

“Inverse” Frustrated Lewis Pairs – Activation of Dihydrogen with Organosuperbases and Moderate to Weak Lewis Acids

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S Supporting Information

ABSTRACT: A new approach to intermolecular frustrated Lewis pairs (FLPs) that combines readily available bulky organosuperbases with moderate to weak boron-containing Lewis acids is reported. These so-called “inverse” FLPs are demonstrated to heterolytically cleave dihydrogen, allowing for the isolation and structural characterization of various phosphonium borohydride salts; two FLPs proved to be efficient catalysts in the metal-free hydrogenation of *N*-benzylideneaniline.

Frustrated Lewis pairs (FLPs) are sterically encumbered Lewis acid–base pairs unable to form classical Lewis acid–base complexes due to unfavorable steric interactions (frustration). As a result, Lewis acidity and basicity of the individual FLP components remain unquenched thus enabling stoichiometric and catalytic activation of small molecules.^{1,2} Arguably, the most striking example is the heterolytic cleavage of dihydrogen discovered by Stephan et al.³ a few years ago, which paved the way to the successful design of various active FLP-based catalysts for the hydrogenation of imines, alkenes, alkynes, and ketones.⁴

While a number of Lewis basic amines and phosphines have been successfully utilized in constructing FLPs for H₂ cleavage, the Lewis acid component with a few exceptions^{5–7} has been limited to expensive, highly fluorinated, but strongly Lewis acidic boranes such as B(C₆F₅)₃, B(C₆F₅)₂R (alkyl, aryl), and related systems. Further, reductions in the Lewis acidity of the borane resulted in inactive FLPs with the commonly used base components.⁸ Nonetheless, recent work from the groups of Papai,⁹ Bercaw/Labinger,¹⁰ and Krempner⁷ has indicated that moderate to weak Lewis acids may be utilized in FLP-mediated H₂-cleavage, provided a sufficiently strong base is present. Such an “inverse” approach may open up new ways to the design of efficient FLP-based hydrogenation catalysts as many weak boron-containing Lewis acids are readily available, inexpensive, and can easily synthetically be modified.

With the aim of identifying moderate to weak Lewis acids capable of reversibly cleaving H₂ in a combination with a strong base, the gas-phase hydride affinities of various organoboranes were calculated. The results are summarized in Table 1 and show that BPh₃ and HBMe₂ are significantly weaker hydride acceptors than their perfluorinated counterparts B(C₆F₅)₃ and HB(C₆F₅)₂. Note also that 9-BBN and its readily accessible alkyl and aryl

Table 1. Calculated Gas-Phase Hydride Affinities, ΔH_{HA} (kcal/mol), of Selected Boranes

borane	ΔH_{HA}	borane	ΔH_{HA}
B(C ₆ F ₅) ₃	−112.0 ^a	9-Et-BBN	−65.2 ^c
HB(C ₆ F ₅) ₂	−97.2 ^a	9-Me-BBN	−62.4 ^c
BPh ₃	−74.4 ^b	BET ₃	−58.5 ^b
HBMe ₂	−74.7 ^b	9-MeO-BBN	−54.1 ^c
9-BBN	−70.2 ^c	9-H ₂ N-BBN	−39.9 ^c
9-Ph-BBN	−69.0 ^c	B(OMe) ₃	−38.2 ^b

^aRef 11. ^bRef 7. ^cThis work.

derivatives are weaker hydride acceptors than HBMe₂ and BPh₃ but still stronger than acyclic BEt₃.

First, we tested the moderate Lewis acids BPh₃ and HBMe₂, respectively, in combination with phosphazene **1** (Figure 1), a strong and bulky Brønsted base (pK_a = 28.4; in CH₃CN). No Lewis acid–base adducts were obtained, and C₆D₆ solutions of each of these FLPs proved stable over prolonged periods of time. However, upon adding H₂ (2.5 atm) to hexanes/benzene solutions of the FLPs **1**/BPh₃ and **1**/HBMe₂, respectively,

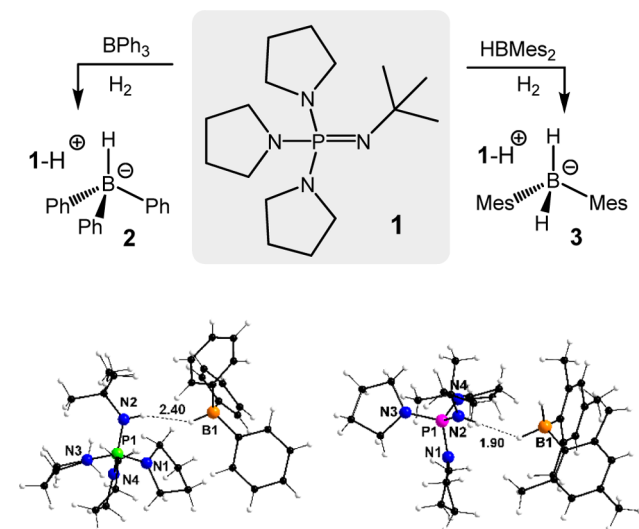


Figure 1. Formation and solid-state structures of **2** (left) and **3** (right) [black = carbon, white = hydrogen].

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crystalline solids were isolated from solution and characterized by multinuclei NMR spectroscopy and combustion analysis as the phosphazanium borates **2** and **3** (Figure 1). The cations of **2** and **3** exhibit ^{31}P NMR resonances at ~ 22 ppm. The anions of **2** and **3**, $[\text{HBPh}_3]^-$ and $[\text{H}_2\text{BMes}_2]^-$, give rise to ^{11}B resonances at -9.1 and -23.0 ppm with scalar B–H coupling constants of ≈ 79 Hz (doublet) and ≈ 76 Hz (triplet), respectively, unambiguously demonstrating the ability of these FLPs to cleave dihydrogen heterolytically. In addition, **2** and **3** were characterized by single X-ray analysis (Figure 1). The structural parameters are consistent with tetrahedral $[\text{HBPh}_3]^-$ and $[\text{H}_2\text{BMes}_2]^-$ anions with av. C–B–C angles of 111.2° and 115.9° , respectively. The NH and BH units in **2** are oriented toward each other with fairly short $\text{NH}\cdots\text{HB}$ (2.40 Å) and $\text{HN}\cdots\text{BH}$ (4.12 Å) distances. Interestingly, the shortest $\text{NH}\cdots\text{HB}$ and $\text{HN}\cdots\text{BH}$ distances in **3** are only 1.90 and 3.77 Å, respectively, and significantly shorter than those found in $[\text{Bu}_3\text{PH}][\text{HB}(\text{C}_6\text{F}_5)_3]^{3b}$ ($\text{PH}\cdots\text{HB}$, 2.75 Å; $\text{HP}\cdots\text{BH}$, 4.67 Å) as well as $[\text{Bu}_3\text{PH}][\text{HB}(\text{cyclo-hexyl})(\text{C}_6\text{F}_5)_2]^{12}$ ($\text{PH}\cdots\text{HB}$, 2.63 Å; $\text{HP}\cdots\text{BH}$, 4.90 Å). Note that only intramolecular ammonium borate salts, derived from pre-organized intramolecular FLPs, have shorter H \cdots H distances; the shortest are in the range from 1.65 to 1.70 Å.¹³ Nonetheless, despite the proximity of the two H atoms in the solid state, THF solutions of **2** and **3** appeared to be relatively stable toward the release of H_2 . Only at 60°C in THF after 30 h, $\sim 50\%$ of **2** and $\sim 70\%$ of **3** converted into the individual FLP components as judged by ^{31}P NMR spectroscopy (Figures S2 and S5).

The significantly weaker hydride acceptors 9-BBN and BET_3 were also tested with **1**, but did not engage in the cleavage of H_2 , an observation that we attribute to the insufficient Brønsted basicity of **1**. We envisioned that increasing the Brønsted basicity of the base component may permit the utilization of weak Lewis acids in the FLP-mediated cleavage of dihydrogen.

To test our hypothesis, Verkade's superbase **4** ($\text{p}K_a = 33.4$; in CH_3CN)¹⁴ was combined with the moderate to weak hydride acceptors BPh_3 , HBMe_2 , 9-BBN, 9-Hex-BBN, and BET_3 . As in the previous cases, no Lewis acid–base adducts were obtained with this sterically demanding and exceptionally strong Brønsted base. Again, C_6D_6 solutions of each of the respective FLPs proved stable over prolonged periods of time. Hexanes/benzene solutions of the FLPs **4**/ BPh_3 and **4**/ HBMe_2 , however, readily reacted with H_2 (2.5 atm.) to furnish the salts **5** and **6** as crystalline solids (Figure 2). As expected, the ^{11}B NMR spectra of **5** and **6** are very similar to those of **2** and **3**. The ^{31}P NMR spectra of **5** and **6** exhibit resonances at ≈ 10 ppm with a scalar P–H coupling constant of ≈ 500 Hz (doublet). The results of the X-ray analysis of **5** (Figure 2) confirmed the anion and cation to be fully separated from each other, strikingly different from what is seen with **2** and **3**. Nonetheless, the structural parameters are consistent with a tetrahedral HBPh_3^- anion with av. C–B–C angles of 110.1° .

Astonishingly, the FLP 9-BBN/**4** when exposed to H_2 (2.5 atm) reacted similarly generating a crystalline solid, which by multinuclei NMR spectroscopy and X-ray crystallography was identified as **7** (Figure 3). While the results of the X-ray data clearly pointed toward a salt-type structure with $[\text{9,9-H}_2\text{BBN}]^-$ as the counteranion, characterization by ^1H and ^{13}C NMR spectroscopy was not straightforward. Integration of the signals of the protons belonging to the BBN unit and the appearance of multiple signals in the ^{13}C NMR suggested more than one anionic species to coexist in solution.

In the ^{11}B NMR spectrum, **7** displays two signals, suggesting at least two anions present in solution; a sharp triplet at -16.5 ppm

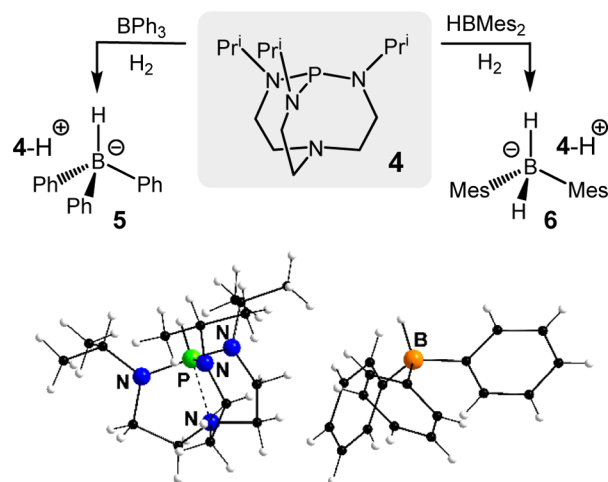


Figure 2. Formation of **5** and **6**; solid-state structure of **5** [black = carbon, white = hydrogen].

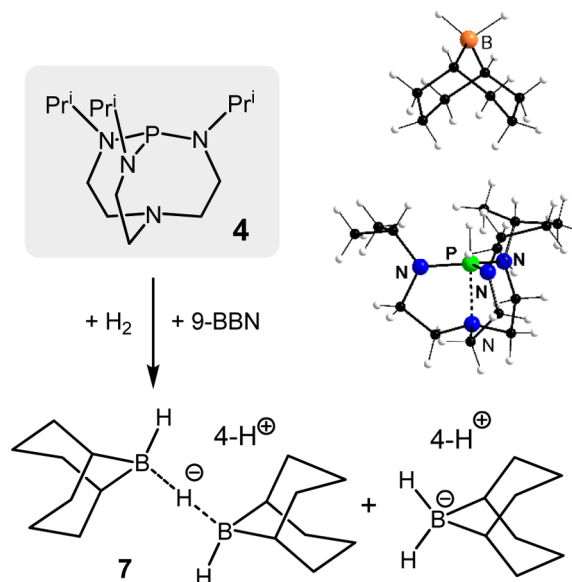


Figure 3. Formation and solid-state structure of **7** [black = carbon, white = hydrogen].

($J_{\text{B-H}} = 78.7$ Hz) due to the monomeric anion $[\text{9,9-H}_2\text{BBN}]^-$ ¹⁵ and a broad singlet at around 4.0 ppm. The latter signal may be assigned to the anion, $[\text{9-H-BBN}\cdots\text{H}\cdots\text{BBN-H-9}]^-$, formed through bridging interactions between $[\text{9,9-H}_2\text{BBN}]^-$ and 9-BBN. In fact, trapping experiments with HBMe_2 , a stronger hydride acceptor than 9-BBN, support this notion. Upon addition of HBMe_2 to **7**, both boron signals disappear in favor of two new signals: a triplet at -23 ppm for $[\text{H}_2\text{BMes}_2]^-$ and two broad signals at 13 and 27 ppm (monomer and dimer of 9-BBN) (Figure 4).

Of further note is the thermal behavior of **7**. Heating THF solutions of **7** at 50°C resulted after 1 day in the complete disappearance of monomeric anion $[\text{9,9-H}_2\text{BBN}]^-$ in favor of bridged anion $[\text{9-H-BBN}\cdots\text{H}\cdots\text{BBN-H-9}]^-$, according to the ^{11}B NMR data (Figure S12). The ^{31}P NMR data (Figure S13) revealed the simultaneous formation of **4** approaching a **4** to 4-H^+ ratio of $\sim 1:1$, after 1 day at 50°C . Further heating for 3 days at 50°C did not change the ^{11}B and ^{31}P NMR spectroscopic

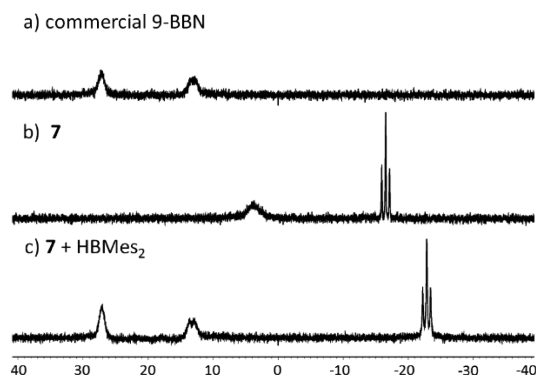
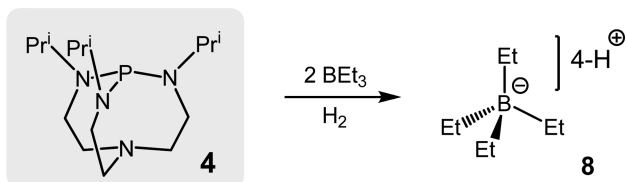


Figure 4. Stack plot of various ^{11}B -NMR spectra in THF at room temperature showing that upon adding HBMe_2 to **7**, the neutral species 9-BBN and the anion $[\text{H}_2\text{BMe}_2]^-$ are formed.

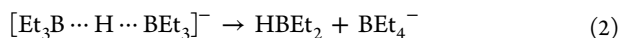
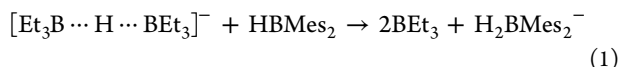
features of the solution, underlining the long-term stability of the salt $[\text{4-H}][\text{9-H-BBN}\cdots\text{H}\cdots\text{BBN-H-9}]^-$.

Surprisingly, when the FLP **4**/ BEt_3 was exposed to H_2 , the hydride-free salt **8** was slowly formed as the major product after a few days at room temperature (Scheme 1); better yields were

Scheme 1. Formation of **8**



achieved when a 2-fold excess of BEt_3 was used. **8** was characterized by multinuclei NMR spectroscopy and the results from X-ray analysis.¹⁶ Its formation can be understood by the intermediate formation of the bridged borohydride $[\text{Et}_3\text{B}\cdots\text{H}\cdots\text{BEt}_3]^-$, which decays into HBEt_2 and $[\text{BEt}_4]^-$ via ethyl transfer (eq 2). In fact, adding HBMe_2 to the reaction mixture after a day generated the anion $[\text{H}_2\text{BMe}_2]^-$ (eq 1), suggesting small quantities of $[\text{Et}_3\text{B}\cdots\text{H}\cdots\text{BEt}_3]^-$ are present and again revealing the ability of the FLP **4**/ BEt_3 to cleave dihydrogen (Figure S17).¹⁷



Finally, 9-Hex-BBN, lower in hydride affinity than 9-BBN and, unlike BEt_3 , reluctant of undergoing alkyl group scrambling, was studied as a Lewis acid component. Indeed, the respective FLP **4**/9-Hex-BBN readily reacted with H_2 (2.5 atm) to furnish a crystalline precipitate identified by NMR spectroscopy as **9** (Figure 5). Note that in the ^{11}B NMR spectrum of **9** instead of the expected doublet at ≈ -13 ppm due to the monomeric anion $[\text{9-Hex-9-H-BBN}]^-$,¹⁸ only one broad signal at ≈ -1 ppm was found (Figure 5). We assign the broad signal to the bridged borohydride anion $[\text{9-Hex-BBN}\cdots\text{H}\cdots\text{BBN-Hex-9}]^-$. That the latter anion contains a hydride is supported by trapping experiments with HBMe_2 , which led to complete disappearance of the broad signal at ≈ -1 ppm in favor of two new signals, a triplet at -23.2 ppm due to the anion $[\text{H}_2\text{BMe}_2]^-$ and a broad signal at ≈ 86 ppm resulting from the formation of 9-Hex-BBN (Figure 5). Regardless of the exact identity of the borohydride

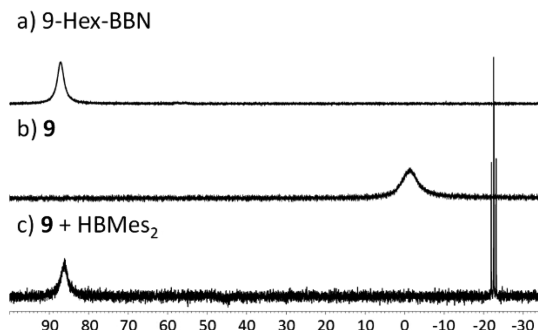
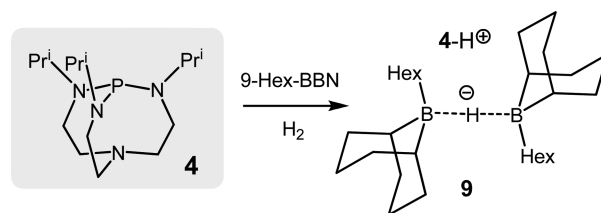


Figure 5. (Top) formation of **9**. (Bottom) Stack plot of various ^{11}B -NMR spectra in THF at room temperature showing that upon adding HBMe_2 to **9**, 9-Hex-BBN and $[\text{H}_2\text{BMe}_2]^-$ are formed.

anion, the trapping experiment confirms the ability of the FLP **4**/9-Hex-BBN to heterolytically cleave H_2 .

Encouraged by the ability of most of our designed “inverse” FLPs to activate H_2 , catalytic hydrogenations using *N*-benzylidenaniline as the model substrate in THF were attempted (Table 2). The FLP’s **2**/ HBMe_2 , **4**/ BEt_3 , and **4**/9-BBN were

Table 2. Catalytic Hydrogenation of *N*-Benzylidenaniline^a

FLP	T ($^\circ\text{C}$)	$p_{(\text{H}_2)}$ (bar)	time (h)	yield ^b (%)
1 / HBMe_2	60	50	16	3
1 / BPh_3	60	50	40	32
1 / BPh_3	80	100	40	>99
4 /9-BBN	60	100	16	7
4 /9-Hex-BBN	25	50	16	10
4 /9-Hex-BBN	60	50	40	>99
4 /9- BEt_3	25	100	16	5
4 /9- BEt_3	60	100	16	11

^aConditions (not optimized): 1.5 mL THF, 6.6 mmol substrate, 0.33 mmol FLP. ^bProducts not isolated; yields determined by ^1H NMR.

found to be inactive even at H_2 pressures of 100 bar and elevated temperatures. The inactivity of **4**/9-BBN is consistent with control experiments that have shown 9-BBN to preferentially react with the substrate to quantitatively generate 9-Bn(Ph)N-BBN (Figure S20). The resulting FLP **4**/9-Bn(Ph)N-BBN did not engage in H_2 -cleavage. This is presumably due to its poor hydride affinity, which is similar if not lower than that of generic 9-NH₂-BBN (Table 1). For the FLPs **1**/ HBMe_2 and **4**/ BEt_3 , similar pathways are assumed to occur leading to largely inactive amino boranes of poor hydride affinity. This is plausible as in both systems hydride-containing boranes either are present (HBMe_2) or generated as a result of alkyl scrambling (HBEt_2).

Much to our delight, the FLPs **1**/ BPh_3 and **4**/9-Hex-BBN at a catalyst loading of 5 mol % showed excellent activity in the hydrogenation of *N*-benzylidenaniline, resulting in the quantitative formation of *N*-benzylaniline. For both FLP systems to be

efficient catalysts, higher temperatures were required consistent with the observation that the release of H₂ from their respective phosphonium borate salts **2** and **9** occurs more rapidly at elevated temperatures.¹⁹

In conclusion, we have demonstrated that structurally simple moderate to weak Lewis acids in combination with commercially available organosuperbases generate “inverse” FLPs, capable of reversibly cleaving H₂. In particular, the ability of 9-Hex-BBN to engage not only in the FLP-mediated cleavage of H₂ but also in the catalytic hydrogenation of *N*-benzylidenaniline is encouraging as the electronic and steric properties of 9-alkyl-substituted BBN derivatives can easily be modified through chemical synthesis. Studies regarding the design and application of these “inverse” FLPs as hydrogenation catalysts along with detailed kinetic and computational investigations to gain mechanistic insight are currently underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b13545.

Experimental details and data (PDF)

Characterization data for **2**, **3**, **5** and **7** (CIF)

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Notes

The authors declare no competing financial interest.

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