Organic & Biomolecular Chemistry

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Cite this: *Org. Biomol. Chem.*, 2021, **19**, 4796

The synthesis, properties, and reactivity of Lewis acidic aminoboranes†

Jordan N. Bentley, Selvyn A. Simoes, Ekadashi Pradhan, Tao Zeng and Christopher B. Caputo *

Received 17th March 2021,
Accepted 4th May 2021

DOI: 10.1039/d1ob00520k

rsc.li/obc

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 that bis(pentafluorophenyl)phenothiazylborane (**1**) could be used as a Lewis acid catalyst 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 application 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 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 sensitive to ambient atmospheric conditions and require strict air- and moisture-free storage and reaction conditions. Heteroatoms, such as oxygen or nitrogen, 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; though their lone pairs can donate electron density back into the empty p-orbital, increasing the bond order and reducing the Lewis acidity. From an FLP perspective, pentafluorophenyl esters of borinic, boronic and boronate derivatives have been shown to exhibit Lewis acidity towards harder bases,[8] however they show limited efficacy in hydrogen activation.[9] Nevertheless, Gellrich was able to overcome this through the use of a non-innocent pyridonate borane complex to reversibly activate hydrogen.[10] This was attributed to a change in the coordination mode from an anionic alkoxypyridine donor to a neutral pyridinone ligand.[10]

Aminoboranes have also garnered interest due to their isoelectronic relationship to olefins.[11] Specifically, sterically encumbered aminoboranes have found applications in organic materials as they have interesting photochemical properties.[12–16] In these applications, the steric hinderance prevents the aminoborane from oligomerizing and precludes any Lewis acidity (Yamaguchi, Fig. 1). However, Erker and coworkers reported the use of pentafluorophenyl substituents on boron to increase the Lewis acidity of aminoboranes, synthesizing (*N*-pyrrolyl)B(C_6F_5)$_2$ and the saturated (*N*-pyrrolidinyl)B

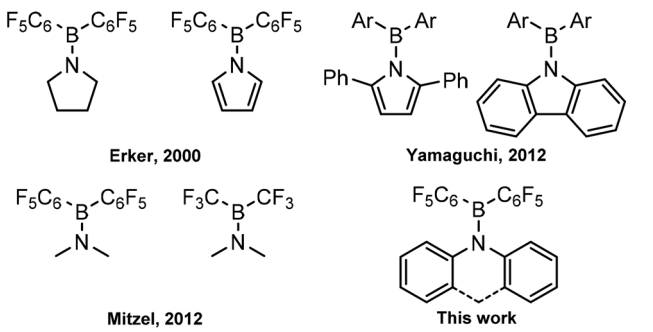

Fig. 1 Examples of sterically encumbered aminoboranes (Ar = Mes, $MesF_9$).

York University, Department of Chemistry, 4700 Keele St., Toronto, ON, Canada, M3J 1P3. E-mail: caputo@yorku.ca

†Electronic supplementary information (ESI) available: Stannanes are toxic and care should be taken when working with them, including careful disposal of waste. CCDC 2068070–2068072, 2068074 and 2068077. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1ob00520k

$(C_6F_5)_2$ analogue (Fig. 1).[17,18] 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 $(C_6F_5)_2BNMe_2$ and $(CF_3)_2BNMe_2$, reporting that the latter will undergo an insertion with diazomethane whereas the pentafluorophenyl derivative was unreactive (Fig. 1).[19]

We previously reported the synthesis and Lewis acidic behaviour of (*N*-phenothiazyl)$B(C_6F_5)_2$ aminoborane (**1**), that demonstrated unique reactivity as an intramolecular frustrated Lewis pair for the catalytic dehydrocoupling of stannanes.[20]

Given this context, we sought to expand the scope of aminoboranes studied with electron withdrawing pentafluorophenyl substituents and herein examine several aminoboranes containing the N–$B(C_6F_5)_2$ core. We computationally and experimentally investigated their Lewis acidic properties contrasting our finding with the ubiquitous Lewis acid $B(C_6F_5)_3$. 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.

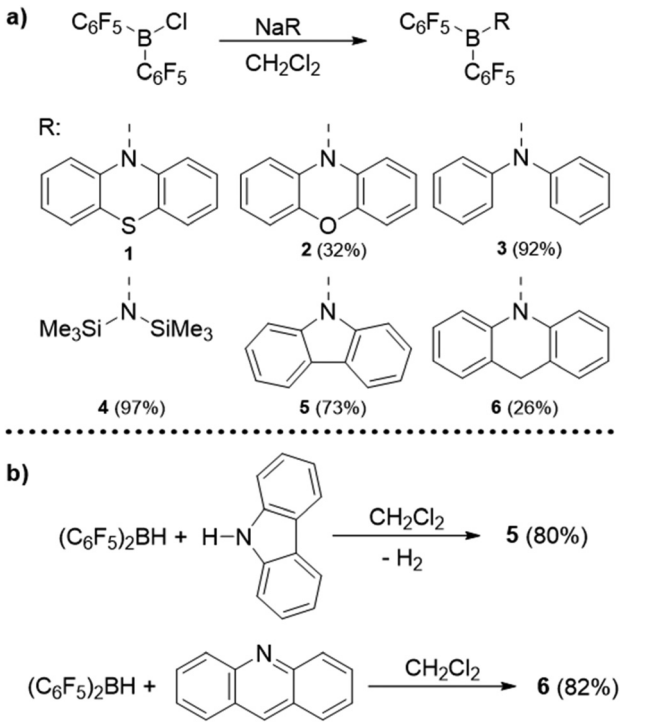

Fig. 2 (a) Synthesis and yields of aminoboranes **1–6** *via* salt metathesis. (b) Synthesis of **5** and **6** using $HB(C_6F_5)_2$.

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**)[20] and we further synthesized aminoboranes containing phenoxazine (**2**), diphenylamine (**3**),[21] trimethylsilyl (**4**),[22] carbazole (**5**), and acridane (**6**) motifs (Fig. 2). These amines provide a platform to understand the impact that fused ring systems have on the Lewis acidity. Similar to the preparation of **1**, these new aminoboranes could be synthesized *via* salt metathesis, with the addition of the respective sodium amide precursor to $ClB(C_6F_5)_2$, yielding compounds **2–6** in moderate to high yields (26–97%, Fig. 2a).

We have also developed alternative synthetic pathways for **5** and **6** utilizing $HB(C_6F_5)_2$. Where compound **5** can be prepared *via* the dehydrocoupling of $HB(C_6F_5)_2$ with carbazole and **6** can be prepared *via* hydride transfer from the addition of HB $(C_6F_5)_2$ to acridine, resulting in a significantly higher yield (Fig. 2b). To further explore this synthetic route, we attempted to facilitate the dehydrocoupling with all the respective amines and $HB(C_6F_5)_2$ in C_6D_6. Unfortunately, this process was not found to be applicable in the synthesis of **1–4** or **6**. In all these cases, no changes were observable by NMR spectroscopy apart from the reaction of $HB(C_6F_5)_2$ with acridane where it was evident that a Lewis acid base adduct was formed. We were able to crystallographically characterize the adduct $\mathbf{6H_2}$ (Fig. 3 and ESI, Fig. S65, S67†). All compounds synthesized were fully characterized by multinuclear NMR spectroscopy and showed similar features to that of **1**, as reported in our earlier work.

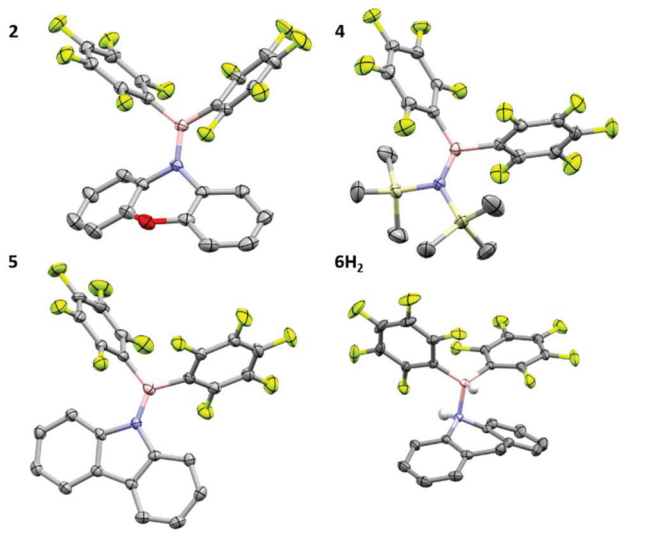

Fig. 3 Solid state structure of the adduct **2**, **4**, **5** and $\mathbf{6H_2}$. B: pink, C: grey, F: yellow-green, N: blue. H-atoms omitted for clarity with the exception of $\mathbf{6H_2}$.

The ^{1}H 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 –$SiMe_3$ groups. Compound **5** showed a doublet 7.99, a triplet at 7.40, a multiplet from 7.27–7.21, and a doublet at 7.00 ppm integrating to the eight protons of the carbazole. Finally, compound **6** showed a doublet at 7.33 and 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 B═N bond character as indicated by their respective distance between the *para* and *meta* fluorine resonances as these ranged from $\Delta\delta_{pm}$ 8.81 to 10.64 ppm, indicating a pseudo 4-coordinate environment around the boron centre.[23,24] Anomalously, 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. The appearance of these additional resonances can be attributed to the steric demand of the acridane functionality restricting the rotation of the C_6F_5 rings.[25]

Crystals suitable for X-ray diffraction were also obtained for **2**, **4**, and **5** (Fig. 3) It should be noted the structure of **4** was previously elucidated by Green and co-workers[22] 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*).

Finally, **$6H_2$** 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 **$6H_2$**.

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.[21,26–28] 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.[29] Structures of **1–6** were optimized at the PBEh-3c/DEF2-mSVP level of theory.[30,31] 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.[32,33] 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 co-workers,[29] whose TMS-isodesmic reaction is used to calculate FIA's here. All calculations in this work except the Natural Bond Orbital (NBO) analyses were performed using the ORCA 4.2 program package.[34] The NBO analyses were done using the GAMESS-US and NBO 7.0 packages.[35] 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. NBO analysis was performed on all structures to gauge the level of donation from the N lone pair to the vacant B p_z-orbital.[36] 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^{-1}. However, **4** only has a stabilization energy of 22 kcal mol^{-1} which can be attributed to the steric hindrance between the trimethylsilyl and pentafluorophenyl substituents, which twists the B–N bond, increasing 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^{-1}. 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 a 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^{-1} (Table 1). Comparatively, $B(C_6F_5)_3$ has a reported FIA of −448 kJ mol^{-1}.[29] Such a wide range of FIA's was unexpected given the small range of N→B π donations and the similar BN bond lengths. This indicates 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 aro-

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
B–N dihedral angle (°)	8	13	10	29	23	8
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[a] (kcal mol^{-1})	−107	−106	−102	−22	−85	−113
FIA (kJ mol^{-1})	−385	−389	−360	−353	−413	−381

[a] Estimated at the level of NBO 2nd order perturbation theory.

maticities of the groups that are connected to N. The Nucleus-Independent Chemical Shifts ($NICS(1)_{zz}$) calculations were performed for those π cyclic groups,[37] and the results are summarized in Fig. 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^-, a phenyl ring rotates to be coplanar with the N $2p_\pi$ and bears all of the destabilization from 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 thus show similar FIA's, which are greater 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 ppm upon 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,[38] which showed fluorene-substituted allenes can delocalize negative charge into the rings, increasing the partial positive character of the allenyl carbon. This observation is in line with 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.[17] Without any π system attached to N to stabilize its pushed-back lone pair, **4** features a low FIA.

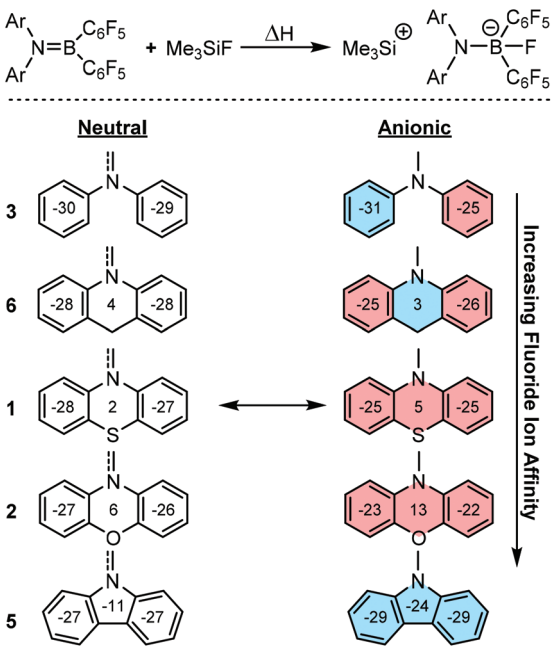

Fig. 4 Top: Computed reaction for FIA values; bottom: NICS values for the neutral and fluoride bound aminoboranes (in ppm).

Behaviour of aminoboranes as Lewis acids

The calculations predict that these aminoboranes will have varying degrees of Lewis acidity thus, we began exploring reactivity with exogenous Lewis bases as it is generally understood that Lewis acids have poor tolerance for donor solvents and Lewis basic functional groups. This reactivity often narrows substrate scopes when they are applied as catalysts. Contrary to conventional Lewis acids, these Lewis acidic aminoboranes appear more tolerant of donor solvents. 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 CD_3CN as observed in the ^{11}B NMR spectrum with a sharper upfield resonance at −3.2 ppm (ESI, Fig. 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 is 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 (Fig. 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

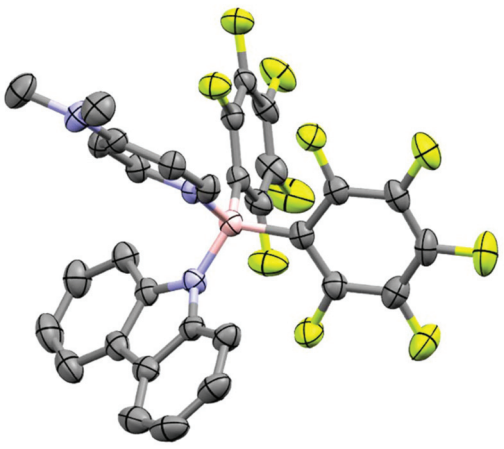

Fig. 5 Solid state structure of the adduct **7**. B: pink, C: grey, F: yellow-green, N: blue. H-atoms omitted for clarity.

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.

As noted above, the adduct of $HB(C_6F)_2$ and acridane (**6H$_2$**) 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 the formation of a 4-coordinate boron species (ESI Fig. S52–S54†). However, this was a minor product, and most of the starting material remained 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 suggests that this aminoborane may be able to reversibly activate H_2. Attempts to utilize **5** as a hydrogenation catalyst were thus far unsuccessful.

We previously reported that **1** was able to catalyze the dehydrocoupling of stannanes.[20] 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).[39] 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 $Ph_3SnSnPh_3$ resonance at δ: −141 ppm in the ^{119}Sn NMR spectrum (Fig. 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 reaction 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.[40] We monitored these reactions *via* ^{1}H NMR spectroscopy for up to 6 hours, however it was observed that most of these reductions proceeded to >90% conversion within 1 hour (ESI Fig. S41–S46†). 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 resulting in near complete conversion in under 6 h (ESI Fig. S49–S51†). 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, $B(C_6F_5)_3$, 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.[41]

Finally, to further explore the hypothesis that the B=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.[42–44] The subsequent NBO analysis was performed at the CAM-B3LYP/cc-pVTZ level. **5**·H_2O has its rBO = 1.64 Å, larger than the typical 1.34 Å 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^{-1} 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^{-1} 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 favorable by −5.0 kcal mol^{-1} energy with ZPE correction. Though we emphasize, again, the overestimating nature of the perturbation theory analysis. The 5.0 kcal mol^{-1} here does not contradict the 201 kcal mol^{-1} mentioned above, as they are obtained with respect to different references. The orbitals discussed above can be seen in Fig. S66 in the ESI.†

These computations were supported by experimental evidence, **5** was dissolved in undried $CDCl_3$ and left for 7 days in solution open to ambient atmosphere, as well as a solid sample of **5** that was also left out on the bench. In both cases, an apparent weak water adduct was observed in the ^{1}H, ^{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 Fig. 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 Å long BO bond and relative −5.0 kcal mol^{-1} energy of the adduct. Encouragingly, decomposition of the aminoborane was not observed. Furthermore, addition of acetophenone and triethylsilane to a solution of **5**·H_2O in $CDCl_3$ (5 mol%) led to the near complete reduction (~89% conversion) of the acetophenone after 48 h at 60 °C (ESI Fig. S47 and S48†). Similar to the reaction done in CD_3CN, some catalyst decomposition occurred, nevertheless, these results are encouraging with respect to aminoborane Lewis acidic capabilities.

Conclusions

We demonstrate the synthesis, characterization of Lewis acidic aminoboranes. Through analysis of the Fluoride Ion Affinity we surmised that the Lewis acidity of these aminoboranes is not immediately related to B–N bond length, but instead the resulting change in aromaticity of the N-contained rings upon adduct formation. All of the tested aminoboranes, with the exception of **4**, showed catalytic activity in the hydrosilylation of acetophenone, though only **2** proved effective in 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 Lewis basic donors and donor solvents. This activity, despite the presence of water and donor solvent could open the doors to new, kinetically 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.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are grateful to York University, the Natural Sciences and Engineering Research Council of Canada, the Canada Foundation for Innovation, and the Canada Research Chairs program.

Notes and references

1 J. W. B. Fyfe and A. J. B. Watson, *Chem*, 2017, **3**, 31–55.
2 A. Dasgupta, R. Babaahmadi, B. Slater, B. F. Yates, A. Ariafard and R. L. Melen, *Chem*, 2020, **6**, 2364–2381.
3 H. C. Brown, K. W. Kim, M. Srebnik and S. Bakthan, *Tetrahedron*, 1987, **43**, 4071–4078.
4 Y. Soltani, L. C. Wilkins and R. L. Melen, *Angew. Chem., Int. Ed.*, 2017, **56**, 11995–11999.
5 W. Meng, X. Feng and H. Du, *Acc. Chem. Res.*, 2018, **51**, 191–201.
6 D. W. Stephan, *Science*, 2016, **354**, aaf7229.
7 J. R. Lawson and R. L. Melen, *Inorg. Chem.*, 2017, **56**, 8627–8643.
8 G. J. P. Britovsek, J. Ugolotti and A. J. P. White, *Organometallics*, 2005, **24**, 1685–1691.
9 R. C. Neu, E. Y. Ouyang, S. J. Geier, X. Zhao, A. Ramos and D. W. Stephan, *Dalton Trans.*, 2010, **39**, 4285–4294.
10 U. Gellrich, *Angew. Chem., Int. Ed.*, 2018, **57**, 4779–4782.
11 A. J. V. Marwitz, M. H. Matus, L. N. Zakharov, D. A. Dixon and S.-Y. Liu, *Angew. Chem., Int. Ed.*, 2009, **48**, 973–977.
12 M. E. Glogowski, P. J. Grisdale, J. L. R. Williams and L. Costa, *J. Organomet. Chem.*, 1974, **74**, 175–183.
13 J. Wang, Y. Wang, T. Taniguchi, S. Yamaguchi and S. Irle, *J. Phys. Chem. A*, 2012, **116**, 1151–1158.
14 T. Taniguchi, J. Wang, S. Irle and S. Yamaguchi, *Dalton Trans.*, 2013, **42**, 620–624.
15 N. M. D. Brown, F. Davidson and J. W. Wilson, *J. Organomet. Chem.*, 1980, **192**, 133–138.
16 C. Arivazhagan, A. Maity, K. Bakthavachalam, A. Jana, S. K. Panigrahi, E. Suresh, A. Das and S. Ghosh, *Chem. – Eur. J.*, 2017, **23**, 7046–7051.
17 G. Kehr, R. Fröhlich, B. Wibbeling and G. Erker, *Chem. – Eur. J.*, 2000, **6**, 258–266.
18 J. W. Strauch, J. L. Fauré, S. Bredeau, C. Wang, G. Kehr, R. Fröhlich, H. Luftmann and G. Erker, *J. Am. Chem. Soc.*, 2004, **126**, 2089–2104.
19 D. Winkelhaus, Y. V. Vishnevskiy, R. J. F. Berger, H.-G. Stammler, B. Neumann and N. W. Mitzel, *Z. Anorg. Allg. Chem.*, 2013, **639**, 2086–2095.
20 J. N. Bentley, E. Pradhan, T. Zeng and C. B. Caputo, *Dalton Trans.*, 2020, **49**, 16054–16058.
21 J. N. Bentley, S. A. Elgadi, J. R. Gaffen, P. Demay-Drouhard, T. Baumgartner and C. B. Caputo, *Organometallics*, 2020, **39**, 3645–3655.
22 J. R. Galsworthy, M. L. H. Green, V. C. Williams and A. N. Chernega, *Polyhedron*, 1998, **17**, 119–124.
23 A. G. Massey and A. J. Park, *J. Organomet. Chem.*, 1966, **5**, 218–225.
24 M. G. Hogben and W. A. G. Graham, *J. Am. Chem. Soc.*, 1969, **91**, 283–291.
25 F. Blank, H. Scherer, J. Ruiz, V. Rodríguez and C. Janiak, *Dalton Trans.*, 2010, **39**, 3609–3619.
26 U. Mayer, V. Gutmann and W. Gerger, *Monatsh. Chem.*, 1975, **106**, 1235–1257.
27 M. A. Beckett, G. C. Strickland, J. R. Holland and K. S. Varma, *Polymer*, 1996, **37**, 4629–4631.
28 J. R. Gaffen, J. N. Bentley, L. C. Torres, C. Chu, T. Baumgartner and C. B. Caputo, *Chem*, 2019, **5**, 1567–1583.
29 P. Erdmann, J. Leitner, J. Schwarz and L. Greb, *ChemPhysChem*, 2020, **21**, 987–994.
30 S. Grimme, J. G. Brandenburg, C. Bannwarth and A. Hansen, *J. Chem. Phys.*, 2015, **143**, 054107.
31 R. Sure, J. G. Brandenburg and S. Grimme, *ChemistryOpen*, 2016, **5**, 94–109.
32 Y. Zhao and D. G. Truhlar, *J. Phys. Chem. A*, 2005, **109**, 5656–5667.
33 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.
34 F. Neese, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2018, **8**, 4–9.

35 E. D. Glendening, C. R. Landis and F. Weinhold, *J. Comput. Chem.*, 2019, **40**, 2234–2241.
36 A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899–926.
37 Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta and P. von Ragué Schleyer, *Chem. Rev.*, 2005, **105**, 3842–3888.
38 B. Inés, S. Holle, R. Goddard and M. Alcarazo, *Angew. Chem., Int. Ed.*, 2010, **49**, 8389–8391.
39 F. Holtrop, A. R. Jupp, B. J. Kooij, N. P. Leest, B. Bruin and J. C. Slootweg, *Angew. Chem., Int. Ed.*, 2020, **59**, 22210–22216.
40 D. J. Parks and W. E. Piers, *J. Am. Chem. Soc.*, 1996, **118**, 9440–9441.
41 V. Fasano and M. J. Ingleson, *Chem. – Eur. J.*, 2017, **23**, 2217–2224.
42 T. Yanai, D. P. Tew and N. C. Handy, *Chem. Phys. Lett.*, 2004, **393**, 51–57.
43 S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456–1465.
44 J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999–3094.