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# Heterolytic Cleavage of $H_2$ by Frustrated B/N Lewis Pairs

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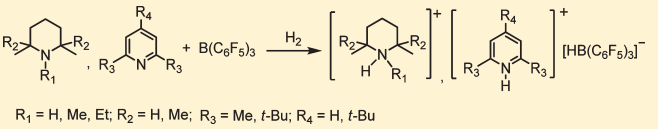
Supporting Information

**ABSTRACT:** Treatment of the Lewis acid $B(C_6F_5)_3$ with the Lewis base 2,6-dimethylpiperidine (DMP) resulted in the formation of the classical Lewis acid·base adduct DMP-B-$(C_6F_5)_3$, **1a**, which was anticipated to undergo thermal dissociation to the "unquenched" Lewis centers. The free Lewis pair was able to form a frustrated Lewis pair (FLP), which induced heterolytic splitting of $H_2$, affording the ionic product $[DMPH][HB(C_6F_5)_3]$, **1b**. FLPs, derived from $B(C_6F_5)_3$ and the bulky Lewis bases 2,2,6,6-tetramethylpiperidine (TMP) and 1,2,2,6,6-pentamethylpiperidine (PMP), could also heterolytically activate $H_2$, affording the salts $[TMPH][HB(C_6F_5)_3]$, **2**, and $[PMPH][HB(C_6F_5)_3]$, **3**, respectively. In a VT NMR study the TMP/$B(C_6F_5)_3$ reaction was studied in greater detail, trying to trace intermediates. The supposed most prominent intermediate, the TMP/$H_2$/$B(C_6F_5)_3$ complex, could, however, not be detected. The combination of $B(C_6F_5)_3$ with the even more sterically demanding Lewis base 1-ethyl-2,2,6,6,-tetramethylpiperidine (Et-TMP) displayed FLP reactivity with $H_2$, but required the high temperature of 110 °C, forming $[2,2,6,6\text{-}(CH_3)_4C_5H_6NH(CH_2CH_3)][HB(C_6F_5)_3]$, **4a**. In the absence of $H_2$ the combination of $B(C_6F_5)_3$ and Et-TMP generated at room temperature a mixture of **4a** and $[2,2,6,6\text{-}(CH_3)_4C_5H_6N{=}CHCH_2\text{-}B(C_6F_5)_3]$, **4b**. **4b** was formed via consecutive hydride and proton abstractions with Et-**TMP** as the base, generating **4a**. 2,4,6-Tri-*tert*-butylpyridine (TTBP), exhibiting reduced Lewis basicity as compared to piperidine derivatives, showed FLP reactivity with $B(C_6F_5)_3$, which gave in the presence of $H_2$ the $[TTBPH][HB(C_6F_5)_3]$, **5**, salt as the only product after several hours. The steric demand of the Lewis bases was evaluated by aid of DFT calculations on borane adducts, which roughly correlated with the reaction temperature of $H_2$ splitting. **1a**, **1b**, **3**, **4a**, and **4b** were studied by single-crystal X-ray diffraction analyses.




$R_1$ = H, Me, Et; $R_2$ = H, Me; $R_3$ = Me, *t*-Bu; $R_4$ = H, *t*-Bu

## INTRODUCTION

The concept of frustrated Lewis pairs (FLPs) was put forth by D. W. Stephan et al. after their remarkable discovery that $H_2$ can reversibly be activated by $[(2,4,6\text{-}C_6H_2Me_3)_2PC_6F_4B(C_6F_5)_2]$,[1] which led to development of the first metal-free catalyst for hydrogenations of bulky imines as one of the fruitful applications of this concept.[2] The steric congestion of Lewis donors and acceptors precludes the formation of classical Lewis adducts, but provokes formation of FLPs with "unquenched" reactivity toward small molecules.[3−5] For instance, the mixture of appropriate phosphines and boranes can activate $H_2$ heterolytically under often mild conditions[6] and can undergo 1,2-addition reactions with olefins, as well.[7,8] After the pioneering work of Stephan et al., an increasing number of related FLP systems were found. The frustrated Lewis pairs were extended from the initial boron/phosphine species[9−20] to boron/carbene systems and borane/amine species.[21−24] Some of the resulting ionic products were shown to serve as active catalysts for the hydrogenation of imines, nitriles, and aziridines, as well as enamines and silyl enol ethers.[12,24,25] However, the mechanism of the $H_2$ activation by FLPs is still not fully understood. Theoretical studies proposed that the Lewis donor and acceptor initially form an "encounter complex" with long nonbonding distances between the Lewis centers frequently supported by multiple CH···F interactions. Such relatively weak specific forces, as well as the global electrostatic field of the Lewis pair, caused in sum too small interaction energies to allow proper identification by conventional analytical methodologies. $H_2$ can insert into this encounter complex, being thus activated by heterolytic H−H splitting.[26,27] Recent sophisticated DFT studies by Grimme et al., which included dispersion forces, pointed out that the intermediate formed between $H_2$ and for instance a P/B FLP could show kinetic stabilization and would thus be spectroscopically detectable under the condition that the P···B nonbonding distance is over 4.5 Å. Otherwise, the $H_2$ heterolysis would be practically barrierless, once the $H_2$ molecule had "sneaked" into the FLP complex.[28] Herein, we explore several sterically hindered Lewis bases, mainly piperidine and pyridine derivatives, to modulate the B···N nonbonding distance of the FLP and to study the impact of varying the B···N distance on their ability to activate $H_2$.

## RESULTS AND DISCUSSION

The reaction of the cyclic *sec*-amine piperidine and $B(C_6F_5)_3$ produced the classical Lewis acid·base adduct $C_5H_{10}N(H)$-$B(C_6F_5)_3$.[29] This adduct turned out to be too stable, preventing thermal dissociation and subsequent FLP-induced heterolysis of $H_2$. Consequently the steric bulk of the Lewis base was increased employing 2,6-dimethylpiperidine (DMP) in conjunction with $B(C_6F_5)_3$ in toluene. However, formation of the classical Lewis

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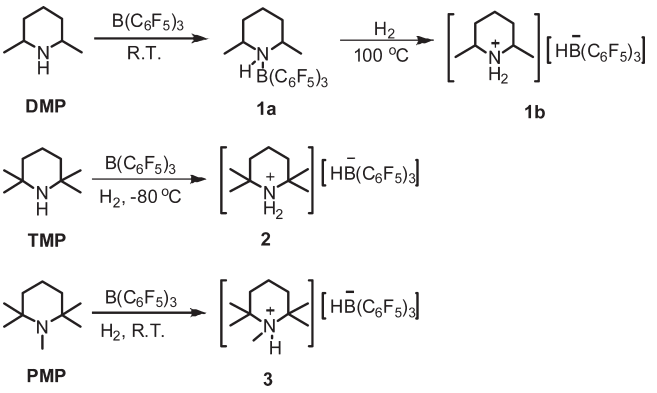
**Scheme 1**




acid·base adduct DMP-$B(C_6F_5)_3$, **1a**, was still observed (Scheme 1). In addition FLP-type intermediates could not be traced along the adduct formation process. The $^{19}F$ NMR spectrum of **1a** was consistent with a Lewis adduct structure revealing, however, three signals attributed to the *ortho*- (−128.2, −128.5, −138.6 ppm) and *meta*-F (−162.4, −164.4 to −164.6 ppm) and two signals for the *para*-F (−155.2, −157.6 ppm) atom, indicating molecular dissymmetry in solution. This was interpreted in terms of hindered rotation of the $C_6F_5$ rings around the B−C bonds, which apparently arose from steric conflicts between the methyl substituents on the piperidine side and the fluorine atoms on the boron side of the molecule. A singlet resonance in the $^{11}B$ NMR spectrum at −4.3 ppm witnessed the presence of a four-coordinated boron center.

An X-ray crystallographic study of **1a** confirmed the Lewis adduct structure (Figure 1). Of particular significance was the B−N bond length of 1.654(4) Å, being slightly longer than that of the very stable piperidine-$B(C_6F_5)_3$ adduct (1.629(3) Å). This small bond elongation was, however, suspected to indicate the possibility of a thermal dissociation of the B−N bond. Indeed at 100 °C **1a** turned out to be thermally unstable in the presence of $H_2$ (1 bar) with the Lewis adduct partly dissociating into the "unquenched" donor and acceptor centers. Subsequent formation of a FLP and reaction with $H_2$ heterolysis were anticipated to induce formation of the $[DMPH][HB(C_6F_5)_3]$ salt **1b**. In the $^1H$ NMR spectrum **1b** featured a broad N*H*$_2$ resonance at 4.52 ppm and a broad quartet B*H* resonance at 3.44 ppm with a $J$(B,H) coupling constant of 88 Hz. In addition, the narrowing gap between the *meta*- and *para*-fluorine $^{19}F$ NMR signals (−135.0 (*o*-), −162.5 (*p*-), −166.6 (*m*-$C_6F_5$) ppm) and a doublet $^{11}B$ NMR signal at −23.9 ppm were pointing to the formation of the tris(pentafluorophenyl)hydridoborate anion. An X-ray diffraction analysis revealed in **1b** an elongated B−N distance of 3.949(2) Å with respect to **1a** (in agreement also with free rotation of the $C_6F_5$ rings in solution) and a H1···H2 separation of 1.945 (1) Å, which could indicate a weak dihydrogen bonding contact. The N1−H2 (1.01(4) Å) and N1−H3 (1.06(4) Å) bond lengths are longer than the N−H distance in **1a** (0.89(4) Å (N1−H)) (Figure 2).

It is noteworthy that in the absence of $H_2$ dissociation of the **1a** Lewis pair did not become evident by spectroscopic or chemical means. For instance, no apparent changes of mixture were noticed when heated to 110 °C for 20 h. Only trace amounts of the anion $[HB(C_6F_5)_3]^-$ were then formed as observed in the $^{19}F$ NMR and $^{11}B$ NMR spectra, which could originate from a

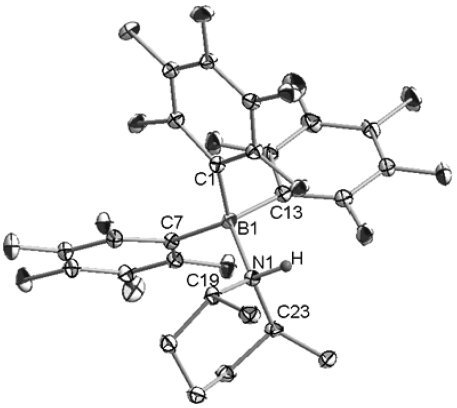



**Figure 1.** Molecular structure of **1a** with 30% probability thermal ellipsoids. Hydrogen atoms except N*H* are omitted for clarity.

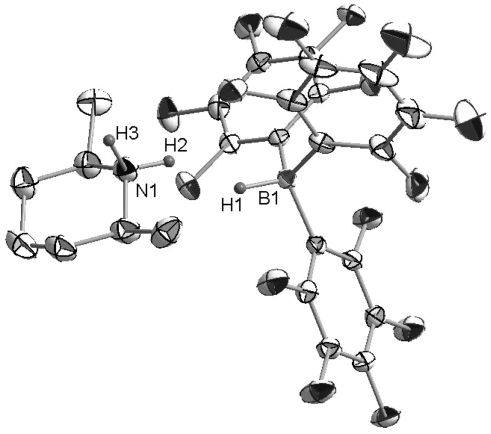



**Figure 2.** Molecular structure of **1b** with 30% probability thermal ellipsoids. Hydrogen atoms expect N*H* and B*H* are omitted for clarity.

$B(C_6F_5)_3$-induced α-hydride abstraction from DMP after rupture of the B−N bond, similar to the chemistry leading to **4a** (Scheme 2), but the major part of the adduct remained intact.

From all these observations it was concluded that any kind of reaction of **1a** requires dissociation of the Lewis adduct at higher temperatures, and the dissociated parts form a FLP, which in the presence or absence of $H_2$ can react further. The reaction barrier seems to be mainly due to the dissociation of the B−N bond, and for instance the $H_2$ insertion and the $H_2$ splitting steps are without barrier. Nevertheless, this observation further proved that classic and frustrated Lewis pair reactivity are mutually not exclusive, and previously "thought to be unreactive" classic Lewis acid···base adducts may be converted thermally to frustrated Lewis pairs, thus offering access to new reactivity.

As Rieger et al. have reported, 2,2,6,6-tetramethylpiperidine (TMP), exhibiting a still higher steric demand than DMP, can heterolytically activate $H_2$ at room temperature in the presence of $B(C_6F_5)_3$.[23] To gain more quantitative insight and to trace intermediates, a VT $^1H$ NMR study was carried out on this reaction in toluene solution starting at 193 K. A broad signal attributed to the $H_B$ nuclei at 3.56 ppm was immediately observed after filling $H_2$ into the NMR tube containing the toluene solution of TMP and $B(C_6F_5)_3$ at 193 K (Figure 3, spectrum a). The N$H_2$ resonance appeared at this temperature as a quite broad signal at around 3.05 ppm. As the temperature was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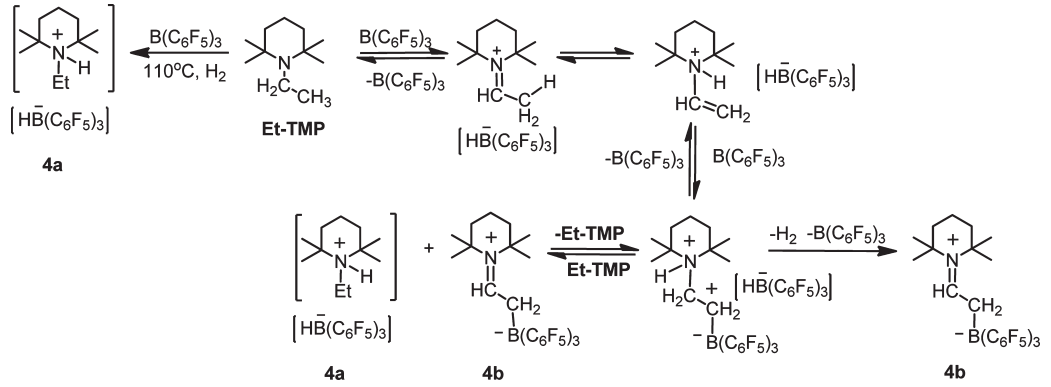
**Scheme 2**



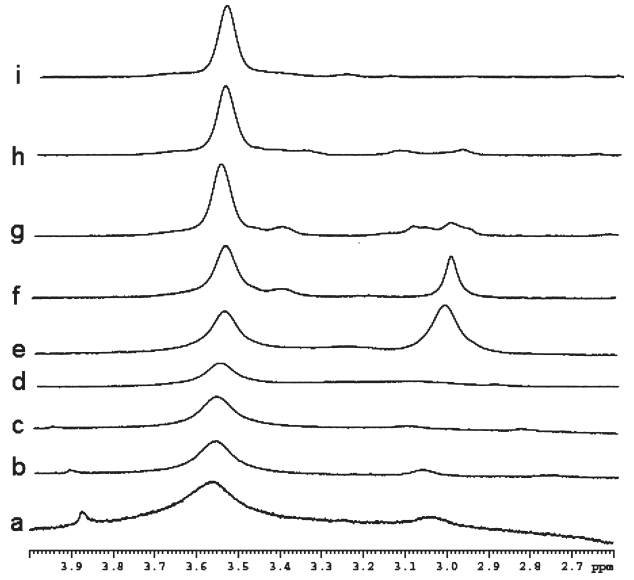




**Figure 3.** 500 MHz VT $^1$H NMR spectra of TMP and $B(C_6F_5)_3$ (1:1) with $H_2$ (1 bar) in [$D_8$]toluene. a: 193 K; b: 203 K, c: 213 K, d: 223 K, e: 233 K, f: 243 K, g: 253 K, h: 263 K, i: 273 K.

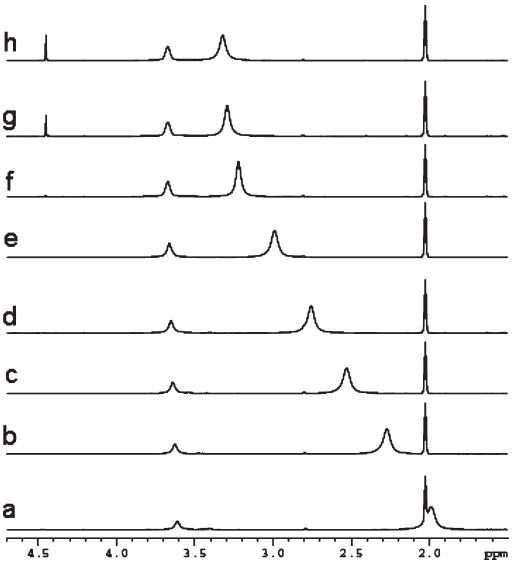



**Figure 4.** 500 MHz $^1$H NMR spectra of the reaction of TMP and $B(C_6F_5)_3$ (1:1) with $H_2$ (1 bar) in toluene [$D_8$] at 283 K. a: start; b: after 2 h; c: after 4 h; d: after 6 h; e: after 8 h; f: after 10 h; g: after 12 h; h: after 14 h.

raised to 233 K, this broad signal became sharper and then gradually vanished with rising temperatures (Figure 3, spectra e−h). Initially, we thought this variable signal may be assigned to the $H_2$-enclosed FLP transient TMP···H$^{\delta+}$−H$^{\delta-}$···B-$(C_6F_5)_3$. But continuing studies disproved this assumption, and this signal was assigned to overlapping signals of N*H*(ax) and N*H*(eq) protons originating from a "frozen-out" chair conformation of the highly substituted piperidinium ring (see ground-state conformations of the X-ray diffraction studies of **1b**, **2**, **3**, **4a**) in the temperature range between 193 and 203 K. Assuming ring inversion at a rate comparable to the NMR time scale, this signal at around 3 ppm coalesces at 213/223 K. At still higher temperatures the $NH_2$ signal gets sharper again (spectra e and f of Figure 3) with now signal averaging over various ring conformations fast on the NMR time scale. At still higher temperatures spectra g and h show that this resonance coalesces again, now due to fast proton exchange with the piperidine N*H* resonance, which was supposed to appear at around 0.5−1.5 ppm buried under the $CH_3$− and −$CH_2$− signals. The progressing $H_2$ splitting process produces an increasing amount of the piperidinium $NH_2$ moiety at the expense of the piperidine N*H* group, shifting the N*H*/$NH_2$ averaged signal more and more to the piperidinium signal side, as evidenced by the sequence of the $^1$H NMR spectra a−f at 283 K of Figure 4.

At the stage of spectra g and h the reaction is completed, with the $NH_2$ signal of the piperidinium cation appearing at 3.4 ppm. At this point also the signal of free $H_2$ becomes visible, which during the progressing reaction was equilibrating with some yet unidentified resonance.

Similar conclusions were drawn from a related VT $^2$H NMR study of the splitting reaction of $D_2$ using TMP and $B(C_6F_5)_3$ with the decoalescing signals to expectedly appear at about 20 °C higher than in the case of the splitting reaction of $H_2$. The $^2$H NMR spectra provided evidence for the position of the N*D* signal appearing temperature dependent in the range 0.3 to 1.1 ppm. The reaction of the TMP/$B(C_6F_5)_3$ pair with HD was then carried out with VT $^1$H NMR monitoring. The development of the spectra looked roughly similar to those of the $H_2$ experiments. We hoped to see resonances with *J*(HD) coupling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patterns being attributable to an intact H−D connection, but no such signal was detected. All the given NMR pursuits pointed to the absence of a FLP/$H_2$ intermediate, and it seemed therefore reasonable to assume that the splitting of the $H_2$ molecule occurs with no or almost no barrier. Within the given FLP model it was therefore anticipated that the B···N distance of the TMP···B-$(C_6F_5)_3$ encounter complex is too short to create a substantial NMR-relevant barrier of >12 kcal/mol.

The X-ray crystallographic study of **2** revealed a B−N distance of 4.565(3) Å, setting the upper limit for a B···N distance in the corresponding FLP in solution.[23] However, as we discussed in the earlier context the nonbonding B···N distance in the TMP···$B(C_6F_5)_3$ encounter complex should be longer than 4.5 Å to generate a substantial barrier in the $H_2$ activation and make the FLP/$H_2$ complex long-lived enough for spectroscopic characterization. It should also be mentioned that the H1A···H1 distance of 2.924 Å in the structure of **2** is too long for a dihydrogen bonding interaction.[23]

In order to expand the B···N nonbonding distance of the B/N FLPs further, increase of the steric bulk around the N center was sought. Thus, we employed 1,2,2,6,6-pentamethylpiperidine (PMP) together with $B(C_6F_5)_3$ to react with $H_2$. The resulting reaction conditions for the $H_2$ heterolysis were expected to be much tougher in comparison with the TMP/$B(C_6F_5)_3$ system. $^1$H NMR spectroscopy of the initial reaction solution in the absence of $H_2$ at 193 K did not provide any evidence for the existence of a FLP intermediate. Only NMR resonances for the free components PMP and $B(C_6F_5)_3$ were observed, and at 213 K the reaction with $H_2$ started to proceed, revealing trace amounts of the product [PMPH][$HB(C_6F_5)_3$], **3**, but no FLP/$H_2$ intermediate. At room temperature the reaction went to completion within 1 h, giving a 90% yield of **3**. Thus, the PMP/$B(C_6F_5)_3$ reaction with $H_2$ required more severe reaction conditions, confirming a higher energetic barrier to cleave the $H_2$ molecule than the TMP/$B(C_6F_5)_3$ system. The pure [PMPH][$HB(C_6F_5)_3$] product **3** featured in the $^1$H NMR spectrum a broad N*H* resonance at 4.49 ppm. The $^{11}$B NMR spectrum showed a doublet resonance at −18.5 ppm with a B−H coupling constant of 82 Hz, and in the $^1$H NMR spectrum the corresponding $H_B$ resonance was found at 3.78 ppm. Moreover, the relatively small $\Delta\delta$(*m*-F)−(*p*-F) separation was consistent with the presence of an anionic four-coordinate boron atom. A crystallographic study of **3** revealed face-to-face orientation of the [NH] and [BH] units with a H1···H2 separation of 2.191(1) Å (Figure 5) still in the range for dihydrogen bonding. It is interesting to see that the H1···H2 and B1···N1 (4.064 (2) Å) distances of **3** are both shorter than the corresponding ones of **2**, indicating a closer packing of the ion pair. From this observation one might be inclined to predict a shorter B···N distance for the PMP···$B(C_6F_5)_3$ FLP and consequently a $H_2$ activation process without barrier, which however does not match with reality.

Enlarging the Lewis base further, 1-ethyl-2,2,6,6-tetramethylpiperidine (Et-TMP) was employed to potentially increase within the given FLP model the distance to $B(C_6F_5)_3$. Indeed the mixture of Et-TMP and $B(C_6F_5)_3$ reacted in the presence of $H_2$ (1 bar) in benzene only at 110 °C to cleanly produce the $H_2$ split salt [2,2,6,6-$(CH_3)_4C_5H_6N(H)(CH_2CH_3)$][$HB(C_6F_5)_3$], **4a** (Scheme 2). A still higher activation barrier was noticed in comparison with the PMP/$B(C_6F_5)_3$ reaction. This decrease in reaction rates might again be explained in the same way as for the given difference in reaction rates between the TMP/$B(C_6F_5)_3$ and the PMP/$B(C_6F_5)_3$ pairs. In continuation of this series of sterically hindered piperidines as FLP base components, we also attempted preparation of a phenyl-substituted TMP possessing no α-hydrogen. This endeavor however failed by many synthetic routes and was finally given up.

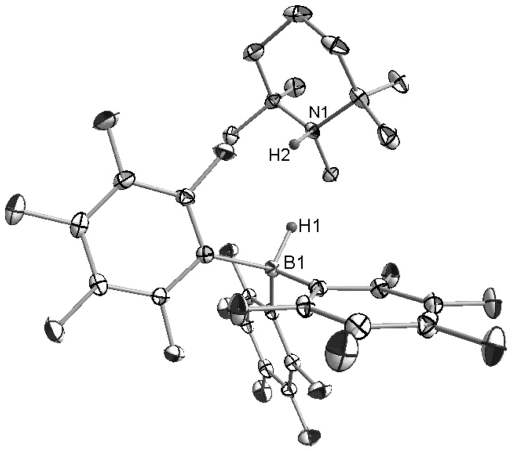



**Figure 5.** Molecular structure of **3** with 30% probability thermal ellipsoids. Hydrogen atoms except N*H* and B*H* atoms are omitted for clarity.

To conclude on this piperidine series for $H_2$ heterolysis, we found increasing temperature limits for the reactions to proceed in follow the order TMP(−80 °C) < PMP(25 °C) < Et-TMP-(110 °C). This order is not in line with the extrapolated nonbonding B···N distances of the FLPs as derived from the X-ray structures of the products, the B/N ion pairs. This discrepancy let us assume that our structural extrapolation failed or other factors are to a significant extent responsible for the unexpected lower limits of the reaction temperatures of the piperidine···$B(C_6F_5)_3$ FLPs. To explain the above order of the piperidine···$B(C_6F_5)_3$ FLPs, one could, among other possibilities, assume on the basis of not too different FLP association energies decreasing FLP associations with increasing temperatures and consequently lowered actual FLP concentrations at higher reaction temperatures, which are anticipated to lead to reduced overall reaction rates.

It was intriguing to see that in the absence of $H_2$ the stoichiometric mixture of Et-TMP and $B(C_6F_5)_3$ reacted, giving **4a** and [2,2,6,6-$(CH_3)_4C_5H_6N$=$CHCH_2$-$B(C_6F_5)_3$], **4b**, in a ratio of about 3:7 based on the NMR spectroscopic analysis (Scheme 2). **4b** featured a =C*H* resonance at 8.07 pm and a =CH−C$H_2$ resonance of 3.17 ppm in the $^1$H NMR spectrum. In addition, the $^{19}$F NMR resonances at −133.5 (*o*-), −160.8 (*p*-), −165.7 ppm (*m*-$C_6F_5$) and a singlet at −13.9 ppm in the $^{11}$B NMR spectrum were consistent with the formation of a four-coordinate boron anion. A single-crystal X-ray diffraction analysis of **4b** revealed a *transoid* structure of the [2,2,6,6-$(CH_3)_4C_5H_6N$=$CHCH_2$−$B(C_6F_5)_3$] molecule in the solid state with a N1····B1 nonbonding distance of 3.865(1) Å (Figure 6).

So in the absence of $H_2$, the Lewis acid $B(C_6F_5)_3$ actually effected α-hydride abstraction from the Et-TMP molecule, which might indicate that the B···N distance in the Et-TMP···$B(C_6F_5)_3$ FLP could be shorter than compared to those in the PMP···$B(C_6F_5)_3$ or TMP···$B(C_6F_5)_3$ encounter complexes, because the reactants had to come very close to

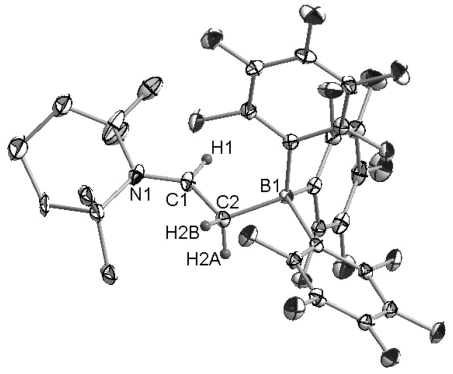



**Figure 6.** Molecular structure of **4b** with 30% probability thermal ellipsoids. Hydrogen atoms except C1*H* and C2*H* are omitted for clarity.

initiate α-hydride abstraction. A similar reaction to that for Et-TMP/$B(C_6F_5)_3$ was observed between bulky amines and $B(C_6F_5)_3$,[23,30−32] and by analogy the reaction of the trityl cation with sterically hindered amines afforded also an iminium cation rather than formation of a FLP with subsequent typical reactivity.[33] Subsequent to the α-hydride abstraction of Et-TMP the intermediate $[2,2,6,6\text{-}(CH_3)_4C_5H_6N{=}CHCH_3]$-$[HB(C_6F_5)_3]$ was envisaged to undergo a 1,3-H-shift to the vinyl ammonium salt $[2,2,6,6\text{-}(CH_3)_4C_5H_6NH\text{-}CH{=}CH_2][HB(C_6F_5)_3]$ (Scheme 2). The remaining Lewis acid $B(C_6F_5)_3$ then attacked the *β*-carbon atom of the cation and promoted proton transfer to a base from the acidic N*H* function to yield **4b**. The released proton either was accepted by free Et-TMP, affording $[2,2,6,6\text{-}(CH_3)_4C_5H_6N(H)CH_2CH_3][HB(C_6F_5)_3]$, **4a**, or reacted with the anion $[HB(C_6F_5)_3]^-$ as a base to generate $H_2$ and free $B(C_6F_5)_3$; the latter could re-enter reactions as a starting material.

Interestingly, at 110 °C the reaction of **4a** and **4b** got reversed within 24 h, and in the presence of $H_2$ **4a** was formed in a total yield of more than 80%. In the initial mixture **4a** is thus proposed to act as a proton and hydride transfer reagent ("ionic hydrogenation" conditions)[34] to the iminium α- and *β*-carbon, regenerating Et-TMP and $B(C_6F_5)_3$, which could then in a FLP-type reaction activate $H_2$ heterolytically, producing **4a** (Scheme 2). In $C_6D_6$ solution **4a** showed two sets of $^{19}F$ NMR signals (−134.1, −164.5, −167.7 and −134.4, −165.5, −168.4 ppm) in an approximate 1:1 ratio attributed to the *o*-, *p*-, and *m*-substituted fluorine atoms, which indicated two different arrangements of the ions: ion-paired structures based on slowly inverting axial and equatorial positions of the Et substituent. In the crystal of **4a** the equatorial "ion pair" seemed to prevail (*vide infra*). The ion pairing is proposed to stabilize these conformers each in its own way. The polar solvent $CDCl_3$ prevented formation of ion pairs by solvation effects; thus only the free ions of **4a** with a piperidinium ring inverting fast on the NMR time scale could be identified, which exhibited $^{19}F$ NMR resonances at −134.8 (*o*-), −164.5 (*p*-), and −167.8 (*m*-$C_6F_5$) ppm in $CDCl_3$ solution.

The single-crystal X-ray diffraction study of **4a** revealed that the cation and anion are oriented face-to-face to each other. The H1···H2 and B1···N1 nonbonding distances amount to 3.88(1) and 5.38(2) Å, respectively (Figure 7). These separations are quite long as compared with those in **2** and **3**, but seemed not particularly meaningful in terms of a retrospective estimate of the FLP distance from which **4a** was assumed to be formed.

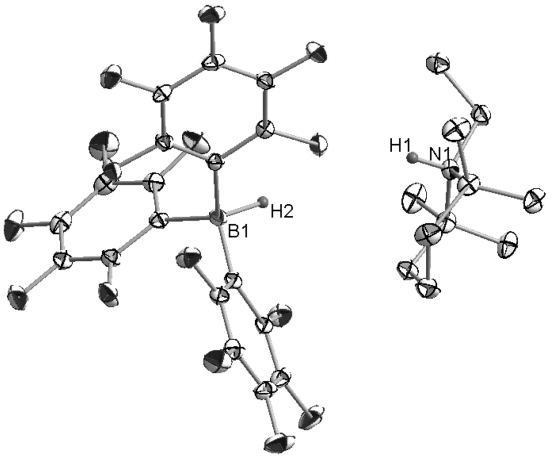
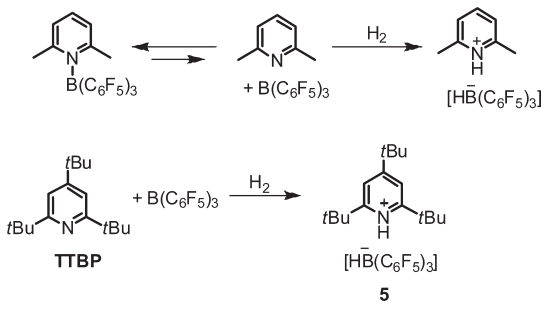



**Figure 7.** Molecular structure of **4a** with 30% probability thermal ellipsoids. Hydrogen atoms except N*H* and B*H* are omitted for clarity.

**Scheme 3**




Lutidine (LUT) shows lower basicity compared to piperidine. It has been reported to exhibit "border" reactivity of classical and frustrated Lewis pair properties with $B(C_6F_5)_3$ at room temperature.[35] We repeated the reaction at 25 °C in toluene solvent and tried to trace the intermediacy of the FLP/$H_2$ complex in the $H_2$ splitting process via $^1H$ NMR and $^{11}B$ NMR pursuits, but could not find any hint to the existence of intermediates. In the $^{11}B$ NMR spectrum at room temperature in toluene solution a singlet and a doublet at −4.5 and −25.2 ppm indicated the formation of the classical Lewis adduct $(2,6\text{-}Me_2C_5H_3N)B(C_6F_5)_3$ and the ionic product $[2,6\text{-}Me_2C_5H_3NH]$-$[HB(C_6F_5)_3]$, which were similar to those found by Stephan.[35]

We also tested the pyridine derivative 2,4,6-tri-*tert*-butylpyridine (TTBP), as a Lewis base. In combination with $B(C_6F_5)_3$ it was capable of activating $H_2$ heterolytically at 1 bar pressure at room temperature, but it required 24 h to reach a yield of 80%. The isolated product $[TTBPH][HB(C_6F_5)_3]$, **5**, is the same as the previously reported compound.[36] The B1···N1 nonbonding distance in the solid state is 4.78 (2) Å, and the H1···H2 distance was found to be 3.51(1) Å. Both lengths are consistent with isolated ions rather than a contact ion pair.

On the basis of the FLP concept we attempted quantification of the steric influence of the Lewis bases by attributing to them a cone angle derived from their adduct with $B(C_6F_5)_3$ (or with $BH_3$ for PMP and Et-TMP). A B−N bond distance of 1.7 Å was used in the DFT calculations of the cone angles (Table 1). The DMP showed relatively small cone angles of 152°, which nicely mirrors the fact that it forms a Lewis adduct with $B(C_6F_5)_3$. The


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**Table 1. Cone Angles[a] for Piperidine and Pyridine Derivatives**

| compound | cone angle (deg) |
|---|---|
| 2,6-dimethylpiperidine (DMP) | 152 |
| 2,2,6,6-tetramethylpiperidine (TMP) | 169 |
| 1,2,2,6,6-pentamethylpiperidine (PMP) | 194 |
| 1-ethyl-2,2,6,6-tetramethylpiperidine (Et-TMP) | 203 |
| 2,6-lutidine (LUT) | 164 |
| 2,4,6-tri-*tert*-butylpyridine (TTBP) | 166 |

[a] Cone angles of the piperidine and pyridine derivatives X based on the DFT-optimized geometries of X-$B(C_6F_5)_3$ (or X-$BH_3$ for X = PMP and Et-TMP). A fixed B−N bond distance of 1.7 Å was used in the calculations of the cone angles

LUT possesses a cone angle of 164°, which together with $B(C_6F_5)_3$ led to an equilibrium between free LUT/$B(C_6F_5)_3$ and the Lewis acid·base adduct at room temperature. According to the calculation results, the TTBP's cone angle (166°) is only a little larger than that for LUT, but no Lewis adduct was observed, only FLP chemistry, in the presence of $B(C_6F_5)_3$. This might demonstrate that the Lewis adduct formation is reacting to even small changes in the cone angles, while FLP reactivity first of all demands the free Lewis pair and in a secondary way influences the FLP reactivity. Assuming TMP and TTBP bases have similar cone angles, they should have similar B···N distances in the FLP encounter complexes. The quite fast reaction between TMP···$B(C_6F_5)_3$ and $H_2$ in comparison with the TTBP···B-$(C_6F_5)_3$ case is presumably also due to the much stronger Lewis basicity of TMP, which causes a high electrostatic field in the FLP cage.[28] Comparing the cone angles of TMP and PMP, the B···N distance in the PMP···$B(C_6F_5)_3$ FLP seemed to be necessarily longer than in the TMP···$B(C_6F_5)_3$ one, which might explain why PMP···$B(C_6F_5)$ FLP requires more severe reaction conditions to activate $H_2$. Nevertheless, the picture derived from the nonbonding B···N distance in the crystal structures of the $H_2$ splitting products gave a different order. This might be explained with a considerable structural flexibility of the bases in the encounter complexes. Et-TMP, though, has a larger cone angle than PMP, but the reaction course with the α-hydride abstraction by $B(C_6F_5)_3$ suggested the possibility of a closer B···N contact in the transition state, being presumably related to the "frustration" state. Thus, the cone angle determination combined with the experimental evidence point to a great structural flexibility in the FLP, which would not easily allow one to take the B···N distance as the decisive parameter for FLP reactivity.

## CONCLUSION

We applied several pyridine and piperidine derivatives to find correlations between the bulk of Lewis bases in FLP contact with $B(C_6F_5)_3$ and their reactivity in heterolytic $H_2$ activation. DMP with $B(C_6F_5)_3$ forms a classical Lewis pair. The Lewis acid combines with the Lewis base, resulting in the adduct DMP-$B(C_6F_5)_3$ at low temperature; but at a higher temperature of 110 °C, this pair dissociates, forming the encountering FLP, which then can activate $H_2$ heterolytically. The sterically demanding TMP, PMP, and Et-TMP together with $B(C_6F_5)_3$, however, formed encounter complexes that apparently activated the $H_2$ molecule without barrier. Especially the TMP···$B(C_6F_5)_3$ system was found capable of splitting $H_2$ even at 193 K. The strong Lewis acid $B(C_6F_5)_3$ encountered with the sterically highly demanding amine ethyltetramethylpiperidine underwent, in the absence of $H_2$, hydride abstraction of the α-H. After a 1,3-H-shift a vinyl ammonium cation was formed, which adds $B(C_6F_5)_3$ at the $C_\beta$ atom. Its acidic character promotes deprotonation of the $H_N$ atom by bases present in the reaction mixture, either the $[HB(C_6F_5)_3]$ anion or Et-TMP. Pyridine derivatives exhibit weaker Lewis basicity compared to piperidine derivatives, but still possess the ability to activate $H_2$ with $B(C_6F_5)_3$ under certain reaction conditions. Our studies suggest that the FLPs have the characteristic feature of structural flexibility, allowing variation of the B···N distance in a quite broad range. Whether or not this distance or the cones of the bases would have influence on the FLP reactivity could not be unravelled by these studies. In addition, detection of LB···$H_2$···LA intermediates through variation of the bases's cone angles remains a challenge.

## EXPERIMENTAL SECTION

**General Considerations.** All manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk techniques or in a glovebox (M. Braun 150B-G-II) filled with dry nitrogen. Solvents were freshly distilled under $N_2$ by employing standard procedures and were degassed by freeze−thaw cycles prior to use. DMP, TMP, PMP, LUT, and TTBP were purchased from Aldrich and stored over molecular sieves. $B(C_6F_5)_3$ was prepared according to the literature.[37] $^1H$ NMR, $^{19}F$ NMR, and $^{11}B\{^1H\}$ NMR data were recorded on a Varian Gemini-300 spectrometer. VT NMR data were recorded on a Bruker DRX 500 spectrometer. Chemical shifts are expressed in parts per million (ppm) referenced to deuterated solvent used. $^{19}F$ and $^{11}B$ were referenced to $CFCl_3$ and $BF_3OEt_2$, respectively. Microanalyses were carried out at the Anorganisch-Chemisches Institut of the University of Zürich.

Crystallographic data were collected at 183(2) K on an Oxford Xcalibur diffractometer (4-circle kappa platform, Ruby CCD detector and a single-wavelength Enhance X-ray source with Mo Kα radiation, $\lambda$ = 0.71073 Å).[38] Selected suitable single crystals were mounted using polybutene oil on the top of a glass fiber fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, absorption correction,[39,40] and data reduction were performed with the Oxford program suite CrysAlisPro.[40] The structures were solved with the direct methods and were refined by full-matrix least-squares methods on $F^2$ with SHELXL-97.[41] All programs used during the crystal structure determination process are included in the WINGX software.[42] The program PLATON[43] was used to check the results of the X-ray studies and to analyze the hydrogen-bonding systems. The hydrogen atoms bound to nitrogen or phosphorus were located in a difference Fourier map and refined without restraints. All other hydrogen positions were calculated after each cycle of refinement using a riding model with C−H distances in the range 0.93−0.98 Å and their isotropic displacement parameters constrained to 1.2 to 1.5$U_{eq}$(C).

**Synthesis of Et-TMP.** 2,2,6,6-Tetramethylpiperidine (2.82 g, 20 mmol), $K_2CO_3$ (3.45 g, 25 mmol), and 5 mL of $CH_3CN$ were added to a 50 mL round-bottom flask. The mixture was refluxed for 1 h at 85 °C in an oil bath with continuous stirring, after which the $CH_3CH_2I$ (3.12 g, 20 mmol) was added to the mixture. The mixture was refluxed for an additional 2 days and then cooled to room temperature. After filtration, the solvent was removed under vacuum to give a viscous liquid. The product was purified by silica gel flash column chromatography, eluting with an ethyl acetate/hexane mixture (1:20 v/v). The fraction containing the product was collected after removing the solvent *in vacuo*. Yield: 65%. The product Et-TMP was stored over molecular sieves. $^1H$ NMR

(toluene-$d_8$, 300 MHz, 293 K): $\delta$ 0.93 (s, 12H, $CH_3$), 1.00 (t, 3H, $^3J_{HH}$ = 6 Hz, $CH_3$), 1.32 (m, 4H, $CH_2$), 1.38 (m, 2H, $CH_2$), 2.33 (q, 2H, $^3J_{HH}$ = 6 Hz, $CH_2$).

**Generation of DMP-B($C_6F_5$)$_3$, 1a.** B($C_6F_5$)$_3$ (0.013 g, 0.025 mmol) and 2,6-dimethylpiperidine (0.0028 g, 0.025 mmol) were dissolved in $C_6D_6$ (0.5 mL), giving a colorless solution. The solution was characterized by NMR spectroscopy. $^1$H NMR ($C_6D_6$, 300 MHz, 293 K): $\delta$ 0.54 (m, 2H, $-CH_2$), 0.71 (m, 2H, $-CH_2$) 0.87 (d, 6H, $^3J_{HH}$ = 6 Hz, $-CH_3$), 3.42 (m, 2H, $-CH$), 5.35 (br, 1H, N*H*). $^{11}$B{$^1$H} NMR ($C_6D_6$, 96 MHz, 293 K): $\delta$ −4.3 (s). $^{19}$F NMR ($C_6D_6$, 282 MHz, 293 K): $\delta$ −128.2 (br, 2F, *o*-$C_6F_5$), −128.5 (d, 2F, $^3J_{FF}$ = 23 Hz, *o*-$C_6F_5$), −138.6 (br, 2F, *o*-$C_6F_5$), −155.2 (t, 1F, $^3J_{FF}$ = 21 Hz, *p*-$C_6F_5$), −157.6 (t, 2F, $^3J_{FF}$ = 21 Hz, *p*-$C_6F_5$), −162.4 (br, 2F, *m*-$C_6F_5$), −164.4 to −164.6 (m, 4F, *m*-$C_5F_5$). $^{13}$C{$^1$H} NMR ($C_6D_6$, 75 MHz, 293 K): $\delta$ 149.7 (dm, $^1J_{C-F}$ = 240 Hz, *o*-$C_6F_5$), 139.4 (dm, $^1J_{C-F}$ = 245 Hz, *p*-$C_6F_5$), 136.3 (dm, $^1J_{C-F}$ = 243 Hz, *m*-$C_6F_5$), 51.7 (*o*-$C_5H_9N$), 26.5 (*m*-$C_5H_9N$), 22.8 ($CH_3$), 10.8 (*p*-$C_5H_9N$). Anal. Calcd for $C_{25}H_{15}BF_{15}N$: C, 48.03; H, 2.42; N, 2.24. Found: C, 48.20; H, 2.47; N, 2.18.

**X-ray crystal structure analysis of 1a:** formula $C_{25}H_{15}BF_{15}N$, $M_r$ = 625.19, orthorhombic, *Pca*2$_1$, $a$ = 17.8991(4) Å, $b$ = 9.0917(2) Å, $c$ = 14.4468(3) Å, $V$ = 2350.97(9) Å$^3$, $Z$ = 4, $D_c$ = 1.766 g cm$^{-3}$, $\mu$ = 0.186 mm$^{-1}$, $\lambda$ = 0.71073 Å, $T$ = 183(2) K, 23 274 reflections collected, 3713 independent ($R_{int}$ = 0.0710) and 2972 observed reflections, 385 refined parameters, $R[F^2 > 2\sigma(F^2)]$ = 0.0431, $wR_2(F^2)$= 0.1172. CCDC 698951.

**Preparation of [DMPH][HB($C_6F_5$)$_3$], 1b.** Solid B($C_6F_5$)$_3$ (0.256 g, 0.5 mmol) and 2,6-dimethylpiperidine (0.0566 g, 0.5 mmol, 0.067 mL) were added to a 50 mL Schlenk tube and dissolved in toluene (10 mL), giving a colorless solution. The Schlenk tube was filled with $H_2$ (1 bar), and the solution was allowed to stir at 110 °C for 20 h. There was no precipitation formed during this period of time. Then the solvent was removed under reduced pressure, and a white solid was obtained, which was washed with pentane. The product was collected as a white solid. Yield: 71%. $^1$H NMR ($C_6D_6$, 300 MHz, 293 K): $\delta$ 0.35 (m, 4H, $-CH_2$), 0.52 (d, 6H, $^3J_{HH}$ = 6 Hz, $-CH_3$), 0.72 (m, 2H, $-CH_2$), 2.01 (br, 2H, $-CH$), 3.44 (q, 1H, $^1J_{HB}$ = 88 Hz, $-BH$), 4.52 (br, 2H, $-NH$). $^{11}$B{$^1$H} NMR ($C_6D_6$, 96 MHz, 293 K): $\delta$ −23.9 (s). $^{19}$F NMR ($C_6D_6$, 282 MHz, 293 K): $\delta$ −135.0 (d, 6F, $^3J_{FF}$ = 23 Hz, *o*-$C_6F_5$), −162.5 (t, 3F, $^3J_{FF}$ = 23 Hz, *p*-$C_6F_5$), −166.6 (t, 6F, $^3J_{FF}$ = 21 Hz, *m*-$C_6F_5$). $^{13}$C{$^1$H} NMR ($C_6D_6$, 75 MHz, 293 K): $\delta$ 148.8 (dm, $^1J_{C-F}$ = 248 Hz, *o*-$C_6F_5$), 139.1 (dm, $^1J_{C-F}$ = 250 Hz, *p*-$C_6F_5$), 137.3 (dm, $^1J_{C-F}$ = 247 Hz, *m*-$C_6F_5$), 56.7 (*o*-$C_5H_9N$), 29.6 (*m*-$C_5H_9N$), 22.7 ($CH_3$), 18.8 (*p*-$C_5H_9N$). Anal. Calcd for $C_{25}H_{17}BF_{15}N$: C, 47.87; H, 2.73; N, 2.23. Found: C, 47.92; H, 2.54; N, 2.10.

**X-ray crystal structure analysis of 1b:** formula $C_{63}H_{48}B_2F_{30}N_2$, $M_r$ = 1424.65, monoclinic, $P2_1/n$, $a$ = 12.3238(2) Å, $b$ = 16.6160(2) Å, $c$ = 15.7963(2) Å, $\beta$ = 107.804(2)°, $V$ = 3079.73(8) Å$^3$, $Z$ = 2, $D_c$ = 1.536 g cm$^{-3}$, $\mu$ = 0.153 mm$^{-1}$, $\lambda$ = 0.71073 Å, $T$ = 183(2) K, 41 687 reflections collected, 6301 independent ($R_{int}$ = 0.0281) and 4570 observed reflections, 443 refined parameters, $R[F^2 > 2\sigma(F^2)]$ = 0.0632, $wR_2(F^2)$ = 0.1882. CCDC 790973.

**Preparation of [PMPH][HB($C_6F_5$)$_3$], 3.** B($C_6F_5$)$_3$ (0.1024 g, 0.2 mmol) and 1,2,2,6,6-pentamethylpiperidine (0.031 g, 0.2 mmol) were added to a 50 mL Schlenk tube and dissolved in toluene (5 mL), giving a yellow solution. The Schlenk tube was filled with $H_2$ (1 bar), and the solution was allowed to stir at rt for 2 h. There was no precipitate formed during this process. The reaction was then concentrated to half of its volume, and hexane was added to induce precipitation. The product was washed with hexane after filtration and dried *in vacuo*. Yield: 82%. $^1$H NMR (toluene-$d_8$, 300 MHz, 293 K): $\delta$ 0.28 (s, 6H, $CH_3$), 0.57 (s, 6H, $CH_3$), 0.84 (m, 4H, $CH_2$), 1.08 (m, 2H, $CH_2$), 1.80 (d, 3H, $^3J_{HH}$ = 6 Hz, N-$CH_3$), 3.78 (q, 1H, $^1J_{HB}$ = 82 Hz, B*H*), 4.49 (br, 2H, N*H*). $^{19}$F NMR (toluene-$d_8$, 282 MHz, 293 K): $\delta$ −134.3 (d, 6F, $^3J_{FF}$ = 23 Hz, *o*-$C_6F_5$), −163.6 (t, 3F, $^3J_{FF}$ = 23 Hz, *p*-$C_6F_5$), −167.3 (t, 6F, $^3J_{FF}$ = 23 Hz, *m*-$C_6F_5$). $^{11}$B{$^1$H} NMR (toluene-$d_8$, 96 MHz, 293 K): $\delta$ −18.5 (s). $^{13}$C{$^1$H} NMR (toluene-$d_8$, 75 MHz, 293 K): $\delta$ 148.2 (dm, $^1J_{C-F}$ = 245 Hz, *o*-$C_6F_5$), 138.7 (dm, $^1J_{C-F}$ = 242 Hz, *p*-$C_6F_5$), 137.3 (dm, $^1J_{C-F}$ = 240 Hz, *m*-$C_6F_5$), 65.6 (*o*-$C_5H_6N$), 37.5 (*m*-$C_5H_6N$), 29.1 ($CH_3$), 18.8 (N-$CH_3$), 15.2 (*p*-$C_5H_6N$). Anal. Calcd for $C_{28}H_{23}BF_{15}N$: C, 50.25; H, 3.46; N, 2.09. Found: C, 50.52; H, 3.32; N, 1.90.

**X-ray crystal structure analysis of 3:** formula $C_{28}H_{23}BF_{15}N$, $M_r$ = 669.28, triclinic, $P\bar{1}$, $a$ = 10.7424(1) Å, $b$ = 11.2219(1) Å, $c$ = 13.6153(1) Å, $\alpha$ = 81.196(1)°, $\beta$ = 72.844(1)°, $\gamma$ = 63.415(1)°, $V$ = 1402.06(3) Å$^3$, $Z$ = 2, $D_c$ = 1.585 g cm$^{-3}$, $\mu$ = 0.162 mm$^{-1}$, $\lambda$ = 0.71073 Å, $T$ = 183(2) K, 30 255 reflections collected, 8556 independent ($R_{int}$ = 0.0248) and 5955 observed reflections, 419 refined parameters, $R[F^2 > 2\sigma(F^2)]$ = 0.0396, $wR_2(F^2)$ = 0.1098. CCDC 790974.

**Preparation of [2,2,6,6-($CH_3$)$_4$-$C_5H_6$NH($CH_2CH_3$)][HB($C_6F_5$)$_3$], 4a, and [2,2,6,6-($CH_3$)$_4$-$C_5H_6$N=CH$CH_2$-B($C_6F_5$)$_3$], 4b.** B($C_6F_5$)$_3$ (0.1024 g, 0.2 mmol) and 1-ethyl-2,2,6,6-pentamethylpiperidine (0. 034 g, 0.2 mmol) were added to a 50 mL Schlenk and dissolved in toluene (5 mL), giving a yellow solution. After stirring for 10 min at rt, the reaction was then concentrated to half volume, and hexane was added to promote precipitation. The product was washed with hexane after filtration and dried *in vacuo*. The white product contains a mixture of **4a** and **4b** in an approximate 3:7 ratio. Yield: 82%. **4b**: $^1$H NMR ($C_6D_6$, 300 MHz, 293 K): $\delta$ 0.47 (s, 6H, $-CH_3$), 0.72 (s, 6H, $-CH_3$), 0.89 (m, 4H, $-CH_2$), 1.25 (m, 2H, $-CH_2$), 3.17 (br, 2H, =CH$-CH_2$), 8.07 (br, 1H, =C*H*-$CH_2$). $^{11}$B{$^1$H} NMR ($C_6D_6$, 96 MHz, 293 K): $\delta$ −13.9 (s). $^{19}$F NMR ($C_6D_6$, 282 MHz, 293 K): $\delta$ −133.5 (d, 6F, $^3J_{FF}$ = 23 Hz, *o*-$C_6F_5$), −160.8 (t, 3F, $^3J_{FF}$ = 21 Hz, *p*-$C_6F_5$), −165.7 (t, 6F, $^3J_{FF}$ = 21 Hz, *m*-$C_6F_5$).

**X-ray crystal structure analysis of 4b:** formula $C_{29}H_{21}BF_{15}N$, $M_r$ = 679.28, monoclinic, $C2/c$, $a$ = 23.0895(3) Å, $b$ = 11.0393(2) Å, $c$ = 21.5309(3) Å, $\beta$ = 90.593(1)°, $V$ = 5487.76(14) Å$^3$, $Z$ = 8, $D_c$ = 1.644 g cm$^{-3}$, $\mu$ = 0.167 mm$^{-1}$, $\lambda$ = 0.71073 Å, $T$ = 183(2) K, 26 356 reflections collected, 6799 independent ($R_{int}$ = 0.0216) and 4967 observed reflections, 435 refined parameters, $R[F^2 > 2\sigma(F^2)]$ = 0.0460, $wR_2(F^2)$ = 0.1314. CCDC 790976.

**Preparation of [2,2,6,6-($CH_3$)$_4$-$C_5H_6$NH($CH_2CH_3$)][HB($C_6F_5$)$_3$], 4a.** Solid B($C_6F_5$)$_3$ (0.1024 g, 0.2 mmol) and 1-ethyl-2,2,6,6-pentamethylpiperidine (0.034 g, 0.2 mmol) were added to a 50 mL Schlenk and dissolved in toluene (5 mL), giving a colorless solution. The solution was filled with $H_2$ (1 bar), and the solution was allowed to stir at 110 °C for 24 h. There was no precipitate formed during this process. The reaction was then concentrated to half of its original volume, and pentane was added to induce precipitation. The product was washed with pentane after filtration and dried *in vacuo*. The product was collected as a white solid. Yield: 81%. $^1$H NMR ($C_6D_6$, 300 MHz, 293 K): $\delta$ 0.28 (s, $-CH_3$), 0.39 (s, $-CH_3$), 0.46 (s, $-CH_3$), 0.52 (s, $-CH_3$), 0.55 (t, $^3J_{HH}$ = 6 Hz, $-CH_2$-$CH_3$), 0.64 (t, $^3J_{HH}$ = 6 Hz, $-CH_2$-$CH_3$), 0.86 (m, $-CH_2$), 1.91 (m, $-CH_2$-$CH_3$), 2.03 (m, $-CH_2$-$CH_3$), 2.37 (br, B*H*), 4.24 (br, N*H*). $^{19}$F NMR ($C_6D_6$, 282 MHz, 293 K): $\delta$ −134.1 (d, $^3J_{FF}$ = 21 Hz, *o*-$C_6F_5$), −134.4 (d, $^3J_{FF}$ = 21 Hz, *o*-$C_6F_5$), −164.5 (t, $^3J_{FF}$ = 23 Hz, *p*-$C_6F_5$), −165.5 (t, $^3J_{FF}$ = 23 Hz, *p*-$C_6F_5$), −167.7 (t, $^3J_{FF}$ = 21 Hz, *m*-$C_6F_5$), −168.4 (t, $^3J_{FF}$ = 21 Hz, *m*-$C_6F_5$). $^{11}$B{$^1$H} NMR ($C_6D_6$, 96 MHz, 293 K): $\delta$ −25.1 (s). $^1$H NMR ($CDCl_3$, 300 MHz, 293 K): $\delta$ 1.46 (s, 6H, $-CH_3$), 1.53 (s, 6H, $-CH_3$), 1.56 (t, 3H, $^3J_{HH}$ = 6 Hz, $-CH_2$-$CH_3$), 1.86 (qd, 2H, $J_{HH}$ = 6, 3 Hz, $-CH_2$-$CH_3$), 3.51 (br, B*H*), 4.00 (br, N*H*). $^{19}$F NMR ($CDCl_3$, 282 MHz, 293 K): $\delta$ −134.8 (d, $^3J_{FF}$ = 21 Hz, *o*-$C_6F_5$), −164.5 (t, $^3J_{FF}$ = 21 Hz, *p*-$C_6F_5$), −167.8 (t, $^3J_{FF}$ = 20 Hz, *m*-$C_6F_5$). $^{11}$B{$^1$H} NMR ($C_6D_6$, 96 MHz, 293 K): $\delta$ −25.2 (s).

**X-ray crystal structure analysis of 4a:** formula $C_{29}H_{25}BF_{15}N$, $M_r$ = 683.31, monoclinic, $P2_1$, $a$ = 10.2209(6) Å, $b$ = 15.4745(6) Å, $c$ = 10.1157(6) Å, $\beta$ = 114.872(7)°, $V$ = 1451.54(16) Å$^3$, $Z$ = 2, $D_c$ = 1.563 g cm$^{-3}$, $\mu$ = 0.158 mm$^{-1}$, $\lambda$ = 0.71073 Å, $T$ = 183(2) K, 23 737 reflections collected, 3742 independent ($R_{int}$ = 0.0365) and 3418 observed

reflections, 426 refined parameters, $R[F^2 > 2\sigma(F^2)] = 0.0356$, $wR_2(F^2) = 0.1018$. CCDC 790975.

**Preparation of [TTBPH][HB($C_6F_5$)$_3$], 5.** Solid B($C_6F_5$)$_3$ (0.256 g, 0.5 mmol) and 2,4,6-tri-*tert*-butylpyridine (0.123 g, 0.5 mmol) were added to the a 50 mL Schlenk and dissolved in toluene (10 mL), giving a colorless solution. The solution was filled with $H_2$ (1 bar) and allowed to stir at room temperature for 24 h. There was no precipitate formed during this process. Then solvent was removed through reduced pressure to leave behind a white solid, which was then washed with hexane and diethyl ether. The product was collected as a white solid. Yield: 80%. $^1$H NMR ($CD_3CN$, 300 MHz, 293 K): $\delta$ 1.39 (s, 9H, *p*-*t*Bu), 1.50 (s, 18H, *o*-*t*Bu), 3.56 (q, 1H, $^1J_{H-B}$ = 90 Hz, B*H*), 7.78 (s, 2H, $C_5H_2N$), 10.8 (br, 1H, N*H*). $^{11}$B{$^1$H} NMR ($CD_3CN$, 96 MHz, 293 K): $\delta$ −24.59 (d, $^1J_{H-B}$ = 90 Hz). $^{19}$F NMR ($CD_3CN$, 282 MHz, 293 K): $\delta$ −135.2 (d, 6F, $^3J_{FF}$ = 18 Hz, *o*-$C_6F_5$), −165.6 (t, 3F, $^3J_{FF}$ = 20 Hz, *p*-$C_6F_5$), −168.9 (t, 6F, $^3J_{FF}$ = 25 Hz, *m*-$C_6F_5$). $^{13}$C{$^1$H} NMR ($CD_3CN$, 75 MHz, 293 K): $\delta$ 163.7 (*o*-$C_5H_2N$), 151.0 (*p*-$C_5H_2N$), 147.8 (*o*-$C_6F_5$), 139.3 (*p*-$C_6F_5$), 136.0 (*m*-$C_6F_5$), 120.7 (*m*-$C_5H_2N$), 37.9 (*o*-C($CH_3$)), 37.7 (*p*-C($CH_3$)), 30.2 (*p*-C($CH_3$)), 29.0 (*o*-C($CH_3$)). Anal. Calcd for $C_{35}H_{31}BF_{15}N$: C, 55.21; H, 4.10; N, 1.84. Found: C, 55.60; H, 4.18; N, 1.87.

## ■ ASSOCIATED CONTENT

**Ⓢ Supporting Information.** Computational details, Cartesian coordinates of the DFT-optimized species, description of the cone angle measurements, and CIF files giving details of the X-ray crystal structure analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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