Frustrated Lewis Pairs

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Spontaneous Reduction of a Hydroborane To Generate a B–B Single Bond by the Use of a Lewis Pair

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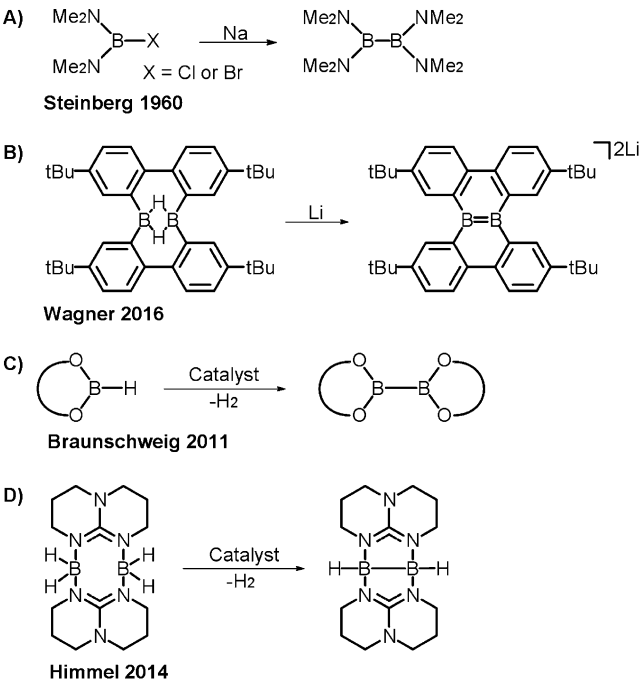
Abstract: *The ansa-aminohydroborane 1-NMe$_2$-2-(BH$_2$)C$_6$H$_4$ crystallizes in an unprecedented type of dimer containing a B–H bond activated by one FLP moiety. Upon mild heating and without the use of any catalyst, this molecule liberates one equivalent of hydrogen to generate a diborane molecule. The synthesis and structural characterization of these 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 co-workers, 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 promotes cooperativity between a Lewis acid (Z) and a Lewis base (L) to activate R–H substrates, thus generating the respective ion pair $[Z–R]^-[L–H]^+$. Such cooperativity is possible with weak Lewis adducts if L–Z bond dissociation is readily accessible.[2d] However, the functionalization of a R group bound to a Group XIII Lewis acids, often used as the Z moiety in FLP chemistry, is more difficult than when bound to transition metal species, thus making catalyst design more difficult.

Although the chemistry of boron is mostly limited to its +3 oxidation state, boron(II) species, such as diboranes, are known.[6] These molecules are useful reagents for borylation[7] and diboration[8] reactions. Diboranes are normally synthesized under highly reducing conditions (Scheme 1 A,B).[9] Other routes to generate these molecules are available,[6b] such as metal-catalyzed dehydrogenative coupling reactions of hydroboranes, as notably reported by Braunschweig and co-workers (Scheme 1 C).[10] Himmel and co-workers were able to use homogeneous catalysts to generate such a B–B bond from a guanidine–BH$_3$ adduct (Scheme 1 D).[11] Other examples of dehydrogenative coupling were observed in the chemistry of carboranes[12a] and proposed in the dehydrogenation of amine–boranes.[12b,c]



Scheme 1. Previously reported approaches to the formation of B–B bonds.

ansa-Aminohydroborane derivatives of the general formula 1-NR$_2$-2-(BR'$_2$)C$_6$H$_4$ 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 focusing 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$_6$F$_5$)$_2$ 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 report herein that the derivative 1-NMe$_2$-2-(BH$_2$)C$_6$H$_4$ (compound **1**) crystallizes in an unprecedented type of dimer, in which 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$_2$, in the first completely characterized example of an uncatalyzed borane dehydrocoupling reaction, thus opening the way to a whole new range of reactivities for frustrated Lewis pairs and diboranes.

As based on the work of Wagner and co-workers,[16] the addition of LiAlH$_4$ to the boronic ester 1-NMe$_2$-2-(B(OMe)$_2$)C$_6$H$_4$ led to **1-LiH**, the LiH adduct of 1-NMe$_2$-2-(BH$_2$)C$_6$H$_4$ (**1**), which was isolated in 60 % yield (Scheme 2).

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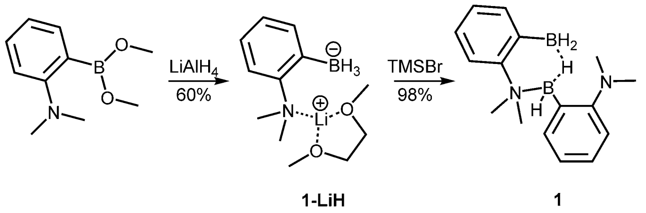


Scheme 2. Synthesis of compound **1**.

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. The sharp ^{11}B{^{1}H} NMR signal observed at −29.3 ppm is typical of a tetravalent boron atom. The adduct **1-LiH** was also characterized by X-ray crystallography (see Figure S22 in the Supporting Information). It was possible to remove the LiH salt by the addition of bromotrimethylsilane (TMSBr), which led to the isolation of species **1** in 98 % yield.

A striking feature of the ^{1}H NMR spectrum of **1** is the presence of eight resonances that were assigned to the hydrogen atoms of the aromatic rings. Furthermore, one sharp resonance at 2.7 ppm integrating for 6 H was attributed to one −NMe$_2$ moiety, whereas the other −NMe$_2$ moiety included in the six-membered ring appears as two broad singlets at 3.1 and 2.8 ppm. These two signals coalesced at 40 °C in [D]chloroform. Two resonances are present in the ^{11}B{^{1}H} NMR spectrum at −10.4 and 3.3 ppm, thus demonstrating the unsymmetrical nature of **1**. It was possible to obtain X-ray quality crystals of **1** from a cold saturated solution in toluene. The ORTEP structure (Figure 1) confirms the unprecedented dimeric arrangement of **1** that derives from the formation of a six-membered ring 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 that 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 was possible to measure the B1–μH and B2–μH distances of 1.27(1) and 1.30(1) Å, respectively.

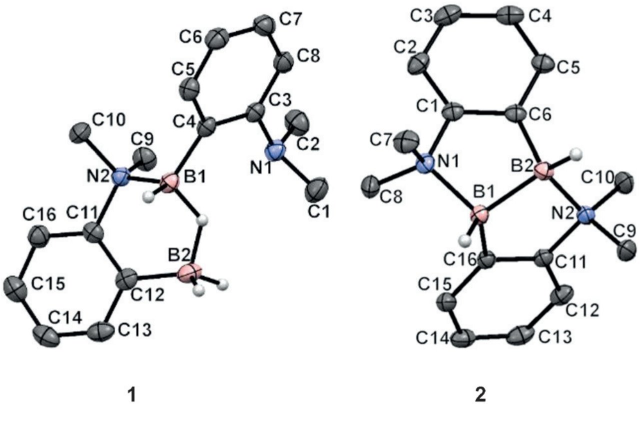
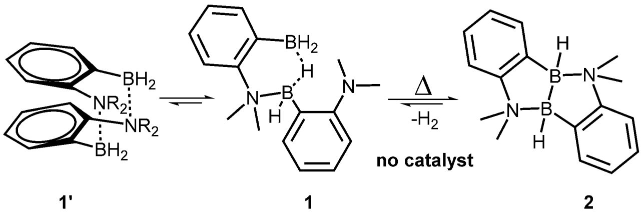


Figure 1. Crystal structure of compounds **1** and **2**. Ellipsoids are drawn at 50 % probability. Hydrogen atoms linked to carbon atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for **1**: N2–B1 1.615(2), B1–μH 1.27(2), B2–μH 1.30(1), B2–C12 1.584(3), C12–C11 1.390(2), C11–N2 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); for **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 previously proposed the dimeric head-to-tail isomer **1′** (Scheme 3) as the product of the thermal degradation of 1-NMe$_2$-2-(BAr$_2$)C$_6$H$_4$ (Ar = 2,4,6- and 2,4,5-trimethylbenzene) under an atmosphere of molecular hydrogen.[15] Although that symmetrical structure was consistent with the NMR data, no other characterization was possible for this degradation product. Computational analysis of the various possible dimeric forms of 1-NMe$_2$-2-(BH$_2$)C$_6$H$_4$ was also part of this previous 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 the solvent toluene (SMD),[19] and it was found that isomer **1** is only slightly more stable than **1′** with ΔH and ΔG values of 0.1 and −3.3 kcal mol^{-1}, respectively. Careful analysis of the ^{1}H NMR spectrum of **1** confirmed the presence of **1′** as a minor component (see the Supporting Information for details). The thermodynamic parameters for the equilibrium were determined by variable-temperature ^{1}H NMR spectroscopy in [D$_6$]benzene ($\Delta H° = (3.8 \pm 0.1)$ kcal mol^{-1} and $\Delta S° = (0.02 \pm 0.01)$ cal mol^{-1} K^{-1}) and are within the expected margin of error of the calculations (Scheme 3).



Scheme 3. Equilibrium between **1** and **1′** and synthesis of compound **2**.

Heating a solution of **1** in [D$_8$]toluene led to the formation of a new compound, **2** (Scheme 3) along with the release of molecular hydrogen (^{1}H NMR: $\delta = 4.5$ ppm). 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 identified **2** as {1-NMe$_2$-2-(BH)C$_6$H$_4$}$_2$. Compound **2** is a rare example of a diborane bearing both a hydrogen atom and an aryl substituent on boron (Figure 1).[20] The B−B bond length (1.740 Å) and the ^{11}B NMR signal of **1** ($\delta = 1.79$ ppm) are similar to those reported by Himmel and co-workers for the guanidine-based derivative (1.772 Å and $\delta = -1.14$ ppm; Scheme 1 D).[11] Unfortunately, our attempts to observe $^{1}J_{B-H}$ coupling in **2** proved unsuccessful, since 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,[12c] this rearrangement is to the best of our knowledge the first structurally characterized example of such a transformation.

To get more insight into the reaction mechanism, we studied the reactivity of **1** and **2** with hydrogen and deuterium gas. 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 spectroscopy when **1** was stored for 16 h under D_2 (3–4 atm) at room temperature. Moreover, heating at 80 °C for 16 h led to the complete disappearance of the B–H signals, as evidenced by ^{1}H NMR spectroscopy, with only a trace amount of **2**, thus allowing the ready preparation of 1-NMe$_2$-2-(BD$_2$)C$_6$H$_4$ (**1$_D$**). 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 spectroscopy.

We monitored the clean and complete transformation of **1** into **2** by ^{1}H NMR spectroscopy at various temperatures 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. An Eyring plot gave a $\Delta H^{\neq}$ value of (24.3 ± 0.7) kcal mol^{-1} and a $\Delta S^{\neq}$ value of (-0.03 ± 0.02) cal mol^{-1} K^{-1} (Figure 2). The first-order rate is consistent with an intramolecular process, and the negligible entropy contribution at the transition state indicates that no significant change in geometry occurs at the transition state during B–B bond formation. We also measured the rate of the reaction at 90 °C under H_2 (3–4 atm), 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 the Supporting Information for details). The slower transformation under a large concentration of hydrogen indicates that the rate for the reverse reaction is significantly enhanced, thus suggesting the reversibility of the process. Finally, by studying the transformation of **1$_D$** into **2$_D$**, we were able to calculate a kinetic isotopic effect of 2.0 ± 0.4.

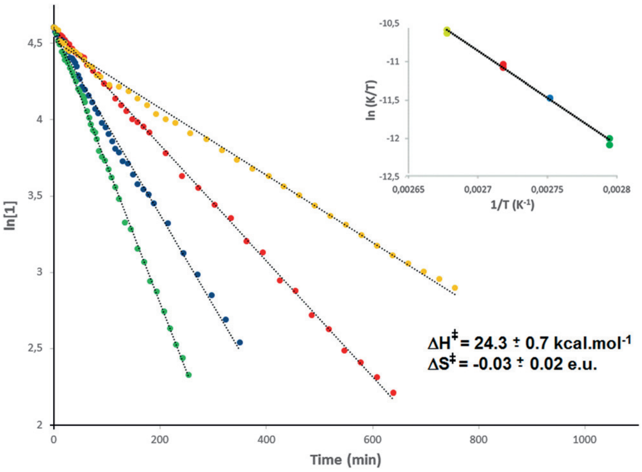


Figure 2. Reaction rate of the transformation of compound **1** into compound **2** at different temperatures (● 85 °C, ● 90 °C, ● 95 °C, ● 100 °C) and Eyring plot of the transformation. Two duplicates were measured for each temperature (see the Supporting Information).

We investigated two main pathways computationally (DFT at the ωB97XD/6-31++G** level of theory with continuum solvation in toluene according to the electron-density-based universal solvation model SMD)[19] to rationalize this transformation. The direct loss of hydrogen to generate a boron–boron homocoupling product was previously postulated by Himmel and co-workers with the guanidine–BH$_3$ adducts.[11a] In that study, the calculated value of the transition state ($\Delta G^{\neq} = 39.0$ kcal mol^{-1}) is too elevated for a significant rate of spontaneous reaction, and transition-metal catalysts were needed to generate the diborane product. We calculated a similar transition state to be significantly more accessible in our system, with respective $\Delta H^{\neq}$ and $\Delta G^{\neq}$ values of 30.6 and 30.4 kcal mol^{-1} (Figure 3, **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 formally deprotonates the bridging hydride with simultaneous formation of a boron–boron bond (Figure 3, **TS2A**). After the corresponding zwitterionic intermediate is formed (Figure 3, **2-H$_2$**), the release of hydrogen could occur by a typical FLP transition state (Figure 3, **TS2B**) similar to that proposed for amine–borane dehydrogenation.[21] There are two possible pathways, depending on the nature of the rotamer present (see the Supporting Information). The two pathways were found to differ slightly in energy, with respective $\Delta H^{\neq}$ and $\Delta G^{\neq}$ 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 have formed (ΔH (ΔG) for **2-H$_2$** and **2-H$_2$′** are 19.3 kcal mol^{-1} (20.8 kcal mol^{-1}) and 18.9 kcal mol^{-1} (20.1 kcal

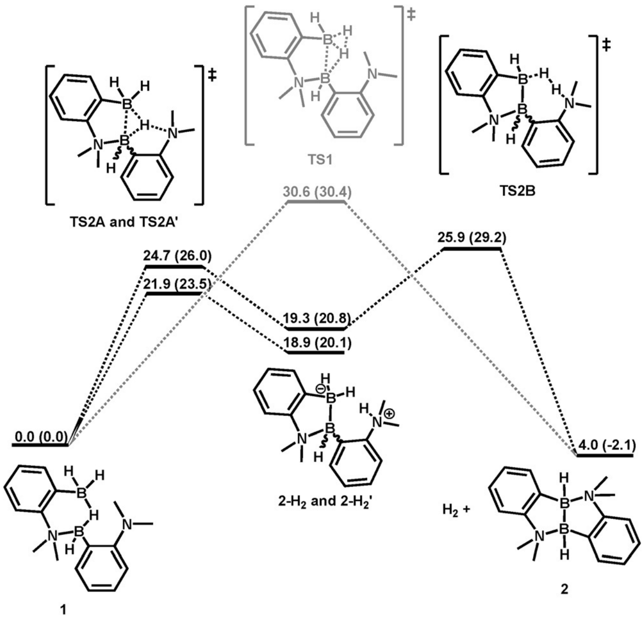


Figure 3. Computed reaction profile of the thermal dehydrocoupling of **1** into **2** at the ωB97XD/6-31++G** level of theory (SMD, toluene); ΔH (ΔG) in kcal mol^{-1}.

mol^{-1}), respectively), 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 it to be lower in energy 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 kinetic isotope effect (KIE),[22] whereas the loss of H_2 from species M–NH_2BH_3, in which the rate-determining step was the cleavage of a B–H bond, exhibits a KIE value close to 1.6.[23] These precedents suggest that either **TS1** or **TS2A** is the rate-limiting step. The complex kinetic profile for the formation of **2** in the presence of H_2 supports 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) eu suggest that pathway **TS2** is slightly more favorable, with both steps of comparable energy.

The pathway **TS2** is somewhat surprising, since hydrogen is more electronegative than boron (2.1 for H and 2.0 for B according to the Pauling scale),[24] thereby making a hydrogen atom bound to boron hydridic rather than protic. Although the deprotonation of metal hydrides is not rare,[25] FLP systems tend to abstract an hydrogen atom from a B–H moiety to generate borenium species.[26] Whereas the deprotonation of a B–H bond in carboranes having boron atoms at lower-oxidation state is known,[27] to the best of our knowledge, the deprotonation of a B^{III}–H bond was only reported once before by Bertrand and co-workers when a carbene $BH(CN)_2$ adduct was treated with the strong base KHMDS to form an isolable boryl anion.[28]

Analysis of the electron density according to the Bader QTAIM theory[29] revealed 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 the Supporting Information). In **TS2A**, it was observed that the nature of the bridging hydrogen atom switches from hydridic to protic $(+0.3240)$, but that the electron population is transferred equally to the two boron atoms, whose respective charge varies 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 those in **TS2A**: The proton has a charge of $+0.5246$ and the boron atoms a charge of $+1.2318$ and $+1.3593$, respectively. Nevertheless, 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; however, the FLP character can facilitate the H_2-elimination process, thus 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 shed some light on the unexpected transformation, which is a rare example of the deprotonation of a B–H bond. The transformation is made possible by the FLP molecule, which aids 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 possibility for B–B bond formation to be reversible suggests a new scaffold in metal-free catalysis. Such systems would enable a variety of multiple redox transformations for which transition-metal catalysts are usually required.

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