EurJIC
European Journal of Inorganic Chemistry

Research Article
doi.org/10.1002/ejic.202500104

Chemistry Europe
European Chemical Societies Publishing

www.eurjic.org

Activation of Small Molecules by Readily Accessible Alkylborane-Based Frustrated Lewis Pairs

Arthur Averdunk, Felix Wech, Jonathan Becker, and Urs Gellrich*

Herein, we report that sterically encumbered (thio)imidazolones react with simple aliphatic boranes, such as 9-borabicyclo[3.3.1] nonane (H-*B*-9-BBN) or dicyclohexylborane ($HBCy_2$), at room temperature to form (thio)imidazolonate boranes,which function as intramolecular frustrated lewis pairs (FLPs). Although direct observation of hydrogen activation by these FLPs is not possible, alkene hydroboration occurs when they are reacted with styrene under hydrogen pressure, suggesting that hydrogen activation is kinetically feasible. In addition, these FLPs rapidly activate N—H bonds, as demonstrated by the activation of ammonia and amines under mild conditions. They also cleave the C—H bond of terminal alkynes. Density functional theory (DFT) calculations are used to investigate the thermodynamics and kinetics of hydrogen and ammonia activation by these FLPs.

1. Introduction

Since Stephan and coworkers reported the first metal-free reversible hydrogen activation with phosphinoborane **1** in 2006 (**Scheme 1**a),[1] there has been significant interest in developing frustrated Lewis pairs (FLPs) for small-molecule activation.[2] In particular, FLPs have been extensively investigated for metal-free catalytic hydrogenations.[3,4] Generally, FLPs are sterically hindered Lewis pairs that cannot form a classical Lewis acid–base adduct due to steric repulsion. As a result, the Lewis acidic and basic properties of the FLP components remain unquenched, enabling bond activation and cleavage.[5] Many of the inter- and intramolecular FLPs developed to date combine relatively weak bases, such as aliphatic amines and phosphines, with strongly Lewis acidic boranes, which often contain fluorinated or chlorinated aryl groups. The synthesis of these boranes typically requires considerable synthetic effort.[4,6]

However, experimental and computational studies have shown that weaker Lewis acids can be employed in intra- or intermolecular FLPs if sufficiently strong bases are used.[7]

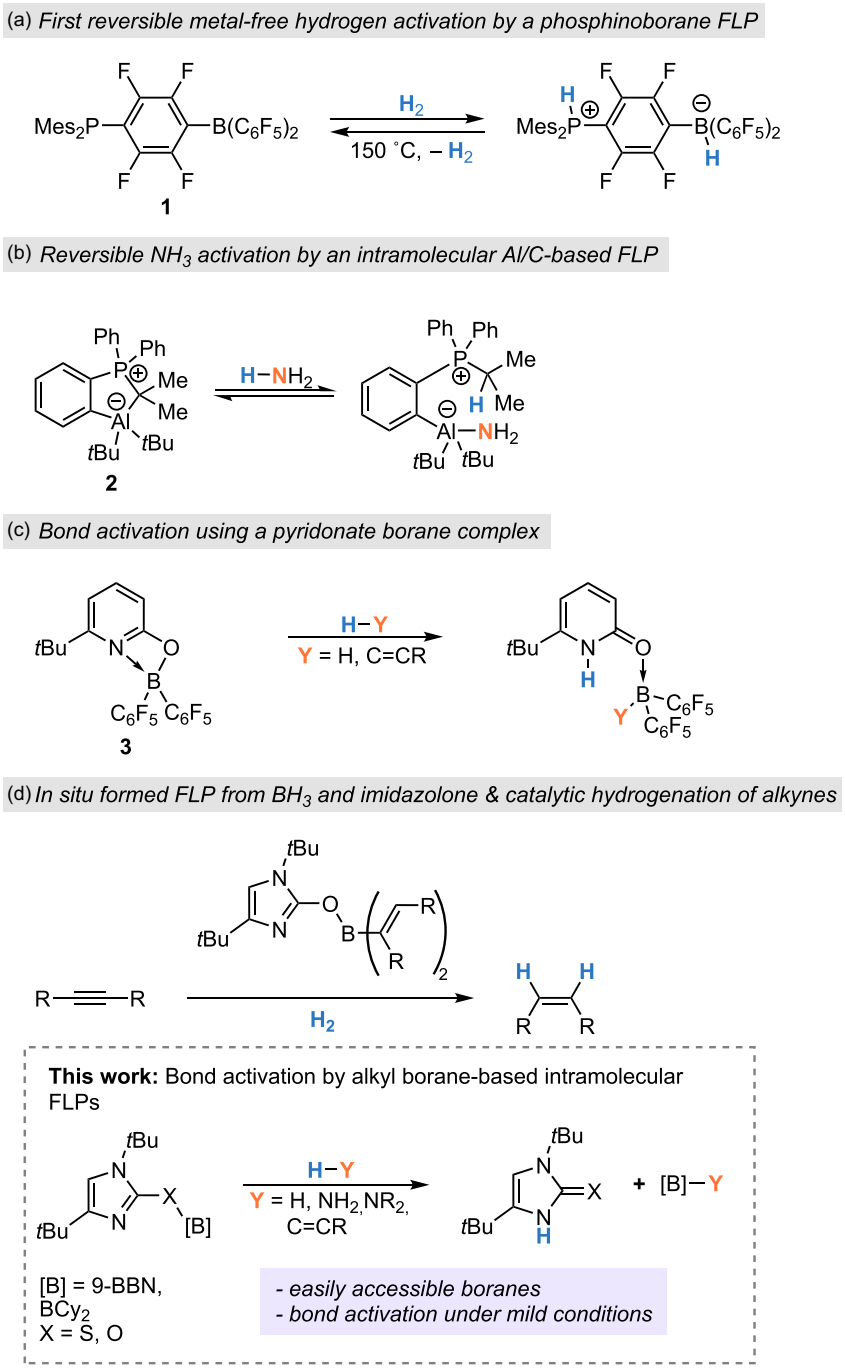
Despite significant progress in FLP-mediated hydrogen activation over the past decades, only a few examples of N—H activation of ammonia and amines by FLPs exist. Notably, in 2013, Stephan and coworkers demonstrated that tris(pentafluorophenyl)borane ($B(C_6F_5)_3$), also known as BCF, catalyzes the intra- and intermolecular hydroamination of alkynes by various secondary arylamines, providing a metal-free route to enamines.[8] Building on this concept, a one-pot strategy for functionalizing amines and *N*-heterocycles under H_2 atmosphere was developed.[9] Recently, the Braunschweig group reported the first catalyst-free and stereoselective intermolecular aminoboration of alkynes using (amino)dihaloboranes and aminoboronic esters under mild conditions.[10] Milstein and coworkers reported an intramolecular aminoborane that undergoes an aromaticity shift upon N—H σ-bond activation.[11] The Breher group later demonstrated the first reversible activation and transfer of non-aqueous ammonia to cyclic ketones, amides, and aziridines, catalyzed by the aluminum/carbon-based intramolecular FLP **2** (Scheme 1b).[12] Beyond FLPs, carbenes, geometrically constrained phosphines, and bismuth complexes have also been explored for metal-free N–H activation of ammonia.[13] In 2018, we reported the reversible activation of molecular hydrogen by pyridonate borane-based FLP **3** (Scheme 1c).[14] Unlike classical FLPs that form a borate salt upon hydrogen activation, this FLP forms a pyridone borane complex that can dissociate, enabling subsequent hydroboration. Compound **3** was used for catalytic hydrogenation of internal and terminal alkynes and catalytic allylboration of acetonitrile.[15,16] In addition to hydrogen activation, this FLP cleaves Csp—H bonds of acetylenes, forms an alkynyl borane complex (Scheme 1c), and enables the first metal-free catalytic dimerization of alkynes.[17] Since the pyridonate substituent transforms into a neutral pyridone-donor ligand during bond activation, reminiscent of the X-to-L-type ligand transformation in metal-ligand cooperation,[18] the reactivity of **3** has been described by the term boron-ligand cooperation.[19] In this context, our team found that sterically hindered imidazolones react with the simplest borane, $BH_3{\cdot}SMe_2$, in the presence of internal alkynes at elevated temperatures to form in situ imidazolonate boranes that function as FLPs and catalyze the hydrogenation of alkynes (Scheme 1d).[20] Building on these results, we investigated whether combining weakly Lewis acidic boranes (H—B-9-BBN or $HBCy_2$) with thioimidazolone **4** and imidazolone **5** would yield intramolecular FLPs capable of bond activation. Herein, we report their synthesis, structural characterization, and reactivity toward small molecules.

A. Averdunk, U. Gellrich
Department of Organic Chemistry
University of Hohenheim
Garbenstrasse 30, 70599 Stuttgart, Germany
E-mail: urs.gellrich@uni-hohenheim.de

F. Wech, J. Becker
Department of Organic and Inorganic Chemistry
Justus-Liebig Universität
Heinrich-Buff-Ring 17, 35392 Gießen, Germany

Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejic.202500104

Research Article
doi.org/10.1002/ejic.202500104



Scheme 1. The context of this work: a) The first reversible metal-free dihydrogen activation reported by Stephan; b) reversible ammonia activation reported by Breher and coworkers; c) H_2 and C–H activation by a pyridonate borane complex; d) catalytic hydrogenation by an FLP formed in situ from BH_3 and imidazolone; and the investigation of small molecule activation by alkylborane-based FLPs reported herein.

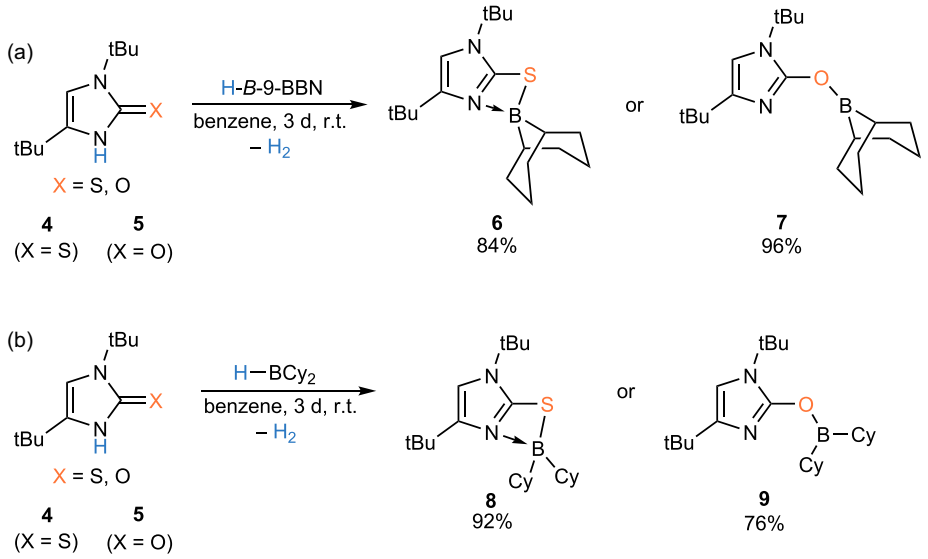
2. Results and Discussion

2.1. Syntheses and Structures of Intramolecular FLPs

We commenced this study with the synthesis of the four intramolecular FLPs shown in **Scheme 2**.

The reaction of H-*B*-9-BBN with thioimidazolone **4** in benzene at ambient temperature produces the intramolecular FLP **6** after hydrogen evolution. This compound was isolated as a crystalline solid in 84% yield following crystallization from DCM at −36 °C (Scheme 2a). Likewise, H-*B*-9-BBN reacts with imidazolone **5** to afford the dehydrogenated product **7** as a viscous oil in 96% yield. Using **4** and $HBCy_2$, the corresponding FLP **8** forms as a crystalline solid in 92% yield, while the reaction of **5** with $HBCy_2$ yields **9** as a crystalline solid in 76% yield (Scheme 2b). The FLPs **6**–**9** were fully characterized by nuclear magnetic resonance (NMR) spectroscopy (^1H, ^{13}C, ^{11}B, HH correlation spectroscopy (COSY), heteronuclear single quantum coherence (HSQC), and heteronuclear

Research Article
doi.org/10.1002/ejic.202500104



Scheme 2. Synthesis of four intramolecular FLPs **6**–**9** from a) H-*B*-9-BBN or b) $HBCy_2$ and thioimidazolone **4** and imidazolone **5**.

multiple bond correlation (HMBC)). The ^{11}B NMR chemical shifts of **6** (23.6 ppm) and **8** (21.5 ppm) indicate nitrogen coordination to boron, whereas the imidazolonate boranes **7** and **9** exhibit shifts of 60.2 and 55.0 ppm, respectively, consistent with trigonal borane structures. Single-crystal X-ray diffraction (SCXRD) confirmed the structures of FLPs **6**, **8**, and **9** (**Figure 1**).

2.2. Activation of Molecular Hydrogen

With FLPs **6**–**9** in hand, we evaluated their ability to activate dihydrogen. As mentioned, the reaction between (thio)imidazolones and boranes at ambient temperature releases molecular hydrogen, indicating that hydrogen release is exergonic. Therefore, hydrogen activation by these FLPs cannot be observed directly. However, when a solution of FLP **6** and one equivalent of styrene **10** was pressurized with H_2 (2.5 bar), a colorless precipitate was observed immediately. After 24 h at room temperature, a ^1H and ^{11}B NMR spectrum of the supernatant was recorded, confirming the formation of alkylborane **11a**, which indicates successful hydrogen activation (**Scheme 3**).[21]

The ^{11}B NMR spectrum shows a shift at 88.2 ppm, which is characteristic of a trivalent alkylborane. This indicates that **4** does

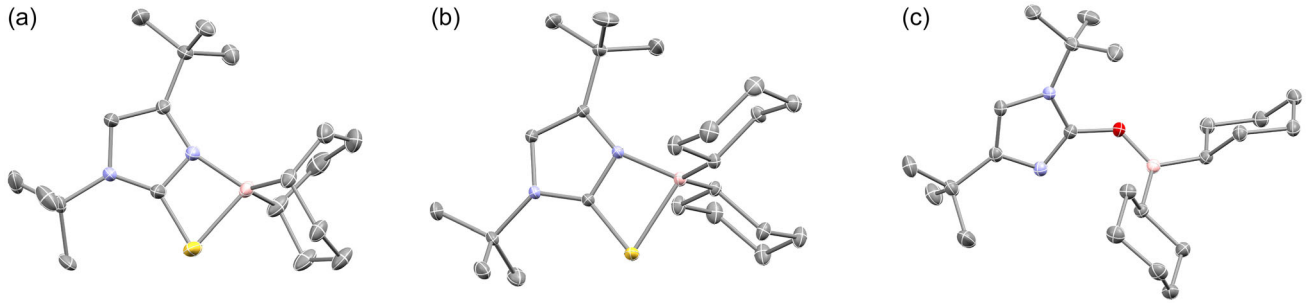
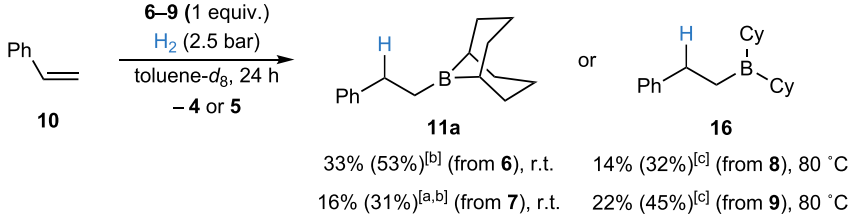


Figure 1. Molecular structures of FLPs **6**, **8**, and **9** derived from SCXRD (50 % probability ellipsoids, all hydrogens are omitted for clarity). Selected bond lengths: a) C–S: 1.7145(16) Å, S–B: 2.0962(18) Å, B–N: 1.635(2) Å. b) C–S: 1.7171(5) Å, S–B: 2.1364(6) Å, B–N: 1.6135(7). c) C–O: 1.3627(11) Å, O–B: 1.3898(12) Å.



Scheme 3. Activation of dihydrogen by FLPs **6**–**9**, followed by hydroboration of styrene into toluene-d_8. Yields were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. a) FLP **7** was formed in situ. b) In situ yields in parentheses are given for a 5-day reaction time. c) In situ yields in parentheses are given for a 4-day reaction time.

Research Article
doi.org/10.1002/ejic.202500104

not coordinate to borane **11a** to form a Lewis acid/Lewis base adduct. The in situ yield of **11a** after 24 h was 33%. In a scale-up experiment using **6** and **10** under hydrogen pressure (2.5 bar), the formed colorless precipitate was separated after 3 days at room temperature and analyzed by ^{1}H and ^{11}B NMR spectroscopy, confirming the formation of **4** in 48% isolated yield while **11a** was obtained with an in situ yield of 44% after the prolonged reaction time (see SI chapter 4.5). To gain further insight into the thermodynamic and kinetic aspects of hydrogen activation by **6**, we performed DFT calculations at the revDSD-PBEP86-D4/def2-QZVPP/PBEh-3c level of theory (**Figure 2**, for details of the calculation methods see SI chapter 9). In agreement with the conclusions drawn from the NMR studies, the calculations show that a B—S bond is present in the minimum structure of **6**. The calculated B—S bond distance of 2.11 Å is in good agreement with the bond distance of 2.10 Å determined by SCXRD (Figure 1a). The calculated small C–S–B angle of 70.0° also agrees well with the experimentally determined angle of 71.1°. The open form with a trivalent borane, which is required for FLP-like bond activation, is thermodynamically disfavored by 3.5 kcal mol^{-1}, but kinetically accessible via $\mathbf{TS_{6/6'}}$, which imposes a barrier of 11.4 kcal mol^{-1} on this transformation. Likewise, the transition state for hydrogen activation is kinetically accessible from **6** with a total activation barrier of 21.5 kcal mol^{-1}. This elementary step is predicted to be slightly endergonic, which is consistent with the experimental result that **12** cannot be observed directly. The dissociation of **12** and the hydroboration of propene **13**, which we used as a model alkene for the calculations, require overcoming a barrier of 22.8 kcal mol^{-1}. The hydroboration itself is exergonic and thus represents the driving force for hydrogen activation by **6**. The coordination of **4** to the alkylborane **11b** to form complex **14** is calculated to be slightly endergonic, which again agrees with the results of the NMR studies.

Similarly, when FLP **7** was exposed to hydrogen pressure (2.5 bar) in the presence of **10**, borane **11a** formed in 16% in situ yield after 24 h. Additionally, a new ^{11}B NMR signal emerged, which shifted significantly to a higher field over the course of the reaction, while the intensity of the signal assigned to FLP **6** decreased. This observation suggests the formation of a bis-complex via coordination of in situ generated **5** to unreacted **6** (see SI, chapters 4.2 and 8.2). To further investigate this process,

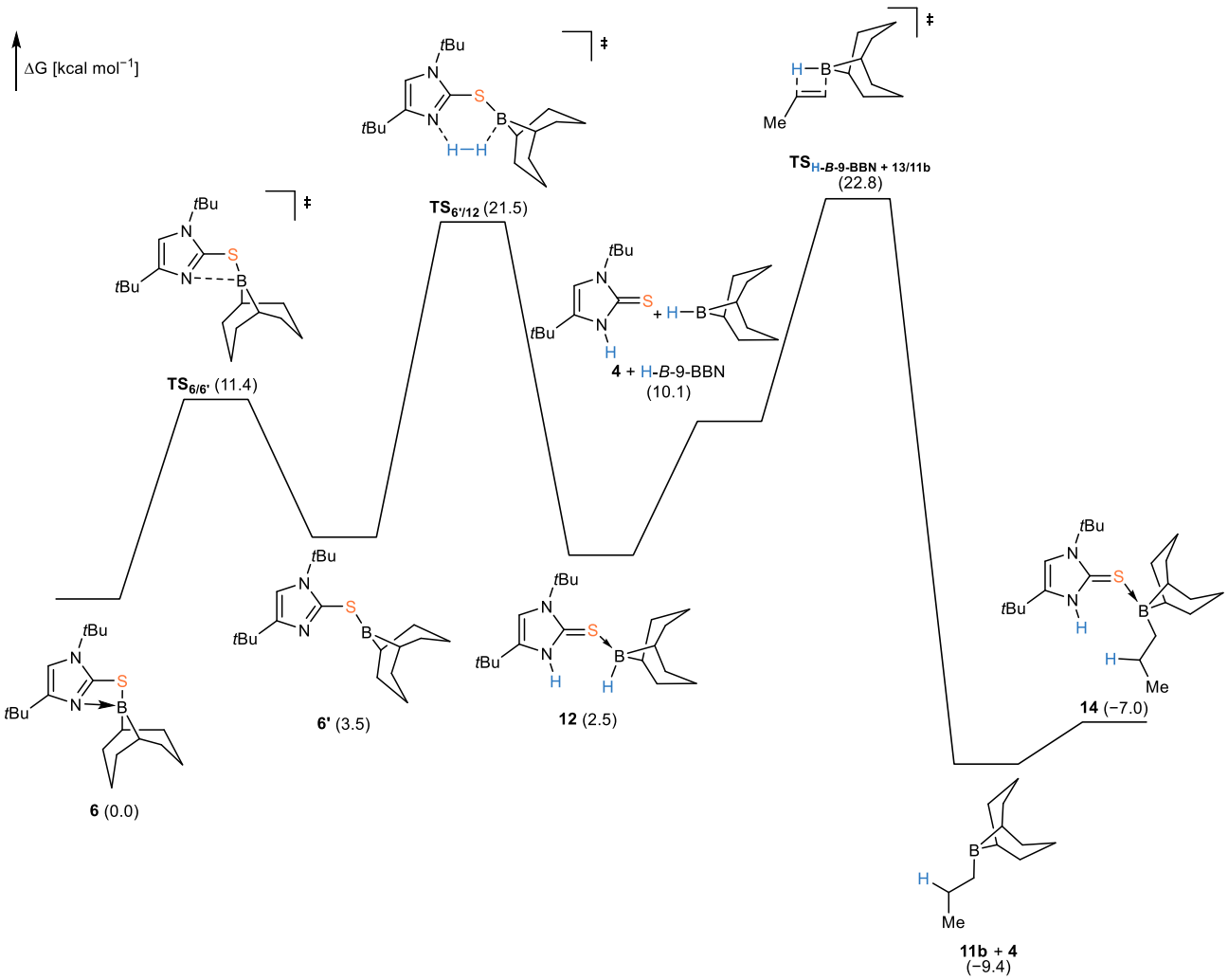
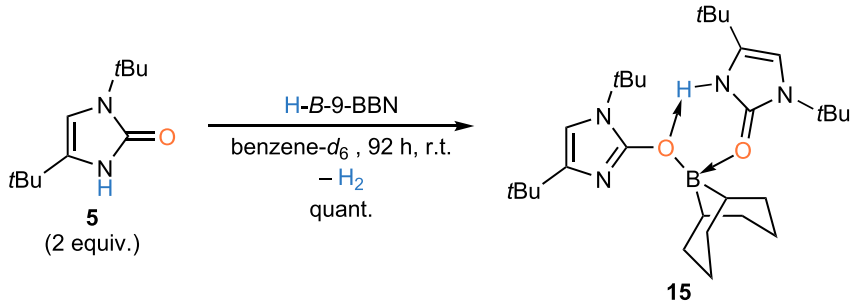


Figure 2. Potential energy surface for the activation of molecular hydrogen by **6** and the subsequent hydroboration of propene. Gibbs free energies computed at the revDSD-PBEP86-D4/PBEh-3c level of theory are given in brackets. The SMD model for toluene was used to implicitly account for solvation.

Research Article
doi.org/10.1002/ejic.202500104



Scheme 4. In situ formation of bis-complex **15**.

two equivalents of **5** were reacted with one equivalent of H-B-9-BBN in benzene-d_6 (**Scheme 4**). The resulting ^{11}B NMR signal at 22.8 ppm supports the formation of bis-complex **15**, which was characterized in situ by NMR.

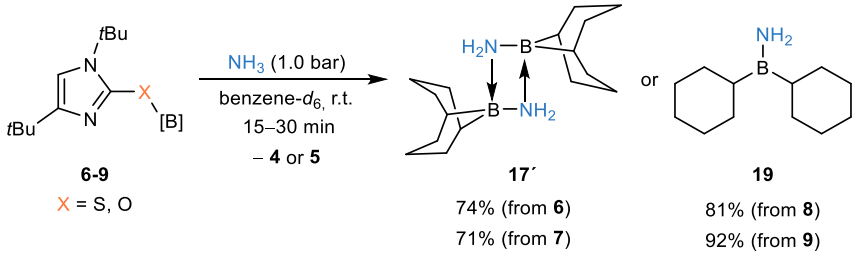
No reaction was observed when **8** and **10** were exposed at room temperature to hydrogen pressure (2.5 bar). However, at 80 °C, **8** produced alkylborane **16** in 14% in situ yield after 24 h. Likewise, with FLP **9**, only trace amounts of **16** were detected at room temperature after 24 h. Upon heating a solution of **9** and **10** for 24 h under hydrogen pressure to 80 °C, **16** was formed in 22% in situ yield. Additionally, spectroscopic analysis of the reaction mixtures with FLPs **8** and **9** revealed traces of cyclohexene in the ^{1}H NMR spectrum after 96 h at 80 °C, suggesting a retrohydroboration process (Figure S102 and S107, Supporting Information).

2.3. N–H Activation of Ammonia and Secondary Amines

We then focused on the N–H activation of ammonia and secondary amines. When complex **6** was exposed to NH_3 (1.0 bar) at room temperature, a colorless precipitate formed immediately. The ^{1}H NMR spectrum indicated the formation of **4** and aminoborane dimer **17′** in 74% in situ yield (**Scheme 5**). The newly formed borane species showed a ^{11}B NMR shift at −1.7 ppm, characteristic of a tetracoordinated borane center, confirming the respective dimeric structure.

The ^{13}C NMR data are consistent with data reported from the independent synthesis of **17′** from H-*B*-9-BBN and NH_3.[22,23] Compound **17′** was fully characterized in situ by NMR spectroscopy. We have also modeled the NH_3 cleavage by thioimidazolonate borane **6** with DFT calculations (**Figure 3**). The reaction begins with the exergonic coordination of ammonia to the borane and the formation of the NH_3 complex **18**. In a concerted process, both the N—H and S—B bonds of **18** are then cleaved in the transition state $\mathbf{TS_{18/4+17}}$. This reaction is exergonic and results in the release of thioimidazolone **4** and the formation of the aminoborane monomer **17**. The dimerization of **17** is also exergonic according to the calculations, which is consistent with experimental observations. The computed barrier for the concerted cleavage of the N—H and S—B bonds is only 10.3 kcal mol^{-1}, which agrees with the experimental observation that ammonia activation by **6** proceeds rapidly at room temperature. The reaction of FLP **7** under the same conditions gives **17′** in 71% in situ yield. Notably, while the reaction of ammonia with H-*B*-9-BBN yields **17′** after prolonged heating in benzene, the reaction of NH_3 (1 bar) with FLPs **6** and **7** occurs within minutes at room temperature.[23] Likewise, the activation of ammonia with FLPs **8** and **9** gives aminodicyclohexylborane **19** via heterolytic N-H cleavage in 81% and 92%, respectively.

The ^{11}B and ^{13}C NMR data of **19** obtained in this study are consistent with literature values.[24] To further explore this reactivity, we investigated the N–H activation of three secondary amines: bis(4-methoxyphenyl)amine (**20a**), diisopropylamine (**20b**), and *N*-methyl-2-(phenylethynyl)benzenamine (**20c**). FLP **8** reacts smoothly with **20a** at room temperature, affording aminoborane **21a** in 84% yield (**Figure 4**). The FLPs reported herein also activate sterically demanding amines, as demonstrated by the formation of aminoborane **21b** from **6** and diisopropylamine **20b** in 94% in situ yield under ambient conditions. Likewise, **7** reacts with **20c** under standard conditions to afford aminoborane **21c** in good yield. The NMR data of **21a**–**21c** are in agreement with literature values, and the observed ^{11}B NMR shifts suggest monomeric structures (Figure 4).[25]



Scheme 5. Activation of ammonia by FLPs **6**–**9** at room temperature in benzene-d_6. Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard. FLPs were formed in situ.

Research Article
doi.org/10.1002/ejic.202500104

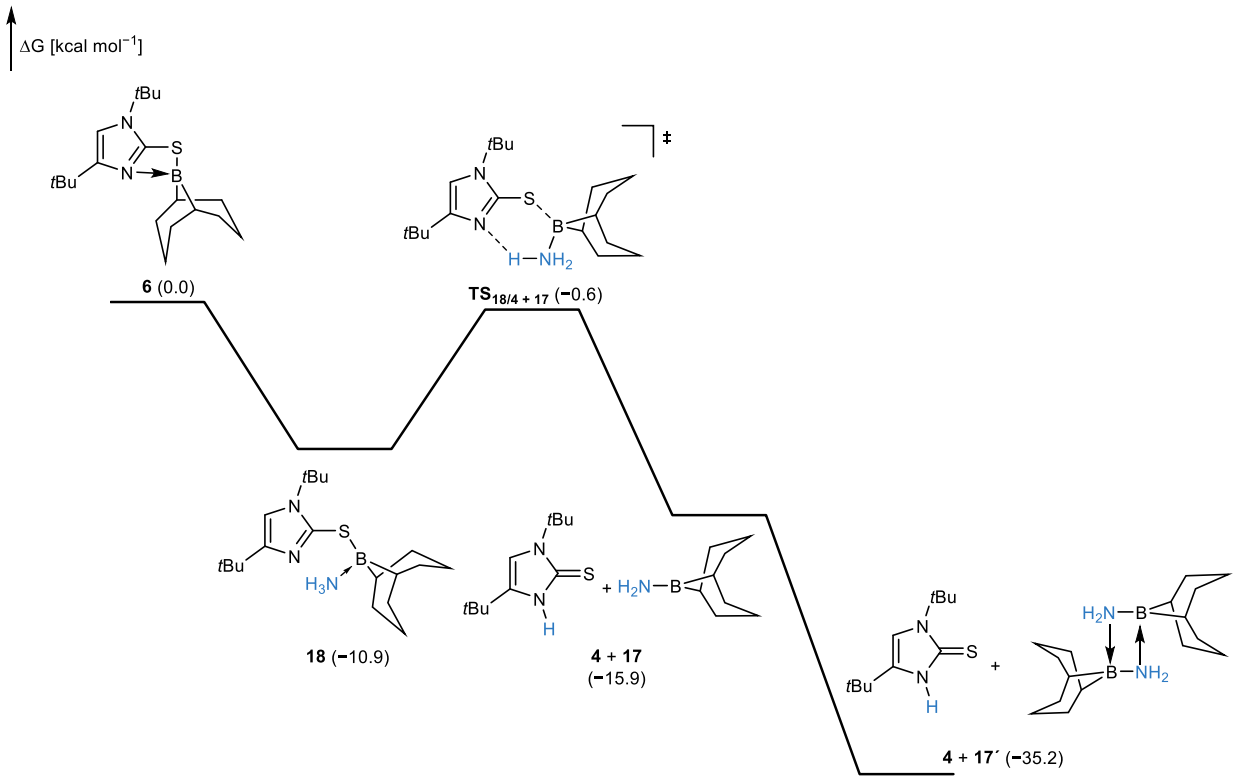
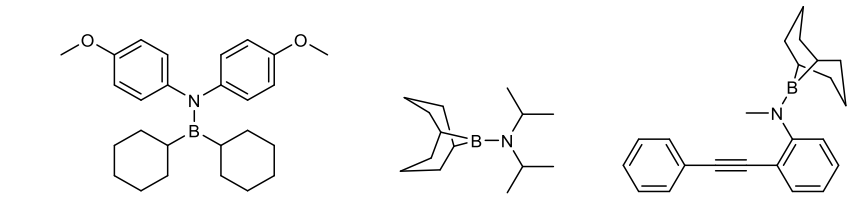
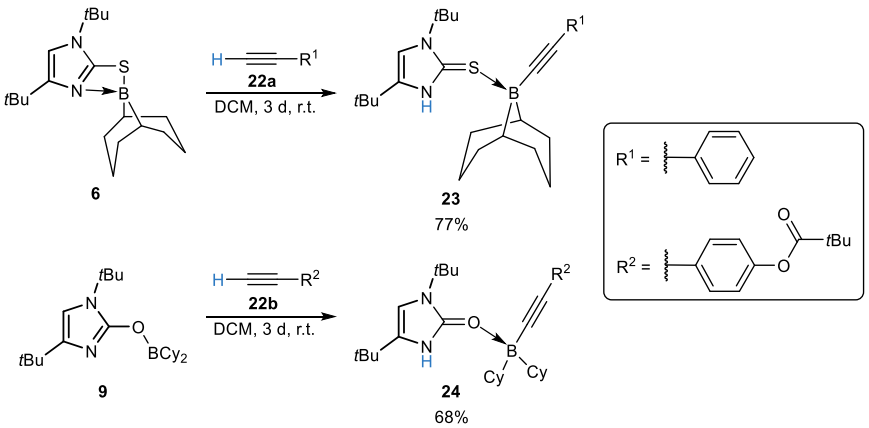


Figure 3. Potential energy surface for the NH-activation of ammonia by **6**. Gibbs free energies computed at the revDSD-PBEP86-D4/PBEh-3c level of theory are given in parentheses. The SMD model for toluene was used to implicitly account for solvation.



	21a	**21b**	**21c**
	84% (from **8**)	94% (from **6**)	78% (from **7**)[a]
^{11}B NMR [ppm]	46.3	48.1	49.4

Figure 4. Aminoboranes are synthesized by the reaction of alkylborane-based FLPs **6**–**8** with secondary amines at room temperature in benzene-d_6. Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard. ^{11}B NMR shifts are given in benzene-d_6. [a] FLP **7** was formed in situ.



Scheme 6. CH activation of terminal alkynes is mediated by FLP **6** and **9**. Isolated yields are given.

2.4. C–H Activation of Alkynes

To test whether the alkylborane-based FLPs reported herein are able to activate the C—H bonds of terminal alkynes, **6** was reacted with phenylacetylene **22a** for three days in DCM at room temperature. When the reaction mixture was stored at −36 °C, a colorless crystalline solid, which was assigned to be the alkynyl borane complex **23**, was obtained in 77% yield (**Scheme 6**).

The formation of the alkynyl borane complex **23** is indicated by an NMR shift of the NH group at 12.43 ppm and an ^{11}B NMR shift at −1.5 ppm and further substantiated by HH-COSY, HSQC, and HMBC spectroscopy. To investigate the generality of this reaction, **9** was reacted with alkyne **22b** to give complex **24** in 68% yield.

3. Conclusion

In summary, we have demonstrated that the simple alkylborane-based FLPs **6**–**9** effectively activate hydrogen and ammonia. While hydrogen activation occurs at room temperature for the 9-BBN-based FLPs **6** and **7**, the cyclohexylborane-based FLPs **8** and **9** require elevated temperatures. In contrast, all FLPs readily activate ammonia. Additionally, FLPs **6**–**8** react with secondary amines to afford aminoboranes **21a**–**21c** in good yields. Notably, FLPs **6** and **9** also facilitate C—H bond cleavage of terminal alkynes. These findings highlight the potential of readily accessible alkylboranes in the development of new FLP-type catalysts.

Acknowledgements

This work was supported by the German Research Foundation (Emmy–Noether program, GE 3117/1-1 and GE 3117/1-2). The authors acknowledge the Mass Spectrometry Unit of the Core Facility Hohenheim (University of Hohenheim, Stuttgart, Germany) for their support in mass spectrometry analysis.

Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: ammonia activation · density functional theory calculations · frustrated Lewis pairs · hydroboration · hydrogen activation

[1] G. C. Welch, R. R. San Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124.
[2] a) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2010**, *49*, 46; b) D. W. Stephan, G. Erker, *Chem. Sci.* **2014**, *5*, 2625; c) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2015**, *54*, 6400; d) D. W. Stephan, *J. Am. Chem. Soc.* **2015**, *137*, 10018; e) D. W. Stephan, *Acc. Chem. Res.* **2015**, *48*, 306; f) J. Lam, K. M. Szkop, E. Mosaferi, D. W. Stephan, *Chem. Soc. Rev.* **2019**, *48*, 3592.
[3] a) L. Greb, P. Oña-Burgos, B. Schirmer, S. Grimme, D. W. Stephan, J. Paradies, *Angew. Chem. Int. Ed.* **2012**, *51*, 10164; b) D. Chen, Y. Wang, J. Klankermayer, *Angew. Chem. Int. Ed.* **2010**, *49*, 9475; c) D. Chen, J. Klankermayer, *Chem. Commun.* **2008**, *18*, 2130; d) P. A. Chase, T. Jurca, D. W. Stephan, *Chem. Commun.* **2008**, *14*, 1701; e) K. Chernichenko, A. Madarász, I. Pápai, M. Nieger, M. Leskelä, T. Repo, *Nat. Chem.* **2013**, *5*, 718; f) Z. M. Heiden, D. W. Stephan, *Chem. Commun.* **2011**, *47*, 5729; g) T. Mahdi, D. W. Stephan, *J. Am. Chem. Soc.* **2014**, *136*, 15809; h) D. J. Scott, M. J. Fuchter, A. E. Ashley, *J. Am. Chem. Soc.* **2014**, *136*, 15813; i) P. A. Chase, G. C. Welch, T. Jurca, D. W. Stephan, *Angew. Chem. Int. Ed.* **2007**, *46*, 8050; j) H. Wang, R. Fröhlich, G. Kehr, G. Erker, *Chem. Commun.* **2008**, *45*, 5966; k) L. Greb, P. Oña-Burgos, A. Kubas, F. C. Falk, F. Breher, K. Fink, J. Paradies, *Dalton Trans.* **2012**, *41*, 9056; l) T. Mahdi, Z. M. Heiden, S. Grimme, D. W. Stephan, *J. Am. Chem. Soc.* **2012**, *134*, 4088.
[4] D. J. Scott, M. J. Fuchter, A. E. Ashley, *Angew. Chem. Int. Ed.* **2014**, *53*, 10218.
[5] G. C. Welch, L. Cabrera, P. A. Chase, E. Hollink, J. D. Masuda, P. Wei, D. W. Stephan, *Dalton Trans.* **2007**, *31*, 3407.
[6] H. Zaher, A. E. Ashley, M. Irwin, A. L. Thompson, M. J. Gutmann, T. Krämer, D. O'Hare, *Chem. Commun.* **2013**, *49*, 9755.
[7] a) T. A. Rokob, A. Hamza, I. Pápai, *J. Am. Chem. Soc.* **2009**, *131*, 10701; b) A. J. M. Miller, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **2010**, *132*, 3301; c) H. Li, A. J. A. Aquino, D. B. Cordes, F. Hung-Low, W. L. Hase, C. Krempner, *J. Am. Chem. Soc.* **2013**, *135*, 16066; d) S. Mummadi, D. K. Unruh, J. Zhao, S. Li, C. Krempner, *J. Am. Chem. Soc.* **2016**, *138*, 3286; e) G. Durin, J.-C. Berthet, P. Thuéry, E. Nicolas, T. Cantat, *Chem. Eur. J.* **2023**, *29*, e202302155; f) C. Manankandayalage, D. K. Unruh, C. Krempner, *Chem. Eu. J.* **2021**, *27*, 6263; g) S. Mummadi, A. Brar, G. Wang, D. Kenefake, R. Diaz, D. K. Unruh, S. Li, C. Krempner, *Chemm Eur. J.* **2018**, *24*, 16526.
[8] T. Mahdi, D. W. Stephan, *Angew. Chem. Int. Ed.* **2013**, *52*, 12418.
[9] T. Mahdi, D. W. Stephan, *Chem. Eur. J.* **2015**, *21*, 11134.
[10] S. Dotzauer, A. Jayaraman, D. Reinhart, H. Braunschweig, *Angew. Chem. Int. Ed.* **2024**, *63*, e202413370.
[11] U. Gellrich, Y. Diskin-Posner, L. J. W. Shimon, D. Milstein, *J. Am. Chem. Soc.* **2016**, *138*, 13307.
[12] F. Krämer, J. Paradies, I. Fernández, F. Breher, *Nat. Chem.* **2024**, *16*, 63.
[13] a) G. D. Frey, V. Lavallo, B. Donnadieu, W. W. Schoeller, G. Bertrand, *Science* **2007**, *316*, 439; b) Y. Wang, P. M. Tran, M. E. Lahm, Y. Xie, P. Wei, E. R. Adams, J. N. Glushka, Z. Ren, V. V. Popik, H. F. Schaefer, G. H. Robinson, *J. Am. Chem. Soc.* **2022**, *144*, 16325; c) X. Yang, E. J. Reijerse, K. Bhattacharyya, M. Leutzsch, M. Kochius, N. Nöthling, J. Busch, A. Schnegg, A. A. Auer, J. Cornella, *J. Am. Chem. Soc.* **2022**, *144*, 16535; d) J. Abbenseth, O. P. E. Townrow, J. M. Goicoechea, *Angew. Chem. Int. Ed.* **2021**, *60*, 23625; e) A. Brand, W. Uhl, *Chem. Eur. J.* **2019**, *25*, 1391.
[14] U. Gellrich, *Angew. Chem. Int. Ed.* **2018**, *57*, 4779.
[15] F. Wech, M. Hasenbeck, U. Gellrich, *Chem. Eur. J.* **2020**, *26*, 13445.
[16] M. Hasenbeck, S. Ahles, A. Averdunk, J. Becker, U. Gellrich, *Angew. Chem. Int. Ed.* **2020**, *59*, 23885.
[17] M. Hasenbeck, T. Müller, U. Gellrich, *Catal. Sci. Technol.* **2019**, *9*, 2438.
[18] a) C. Gunanathan, D. Milstein, *Chem. Rev.* **2014**, *114*, 12024; b) J. R. Khusnutdinova, D. Milstein, *Angew. Chem. Int. Ed.* **2015**, *54*, 12236; c) D. Milstein, *Philos. Trans. R. Soc. A* **2015**, *373*; d) J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **2005**, *127*, 10840.
[19] M. Hasenbeck, U. Gellrich, *Chem. Eur. J.* **2021**, *27*, 5615.
[20] F. Wech, U. Gellrich, *ACS Catal.* **2022**, *12*, 5388.
[21] H. Ohmiya, M. Tanabe, M. Sawamura, *Org. Lett.* **2011**, *13*, 1086.
[22] M. W. Drover, L. L. Schafer, J. A. Love, *Angew. Chem. Int. Ed.* **2016**, *55*, 3181.
[23] R. Köster, G. Seidel, *Justus Liebigs Ann. Chem.* **1977**, *1977*, 1837.
[24] P. V. Ramachandran, M. P. Drolet, A. S. Kulkarni, *Chem. Commun.* **2016**, *52*, 11897.
[25] K. Yuan, S. Wang, *Org. Lett.* **2017**, *19*, 1462.

Manuscript received: February 28, 2025
Revised manuscript received: April 10, 2025
Version of record online: May 20, 2025