

The Synthesis, Properties, and Reactivity of Lewis Acidic Aminoboranes

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Abstract

The evolution of frustrated Lewis pair chemistry has led to significant research into the development of new Lewis acidic boranes. Much of this has focused on modifying aryl substituents rather than introducing heteroatoms bound to boron. We recently reported unique Lewis acidic behaviour from bis(pentafluorophenyl)phenothiazylborane (1) for the heterolytic dehydrocoupling of stannanes. In this work, we synthesize and characterize a family of Lewis acidic aminoboranes and explored their reactivity with various Lewis bases as well as their efficacy as catalysts for stannane dehydrocoupling and hydrosilylation. Quantum chemical calculations were undertaken to understand the origins of the Lewis acidity and the most Lewis acidic aminoborane (5) was found to be an effective catalyst even in coordinating solvents such as water or acetonitrile, suggesting the amino substituent provides a level of protection against competing donors.

Introduction

Tri-coordinate boranes have found diverse applications as Lewis acidic reagents for stoichiometric and catalytic transformations.^{1–4} The advent of frustrated Lewis pair (FLP) chemistry has brought the synthesis of novel Lewis acidic boranes into the spotlight.^{5–7} The steric and electronic properties of tri-coordinate boranes can easily be modified through simple organometallic transformations, opening up a substantial library of available Lewis acids.

Though they are powerful synthetic tools, many electrophilic triarylboranes are inherently sensitive to ambient atmospheric conditions and require strict air- and moisture-free storage and reaction conditions. Heteroatoms, such as nitrogen or oxygen, can be introduced adjacent to the boron centre, however this often leads to a substantial reduction in Lewis acidic character. These heteroatoms can inductively withdraw electron density; however, lone pairs will donate electron density back into the empty p-orbital, increasing the bond order and reducing the Lewis acidity. Nevertheless, pentafluorophenyl esters of borinic, boronic and boronate derivatives have been shown to exhibit Lewis acidity towards harder bases,⁸ though they have not been shown to be effective at activating hydrogen in an FLP fashion.⁹ More recently, Gellrich has shown that a non-innocent pyridonate borane complex can reversibly activate hydrogen, however this is attributed to a change in the coordination mode from an anionic alkoxypyridine donor to a neutral pyridinone ligand.¹⁰

On the other hand, aminoboranes have garnered interest due to their isoelectronic relationship to olefins. Specifically, sterically encumbered aminoboranes have found applications in organic materials as they have unique photochemical properties.^{11–15} In these applications, the steric hinderance required to prevent the aminoborane from oligomerizing and precludes any Lewis acidity (Yamaguchi, Figure 1). However, Erker and co-workers reported the use of pentafluorophenyl substituents on boron to increase the Lewis acidity of aminoboranes, synthesizing (*N*-pyrrolyl)B(C₆F₅)₂ and the saturated (*N*-pyrrolidinyl)B(C₆F₅)₂ analogue (Figure 1).^{16,17} They illustrated that the pyrrolyl derivative proved to be Lewis acidic enough to abstract a methyl group from a zirconocene complex, whereas the saturated pyrrolidinyl aminoborane had limited Lewis acidity due to the greater B=N character. Mitzel and co-

workers explored the behaviour of the electrophilic aminoboranes $(\text{C}_6\text{F}_5)_2\text{BNMe}_2$ and $(\text{CF}_3)_2\text{BNMe}_2$, reporting that the latter will undergo an insertion with diazomethane whereas the pentafluorophenyl derivative was unreactive (Figure 1).¹⁸ We previously reported the synthesis and Lewis acidic behaviour a (*N*-phenothiazyl) $\text{B}(\text{C}_6\text{F}_5)_2$ aminoborane (**1**), that showed unique reactivity as an intramolecular frustrated Lewis pair for the catalytic dehydrocoupling of stannanes.¹⁹

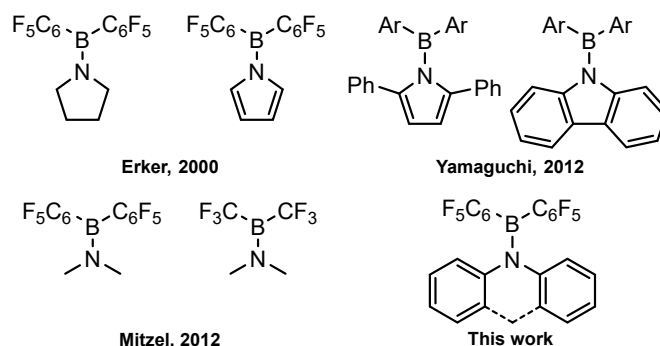


Figure 1 – Examples of sterically encumbered aminoboranes (Ar = Mes, MesF₉).

Given this context, we sought to expand the scope of aminoboranes studied with electron withdrawing pentafluorophenyl substituents and herein examine several aminoboranes containing the $\text{N-B}(\text{C}_6\text{F}_5)_2$ core. We computationally and experimentally investigated their Lewis acidic properties contrasting our finding with the ubiquitous Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$. Further, we explore the role that the neighbouring nitrogen atom plays in tempering the Lewis acidity and investigate if this enhances the stability of these Lewis acids towards donors and exogenous conditions.

Results and Discussion

Synthesis and Characterization

We began by evaluating amines that could provide a comprehensive scope of both steric and electronic properties. As noted above, we previously reported the synthesis of the phenothiazyl aminoborane (**1**) and we further synthesized aminoboranes containing phenoxazine (**2**), diphenylamine (**3**),²⁰ trimethylsilyl (**4**),²¹ carbazole (**5**), and acridane (**6**) motifs (Figure 2). These amines provide a platform to understand the impact that fused ring systems have on the Lewis acidity. Similarly, to the preparation of **1**, these new aminoboranes could be synthesized *via* a salt metathesis reaction, by the addition of the respective sodium amide precursor to $\text{ClB}(\text{C}_6\text{F}_5)_2$, yielding compounds **2** – **6** in moderate to high yields (28 – 91%, Figure 2a).

Curiously, we found alternative synthetic pathways for **5** and **6**. Compound **5** can be easily prepared *via* the dehydrocoupling of $\text{HB}(\text{C}_6\text{F}_5)_2$ with carbazole, resulting in a significantly higher yield and simpler procedure (Figure 2b). To further explore this route, we attempted to facilitate the dehydrocoupling with all the respective amines and $\text{HB}(\text{C}_6\text{F}_5)_2$ in C_6D_6 . Unfortunately, this process was not found to be applicable in the synthesis of **1** – **4** and **6**. In all these cases, no changes were observable by NMR spectroscopy apart from the reaction of $\text{HB}(\text{C}_6\text{F}_5)_2$ with acridane where it was evident a Lewis acid base adduct was formed. We were able to crystallographically characterize the adduct **6H₂** (Figure 3 and ESI, Figures S65-67). Additionally, **6** can be prepared *via* hydride transfer from the addition of $\text{HB}(\text{C}_6\text{F}_5)_2$ to acridine in high yield.

These compounds were fully characterized by multinuclear NMR spectroscopy and showed similar features to that of **1**. The ^1H NMR spectra of **2** – **6** agree with the structures and are otherwise unremarkable. Compound **2** showed a doublet of doublets at 6.83 ppm, and a doublet of triplets at 6.54 ppm as inequivalent resonances that correspond to the eight protons on the phenoxazine motif. Compound **3** showed a doublet at 6.96, a triplet at 6.80, and a multiplet from 6.78-6.71 ppm, which corresponds to the two phenyl substituents. Compound **4** showed a singlet at 0 ppm which corresponds to the two $-\text{SiMe}_3$ groups. Compound **5** showed a doublet 7.99, a triplet at 7.40, a multiplet from 7.27-

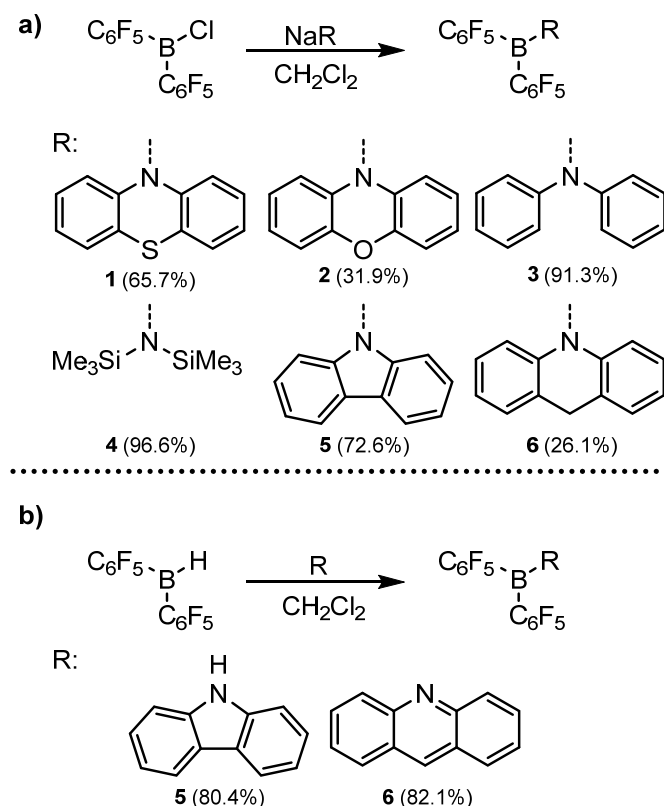


Figure 2 – Synthesis and yields of aminoboranes **1** – **6**.

7.21, and a doublet at 7.00 ppm integrating to the eight protons of the carbazole. Finally, compound **6** showed a doublet at 7.33, a multiplet from 7.21-6.98 for the aromatic protons, and a doublet at 3.92 ppm for the bridgehead CH_2 resonances. The chemical shifts in their respective ^{11}B NMR spectra range from 44.1-37.1 ppm and indicate the pseudo tri-coordinate nature of these species. Most notably the ^{19}F NMR spectra of **2** – **6** support similar degrees of back-donation as indicated by their respective distance between the *para* and *meta* fluorine resonances. These ranged from $\Delta\delta$ 8.81 to 10.64 ppm; further supporting that a degree of B-N double bond character exists in compounds **1** – **6**. Anomalous, the ^{19}F NMR spectrum for compound **6** presents two resonances for each *ortho* and *meta* fluorine atoms at 130.08 & 132.06 ppm and 160.95 & 161.13 ppm. This can be attributed to the steric demand of the acridane functionality restricting the rotation of the C_6F_5 rings.

Crystals suitable for X-ray diffraction were also obtained for **2**, **4**, and **5** (Figure 3) It should be noted the structure of **4** was previously elucidated by Green and co-workers²¹ and our values are in agreement with their reports). These show B–N bond lengths of 1.395(2) Å, 1.402(3) Å, and 1.405(2) Å respectively.

Furthermore, both the boron and nitrogen centres in **2**, **4**, and **5** show trigonal planar geometry with the sum of the bond angles around boron being 359.4 °, 359.9 °, and 360.1 °, and around nitrogen being 359.2 °, 359.9 °, and 359.8 °, respectively. These data compare nicely to previously reported monomeric Lewis acidic aminoboranes with trigonal planar geometries around both boron and nitrogen, as well as B–N bond lengths of ~1.40 Å (*vide supra*).

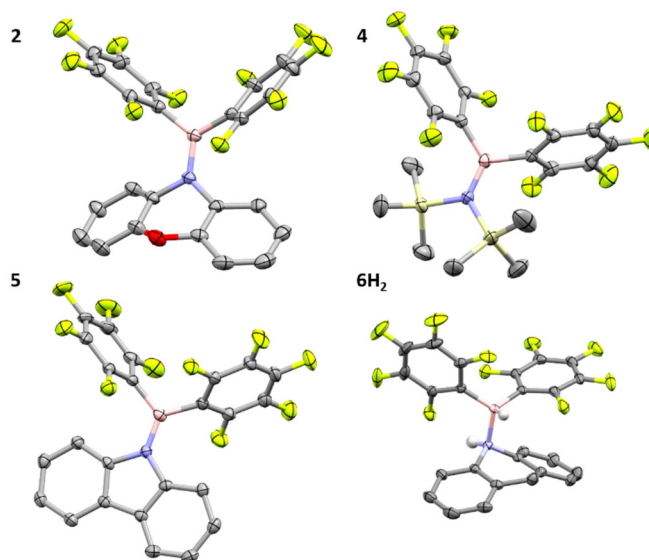


Figure 3 – X-Ray structures of **2**, **4**, **5**, and **6H₂**.

Finally, **6H₂** was found to have two molecules in the unit cell, with substantially longer B–N bond lengths of 1.683(2) Å and 1.665(2) Å. Furthermore, the B and N atoms are tetrahedral in nature, as opposed to trigonal planar, strongly suggesting the ammineborane character of **6H₂**.

Evaluation of the Lewis Acidity of Aminoboranes

We attempted to experimentally assess the Lewis acidity of **1** – **6** using both the Gutmann-Beckett and the Fluorescent Lewis Adduct method.^{20,22–24} Unfortunately both of these methods provided inconclusive results, which we attribute to the steric bulk around the boron as well as the pseudo double bond character of the aminoborane. Therefore, fluoride ion affinity (FIA) calculations were performed to better elucidate the impacts that each amino-substituent has on the Lewis acidity of the boron centre.²⁵ Structures of **1** – **6** were optimized at the PBEh-3c/DEF2-mSVP level of theory.^{26,27} The same method was employed for hessian calculations. There were no imaginary frequencies at the optimized structures. Single point calculations at those structures were done at the PW6B95/DEF2-QZVPP level of theory.^{28,29} Zero-point energy (ZPE) corrections were added to those single point energies to give the final energies of those structures, which were used to calculate FIA's. This selection of methods was inspired by Greb and coworkers,²⁵ whose TMS-isodesmic reaction is used to calculate FIA's here. All calculations in this work except the NBO analyses were performed using the ORCA 4.2 program package.³⁰ The NBO analyses were done using the GAMESS-US and NBO 7.0 packages.³¹ Structurally, the neutral aminoboranes optimized to provide B–N bond lengths of 1.40-1.41 Å (Table 1), which agrees with the experimental crystallographic observations. In all cases, the N atom is planar, and the sum of the angles are ~360°. Such a planar structure may arise from the B=N double bond character and/or the π -interaction between N

and the two aromatic rings connected to it. Natural Bond Orbital (NBO) analysis was performed on all the structures to gauge the level of donation from the N lone pair to the vacant B p_z -orbital.³² The results indicate that all six aminoboranes show similar B–N overlap, ranging from 0.30 – 0.34 electrons being donated from the N lone pair to B (Table 1). Interestingly, the NBO second order perturbation theory analysis indicates a range of energy lowering induced by this donation. In the case of **1**, **2**, **3**, and **6** this stabilization energy ranges from 102 – 113 kcal/mol. However, **4** only has a stabilization energy of 22 kcal/mol which can be attributed to the steric hindrance between the trimethylsilyl and pentafluorophenyl substituents, which twists the B–N bond, increases the dihedral angle between the B and N moieties, and reduces the π -interaction. Aminoborane **5**, bearing a carbazole fragment, proved to have a lower than anticipated stabilization of 85 kcal/mol. Unlike **4**, this can be attributed to the N lone pair being delocalized into the aromatic carbazole ring system. It is important to note that the second order perturbation analysis is of qualitative nature. Those overestimated energies reflect the relative, but not absolute strengths of the BN π bonds. Overall, the BN π interactions are weak (~ 0.3 e donation) and the two smaller donations of **4** and **5** are consistent with their less NBO-estimated BN π interaction energies than the others.

The relative Lewis acidities of **1–6** were estimated by the calculated FIA's: -385 (**1**), -389 (**2**), -360 (**3**), -353 (**4**), -413 (**5**), and -381 (**6**) kJ/mol (Table 1). Comparatively, $B(C_6F_5)_3$ has a reported FIA of 448 kJ/mol.²⁵ Comparing such a large range of FIA's and the overall small N \rightarrow B π donations and the similar BN bond lengths, we see that the different Lewis acidities of the B centres do not directly arise from the BN π interactions. Instead, the acidities are related to the variations of the aromaticities of the groups that are connected to N. The Nucleus-Independent Chemical Shifts (NICS(1)_{zz}) calculations were undertaken for those π cyclic groups.³³ These results are summarized in Figure 4, a blue colouration indicates that a ring becomes more aromatic upon binding a fluoride anion and a red colouration indicates reduced aromaticity. Upon bonding a F^- to B, the N lone pair must be completely pushed back from the BN π bond and get more delocalized into the π groups attached to N. We temporarily leave **4** aside since it has no π groups attached to N. In **3**• F^- , one of the phenyl rings rotate to be coplanar with the N $2p_\pi$ and bears all the destabilization arising from its conjugation with the N lone pair. Such a rotation also leads to steric hindrance between the two phenyls. These two factors result in a lower FIA. **1**, **2**, and **6** are similar, as the ligands attached to N cannot rotate about their CN bonds. The destabilization due to conjugating with the N lone pair is hence attenuated in the two 6-membered side rings. There is no steric hindrance between the side rings induced by the push-back. The three compounds hence share similar FIA's, which are larger than that of **3**. In **5**• F^- , the N lone pair is pushed to a triple-ring 14 electron π system. The number of electrons is consistent with the $4n+2$ Hückel's rule, and the system is aromatic, highlighted by the blue colour across all three rings. The enhancement of aromaticity is most significant in the central ring that contains N, with its NICS(1)_{zz} changing from -11 to -24 in the F^- adduction. This enhancement of aromaticity explains the largest FIA of **5**. This result is reminiscent of the allene derived carbon Lewis acids reported by Alcarazo and co-workers,³⁴ which showed fluorene-substituted allenes can delocalize negative charge into the rings, increasing the partial positive character of the allenyl carbon. This observation could also help to understand the aforementioned dichotomic Lewis acidity of (*N*-pyrrolyl) $B(C_6F_5)_2$ and the saturated (*N*-pyrrolidinyl) $B(C_6F_5)_2$, given that the aromatic amine generates a Lewis acidic aminoborane, whereas the saturated one shows limited Lewis acidic behaviour.¹⁶ Without any π system attached to N to stabilize its pushed-back lone pair, **4** features a low FIA.

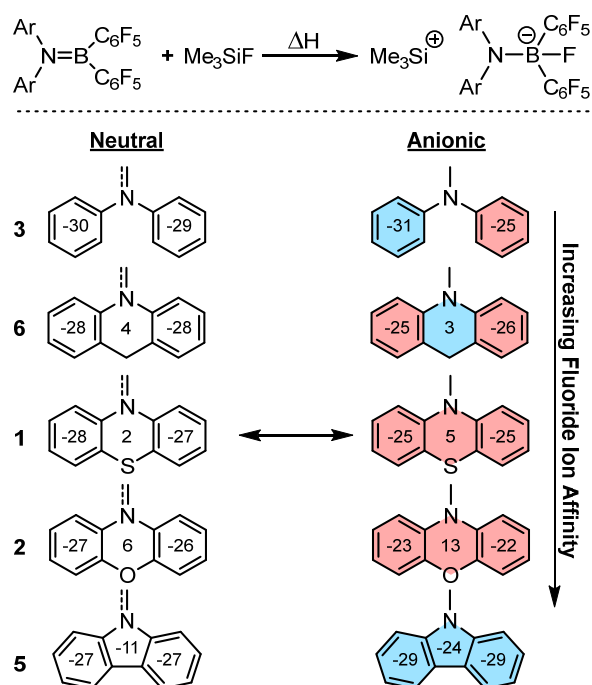


Figure 4 – Top: Computed Reaction for FIA values; Bottom: NICS values for the neutral and fluoride bound aminoboranes.

Table 1 – Computational results for **1-6**

	1	2	3	4	5	6
B–N (Å)	1.40	1.40	1.40	1.40	1.41	1.40
N lp → B p _z Donation (e)	0.34	0.34	0.35	0.31	0.30	0.34
N lp → B p _z Donation Energy (kcal/mol)	-107	-106	-102	-22	-85	-113
FIA (kJ/mol)	-385	-389	-360	-353	-413	-381

¹ Estimated at the level of NBO 2nd order perturbation theory.

Behaviour of Aminoboranes as Lewis Acids

The calculations predict that these aminoboranes will have varying degrees of Lewis acidity and with these data in hand, we sought to understand how these molecules behave. We began by exploring reactivity with exogenous Lewis bases as it is generally understood that Lewis acids have poor tolerance for donor solvents and various functional groups. This often narrows substrate scopes when they are applied as catalysis. Contrary to conventional Lewis acids, these Lewis acidic aminoboranes appear more tolerant of donor solvent. Exposure of aminoboranes **1-4** and **6** to acetonitrile did not appear to show any changes in the multinuclear NMR spectra, indicating that adduct formation is not favourable at room temperature. However, the more Lewis acidic **5** appears to form an adduct with acetonitrile when dissolved in CD₃CN as observed in the ¹¹B NMR spectrum with a sharper upfield resonance at -3.2 ppm (ESI, Figure S50).

Increasing the Lewis base donor abilities, we explored the reactivity of the aminoboranes with 4-dimethylaminopyridine (DMAP). However, again only **5** formed an isolable adduct (**7**), which supports the FIA calculations that it has the greatest Lewis acidity. The evidence for adduct formation was clear by multinuclear NMR analysis, the ^{11}B NMR spectrum has a resonance at δ : -0.60 ppm, indicating a tetracoordinate boron centre. Further, this is supported by the ^{19}F NMR spectrum, with resonances at δ : -130.38, -156.62 and -162.95 ppm. Crystals suitable for X-ray diffraction were grown from a concentrated benzene solution (Figure 5). The B–N bond length for the carbazole substituent was found to be 1.548(3) Å, which is significantly longer than the neutral species (1.405(2) Å) and consistent with the 1.55 Å of **5**•F $^-$ obtained in calculation, indicating that the nitrogen lone pair is no longer being donated to the boron centre. The B–N bond length between the aminoborane and DMAP was found to be slightly longer at 1.607(4) Å, supporting the dative bond formation.

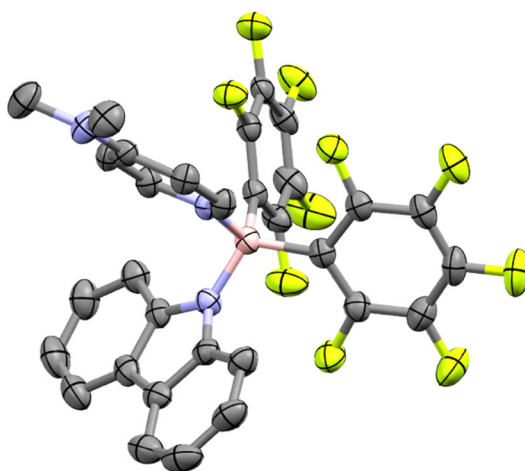


Figure 5 – Solid state structure of the adduct **7**. B: pink, C: grey, F: yellow-green, N: blue. H-atoms omitted for clarity.

As noted above, the adduct of $\text{HB}(\text{C}_6\text{F}_5)_2$ and acridane (**6H₂**) could be synthesized, however **6** could not be generated from this product via H_2 loss, even when heated. The fact that only **5** could be successfully prepared *via* a dehydrocoupling approach led us to explore if **5** could reversibly activate H_2 in an intramolecular FLP fashion. Exposure of **5** to an atmosphere of H_2 in a J-Young NMR tube produced new resonances in the ^{19}F NMR spectrum, indicating a 4-coordinate boron species (ESI Figures S52-54). However, this was a minor product, and most of the starting material stays intact. Isolation of this product was not successful as once the H_2 was released from the system, the only observable product was **5**. Nevertheless, this indicates that this aminoborane may be able to activate H_2 , unfortunately utilizing **5** as a hydrogenation catalyst was unsuccessful.

We previously reported that **1** was able to catalyze the dehydrocoupling of stannanes.¹⁹ This was unexpected because it was the first time an intramolecular FLP was shown to heterolytically facilitate this reaction (there has been subsequent work illuminating the heterolytic nature of this transformation).³⁵ To further understand this reaction, we explored the ability of **2** – **6** to act as catalysts for the dehydrocoupling of Ph_3SnH under similar conditions to our prior report (5 mol %, 50 °C in C_6D_6). Only **2** promoted this reaction to an appreciable extent as evidenced by the increase in the $\text{Ph}_3\text{SnSnPh}_3$ resonance at δ : -141 ppm in the ^{119}Sn NMR spectrum (Figure S28). These results make sense given the structural and

electronic similarities between phenothiazine and phenoxazine. Trace dehydrocoupled product could be observed when **6** is used as a catalyst, however this does not proceed in appreciable yields.

The FIA calculations indicate that the aminoboranes **1-6** are somewhat electrophilic (*vide supra*). To experimentally verify these values, we explored the ability of these Lewis acids to catalyze the hydrosilylation of acetophenone at 5 mol % catalyst loading. We monitored these reactions via ^1H NMR spectroscopy for up to 6 hours, however it was observed that most of these reductions were complete within 1 hour (ESI Figures S41-46). Predictably, aminoborane **4**, which bears a bis(trimethylsilylamido) functionality, was unable to facilitate this reaction given the steric constraints of the trimethylsilyl substituents. These results speak to the ability of the aminoboranes to act as Lewis acid catalysts. Excitingly, we were able to perform this same hydrosilylation reaction with **5** (5 mol%) in CD_3CN at room temperature to complete conversion in under 6 hrs (ESI Figure S49-51). The ^{11}B and ^{19}F NMR spectra indicate that some catalyst decomposition occurs, however at the end of the reaction some catalyst remains. This reaction would not be possible with the more electrophilic Lewis acid, $\text{B}(\text{C}_6\text{F}_5)_3$, and supports our hypothesis that the lone pair donation from the amino substituent provides additional stability to the Lewis acidic boron centre. This finding is reminiscent of work by Ingleson where they report that weakly Lewis acidic boranes can facilitate FLP reductions in wet solvents.³⁶

Finally, to further explore the hypothesis that the $\text{B}=\text{N}$ double bond provides a level of “protection” to the Lewis acidic borane, we computationally explored the sensitivity of **5**, the most Lewis acidic aminoborane, with water. Structural optimizations, hessian, and energy calculations were all performed at the CAM-B3LYP/def2-QZVPP/D3/CPCM(Toluene)) level and there is no imaginary frequency.³⁷⁻³⁹ The subsequent NBO analysis was performed at the CAM-B3LYP/cc-pVTZ level. **5**• H_2O has its $\text{rBO} = 1.64 \text{ \AA}$, larger than the typical 1.34 \AA covalent bond length. For the **5**• H_2O adduct, the NBO analysis assigned a Lewis structure with a coordinate bond between the O lone pair and the B vacant orbital, which features a $s^{0.11}p^{0.89}$ hybridization. The second order perturbation theory analysis indicates a 201 kcal/mol large interaction. Although it is well known that the perturbation theory overestimates interactions between orbitals, such a large magnitude clearly points to a coordinate (dative) bond. The occupancies of the B vacant and the O lone pair orbitals are 0.35 and 1.71 e, respectively. The occupancy of the B vacant orbital does not solely arise from the O lone pair. The perturbation analysis shows that the N lone pair also interacts with the B vacant orbital, with a 23 kcal/mol magnitude. Note that the B and N moieties has been distorted to nonplanar by the H_2O attachment to B, with a 43 degrees dihedral angle. The N-to-B π donation is hence largely reduced. Overall, the DFT calculation showed that the H_2O -addition is favorably by 5.0 kcal/mol energy with ZPE correction. We need to emphasize again the overestimation nature of the perturbation theory analysis. The 5.0 kcal/mol here does not contradict the 201 kcal/mol mentioned above, as they are obtained with respect to different references. The orbitals discussed above can be seen in Figure S66 in the ESI.

These computations were supported by experimental evidence, **5** was dissolved in “wet” CDCl_3 and left for 7 days in solution, as well as a solid sample of **5** was left out on the bench for a week, exposing it to atmospheric conditions. In both cases, a weak water adduct was observed in the ^1H , ^{11}B , and ^{19}F NMR spectra, however the change in the ^{11}B chemical shift from the parent species to the water adduct was less than 1 ppm (40.5 ppm vs 39.9 ppm, see ESI Figure S58 – S60). Similar observations can be seen in the ^{19}F NMR spectrum, supporting that the H_2O adduct is quite weak, consistent with the calculated 1.63 \AA long BO bond and 5.0 kcal/mol low adduction energy. Encouragingly though, decomposition of the aminoborane is not observed. Furthermore, addition of acetophenone and triethylsilane to a wet solution

of **5** in CDCl₃ (5 mol%) led to the near complete reduction (~89% conversion) of the acetophenone after 48h at 60 °C (ESI Figures S47-48). Similarly, to the MeCN example, some catalyst decomposition occurred, however, these results are nevertheless encouraging with respect to aminoborane Lewis acidic capabilities.

Conclusions

In conclusion, we synthesized a series of aminoboranes that exhibit Lewis acidic properties. Fluoride Ion Affinity calculation indicated that the Lewis acidity of these aminoboranes could not be correlated to B-N bond length, but instead the resulting aromaticity of the N-contained/connected rings. As catalysts, all the tested aminoboranes showed efficacy towards the hydrosilylation of acetophenone, but only **2** proved to be effective at the dehydrocoupling of stannanes – owing to the similarity of phenoxazine to phenothiazine. Finally, the carbazole substituted aminoborane **5** was shown to effect catalytic transformations even in the presence of donors. This unexpected behaviour could open the doors to new, more bench stable Lewis acids for frustrated Lewis pair transformations. We have begun investigating this exciting prospect and will report our findings in due course.

Author Contributions

J.N.B., S.S., and E.P. were responsible for data collection. C.B.C., and T.Z. were responsibly for supervision. J.N.B., S.S., E.P., T.Z., and C.B.C. were responsible for writing, reviewing, and editing the manuscript.

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Notes and References

Note, stannanes are toxic and care should be taken when working with them, including careful disposal of waste. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers CCDC: 2068070, 2068071, 2068072, 2068074, 2068077.

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