Spontaneous Reduction of a Hydroborane to Generate a B-B Single Bond using a Lewis Pair

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Abstract: The *ansa*-aminohydroborane 1-NMe_2-2-BH_2-C_6H_4 crystallizes in an unprecedented type of dimer comporting a B-H bond activated by one FLP moiety. Upon mild heating and without the use of any catalyst, this molecule liberates one equivalent of hydrogen to generate a diborane molecule. The synthesis and the structural characterization of those new compounds as well as the kinetic monitoring of the reaction and the DFT investigation of its mechanism are reported.

Since their discovery by Stephan and coworkers, frustrated Lewis pairs (FLPs)[1] have been used to activate many unreactive molecules[2] and to catalyze the hydrogenation,[3] hydroboration,[4] and hydrosilylation[5] of unsaturated substrates. Conceptually, the absence of a Lewis adduct helps the cooperativity between a Lewis acid (Z) and a Lewis base (L) to activate R-H substrates, generating the respective ion pair $[Z\text{-}R]^-[L\text{-}H]^+$. Such cooperativity can also be obtained with weak Lewis adducts if L-Z bond dissociation is readily accessible.[2d] However, group XIII Lewis acids, often used as the Z moiety in FLP chemistry, are limited in the functionalization of the R group, in contrast to transition metal complexes, making catalyst design more difficult.

Although most of boron chemistry is limited to its +3 oxidation state, boron(II) species such as diboranes are known.[6] These molecules are useful reagents for the borylation[7] and diboration[8] reactions. Diboranes are normally synthesized using highly reducing conditions (Figure 1A, B).[9] Other routes to generate these molecules are available,[6b] notably by metal-catalyzed dehydrogenative coupling reactions of hydroboranes, as reported notably by Braunschweig (Figure 1C).[10] Recently, Himmel and coworkers were able to use homogeneous catalysts to generate such a B-B bond from a guanidine-BH_3 starting material (Figure 1D).[11] Other examples of dehydrogenative coupling were observed in the chemistry of carboranes[12a] and proposed in the dehydrogenation of amine-boranes.[12b-c]

Ansa-aminohydroborane derivatives of the general formula 1-NR_2-2-BR'_2-C_6H_4 have a rich chemistry, notably for the hydrogenation of alkynes[13] and the C-H bond activation of arenes.[14] Although FLP chemistry has been focused on molecules possessing very bulky amines, such as the 2,2,6,6-tetramethylpiperidino group, or highly Lewis acidic boranes such as the $B(C_6F_5)_2$ group, we have been interested in the chemistry of BH_2 derivatives bearing smaller amine groups that could exhibit FLP type behavior.[2d] These species were found to play an important role in the hydrogenation of CO_2.[15] We wish to report that derivative 1-NMe_2-2-BH_2-C_6H_4 (compound **1**) crystallizes in an unprecedented type of dimer where a B-H bond of one molecule is activated by the N-B Lewis pair of another molecule. Surprisingly, upon heating above 80 °C this compound undergoes spontaneous release of H_2 to generate the first completely characterized example of an uncatalyzed borane dehydrocoupling reaction, opening the way to a whole new range of reactivities for frustrated Lewis pairs and diboranes.

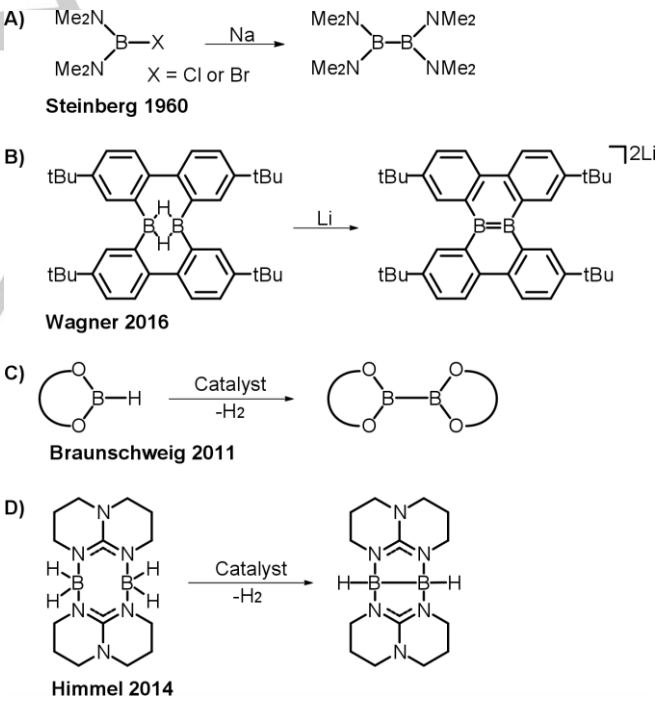

Figure 1. Previously reported formations of B-B bond.

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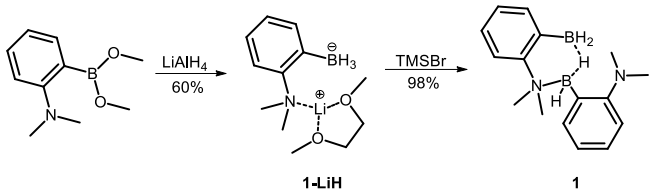


Scheme 1. Synthesis of compound **1.**

Based on the work of Wagner and coworkers,[16] the addition of $LiAlH_4$ on the boronic ester NMe_2-C_6H_4-$B(OMe)_2$ led to **1-LiH**, the LiH adduct of 1-NMe_2-2-BH_2-C_6H_4 (**1**), which was isolated in 60% yield (Scheme 1). The ^{1}H NMR spectrum of **1-LiH** exhibits a characteristic quartet at 1.2 ppm with a B-H coupling constant of 80 Hz. Its sharp $^{11}B\{^1H\}$ NMR signal at -29.3 ppm is typical of a tetravalent boron atom. **1-LiH** was also characterized by X-ray crystallography (Figure S22). It was possible to remove the LiH salt by addition of TMSBr leading to the isolation of species **1** in 98% yield.

A striking feature of the ^{1}H NMR spectrum of **1** is the presence of 8 resonances that could be assigned to the protons of the aromatic rings. In addition, one sharp resonance at 2.7 ppm integrating for 6H can be attributed to one -NMe_2 moiety, whereas the other -NMe_2 moiety included in the 6-membered ring appears as two broad singlets at 3.1 and 2.8 ppm. These two signals coalesce at 40 °C in chloroform-*d*. Two resonances are present in the $^{11}B\{^1H\}$ NMR spectrum at -10.4 and 3.3 ppm demonstrating the unsymmetrical nature of **1**. It was possible to obtain X-ray quality crystals of **1** from a cold saturated toluene solution. The ORTEP structure is depicted in Figure 2, confirming the unprecedented dimeric arrangement of **1** that derives from a 6-membered ring formed by the B-H activation of one monomer by the FLP site of a second. The N2-B1 bond distance of 1.615 Å is significantly shorter than the N1-B1 and N1-B2 distances of 3.044 and 3.705 Å, respectively. The B1-B2 distance of 2.255 Å is significantly longer than the one reported for B_2H_6 (1.776 Å)[17] and the 9-BBN dimer (1.818 Å)[18] and is indicative of the absence of significant interaction between the two boron atoms. Since the bridging hydride could be located in the Fourier map, it is possible to report the B1-μH and B2-μH distances of 1.27(1) and 1.30(1) Å, respectively.

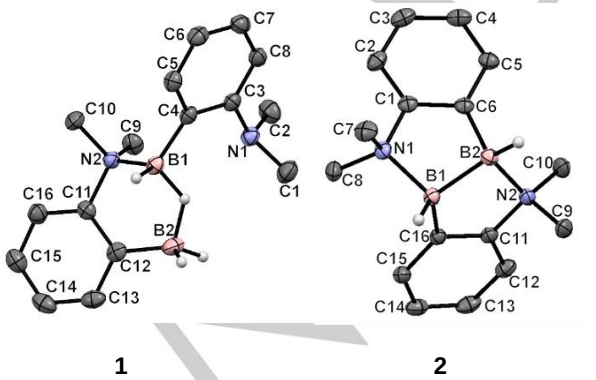
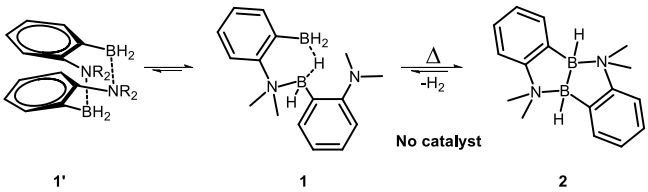


Figure 2. Crystal structure of compounds **1** and **2**. Ellipsoid are drawn at 50% probability. Hydrogens linked to carbon are omitted for clarity. Selected bond lengths (Å) and angles (°) for **1** : N2-B1: 1.615(2), B1-μH: 1.27(2), B2-μH: 1.30(1), B2-C12: 1.584(3), C12-C11: 1.390(2), C11-N2: 1.494(2), C11-N2-B1: 108.7(1), N2-B1-μH: 104.0(7), B1-μH-B2: 123(1), μH-B2-C12: 108.7(7), B2-C12-C11: 121.9(2), C12-C11-N2: 115.7(1); **2** : B1-B2: 1.740(2), N1-B1: 1.671(2), N2-B2: 1.677(1), N1-B1-B2: 101.42(8), B1-B2-N2: 101.20 (8).

Whereas these results present the first fully characterized structure of **1**, we have previously proposed the dimeric head-to-tail isomer **1'** (Scheme 2) as the product of the thermal degradation of 1-NMe_2-2-$B(Ar)_2$-C_6H_4 (Ar = 2,4,6- and 2,4-5-trimethylbenzene) under an atmosphere of molecular hydrogen.[15] While that symmetrical structure was consistent with the NMR data, no other characterization could be obtained for this degradation product. A computational analysis of the various possible dimeric forms of 1-NMe_2-2-BH_2-C_6H_4 was also part of this study. However, isomer **1** was not investigated computationally at that time. Additional DFT calculations were thus performed at the ωB97XD/6-31++G** level of theory in a toluene solvent (SMD)[19] and it was found that the isomer **1** is only slightly more stable than **1'** with ΔH and ΔG of 0.1 and -3.3 kcal.mol^{-1}, respectively. A careful analysis of the ^{1}H NMR spectrum of **1** shows the presence of **1'** as a minor component (see ESI for details). The thermodynamic parameters of the equilibrium were determined using VT ^{1}H NMR in benzene-d_6 (ΔH° = 3.8 ± 0.1 kcal.mol^{-1} and ΔS° = 0.0170 ± 0.0004 cal.mol^{-1}.K^{-1}) and are within the expected margin of error of the calculations (Scheme 2).

Heating a solution of **1** in toluene-d_8 leads to the formation of a new compound (**2**, Scheme 2) along with the release of molecular hydrogen (^{1}H NMR: δ = 4.5). The species **2** was originally misidentified as compound **1'** since all the NMR data were consistent with a symmetric dimer.[15] However, X-ray crystallography unequivocally identifies **2** as [1-NMe_2-2-BH-C_6H_4]$_2$. As can be seen in Figure 2, **2** is a rare example of a diborane bearing both a hydrogen atom and an aryl substituent on boron.[20] The B-B bond length (1.740 Å) and the ^{11}B NMR signal of **1** (δ = 1.79) are similar to those reported by Himmel for the guanidine-based derivative (1.772 Å and δ = -1.14; Fig. 1D).[11] Unfortunately, our attempts to observe the $^1J_{B\text{-}H}$ coupling in **2** proved unsuccessful as only broadening of the resonance was observed in the proton-coupled ^{11}B NMR spectrum. Although thermally induced boron-boron dehydrogenative homocoupling was proposed in amine-borane dehydrogenation,[13c] this rearrangement is to the best of our knowledge the first structurally characterized example of such a transformation.



Scheme 2. Equilibrium between **1** and **1'** and synthesis of compound **2.**

To get more insight into the reaction mechanism, the reactivity of **1** and **2** with hydrogen and deuterium gas was studied. It was found that **1** does not form a stable adduct with hydrogen, but can nevertheless split the molecule at room temperature, as evidenced by the appearance of the characteristic signal of HD by ^{1}H NMR when stored for 16h under 3-4 atm of D_2 at room temperature. Moreover, heating at 80 °C for 16h leads to the complete disappearance of the B-H signals, as evidenced by ^{1}H NMR, with only a trace amount of **2**, allowing the easy

preparation of NMe_2-C_6H_4-BD_2 (**1D**). In a similar experiment, **2** was also able to split hydrogen. However, heating to 80 °C was needed to clearly observe the HD signal by ^{1}H NMR.

The clean and complete transformation of **1** to **2** was monitored using ^{1}H NMR spectroscopy at various temperatures in order to determine the kinetic parameters of the transformation. The disappearance of **1** over time was shown to follow a first-order process with rates varying from 0.0021 to 0.0094 min^{-1} from 85 to 100 °C, respectively. Processing the values using an Eyring plot gave values for $\Delta H^{\ddagger}$ of 24.3 ± 0.7 kcal.mol^{-1} and a $\Delta S^{\ddagger}$ of -0.03 ± 0.02 cal.mol^{-1}.K^{-1}. (Figure 3). The first-order rate is consistent with an intramolecular process and the negligible entropy value of the transition state indicates that no significant change in geometry is occurring at the transition state during the B-B bond formation. We also measured the rate of the reaction at 90 °C under a pressure of 3-4 atm of H_2 and although the kinetic profile was too complex to analyze, the reaction was found to be about 50% slower than under a nitrogen atmosphere (see ESI for details). The slower transformation under a large concentration of hydrogen indicates that the rate for the reverse reaction is significantly enhanced, suggesting the reversibility of the process. Finally, studying the transformation of **1D** to **2D** allowed us to calculate a kinetic isotopic effect of 2.0 ± 0.4.

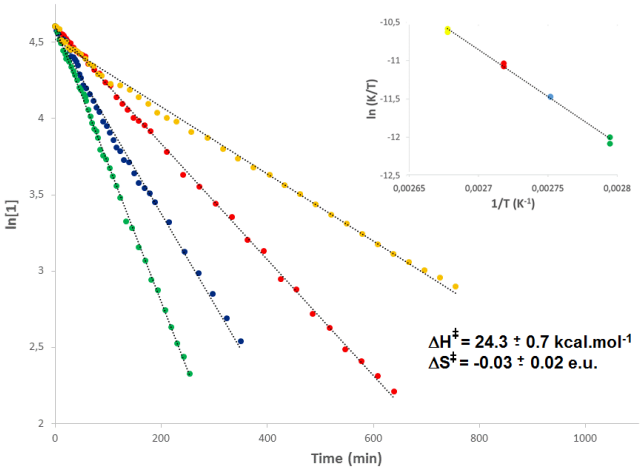


Figure 3: Reaction rate of the transformation of compound **1** in compound **2** at different temperatures (●85 °C, ●90 °C, ●95 °C and ●100 °C) and Eyring plot of the transformation. Two duplicates were measured for each temperature (See ESI).

Two main pathways were investigated computationally (DFT at the ωB97XD/6-31++G**, level of theory with continuum solvation in toluene using the electron density-based universal solvation model SMD)[19] in order to rationalize this transformation. The direct loss of hydrogen to generate a boron-boron homocoupling product was previously postulated by Himmel with the guanidine-BH_3 adducts.[11a] In that report, the calculated value of the transition state ($\Delta G^{\ddagger}$ = 39.0 kcal.mol^{-1}) was too high to spontaneously occur and transition metal catalysts were needed in order to generate the diborane product. We calculated a similar transition state to be significantly more accessible in our system, with respective $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ values of 30.6 and 30.4 kcal/mol^{-1} (Figure 4, **TS1**). Although lower than in the Himmel study, these values are still too high to account for the experimental kinetic data. A second pathway was thus investigated in which the free amine would formally deprotonate the bridging hydride with simultaneous formation of a boron-boron bond (Figure 4, **TS2A**). After obtaining the corresponding zwitterionic intermediate (Figure 4, **2-H$_2$**), the release of hydrogen could occur by a typical FLP transition state (Figure 4, **TS2B**), similar to what has been proposed in amine-borane dehydrogenation.[21] Two possible pathways are probable, depending on the nature of the rotamer present (see ESI). The two pathways were found to differ slightly in energy, with respective $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ values of 24.7 and 26.0 kcal.mol^{-1} for **TS2A** and of 21.9 and 23.5 kcal.mol^{-1} for **TS2A'**. Once the intermediates are obtained (ΔH (ΔG) for **2-H$_2$** and **2-H$_2$'** are respectively of 19.3 kcal.mol^{-1} (20.8 kcal.mol^{-1}) and 18.9 kcal.mol^{-1} (20.1 kcal.mol^{-1})), the release of H_2 occurs with $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ values of 25.9 and 29.2 kcal.mol^{-1}, respectively, for **TS2B**. Both transition states in this pathway are very close in energy. It was not possible to locate **TS2B'** but one might expect for it to be lower than **TS2B** to follow the same trend observed for **TS2A'** and **2H$_2$'**.

It has been postulated that the activation/elimination of H_2 from a FLP does not present a significant KIE,[22] whereas the loss of H_2 from species M-NH_2BH_3, where the rate determining step was the cleavage of a B-H bond, exhibits a KIE close to 1.6.[23] These precedents suggest that either **TS1** or **TS2A** is the rate limiting step. It should be kept in mind that the complicated kinetic profile for the formation of **2** in presence of H_2 support the hypothesis that **TS2A** and **TS2B** are very close in energy. Although we cannot completely rule out the possibility of **TS1** occurring, the experimental values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of 24.3 ± 0.7 kcal.mol^{-1} and -0.03 ± 0.02 e.u. suggest that pathway **TS2** is slightly more favorable with both steps of comparable energies.

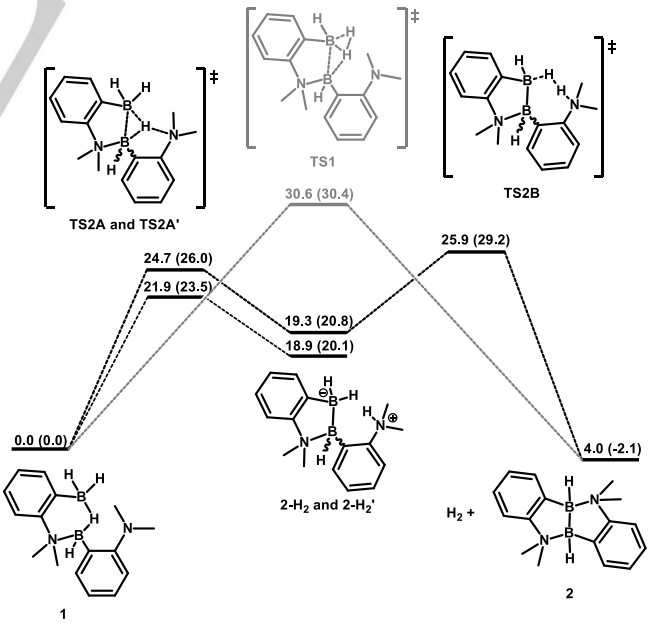


Figure 4. Computed reaction profile of the thermal dehydrocoupling of **1** into **2** at the ωB97XD/6-31++G**, SMD=toluene level of theory ΔH (ΔG), in kcal/mol.

The pathway **TS2** is somewhat surprising since hydrogen is more electronegative than boron (2.1 for H and 2.0 for B according to Pauling's scale),[24] thereby making a hydrogen atom bound to

boron hydridic rather than protic. While the deprotonation of metal hydrides is not rare,[25] FLP systems tend to abstract an hydrogen atom to generate borenium species.[26] While the deprotonation of lower oxidation B-H bond in carboranes was well studied,[27] to the best of our knowledge, the deprotonation of a B(III)-H bond was only reported once before by Bertrand when reacting the strong base KHMDS on a carbene $BH(CN)_2$ adduct to form an isolable boryl anion.[28]

An analysis of the electron density according to Bader's QTAIM theory[29] reveals that for molecule **1,** the bridging hydride has almost the same atomic charge (-0.6438) as the terminal hydrides (-0.6243 to -0.6435; see ESI). In the **TS2A**, it is observed that the hydrogen switch from a hydridic to a protic character (+0.3240), but that the electron population is transferred equally to the two boron atoms where their respective charges vary from +1.8992 and +1.9882 in **1** to +1.3780 and +1.3865 in **TS2A**. The atomic electron populations in **2** are close to **TS2A**, with the proton having a charge of +0.5246 and the boron atoms of +1.2318 and +1.3593, respectively. Nevertheless, it should be kept in mind that the deprotonation of a B-H bond by a rather weak Lewis base such as a dimethylaniline is not thermodynamically favorable since **2-H_2** is higher in energy by 20 kcal.mol^{-1} than the starting material, but the FLP character can facilitate the H_2 elimination process, making the whole transformation thermodynamically possible.

In conclusion, we discovered that the unusual activation of the B-H bond in hydroborane **1** leads to the first spontaneous boron-boron dehydrogenative homocoupling of a hydroborane. The experimental and computational study of the mechanism sheds some light on the unexpected transformation which is a rare example of deprotonation of a B-H bond, which is made possible by the FLP molecule that helps the release of H_2. We have yet to explore the generality of this method and the reactivity of the B-B bond, but the exciting possibility for the B-B bond formation to be reversible opens the way to the addition of a new scaffold in metal-free catalysis. One could imagine activating both an E-H bond, which is readily done by FLPs, and additional E'-X bonds, by the B(II)/B(III) centre. Such system would allow for a variety of multiple redox transformations currently mostly exclusive to transition metal catalysts.

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Keywords: Frustrated Lewis pairs • Boranes • Diboranes • Small molecule activation

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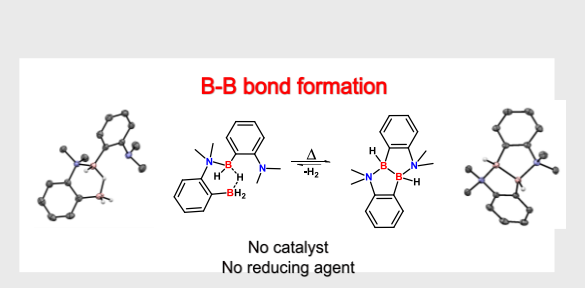

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Page No. – Page No.

Spontaneous Reduction of a Hydroborane to Generate a B-B Single Bond using a Frustrated Lewis Pair

The *ansa*-aminohydroborane 1-NMe_2-2-BH_2-C_6H_4 crystallizes in an unprecedented type of dimer comporting a hydride bridging between two boron centers. Upon mild heating and without the use of any catalyst, this molecule liberates one equivalent of hydrogen to generate a boron-boron bond.

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