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# Frustrated Lewis Pairs

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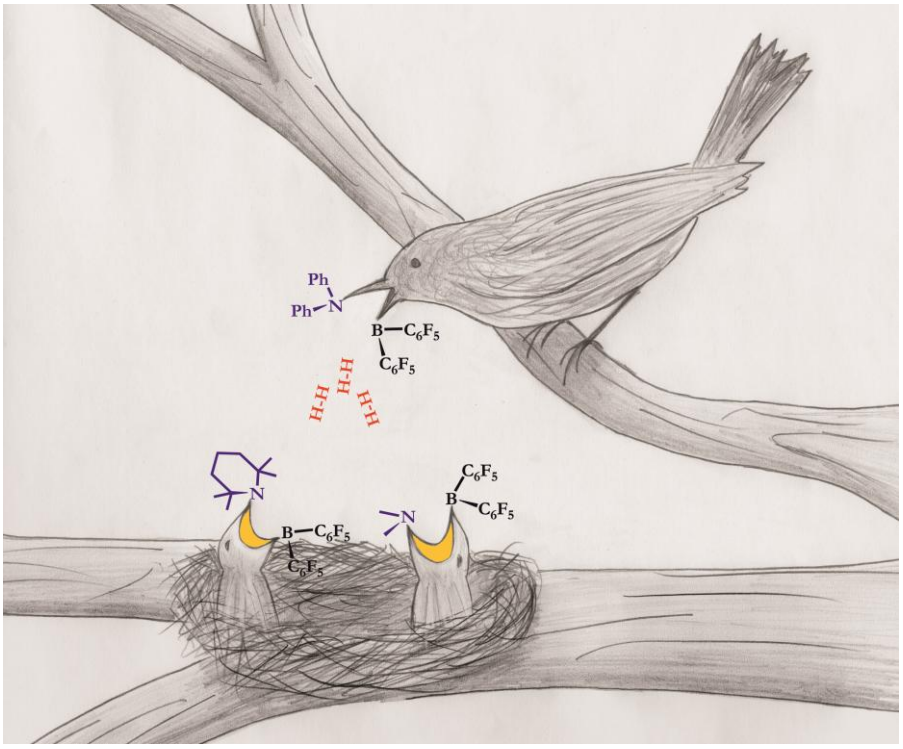


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COMMUNICATION

# Hydrogen activation by 2-boryl-*N*,*N*-dialkylanilines: a revision of Piers' *ansa*-aminoborane†

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**Two 2-[bis(pentafluorophenyl)boryl]-*N*,*N*-dialkylanilines reported here exemplify a new class of intramolecular frustrated B/N Lewis pairs. A structure closely related to this class structure was synthesized in 2003 by Piers *et al.* but was unable to activate $H_2$. The new aminoboranes can activate hydrogen at near ambient conditions; besides, one of them can hydrogenate imines and enamines in a catalytic fashion demonstrating the validity of the original Piers' approach to hydrogen activation with *ansa*-aminoboranes.**

Frustrated Lewis pairs (FLPs) is a rapidly developing concept in contemporary chemistry and catalysis.[1] The idea of the substrate activation by a mutual action of both a Lewis acid and base is not new and has been successfully used in transition metal catalysis.[2] On the other hand, the frustrated Lewis pairs comprising lightweight main-group elements and their reactivity have been known for decades.[3] Nevertheless, a real breakthrough in this area was brought by Stephan *et al.* in 2006 in their pioneering work on the activation of elemental hydrogen with phosphinoborane $(C_6F_5)_2BC_6F_4PMes_2$.[4] This initial finding boosted research activity in this field leading to more than two hundred papers on activation of hydrogen and other small molecules.[5] Whereas a variety of small molecules have been activated by FLPs, the most important achievement and practical application is FLP-catalyzed hydrogenation of polar double bonds.[6]

In 2003, Piers *et al.* described an approach for hydrogen activation by a bridged frustrated aminoborane, emphasizing the importance of the highly Lewis acidic bis(pentafluorophenyl) boryl group. As an example, aminoborane **1** was synthesized (Fig. 1).[7] Attempts to activate hydrogen with **1** were unsuccessful. This paper has presumably therefore been sparingly cited in later publications.

Herein we report two new compounds closely related to the original *ansa*-aminoborane **1**. In these molecules the diphenylamino moiety was substituted with more basic 2,2,6,6-tetramethylpiperidino-1 (TMP) (**2**) or dimethylamino (**3**) groups. Both **2** and **3** readily activate $H_2$ at ambient conditions, demonstrating that Piers *et al.* were very close to successful hydrogen activation using a solely main-group compound (Fig. 1).

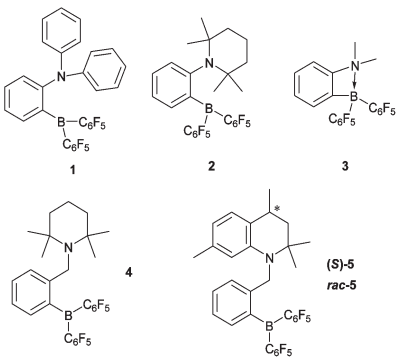


**Fig. 1** *Ansa*-aminoboranes prepared by Piers (**1**), by our group (**4**, **5**) and reported herein (**2**, **3**).

Recently, we have reported the *ansa*-aminoboranes **4** and **5**, which efficiently transfer molecular hydrogen to imines and other nitrogen-containing compounds in a catalytic fashion.[8,9] Asymmetric hydrogenations have been attempted by introducing chiral amines into frameworks of the catalysts (*e.g.* **(*S*)-5**) but only fair enantioselective inductions (up to 38% *ee*) were achieved. We attributed this to excessive conformational freedom of the catalyst molecules (Fig. 1). In this regard removal of the methylene junction between the phenylene ring and the amino groups may lead to more rigid molecules with superior asymmetric effectiveness. To the best of our knowledge, **1** is the only 2-[bis(pentafluorophenyl)boryl]-aniline that has been aimed for $H_2$ activation, although some other structures with nitrogen-containing groups in the *ortho*-position to the bis(pentafluorophenyl)boryl moiety are known.[10] Hence, the achiral *ansa*-aminoboranes **2** and **3** were prepared to test their reactivity towards hydrogen and evaluate potential catalytic activity in hydrogenations.

## Results

The *ansa*-aminoboranes **2** and **3** were prepared in high yield by the standard approach[8,9] from bis(pentafluorophenyl)boron chloride **11**[11] and *o*-*N*,*N*-dialkylaminophenyllithiums **9** and **10** (Scheme 1). A one-step synthesis starting from iodobenzene and LiTMP was previously reported to give 1-(2-iodophenyl)-2,2,6,6-tetramethylpiperidine **7** in 81% yield.[12] Since no exact

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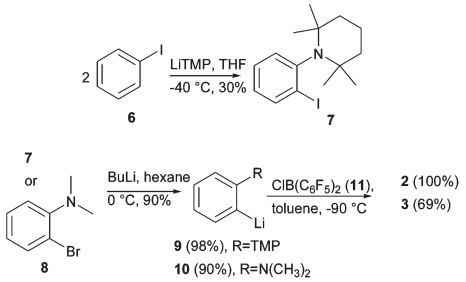
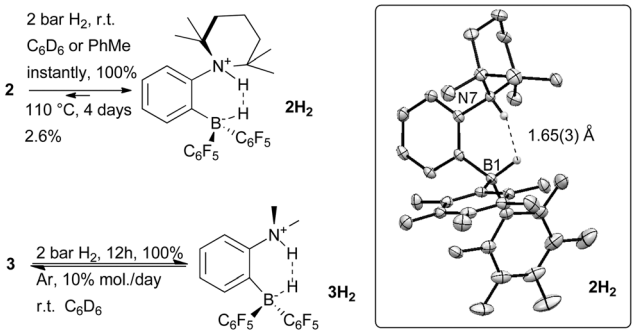
†Electronic supplementary information (ESI) available: Experimental procedures and crystallographic data in CIF. CCDC 875800 (**2**), 875801 (**2H$_2$**) and 875802 (**3**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30926b




**Scheme 1** Synthesis of aminoboranes **2** and **3**.




**Scheme 2** Hydrogen activation by the aminoboranes **2** and **3**: formation of ammonium borohydrides $\mathbf{2H_2}$ and $\mathbf{3H_2}$. ORTEP drawing (displacement parameters drawn at 50% probability level) of the molecule of $\mathbf{2H_2}$ (hydrogen atoms except for N*H* and B*H* are omitted for clarity).†

procedure was reported for **7**, we were able to synthesize it in *ca.* 30% reproducible yield only. The respective lithium compounds **9** and **10** were isolated from the reaction of **7** or *N*,*N*-dimethyl-2-bromoaniline **8** with butyllithium in hexane at 0 °C. It is worth noting that isolation of pure **9** and **10** is beneficial as the subsequent reaction with $(C_6F_5)_2BCl$ **11** gives **3** in high yield, and **2** almost quantitatively.

The aminoborane **2** was isolated as deeply coloured yellow crystals. NMR data, especially the $^{19}$F-NMR spectrum, which contains resonances at −127.2, −149.3 and −162.1 ppm, are consistent with three-coordinated boron species and reveal the "frustration" between the B and N centres. Colours from yellow to deep bloody red are typical for bridged phosphino-[13] and aminoboranes,[8,9] and the aminoborane **2** is not an exception in this respect. In contrast, the *N*,*N*-dimethylaminoborane **3** was isolated as white crystals. In addition, NMR measurements (in ppm $^{13}$C: $\delta = 47.9$ (N($CH_3$)$_2$); $^{10}$B: $\delta = 9.0$; $^{19}$F: $\delta = -156.6$ (*p*-F), −163.4 (*m*-F)) evidence a B–N bonding. It was not clear from the NMR data whether the B–N bonding is intra- or intermolecular, taking into account that the dimethylamino group is sterically benign. Both structures, **2** and **3**, were determined using the X-ray diffraction method (Fig. 2). A four-membered ring with the B–N bond lengths of 1.771(3) and 1.741(3) Å for two different molecules of **3** in a unit cell was found. The formation of four-membered B–N rings was recently reported for the products of hydroboration of enamines with Piers' borane $HB(C_6F_5)_2$.[14] In contrast to **3**, the X-ray diffraction method showed no evidence of the B–N bonding in **2**. Evidently, extreme steric hindrance of the 2,2,6,6-tetramethylpiperidinyl moiety is responsible for this effect.

Though both **2** and **3** activate molecular hydrogen under 2 bar pressure and at room temperature, they do this in a different fashion. The "truly frustrated" **2** absorbs $H_2$ instantly upon exposure. The resultant borohydride $\mathbf{2H_2}$ was produced in toluene and isolated as white crystals, from which the crystal structure was determined (Scheme 2). Attempts to dehydrogenate $\mathbf{2H_2}$ back into **2** were unsuccessful; heating it for 4 days at 110 °C in toluene-$d_8$ led to formation of a minute (2.6 mol% by $^{19}$F NMR) amount of **2**. The irreversible activation of hydrogen by **2** is in sharp contrast with the previously reported **4**, whose corresponding hydrogen adduct $\mathbf{4H_2}$ starts to release hydrogen within minutes at 110 °C and is fully converted to **4** upon heating for 24 h in an open system.[8] The structure of $\mathbf{2H_2}$ in a solid state represents the zwitterionic structure typical for those *ansa*-ammonium borohydrides reported previously by us[9] and Erker *et al.*[14] The counterparts of the intramolecular ion pair are oriented towards each other forming an almost plain 6-membered pseudo-ring with the 1.65(3) Å H–H distance (Scheme 2, Table 2).

The aminoborane **3**, containing the four-membered B–N ring, slowly produces the respective intramolecular ammonium borohydride $\mathbf{3H_2}$ in $C_6D_6$ at the constant rate of about 8 mol% h$^{-1}$ upon exposure to 2 bar of hydrogen. Thus **3** was totally converted into $\mathbf{3H_2}$ within 12 h. When hydrogen is vented off and the solution of $\mathbf{3H_2}$ is left standing under Ar in an open system, it slowly dehydrogenates back to **3** with the rate of about 10% per day. Thus **3** exhibits reversibility of hydrogen uptake at room temperature without any need of thermal promotion for dehydrogenation of $\mathbf{3H_2}$. The thermal behaviour of the borohydride $\mathbf{3H_2}$ is more complicated and is a subject of a separate study which will be published elsewhere.

Catalytic activity of the prepared aminoboranes/ammonium borohydrides in the hydrogenation of imines and enamines was studied. No reaction occurred in an attempted hydrogenation of

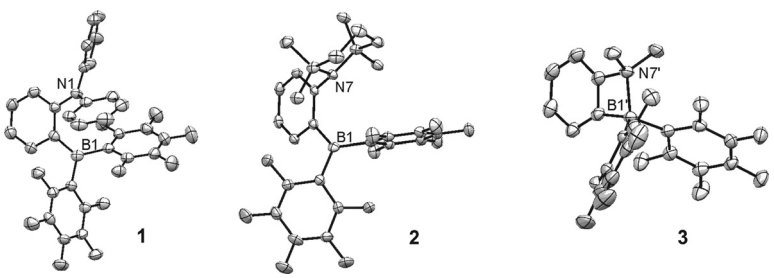



**Fig. 2** ORTEP drawings (displacement parameters drawn at 50% probability level) of the aminoboranes **1** reported by Piers *et al.*,[7] and **2**–**3** (hydrogen atoms are omitted for clarity, one of two crystallographically independent molecules of **3** is shown).†



**Table 1** Hydrogenation of **16** and **17** catalyzed by the aminoborane **3**[a]

| Substrate | Loading of **3**, %mol | Temperature, °C | Time, h | Conversion, % |
|---|---|---|---|---|
| **16** | 4 | 110 | 36 | 30 |
| **16** | 10 | 80 | 18 | 70 |
| **16** | 10 | 100 | 18 | 81 |
| **16** | 15 | 80 | 22 | 100 |
| **17** | 5 | 25 | 18 | 15 |
| **17** | 5 | 80 | 1 | 100 |

[a] 0.25 mmol of the substrate and a catalytic amount of **3** were placed in a Schlenk tube and stirred under 2 bar $H_2$ and respective conditions. Conversions were determined by $^1$H-NMR of crude reaction mixtures.

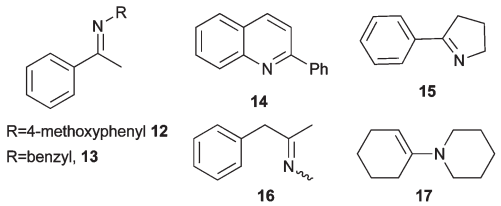



**Fig. 3** Substrates used in the attempted catalytic hydrogenation with the aminoboranes **2**, **3** or ammonium borohydrides $\mathbf{2H_2}$, $\mathbf{3H_2}$.

imines **12–16** (Fig. 3) using **2** or $\mathbf{2H_2}$ as the catalyst (5 mol%, toluene, 110 °C, 2 bar $H_2$, 16 h). Moreover, no reactivity was observed when equimolar amounts of the borohydride $\mathbf{2H_2}$ and benzaldehyde or benzonitrile were heated for 24 h at 110 °C in $C_6D_6$.

The aminoborane **3** was tried as a catalyst for the hydrogenation of imines **12–16** and an enamine **17** (4 mol%, toluene, 110 °C, 2 bar $H_2$, 36 h). As a result, only **16** and **17** were catalytically hydrogenated (Table 1, Fig. 3). To figure out the reason for such a strong difference in reactivity, **12–17** were mixed with equimolar amounts of the ammonium borohydride $\mathbf{3H_2}$ in $C_6D_6$. No reaction occurred between $\mathbf{3H_2}$ and imines **12–15** at room temperature or upon heating for 3 h at 50 °C. In contrast, **16** and **17** react instantly at room temperature, though with different outcome. The enamine **17** produces smoothly *N*-cyclohexylpiperidine ($\mathbf{17H_2}$) and the aminoborane **3**. No interactions were found between **3** and the starting enamine **17** or the product amine $\mathbf{17H_2}$ by NMR. On the other hand, as complete consumption of the borohydride $\mathbf{3H_2}$ occurred upon mixing with imine **16** (1 : 1), the complex mixture comprising the reduced imine $\mathbf{16H_2}$ coordinated to aminoborane **3** was produced. The coordination between **3** and the amine $\mathbf{16H_2}$ or the imine **16** explains the longer reaction times (compared to **17**) and the requirement of thermal promotion to break the Lewis acid–base adduct (Table 1).

## Discussion

Experimental results reported herein and published by Piers *et al.* represent three different examples of 2-[bis(perfluorophenyl)-boryl]-anilines. The aminoborane **1** does not produce an intramolecular B–N bonding and does not activate hydrogen. While frustration of the borane and amine parts is caused, apparently, by steric reasons, the inability to split hydrogen was attributed

**Table 2** Comparison of geometries of the B–C═C–N frames of **2**, $\mathbf{2H_2}$ and **3**, based on X-ray diffraction data

| | **2** | $\mathbf{2H_2}$ | **3**[c] |
|---|---|---|---|
| *d*(B–N), Å | 3.031(4) | 2.941(2) | 1.771(3) [1.741(3)] |
| ∠(C═CB), ° | 126.6(2) | 123.1(1) | 93.0(2) [92.2(2)] |
| ∠(C═CN), ° | 119.1(2) | 116.9(1) | 101.7(2) [101.7(2)] |
| N-dihedral ∠, °[a] | 76.1(2) | 86.0(1) | 89.7(1) [88.7(1)] |
| B-dihedral ∠, °[a] | 49.4(2) | 74.3(1) | 85.6(1) [87.6(1)] |
| *d*($N^+$H), Å[b] | | −0.05(2) | |
| *d*($B^-$H), Å[b] | | −0.33(2) | |

[a] Angle between the least squares planes of the phenylene bridge and the TMP (NCC) or $B(C_6F_5)_2$ (BCC) groups. [b] A declination of hydrogen atoms from the B–C═C–N plane. [c] Values for the second crystallographically independent molecule are in brackets.

by Piers and lately by Pápai to a low basicity of the diphenylamino group. The power of a frustrated Lewis pair stems from the basicity of the basic and the acidity of the acidic counterparts, of which both are crucial for activation of $H_2$. This has been studied theoretically.[15] Besides, in our recent paper we have systematically studied a series of structurally homological intramolecular frustrated Lewis pairs. It was shown that gradual decreasing of the basicity of the amino group (from **4** to **5**) makes the respective ammonium borohydride less stable and hydrogen liberation more facile. This translates into a dramatic rise of the catalytic activity of the respective aminoboranes, for example **5**. Eventually, we have reached the point on the basicity scale of the amine part where the respective ammonium borohydride, the product of $H_2$ activation, was no longer stable at ambient conditions.[9] A relation between the acidity of boranes and reversibility of hydrogen uptake was a matter of an experimental study as well.[16] On the other hand, the mutual geometry of the acid and base counterparts can substantially improve not only kinetic parameters of hydrogen splitting,[13] but also thermodynamic stability of hydrogen adducts. Thus enhanced thermodynamic stability of *ortho*-anilinium borohydrides was emphasized by Pápai *et al.*; the calculated $\Delta G$ value for hydrogenation of **1** is +7.1 kcal mol$^{-1}$. This value is much lower than expected based on evaluation of the Lewis acid and base strengths apart from their intramolecular nature and the mutual geometry. Similarly, surprisingly high thermodynamic stability was calculated for the *ansa*-ammonium borohydride $\mathbf{4H_2}$.[15] In addition, other frustrated *ansa*-B/N systems containing an ethylene or ethynylene bridge and constrained geometry were theoretically designed and claimed to be promising candidates for activation of small molecules, particularly methane.[17]

The *ansa*-aminoborane **2** exemplifies the exceptionally reactive frustrated Lewis pair. Possessing the extremely hindered TMP-moiety, the aminoborane **2** does not form the B–N bonded ring, revealing FLP reactivity in full strength. Other structurally close compounds have either partially quenched reactivity due to the B–N bond formation caused by less hindered amino substituents (**3** or reported by Erker *et al.*)[14] or diminished reactivity due to a lower basicity of the diphenylamino group in **1**. Therefore, aminoborane **2** activates $H_2$ producing the extremely stable adduct $\mathbf{2H_2}$. Comparison of the structures of **2** and $\mathbf{2H_2}$ in a solid state revealed that activation of $H_2$ causes a minor change in geometry of the B–C═C–N frame (Table 2). Thus the rigid

geometry of **2** is optimal for $H_2$ activation, making $\mathbf{2H_2}$ particularly stable due to a large contribution of the entropic factor to the free energy. The formation of the 6-membered pseudo-ring of $\mathbf{2H_2}$ is thermodynamically more favourable than the respective 7-membered ring as evident by different dehydrogenation behaviour of $\mathbf{2H_2}$ and $\mathbf{4H_2}$, mentioned previously. This suggestion requires further experimental verification by direct calorimetric studies which are in progress. Additional stability of the resultant ammonium borohydride $\mathbf{2H_2}$ is supported by its inability to hydrogenate imines or even benzaldehyde. Apparently, an important step in the hydrogenation with *ansa*-ammonium borohydrides is the breakage of the "dihydrogen" bond and the resultant ring-opening of the six-membered pseudo-ring. In the case of $\mathbf{2H_2}$ this step is complicated by rigidity of the B–C═C–N frame and strong electrostatic attraction between counterparts of the intramolecular ion pair. Nevertheless, there are some differences between **2** and $\mathbf{2H_2}$ in orientation of the amine and boryl parts. Due to steric repulsion, the TMP- and $(C_6F_5)_2B$-groups have a sliding orientation in **2** and are turned by 76° and 49° respectively relative to the plane of the bridging $C_6H_4$ ring (Table 2). In the borohydride $\mathbf{2H_2}$ these angles are 86° and 74° respectively, demonstrating geometry close to $C_s$-symmetric.

The *N*,*N*-dimethylaminoborane **3** is an example of a sterically benign *ortho*-borylaniline. The absence of steric repulsion facilitates formation of a four-membered B–N ring. Though the basicity of the dimethylamino group is substantially lower than that of the TMP, and some reactivity is quenched by the intramolecular Lewis B–N adduct, **3** is still able to activate $H_2$ at near ambient conditions. The progress of hydrogen uptake was found to be linear with time under constant pressure, perhaps due to the rate-limiting character of the B–N ring dissociation. The formation of four-membered $(C_6F_5)_2B$–N adducts was reported previously by Erker *et al.* and the B–N ring dissociation energy was measured to be 13–14 kcal $mol^{-1}$.[14] The ease of hydrogen release from the ammonium borohydride $\mathbf{3H_2}$ is remarkable. Evidently, the formation of the B–N bond facilitates the shift of the equilibrium to **3**.

Reversibility of hydrogen uptake by **3** at room temperature resembles those of **5**, which was found to be the most active FLP catalyst for the hydrogenation of various imines (TOF *ca.* 100 $h^{-1}$). While imines **12–15** were smoothly hydrogenated with the *ansa*-aminoboranes **4** and **5** as catalysts, the imine **16** was not hydrogenated catalytically due to coordination of the substrate to the catalyst.[8,9] In contrast, the *ansa*-aminoborane **3** was able to hydrogenate **16** but not **12–15**, demonstrating the opposite selectivity to non-hindered imines. Even though the dimethylamino group is one of the smallest possible secondary amino-groups, $\mathbf{3H_2}$ is much more hindered than $\mathbf{4H_2}$ containing the $TMPCH_2$ group; the diminished accessibility of the ammonium borohydride catalyst $\mathbf{3H_2}$ for a substrate is caused by the tighter *ortho*-connection of the amine and boryl parts and by constrained geometry of the 6-membered pseudo-ring in comparison to the 7-membered one in $\mathbf{4H_2}$. In this respect the smooth hydrogenation of the quite hindered enamine **17** is remarkable. A possible explanation is the influence of steric factors during proton transfer from the catalyst ($\mathbf{3H_2}$) to a substrate, which is considered to be the first step in the catalytic cycle. Indeed, while in the case of imines the protonation occurs at the nitrogen atom and hence the proximity of the catalyst's $NHMe_2^+$ group to the substrate's –N═C– bond is required, in the case of enamines the catalyst protonates the β-carbon, which is much more accessible. This consideration requires further experimental and theoretical support.

In conclusion, two new *ansa*-aminoboranes bridged with a phenylene ring were prepared. The aminoborane **2** containing a highly basic and sterically hindered 2,2,6,6-tetramethylpiperidine moiety instantly activates $H_2$ at ambient conditions producing the extremely stable and unreactive ammonium borohydride $\mathbf{2H_2}$. The *ansa*-aminoborane **3** containing a smaller *N*,*N*-dimethylamino group produces an intramolecular Lewis adduct comprising a four-membered B–N ring. It features reversible $H_2$ activation at room temperature, which is remarkable. **3** or the respective ammonium borohydride $\mathbf{3H_2}$ efficiently catalyzes hydrogenation of some imines and enamines, demonstrating selectivity to non-hindered substrates. The aminoboranes **2** and **3** exemplify the validity of the approach to hydrogen activation by the first intramolecular B/N frustrated pair proposed by Piers *et al.* back in 2003.

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