H_2 Activation

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Hydrogen and Amine Activation by a Frustrated Lewis Pair of a Bulky N-Heterocyclic Carbene and $B(C_6F_5)_3$**

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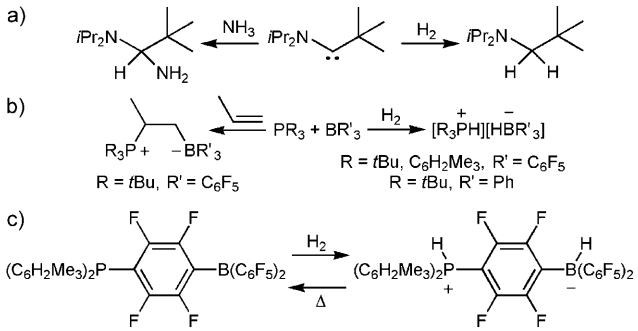
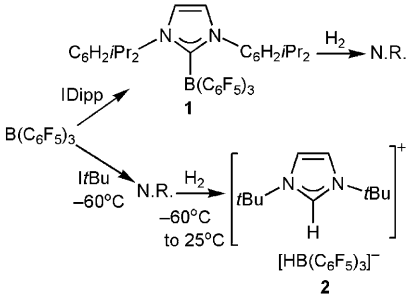
Dedicated to Professor R. J. Puddephatt

N-Heterocyclic carbenes (NHCs),[1] one class of stable and isolable carbenes,[2] are a well-studied ligand that can often replace phosphines in organometallic complexes, which have found extensive use in catalysis.[3,4] NHCs are also utilized as organocatalysts in their own right,[5–7] and there are growing number of reports of unique and unexpected reactivity of a variety of stable carbenes. For example, recent studies from Bertrand and co-workers showed that certain (amino)-(alkyl)carbenes react directly with dihydrogen and ammonia,[8] mimicking metalloid oxidative addition processes (Scheme 1a). Small main-group species, such as P_4[9,10] also react with carbenes. Current work from our group involves the reactivity of "frustrated Lewis pairs" (FLPs),[11,12] a combination of Lewis acids and bases in which steric encumbrance prevents or limits adduct formation. These unquenched sites can have unique reactivity. For example, mixtures of bulky phosphines and boranes react directly with dihydrogen[13,14] and olefins (Scheme 1b).[15,16] Furthermore, the compound $(2,4,6\text{-}Me_3C_6H_2)_2P(C_6F_4)B(C_6F_5)_2$ is the first example of a main group system that can reversibly react with dihydrogen (Scheme 1c).[17] The hydrogen-activating ability of these species has been exploited in metal-free catalytic reduction of imines, nitriles, and aziridines.[18,19] However, the range of compounds known to be reactive in FLP-type chemistry is relatively small to date.[20–22] Herein, we present bulky NHCs which are viable basic partners with the Lewis acid tris(pentafluorophenyl)borane[23–25] in FLP chemistry, showing bond activation reactivity with dihydrogen and amines. In the later case, the NHC also catalyzes an elimination reaction with primary and secondary alkyl amines adducts of tris(pentafluorophenyl)borane to directly and cleanly generate a variety of aminoboranes.



Scheme 1. Selected examples of main-group compounds that activate dihydrogen and other small molecules: a) an (amino)(alkyl)carbene, b) a mixture of bulky phosphines and boranes, c) a *para*-phosphinophenylborane.

In our initial efforts to uncover carbene-based FLPs, the reaction of the NHC 1,3-bis(2,6-diisopropylphenyl)-1,3-imidazol-2-ylidene (IDipp) with $B(C_6F_5)_3$ was performed. The ^{11}B NMR spectrum of the resulting product (**1**) shows a single resonance at −15.6 ppm, which is indicative of a four-coordinate boron center, suggesting the formation of the simple Lewis adduct of formulation $(IDipp)B(C_6F_5)_3$ (Scheme 2). The ^1H, ^{19}F and $^{13}C\{^1H\}$ NMR spectra of **1** are all quite complex, which is attributable to restricted rotation in this bulky adduct. In addition this formulation was confirmed by an X-ray crystal structure determination (Figure 1). Power and Phillips described the only reported $NHC/B(C_6F_5)_3$ adduct, which contains 1,3,4,5-tetramethyl-1,3-imidazol-2-ylidene. This latter species had a B–C(carbene) bond length of 1.6407(18) Å,[26] which compares with the B–C distance of 1.663(5) Å found in **1**. The greater steric demands presented by the *i*Pr groups on the arene substituents in IDipp presumably account for the longer B–C bond. It is noteworthy that Lewis acid–base adduct **1** proved unreactive towards dihydrogen or olefins Scheme 2), and is not stable for extended periods in solution, decomposing to give a mixture of products.



Scheme 2. Reactivity of $B(C_6F_5)_3$ with the NHCs IDipp and I*t*Bu with H_2. N.R. = no reaction.

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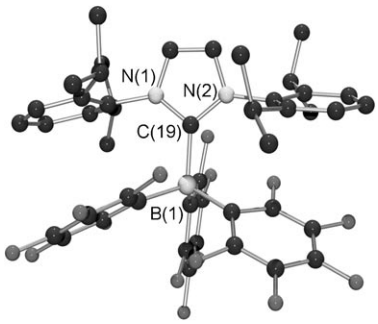


Figure 1. POV-ray depiction of the X-ray crystallographic structure of **1**. Hydrogen atoms have been omitted for clarity.

In a similar fashion to IDipp, reactions of 1,3-di-*tert*-butyl-1,3-imidazol-2-ylidene (I*t*Bu) and $B(C_6F_5)_3$ gave many products upon mixing at room temperature. Based on NMR spectroscopic data, some of these species appear to be the result of nucleophilic attack of aryl carbons in $B(C_6F_5)_3$. However, performance of the reaction at −60 °C in toluene resulted in the ^1H, ^{19}F, and ^{11}B NMR spectra that indicate no interaction between I*t*Bu and $B(C_6F_5)_3$. This observation supports the notion that this combination of carbene and tris(pentafluorophenyl)borane should behave as a FLP capable of reaction with small molecules. Indeed, addition of dihydrogen to a solution of equimolar amounts of I*t*Bu and $B(C_6F_5)_3$ at −78 °C results in the clean formation of the ionic complex $[I\textit{t}BuH][HB(C_6F_5)_3]$ (**2**) in 97% yield (Scheme 2). ^1H NMR signals of **2** for the imidazolium C−H and hydridoborate B−H hydrogen atoms are clearly observed at 8.20 and 3.63 ppm, respectively, with ^{19}F and ^{11}B NMR spectra indicative of the $[HB(C_6F_5)_3]^-$ anion. The formulation of **2** was also confirmed by X-ray crystallography (Figure 2). The geometry of the $[HB(C_6F_5)_3]^-$ anion is unexceptional.[13,18] The structure of the $[I\textit{t}BuH]^+$ cation has not been previously reported, but the metric parameters are similar to those seen in an *N*-adamanyl variant and the complex $[(I\textit{t}Bu)PdI_2PPh_3]$.[27] Unlike $[R_3PH][HB(C_6F_5)_3]$, no proton–hydride dihydrogen bond is observed.[13] The closest ion–ion contact is between the B−H hydride and a proton of the imidazolium *t*Bu group (2.592 Å). Compound **2** has a similar thermal stability to $[R_3PH][HB(C_6F_5)_3]$, failing to liberate dihydrogen upon heating to 150 °C for 4 days. In contrast to the phosphonium salts, **2** does not mediate the stoichiometric or catalytic reduction of imines, such as *t*BuN=CPh(H), over a 13 hour period at 25 °C in CD_2Cl_2. This latter observation is consistent with the greater basicity of carbene in comparison to phosphine, precluding protonation of imine and thus initiation of reduction.[18,19]

It is notable that Bertrand et al. observed no reaction of NHC-type carbenes with dihydrogen.[8] Furthermore, $B(C_6F_5)_3$ alone does not appreciably interact with dihydrogen.[13,14] This fact suggests that approach of the Lewis acid I*t*Bu and base $B(C_6F_5)_3$ is prevented by the steric demands of the *tert*-butyl substituents of the carbene, precluding dative bond formation. Such pairing could provide a reactive pocket for the activation of dihydrogen. Indeed, this proposition is supported by recently published DFT studies for the closely related situation observed for the approach of sterically demanding phosphine and borane.[14,16]

The carbene I*t*Bu also reacts with ammonia, aniline, and diphenylamine adducts of $B(C_6F_5)_3$ to give new species **3**–**5**, respectively, as evidenced by the observation signals in the ^1H NMR spectrum for the imidazolium protons at 9.53, 7.75, and 7.62 ppm, respectively. Owing to the FLP nature of I*t*Bu and $B(C_6F_5)_3$, no base exchange reactions are observed. The $^{11}B\{^1H\}$ NMR spectra for **3**–**5** revealed single resonances at −10.0, −9.7, and −7.6 ppm, respectively, which is consistent with generation of borate anions. For **4**, the ^{19}F NMR spectrum exhibits three peaks for the *ortho*, *para*, and *meta* fluorine atoms at −133.2, −161.9, −165.9 ppm, respectively. The corresponding ^{19}F NMR spectrum for **5** is more complicated at room temperature, which is consistent with restricted rotation arising from the increased steric bulk in the anion. These data support the formulation of the products as $[I\textit{t}BuH][H_2NB(C_6F_5)_3]$ (**3**) and $[I\textit{t}BuH][PhRNB(C_6F_5)_3]$ R = H (**4**), Ph (**5**). In the case of **4,** the structure was confirmed by an X-ray crystallographic study (Figure 3). The disorder of the $[I\textit{t}Bu]^+$ cation in **4** precludes metric comparison with compound **2**. Nonetheless, the closest approach of the cation and anion observed was between a C_6F_5 fluorine atom and a *t*Bu hydrogen atom (2.588 Å). In the anion, the B−N bond length is 1.532(8) Å, which is significantly shorter than the B−N bonds in other crystallographically characterized aminoborates of $B(C_6F_5)_3$ (1.628(3) and 1.636(3) Å in $[Na(OEt_2)_4][H_2N\{B(C_6F_5)_3\}_2]$,[28] 1.576(4) Å in $[LiOEt_2][C_4H_4NB(C_6F_5)_3]$,[29] and 1.565(4) Å in $[HNEt_3][(indolate)B(C_6F_5)_3]$).[30] The ammonia, aniline, and diphenylamine adducts of $B(C_6F_5)_3$[31] are deprotonated by I*t*Bu to generate

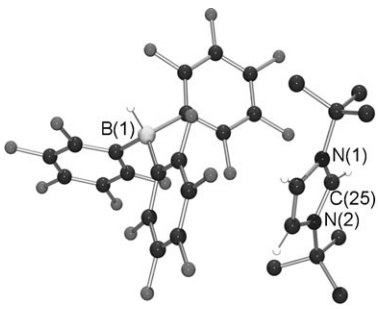


Figure 2. POV-ray depiction of **2**. Hydrogen atoms of the *t*Bu groups omitted for clarity.

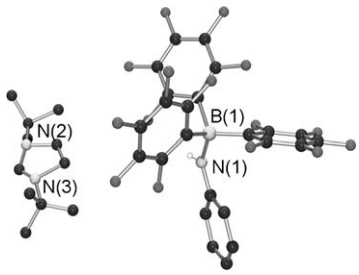
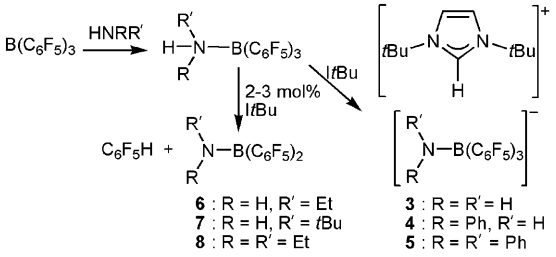


Figure 3. POV-ray depiction of the X-ray crystallographic structure of **4**. Non-N−H hydrogen atoms have been omitted for clarity. One orientation of the disordered cation is shown.

ionic complexes **3**–**5**, respectively, which is analogous to reaction with dihydrogen (Scheme 3).

In the corresponding reactions with the primary and secondary alkyl amines, adducts with I*t*Bu result in the formation of the aminoboranes $RR'NB(C_6F_5)_2$ (R = H, R′ = Et (**6**), *t*Bu (**7**); R = R′ = Et (**8**)). The generated C_6F_5H and unreacted I*t*Bu were observed by ^{19}F and ^{1}H NMR spectra. The observation of a broad signal centered around 33 ppm in the ^{11}B NMR spectra for **6**–**8** suggest three-coordinate monomeric aminoboranes. In addition, restricted rotation about the newly formed covalent B–N bond is evident in the ^{19}F NMR spectra. For example, the unsymmetrical aminoborane **7** has six separate ^{19}F signals at 25 °C. This is consistent with a significant overlap of the orbital occupied by the nitrogen lone pair and the empty boron p_Z orbital.[32,33]



Scheme 3. N–H bond cleavage of amines with I*t*Bu/$B(C_6F_5)_3$.

The presence and necessity of the carbene in the formation of **6**–**8** suggests that these reactions are catalytic in carbene, and indeed formation is readily accomplished with the use of 2–3 mol % of I*t*Bu. In these cases, the quantitative formation of the aminoboranes[33,34] is complete within 2 h at 25 °C. Notably, **6**–**8** are stable in solution under these conditions. The mechanism of these reactions are under study, but it may be that deprotonation of the initially formed amine adduct of $B(C_6F_5)_3$ by I*t*Bu affords an electron-rich aminoborate that then reacts with the transient imidazolium ion to eliminate C_6F_5H and regenerates the carbene. It is important to recognize that Bertrand et al. found that NHCs alone were unreactive towards N–H bonds,[8] although Clyburne and co-workers have observed a carbene C···H–N interaction between IMes and $HNPh_2$.[35] Additionally, phosphine–borane FLPs do not directly react with amines, as the transfer of a phosphonium proton to the nitrogen of an aminoborate anion is a key step in the mechanism of imine hydrogenation catalyzed by phosphonium borates. In marked contrast, the I*t*Bu/$B(C_6F_5)_3$ FLP mixture gives either an aminoborate salt or an aminoborane, depending on the nature of the amine substituents.

In conclusion, the combination of Lewis bases capable of FLP chemistry with tris(pentafluorophenyl)borane, which was previously limited to sterically demanding phosphines and amines, has been expanded to include sterically encumbered NHCs. These systems are shown to effect heterolytic cleavage of the H–H bond to give imidazolium borates. In addition, this FLP combination cleaves amine N–H bonds, affording aminoborate salts, or mediates loss of C_6F_5H to give aminoboranes. The latter case has been shown to be catalytic in carbene. These results provide further evidence that the concept of FLPs can be broadened resulting in the activation of a variety of small molecules and the discovery of new catalytic processes. A variety of new FLP systems are being investigated, and the their utility in stoichiometric and catalytic transformation are the subjects of current investigations.

Experimental Section

General considerations: All manipulations were performed on a double manifold $N_2(H_2)$/vacuum line with Schlenk glassware, or in an N_2-filled M-Braun or Vac Atmospheres glove box. The N_2 and H_2 gases were dried by passage through a Dririte column. Solvents (Aldrich) were dried using an Innovative Technologies solvent system. NMR spectra were obtained on a Bruker Avance 300 MHz spectrometer, and spectra were referenced to residual solvent (^{1}H, ^{13}C) or externally (^{11}B: BF_3OEt_2, ^{19}F: $CFCl_3$, ^{31}P: 85 % H_3PO_4). NMR solvents were purchased from Cambridge Isotopes, dried over CaH_2 or Na/benzophenone, vacuum distilled prior to use and stored over 4 Å molecular sieves in the glovebox. All amines were purchase from Aldrich; liquid amines were dried over 4 Å molecular sieves and solid reagents were used as received. I*t*Bu and IDipp were purchased from Strem Chemicals and used as received. $B(C_6F_5)_3$ was generously provided by Nova Chemicals. The adducts $tBuNH_2B(C_6F_5)_3$, $H_3NB(C_6F_5)_3$ and $EtNH_2B(C_6F_5)_3$ were prepared as previously described.[19,36]

1: A solution of $B(C_6F_5)_3$ (0.100 g, 0.20 mmol) in toluene (5 mL) was cooled to −78 °C. IDipp (0.076 g, 0.20 mmol) was added to the cooled solution in toluene (9 mL) with a syringe. The reaction was stirred for 5 min then allowed to warm to room temperature over 2 h. The solvent was removed in vacuo to give the product as a light brown solid. Note: prolonged stirring led to formation of several other products. Yield 0.161 g (91 %). X-ray quality crystals were obtained by cooling a toluene/hexanes solution to −35 °C. ^{1}H NMR ([D$_8$]toluene, −60 °C): $\delta = 6.97$ (d, 1H, $^{3}J_{HH} = 7.6$ Hz, Ar*H*), 6.92 (t, 1H, $^{3}J_{HH} = 7.0$ Hz, Ar*H*), 6.82 (t, 1H, $^{3}J_{HH} = 7.6$ Hz, Ar*H*), 6.58 (d, 2H, $^{3}J_{HH} = 7.6$ Hz, 2Ar*H*), 6.37 (d, 1H, $^{3}J_{HH} = 7.7$ Hz, Ar*H*), 6.32 (s, 1H, =C*H*), 6.20 (s, 1H, =C*H*), 3.26–3.02 (overlapping m, 3H, C*H*Me$_2$), 1.72 (br m, 1H, C*H*Me$_2$), 1.37 (d, 3H, $^{3}J_{HH} = 6.6$ Hz, CHMe$_2$), 1.31 (d, 3H, $^{3}J_{HH} = 6.4$ Hz, CHMe$_2$), 0.95 (d, 6H, $^{3}J_{HH} = 6.7$ Hz, CHMe$_2$), 0.90 (br, 2H, $^{3}J_{HH} = 6.6$ Hz, 2C*H*Me$_2$), 0.83 (d, 3H, $^{3}J_{HH} = 6.3$ Hz, CH*Me*$_2$), 0.62 ppm (d, 3H, $^{3}J_{HH} = 6.6$ Hz, CH*Me*$_2$). $^{11}B\{^{1}H\}$ NMR ([D$_8$]toluene, −60 °C): $\delta = -15.6$ ppm (s). ^{19}F NMR ([D$_8$]toluene, −60 °C): $\delta = -110.6$ (d, 1F, $^{3}J_{FF} = 24$ Hz, *o*-ArC*F*), −119.4 (dd, 1F, $^{3}J_{FF} = 52, 29$ Hz, *o*-ArC*F*), −126.0 (d, 1F, $^{3}J_{FF} = 24$ Hz, *o*-ArC*F*), −127.8 (d, 1F, $^{3}J_{FF} = 25$ Hz, *o*-ArC*F*), −132.8 (dd, 1F, $^{3}J_{FF} = 51, 25$ Hz, *o*-ArC*F*), −133.5 (d, 1F, $^{3}J_{FF} = 24$ Hz, *o*-ArC*F*), −157.1 (m, 2F, 2*p*-ArC*F*), −158.2 (t, 1F, $^{3}J_{FF} = 21$ Hz, *p*-ArC*F*), −162.5 (m, 1F, *m*-ArC*F*), −163.4 (m, 2F, 2 x *m*-ArC*F*), −164.3 (m, 2F, 2 x *m*-ArC*F*), −166.3 ppm (t, 1F, $^{3}J_{FF} = 21$ Hz, *m*-ArC*F*). Elemental analysis (%) calcd for $C_{45}H_{37}BF_{15}N_2$: C 59.95, H 4.14, N 3.11; found: C 59.51, H 4.14, N 2.95. X-ray analysis: triclinic, $P\bar{1}$, $a = 9.1610(11)$, $b = 11.9932(14)$, $c = 19.725(2)$ Å, $\alpha = 78.645(2)°$, $\beta = 85.995(2)°$, $\gamma = 75.689(2)°$, $V = 2058.3(4)$ Å^3, Data/variables: 7218:563, $R = 0.0559$, $R_w = 0.1226$, $GOF = 0.921$. CCDC-689780.

2: A solution of $B(C_6F_5)_3$ (0.282 g, 0.55 mmol) in toluene (4 mL) was placed in a 25 mL round-bottomed flask equipped with a sealable teflon tap. The solution was freeze–pump–thaw cycled three times, placed under an atmosphere of N_2, and frozen in liquid N_2. Under a strong flow of N_2, the teflon tap was quickly replaced with a septa and a solution of I*t*Bu (0.100 g, 0.55 mmol) in toluene (4 mL) was added quickly with a syringe. The teflon tap was replaced, the flask evacuated, and placed under an atmosphere of H_2. The flask was sealed, the reaction stirred at −78 °C for 2 h and then slowly warmed overnight. The white, turbid reaction mixture was pumped dry to give

a white powder. X-ray quality crystals were grown from layering pentane onto a CH_2Cl_2 solution of the product and cooling to −35 °C. Yield: 0.372 g (97 %). ^{1}H NMR (CD_2Cl_2): δ = 8.20 (t, 1H, $^4J_{HH}$ = 1.8 Hz, N_2CH), 7.50 (d, 2H, $^4J_{HH}$ = 1.8 Hz, =C*H*), 3.63 (1:1:1:1 q, 1H, $^1J_{HB}$ = 89 Hz, B*H*), 1.70 ppm (s, 18H, *t*Bu). ^{13}C{^{1}H} NMR (CD_2Cl_2): 148.7 (d, $^1J_{CF}$ = 244 Hz, *o*-Ar*C*F), 138.5 (d, $^1J_{CF}$ = 244 Hz, *p*-Ar*C*F), 137.2 (d, $^1J_{CF}$ = 245 Hz, *m*-Ar*C*F), 129.8 (s, N_2CH), 126.2 (b, B*C*), 121.3 (s, N*C*H), 61.8 (s, *t*Bu), 30.2 ppm (s, *t*Bu). ^{11}B NMR (CD_2Cl_2): δ = −25.3 ppm (d, $^1J_{BH}$ = 89 Hz, *B*H). ^{19}F NMR (CD_2Cl_2): δ = −133.9 (d, 6F, J_{FF} = 21 Hz, *o*-Ar*C*F), −164.9 (t, 3F, J_{FF} = 21 Hz, *p*-Ar*C*F), −167.5 ppm (m, 6F, *m*-Ar*C*F). Elemental analysis (%) calcd for $C_{29}H_{22}BF_{15}N_2$: C 50.17, H 3.19, N 4.03; found: C 50.39, H 3.03, N 4.10. X-ray analysis: monoclinic, $P2_1/c$, a = 15.4897(14), b = 9.7960(9), c = 20.1789(19) Å, β = 107.0520(10)°, V = 2927.3(5) Å^3, Data/variables: 5167:428, R = 0.0444, R_w = 0.1259, GOF = 0.928. CCDC-689783.

3–**5**: These species were prepared in a similar fashion. For **3**: I*t*Bu (0.017 g, 0.09 mmol) in hexanes (2 mL) was added to a solution of $H_3NB(C_6F_5)_3$ (0.050 g, 0.09 mmol) in toluene (3 mL). After addition, a light yellow solid precipitated from solution. The vial was rinsed with hexanes (3 × 2 mL) and the reaction was stirred for 5 min. The stirring was stopped and the solid was allowed to settle for 30 min after which the solvent was decanted. The remaining solid was dried to give the product as pale yellow solid. **3**: Yield 0.064 g, 95 %. ^{1}H NMR (CD_2Cl_2): δ = 9.53 (s, 1H, N_2CH), 7.42 (s, 2H, =C*H*), 4.00 (br s, 2H, NH_2), 1.72 ppm (s, 18H, *tBu*). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 148.6 (d, $^1J_{CF}$ = 244 Hz, *o*-Ar*C*F), 140.1 (d, $^1J_{CF}$ = 244 Hz, *p*-Ar*C*F), 137.5 (d, $^1J_{CF}$ = 245 Hz, *m*-Ar*C*F), 134.4 (s, N_2CH), 128.7 (b, B*C*), 119.9 (s, N*C*H), 61.4 (s, *t*Bu), 30.4 ppm (s, *t*Bu). ^{11}B NMR (CD_2Cl_2): δ = −10.0 ppm (br s, *B*NH_2). ^{19}F NMR (CD_2Cl_2): δ = −135.5 (br, 6F, *o*-C_6F_5), −161.2 (br, 3F, *p*-C_6F_5), −166.0 ppm (br, 6F, *m*-C_6F_5). Elemental analysis (%) calcd for $C_{29}H_{23}BF_{15}N_3$: C 49.11, H 3.27, N 5.92; found: C 49.33, H 3.50, N 6.12. **4**: Yield 0.063 g (94 %). ^{1}H NMR (C_6D_5Br): δ = 7.75 (s, 1H, N_2CH), 6.96 (t, 2H, $^3J_{HH}$ = 8 Hz, *m*-ArC*H*), 6.75 (s, 2H, =C*H*N), 6.60 (d, 2H, $^3J_{HH}$ = 8 Hz, *o*-ArC*H*), 6.35 (t, 1H, $^3J_{HH}$ = 8 Hz, *p*-ArC*H*), 4.26 (s, 1H, N*H*), 1.18 ppm (s, 18H, *t*Bu). ^{13}C{^{1}H} NMR (C_6D_5Br): δ = 152.4 (s, N_2CH), 148.2 (d, $^1J_{CF}$ = 235 Hz, *o*-Ar*C*F), 138.2 (d, $^1J_{CF}$ = 248 Hz, *p*-Ar*C*F), 136.3 (d, $^1J_{CF}$ = 239 Hz, *m*-Ar*C*F), 128.4 (s, *m*-Ar*C*H), 128.2 (s, =*C*H), 119.9 (s, =*C*HN), 114.4 (s, *o*-Ar*C*H), 114.1 (br s, BAr*C*), 112.6 (s, *p*-Ar*C*H), 60.1 (s, *t*Bu), 28.7 ppm (s, *t*Bu). ^{11}B NMR (C_6D_5Br): δ = −9.7 ppm (br s). ^{19}F NMR (C_6D_5Br): δ = −133.2 (d, 6F, $^3J_{FF}$ = 22 Hz, *o*-Ar*C*F), −161.9 (t, 3F, $^3J_{FF}$ = 21 Hz, *p*-Ar*C*F), −165.9 ppm (m, 6F, *m*-Ar*C*F). Elemental analysis (%) calcd for $C_{35}H_{27}BF_{15}N_3$: C 53.52, H 3.47, N 5.35; found: C 53.25, H 3.42, N 5.23. X-ray analysis: monoclinic, $C2/c$, a = 18.552(2), b = 18.677(2), c = 22.029(2) Å, β = 109.055(2)°, V = 7215.1(13) Å^3, Data/variables: 6363:483, R = 0.0804, R_w = 0.2193, GOF = 0.955. CCDC-689782. **5**: Yield 0.170 g, 98 %. ^{1}H NMR (C_6D_5Br): δ = 7.62 (br s, 1H, N_2CH), 7.21 (d, 4H, $^3J_{HH}$ = 8 Hz, *o*-ArC*H*), 6.98 (t, 4H, $^3J_{HH}$ = 8 Hz, *m*-ArC*H*), 6.77 (s, 2H, =C*H*N), 6.68 (t, 2H, $^3J_{HH}$ = 8 Hz, *p*-ArC*H*), 1.17 ppm (s, 18H, *t*Bu). ^{11}B NMR (C_6D_5Br): δ = −7.6 ppm (s). ^{19}F NMR (C_6D_5Br): δ = −131.4 (d, 2F, $^3J_{FF}$ = 23 Hz, *m*-Ar*C*F), −131.8 (d, 2F, $^3J_{FF}$ = 25 Hz, *o*-Ar*C*F), −132.1 (d, 2F, $^3J_{FF}$ = 26 Hz, *o*-Ar*C*F), −162.0 (t, 2F, $^3J_{FF}$ = 21 Hz, *p*-Ar*C*F), −162.3 (t, 1F, $^3J_{FF}$ = 21 Hz, *p*-Ar*C*F), −166.4 (m, 2F, *m*-Ar*C*F), −166.6 (m, 2F, *m*-Ar*C*F), −167.8 ppm (m, 2F, *m*-Ar*C*F). Elemental analysis (%) calcd for $C_{41}H_{31}BF_{15}N_3$: C 57.16, H 3.63, N 4.88; found: 57 03, H 3.50, N 4.85.

6: A solution of $EtNH_2B(C_6F_5)_3$ (0.012 g, 22 μmol) in C_6D_5Br (0.3 mL) was added to a solution of I*t*Bu (0.004 g, 22 μmol) in C_6D_5Br (0.3 mL). The reaction solution was placed in an NMR tube and NMR spectra were obtained within 5 min of mixing. ^{1}H NMR (C_6D_5Br): δ = 5.41 (br s, 1H, N*H*), 2.92 (quin, 2H, $^3J_{HH}$ = 7.0 Hz, NCH_2), 1.00 ppm (t, 3H, $^3J_{HH}$ = 7.0 Hz, NCH_2CH_3). ^{11}B NMR (C_6D_5Br): δ = 33.3 ppm (br s). ^{19}F NMR (C_6D_5Br): δ = −132.0 (m, 2F, *o*-Ar*C*F), −132.6 (m, 2F, *o*-Ar*C*F), −150.8 (t, 1F, $^3J_{FF}$ = 21 Hz, *p*-Ar*F*),−152.2 (t, 1F, $^3J_{FF}$ = 21 Hz, *p*-Ar*F*), −160.9 (m, 2F, *m*-Ar*C*F), −161.2 ppm (m, 2F, *m*-Ar*C*F).

7: A solution of I*t*Bu (1 mg, 6 μmol, 2 mol %) in dry hexanes (2 mL) was added to a slurry of $tBuNH_2B(C_6F_5)_3$ (0.160 g, 0.27 mmol) in dry hexanes (4 mL). The reaction was stirred at room temperature for 2 h. The solvent was removed in vacuo to give a white powder. Yield 0.111 g, 98 %. ^{1}H NMR (C_6D_5Br): δ = 5.63 (br s, 1H, N*H*), 1.10 ppm (s, 9H, *t*Bu*H*). ^{13}C{^{1}H} NMR (C_6D_5Br): δ = 147.3 (d, $^1J_{CF}$ = 244 Hz, *o*-Ar*C*F), 145.3 (d, $^1J_{CF}$ = 242 Hz, *o*-Ar*C*F), 141.5 (d, $^1J_{CF}$ = 256 Hz, *p*-Ar*C*F), 141.1 (d, $^1J_{CF}$ = 253 Hz, *p*-Ar*C*F), 137.1 (d, $^1J_{CF}$ = 251 Hz, 2 × overlapping *m*-Ar*C*F), 111.2 (br s, Ar*C*B), 52.8 (s, *t*Bu), 31.3 ppm (s, *t*Bu). ^{11}B NMR (C_6D_5Br): δ = 32.7 ppm (br s). ^{19}F NMR (C_6D_5Br): δ = −130.8 (m, 2F, *o*-Ar*C*F), −133.2 (m, 2F, *o*-Ar*C*F), −151.6 (t, 1F, $^3J_{FF}$ = 21 Hz, *p*-Ar*F*), −153.0 (t, 1F, $^3J_{FF}$ = 21 Hz, *p*-Ar*F*), −161.3 ppm (overlapping m, 4F, *m*-Ar*C*F). Satisfactory analytical data could not be obtained owing to air sensitivity.

8: I*t*Bu (1 mg, 0.006 mmol, 3 mol %) was added to a solution of $Et_2NHB(C_6F_5)_3$ (0.096 g, 0.19 mmol) in hexanes (4 mL) and benzene (2 mL). The reaction was stirred for 12 h, after which the solvent was removed in vacuo. The light oil was dissolved in hexanes, and the solvent was removed in vacuo to give the product as a light orange oil. Yield 0.075 g, 96 %. ^{1}H NMR (C_6D_5Br): δ = 3.05 (q, 4H, $^3J_{HH}$ = 7.0 Hz, NCH_2), 0.98 ppm (t, 6H, $^3J_{HH}$ = 7.0 Hz, NCH_2CH_3). ^{13}C{^{1}H} NMR (C_6D_5Br): δ = 145.0 (d, $^1J_{CF}$ = 246 Hz, *o*-Ar*C*F), 140.5 (d, $^1J_{CF}$ = 257 Hz, *p*-Ar*C*F), 136.4 (d, $^1J_{CF}$ = 257 Hz, *m*-Ar*C*F), 111.0 (br s, BAr*C*), 43.4 (s, NCH_2), 14.1 ppm (s, NCH_2CH_3). ^{11}B NMR (C_6D_5Br): δ = 33.5 ppm (br s). ^{19}F NMR (C_6D_5Br): δ = −132.1 (m, 4F, *o*-Ar*C*F), −152.9 (t, 2F, $^3J_{FF}$ = 21 Hz, *p*-Ar*C*F), −161.1 ppm (m, 4F, *m*-Ar*C*F). Elemental analysis (%) calcd for $C_{16}H_{10}BF_{10}N$: C 46.08, H 2.42, N 3.36; found: C 46.23, H 2.39, N 3.24.

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