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Dihydrogen Activation by Frustrated Carbene-Borane Lewis Pairs: An Experimental and Theoretical Study of Carbene Variation

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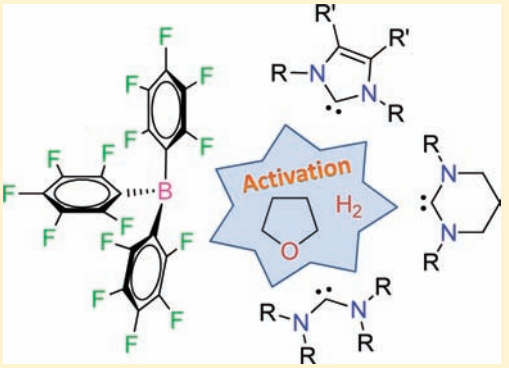
Supporting Information

ABSTRACT: A variety of Lewis acid−base pairs consisting of tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, in combination with sterically demanding five- and six-membered *N*-heterocyclic carbenes (NHCs) of the imidazolin-2-ylidene, imidazolidin-2-ylidene, and tetrahydropyrimidin-2-ylidene types were investigated with respect to their potential to act as frustrated Lewis pairs (FLP) by reaction with dihydrogen (H_2) and tetrahydrofuran (THF). A sufficient degree of "frustration" was usually established by introduction of a 1,3-di-*tert*-butyl or 1,3-diadamantyl carbene substitution pattern, which allows an unquenched acid−base reactivity and thus leads to heterolytic dihydrogen activation and ring-opening of THF. In contrast, 1,3-bis(2,6-diisopropylphenyl)-substituted carbenes showed ambiguous behavior, and the corresponding five-membered imidazolin-2-ylidene formed a stable carbene-$B(C_6F_5)_3$ adduct, whereas fast C−F activation and formation of a zwitterionic pyrimidinium-fluoroborate was observed for the six-membered tetrahydropyrimidin-2-ylidene. A stable adduct was also isolated for the combination of the acyclic carbene bis(diisopropylamino)methylene with $B(C_6F_5)_3$, and consequently no reactivity toward H_2 and THF was observed. To rationalize the reactivity of the carbene-borane Lewis pairs, the thermodynamics of adduct formation with $B(C_6F_5)_3$ were calculated for 10 different carbenes; the stability (or instability) of these adducts can be used as a good measure of the degree of "frustration".

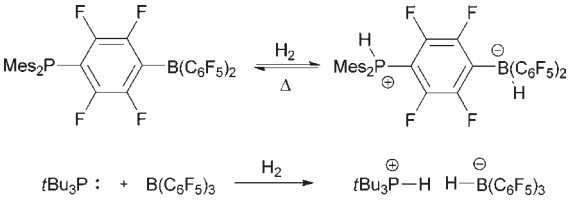


INTRODUCTION

Since 2006, when Stephan and co-workers reported the reversible, metal-free activation of dihydrogen by the phosphine-borane system *para*-$Mes_2P(C_6F_4)B(C_6F_5)_2$ (Mes = 2,4,6-trimethylphenyl, Scheme 1),[1] the use of so-called "frustrated Lewis pairs" (FLPs) for the activation of small molecules has developed into an exceptionally rapidly growing area of research.[2] In such FLP systems, the combination of sterically congested Lewis acids and bases prevents traditional adduct formation and thus allows mutual and unquenched reactivity of the two antagonistic partners. For instance, the formation of a stable P−B bond is suppressed in the well-studied pair $P(tBu)_3$/$B(C_6F_5)_3$,[3] which is therefore capable of heterolytic dihydrogen cleavage to afford cleanly the phosphonium borate salt $[(tBu)_3PH][HB(C_6F_5)_3]$ (Scheme 1).[4] To date, numerous phosphine/borane combinations have been established that can be employed for the activation not only of H_2[5] but also of other small molecules such as tetrahydrofuran (THF),[6] olefins,[7] alkynes,[8] carbon dioxide,[9] nitrous oxide,[10] isocyanates, azides,[11] and singlet dioxygen.[12] In addition, selective S−S and P−P bond activation has been achieved.[13,14]

During the twenty years since the isolation of the first stable carbenes of the imidazolin-2-ylidene type by Arduengo et al.,[15]

Scheme 1



N-heterocyclic carbenes (NHCs) have been used extensively for the replacement of phosphine ligands in organotransition metal chemistry and catalysis as a consequence of their high basicity and ensuing ability to form very strong metal−carbon bonds.[16,17] Accordingly, the combination of a sterically demanding carbene such as 1,3-di-*tert*-butylimidazolin-2-ylidene (**1a**) with the borane $B(C_6F_5)_3$ could be expected to afford a viable FLP system, which indeed proved capable of H−H, C−O, C−H, and N−H bond activation.[18−21] In fact, this Lewis pair exhibits a particularly strong propensity for heterolytic dihydrogen cleavage, which can be ascribed to the strongly exergonic nature of the

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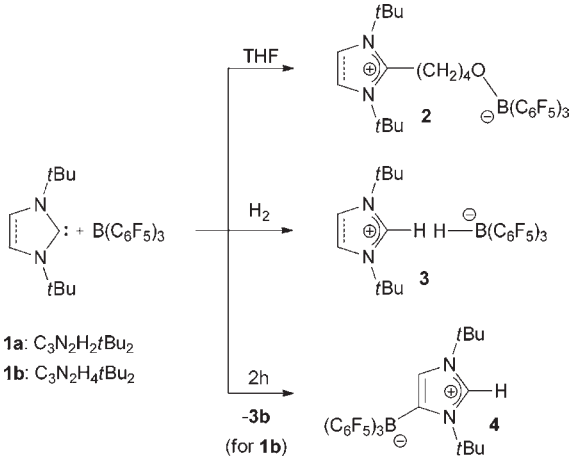
Scheme 2



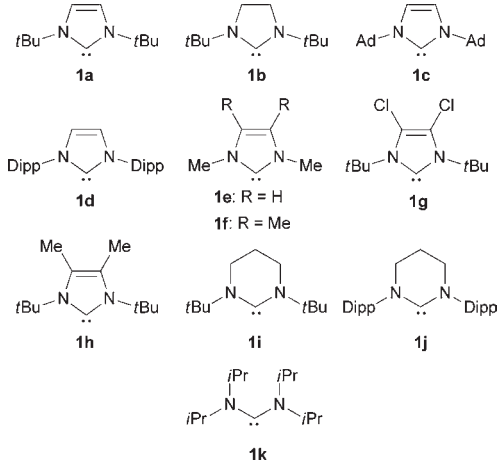


Figure 1. *N*-Heterocyclic carbenes for the preparation of carbene-$B(C_6F_5)_3$ Lewis pairs.

H_2 splitting reaction as a result of an enhanced cumulative acid−base strength.[22] In the absence of H_2 or other substrates, however, this high reactivity leads to self-destruction and irreversible formation of the abnormal carbene-borane adduct **4** by C−H activation, which eliminates mismatching between Lewis acid and base and enables this FLP to circumvent frustration at the expense of its activity (Scheme 2).[18] Similarly, abnormal carbene binding was observed upon P−P bond cleavage of white phosphorus by **1a**/$B(C_6F_5)_3$.[23,24]

To block this deactivation path, the dihydro congener of **1a**, the imidazolidin-2-ylidene **1b**, was employed, which was also successfully used for H_2 and THF activation in combination with $B(C_6F_5)_3$ (Scheme 2).[20] Surprisingly, however, all attempts to isolate a normal carbene-borane adduct from solutions of **1b**/$B(C_6F_5)_3$ failed and again afforded the abnormal adduct **4** together with equimolar amounts of the corresponding imidazolidinium hydroborate **3b**. Although unexpected, the propensity of this system to undergo self-dehydrogenation indicated the potential of carbene-borane FLPs to act as stoichiometric dehydrogenation reagents,[25] and this has indeed been demonstrated for the pair **1a**/$B(C_6F_5)_3$ through the preparation of *N*-heterocyclic germylenes by H_2 or, more precisely, H^+/H^- extraction.[26]

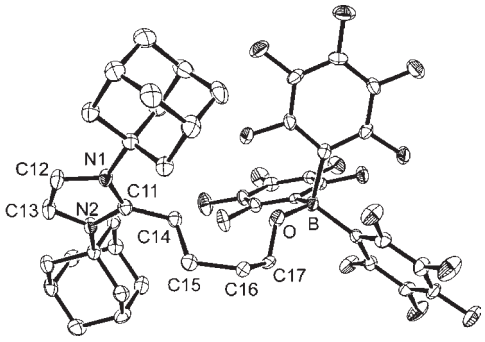


Figure 2. ORTEP diagram of **5** with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å] and angles [deg]: C11−N1 1.3631(17), C11−N2 1.3552(17), C12−C13 1.334(2), C11−C14 1.4946(19), B−O 1.447(2), C17−O 1.354(2), O−C(17′) 1.403(7); N1−C11−N2 107.76(12), O−B−C40 106.87(13), O−B−C50 110.98(13), O−B−C60 112.32(13). Only one position of the disordered atoms C16 and C17 is shown.

According to theoretical calculations, the failure to isolate any normal adducts from mixtures of **1a** and **1b** with $B(C_6F_5)_3$ should not be ascribed solely to their thermodynamic instability but also to the higher stability of the abnormal adduct **4**, whereas the reverse is true for the sterically less demanding carbene **1e** bearing methyl substituents in the 1,3-positions (Figure 1).[18] Accordingly, the related normal adduct [(**1f**)$B(C_6F_5)_3$] was isolated and structurally characterized,[27] as was [(**1d**)$B(C_6F_5)_3$], indicating that the 1,3-diisopropylphenyl substituents in **1d** are not sufficiently bulky to establish a frustrated Lewis pair (Figure 1, vide infra).[19] In view of the many variations that have been applied to phosphine-borane Lewis pairs,[28] the study presented herein was initiated (i) to elaborate the factors leading to "frustration" in related carbene-borane Lewis pairs and (ii) to identify possible deactivation pathways such as normal and abnormal adduct formation or other thermal rearrangements similar to those that have been discovered for P−B systems.[29] Therefore, the reactivity of the carbenes **1c**, **1d**, and **1g**−**1k** toward $B(C_6F_5)_3$ was studied and, if possible, these combinations were employed in THF and H_2 activation. In addition, the thermodynamics of normal adduct formation with $B(C_6F_5)_3$ were calculated for all carbenes **1a**−**1k** to rationalize the experimental results and to establish a measure for the degree of "frustration" (Figure 1).

RESULTS AND DISCUSSION

Lewis Pair 1,3-Bis(1-adamantyl)imidazolin-2-ylidene (1c)/$B(C_6F_5)_3$. As previously described, the carbenes **1a** and **1b** bearing *N*-*tert*-butyl substituents cleanly effect heterolytic cleavage of THF and H_2 in combination with $B(C_6F_5)_3$, and, for steric reasons, similar reactivity was expected for 1,3-bis(1-adamantyl)imidazolin-2-ylidene (**1c**). Hence, mixing **1c** with $B(C_6F_5)_3$ in THF afforded the imidazolium-borate zwitterion **5** in 93% yield as a white crystalline solid. The formation of **5** can be rationalized by nucleophilic attack of the carbene at the Lewis acid−base adduct [(THF)$B(C_6F_5)_3$], followed by ring-opening of the THF ligand. The presence of a $(CH_2)_4O$ moiety is indicated by the four methylene resonances at 1.68, 1.95, 3.23, and 3.54 ppm in the ^1H NMR spectrum and at 27.6, 28.6, 31.6, and 62.7 ppm in the ^{13}C NMR spectrum. The ^{11}B NMR resonance at −1.7 ppm falls in the range observed for similar compounds obtained from carbene- and phosphine-borane

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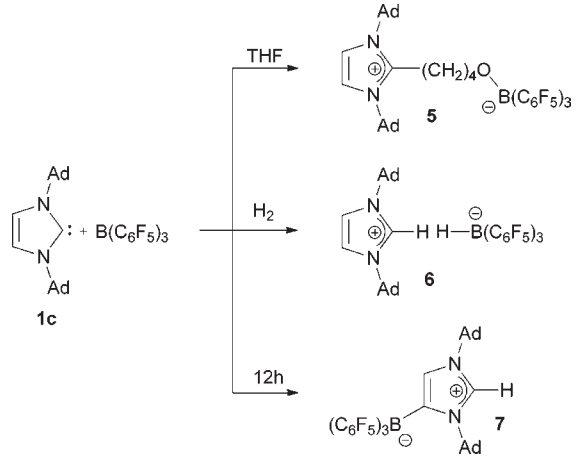
Scheme 3

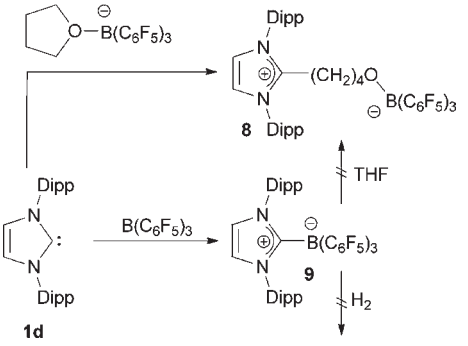


pairs.[6,18,20] The zwitterionic nature of **5** was also confirmed by X-ray diffraction analysis (Figure 2), and the structural parameters with C11−N1 = 1.3631(17) Å, C11−N2 = 1.3552(17) Å, and N1−C11−N2 = 107.76(12)° are typical of imidazolium salts.[15] The ring-opened THF molecule gives rise to a B−O bond of 1.446(2) Å and a C11−C14 bond of 1.494(2) Å. Note however that part of the $(CH_2)_4O$ chain is disordered (see Experimental Section).

The reactivity of **1c**/$B(C_6F_5)_3$ indicated the potential of this Lewis pair for H_2 activation, and purging a toluene solution containing equimolar amounts of **1c** and $B(C_6F_5)_3$ with H_2 at −30 °C resulted in the formation of a white precipitate. After stirring for 8 h under a static H_2 atmosphere, the imidazolium hydroborate salt **6** was isolated by filtration in 89% yield (Scheme 3). In comparison with the carbenes **1a** and **1b**, the reaction seems to be somewhat less efficient, since almost quantitative amounts of **3a** and **3b** were usually obtained within 2 h.[18,20] In the ^{1}H NMR spectrum, the resonances pertaining to the cation are found at 8.29 and 7.47 ppm for the two types of NCH hydrogen atoms, along with three resonances at 1.78, 2.10, and 2.30 ppm for the adamantyl groups, whereas the anion gives rise to a broad quartet at 3.58 ppm. Accordingly, a doublet is observed in the ^{11}B NMR spectrum at −25.2 ppm, with a $^1J(^1H,^{11}B)$ coupling constant of 90 Hz. In addition, the $HB(C_6F_5)_3$ anion generates three ^{19}F NMR resonances at −133.8, −164.6, and −167.5 ppm for the *ortho*, *para* and *meta* fluorine atoms, respectively.

Similar to its *tert*-butyl congener **1a**,[18] **1c** does not form an isolable normal adduct with $B(C_6F_5)_3$, and attempts to crystallize such an adduct under various conditions either led to fractional crystallization of the two components or indicated formation of the abnormal adduct **7**, in which the $B(C_6F_5)_3$ moiety is attached to the 4-position of the imidazole heterocycle (Scheme 3). **7** could be isolated in good yield (79%) as a white solid from a toluene solution of **1c**/$B(C_6F_5)_3$ after stirring for 12 h and precipitation with hexane. Solutions of **7** are inert toward H_2, but slow decomposition was observed in chlorinated solvents and in THF solution. The ^{11}B NMR resonance at −15.4 ppm is in agreement with the presence of a boron atom in a tetrahedral environment, and the ^{19}F NMR spectrum of **7** exhibits six signals each for the *ortho* and *meta* fluorine atoms and three signals for the *para* fluorine, which can be explained by hindered rotation around all four B−C bonds, rendering the 15 fluorine atoms inequivalent at room temperature on the NMR time scale.

Scheme 4



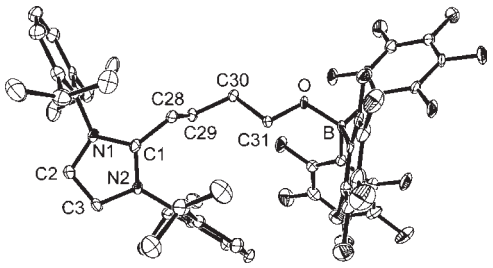


Figure 3. ORTEP diagram of **8** with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å] and angles [deg]: C1−N1 1.345(3), C1−N2 1.338(3), C2−C3 1.338(4), C1−C28 1.479(3), B−O 1.468(3), C31−O 1.412(3); N1−C1−N2 106.8(2), O−B−C41 114.7(2), O−B−C51 104.93(19), O−B−C61 106.4(2).

In agreement with the abnormal binding mode, the ^{1}H and ^{13}C NMR spectra reveal the presence of two different imidazole C−H groups with signals at 6.84 and 8.07 ppm and at 123.7 and 128.2 ppm, respectively. These spectroscopic data are in excellent agreement with those established for **4**,[18] confirming that **7** constitutes another example of an abnormal NHC main group complex,[30] which are much rarer than related abnormal transition metal NHC complexes.[31]

Lewis Pair 1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (1d)/B(C_6F_5)$_3$. The Lewis pair **1d**/$B(C_6F_5)_3$ had already been studied and shown to form the normal adduct $[(\mathbf{1d})B(C_6F_5)_3]$ (**9**), which proved unreactive toward dihydrogen or olefins.[19] Independently, we also studied this pair and initially treated a THF solution of the borane with **1d** to isolate the zwitterion **8** in quantitative yield as a white solid (Scheme 4). The bridging $(CH_2)_4O$ moiety gives rise to four methylene resonances in the ^{1}H (1.19, 1.41, 2.62, 2.84 ppm) and ^{13}C NMR spectra (25.1, 25.7, 33.0, 63.9 ppm), and the ^{11}B NMR resonance at −2.6 ppm is similar to those established for **2a**, **2b**, and **5**. The molecular structure of **8** was additionally established by X-ray diffraction analysis (Figure 3), confirming its imidazolium-borate character with C−N bond lengths of C1−N1 1.345(3) Å and C1−N2 1.338(3) Å and with an N1−C1−N2 angle of 106.8(2)°. The B−O bond length is 1.468(3) Å, which is slightly longer than in **5** [1.447(2) Å].

The observation that the carbene **1d** is not able to replace the THF ligand in the solvate complex $[(THF)B(C_6F_5)_3]$, but effects C−O bond cleavage with formation of **8**, indicated the potential presence of an FLP system. Mixing the two components in toluene, however, afforded the normal adduct **9** as a white solid

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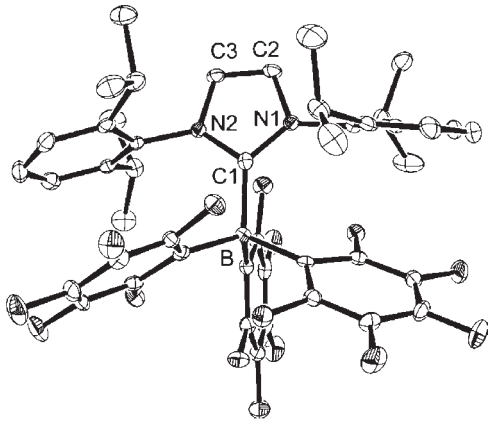
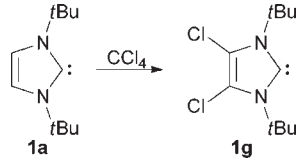


Figure 4. ORTEP diagram of **9** with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å] and angles [deg]: B−C1 1.684(2), C1−N1 1.3672(18), C1−N2 1.3760(17), C2−C3 1.334(2); N1−C1−N2 104.03 (12), C1−B−C31 109.59(11), C1−B−C41 108.79(11), C1−B−C51 112.85(12).

Scheme 5



after precipitation with pentane. As previously described,[19] this compound is not indefinitely stable in solution at room temperature and is not capable of cleaving dihydrogen. The X-ray crystal structure of **9** had also been previously determined, at room temperature in the triclinic space group $P\bar{1}$, and a $C_{carbene}$−B bond length of 1.663(5) Å was found.[21] In our hands, the compound crystallized in the monoclinic space group $P2_1/c$ from a toluene/pentane mixture at −35 °C, and the resulting molecular structure at 100 K is shown in Figure 4 for comparison. The molecular conformations of both forms are closely similar except for slight differences in the orientation of the Dipp groups, but the $C_{carbene}$−B bond length of 1.684(2) Å is longer than previously determined for **9** (vide supra) and for the adduct [(**1f**)B(C_6F_5)$_3$] [1.6407(16) Å] containing the sterically less demanding carbene 1,3,4,5-tetramethylimidazolin-2-ylidene (**1f**).[27] Both forms of **9** are characterized by substantial displacements of the substituents out of the central ring plane (in our structure −0.30 Å for B, 0.17 Å for C4, and 0.33 Å for C16), reflecting the steric overcrowding.

Lewis Pair 1,3-Di-*tert*-butyl-4,5-dichloroimidazolin-2-ylidene (1g)/B(C_6F_5)$_3$. To identify other possibilities of blocking FLP deactivation by C−H activation and abnormal adduct formation, we aimed at the synthesis of the carbene **1g**, bearing two chlorine atoms in the 4,5-positions. In a similar fashion as described for the preparation of 1,3-diaryl-4,5-dichloroimidazolin-2-ylidenes (aryl = 2,4,6-trimethylphenyl, 2,6-diisopropylphenyl),[32] the new carbene **1g** could be obtained from the chlorination reaction of **1a** with 2 equiv of carbon tetrachloride at 40 °C in THF (Scheme 5). After careful evaporation of the solvent and sublimation at 60 °C under high vacuum, **1g** was isolated in moderate yield (43%). In contrast to its 1,3-aryl congeners, **1g** is not air-stable; it decomposes rapidly upon exposure to air and also appears to be light-sensitive at room temperature. **1g** was characterized by NMR

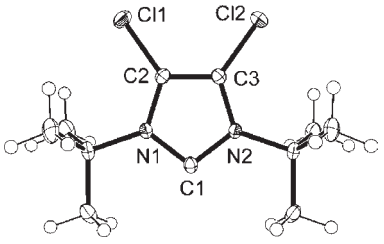
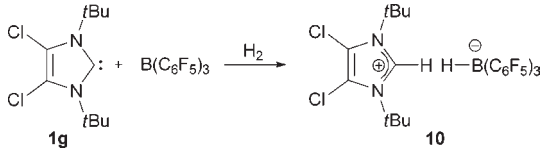


Figure 5. ORTEP diagram of **1g** with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å], bond angles and torsion angles [deg]: N1−C1 1.3677(10), N2−C1 1.3661(10), C2−C3 1.3548(11), C2−Cl1 1.7087(8), C3−Cl2 1.7087(8); N1−C1−N2 104.52(7); C1−N2−C8-C10 −4.1(1), C1−N1−C4-C6 0.9(1).

Scheme 6



spectroscopy, and the ^{13}C NMR resonance of the carbene carbon atom is found at 213.0 ppm in the typical carbene range,[16i] albeit at slightly higher field than observed for the related 1,3-diaryl-4,5-dichloro carbenes.[32] Single crystals suitable for an X-ray diffraction analysis were obtained by sublimation, and the molecular structure (Figure 5), with approximate C_{2v} symmetry (rms deviation 0.03 Å), reveals structural parameters within the imidazole ring [C1−N1 = 1.3677(10) Å, C1−N2 = 1.3661(10) Å, N1−C1−N2 = 104.52(7)°] that are in good agreement with those established for the two related carbenes.[32] It should be noted, however, that the N−C−N angle in **1g** is 3° larger than in the 1,3-diaryl congeners, which could be ascribed to a stronger steric repulsion between the chlorine and *tert*-butyl substituents. Since the *t*Bu groups are forced to adopt a staggered conformation with regard to the C−Cl axes, one methyl group of each substituent is located in the imidazole plane with the corresponding C-Me vector aligned with the carbene lone pair. Consequently, **1g** could be rated as a sterically more demanding carbene ligand than **1a**.

Although the steric properties of **1g** might afford an FLP system with a higher degree of frustration, lower reactivity should be expected, since the electron-withdrawing nature of the chlorine substituents usually affords a substantially reduced basicity and proton affinity.[33] These factors might account for the observation that an equimolar THF solution of **1g** and B(C_6F_5)$_3$ does not give any product with a ring-opened THF molecule; slow decomposition was observed instead. It was anticipated that blocking the 4,5-positions in **1g** might render the isolation of a carbene-borane adduct [(**1g**)B(C_6F_5)$_3$] possible; however, all attempts have failed so far, and mixing **1g** with the borane in benzene or toluene led to the separation of an intractable red oil, which could not be sufficiently characterized because of rapid decomposition upon dissolution in more polar solvents. Nonetheless, the FLP **1g**/B(C_6F_5)$_3$ proved capable of heterolytic dihydrogen cleavage, and purging a toluene solution with H_2 resulted in the slow formation of a white precipitate, containing the imidazolium-hydroborate **10** (Scheme 6). NMR spectroscopic characterization also indicated the presence of the [(HO)B(C_6F_5)$_3$]$^-$ anion, which might stem from moisture and

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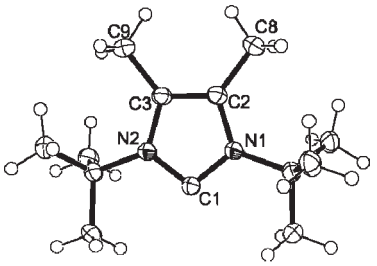


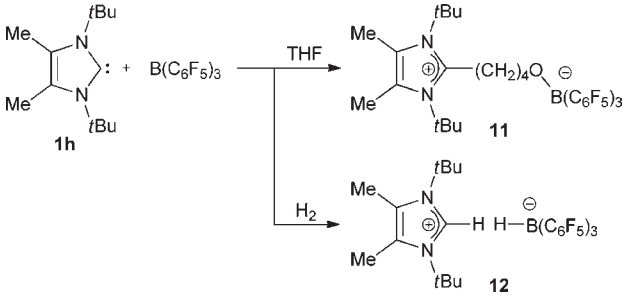
Figure 6. ORTEP diagram of **1h** with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å], bond angles and torsion angles [deg]: N1−C1 1.3638(16), N2−C1 1.3643(16), C2−C3 1.3572(19), C2−C8 1.4963(17), C3−C9 1.4990(18); N1−C1−N2 103.40(10); C1−N1−C4-C5 18.4(2), C1−N2−C10-C11 16.1(2).

H_2O cleavage. Therefore, **10** was only isolated in 40% yield. Optimization of the reaction conditions was not attempted, but the results are sufficient to demonstrate the inferior dihydrogen activation properties of **1g**.

Lewis Pair 1,3-Di-*tert*-butyl-4,5-dimethylimidazolin-2-ylidene (1h)/B(C_6F_5)$_3$. Another possibility of blocking side reactions at the 4/5-positions of carbenes such as **1a** was recently introduced by Polyakova and co-workers,[34] who reported a new synthetic route to 4,5-disubstituted *N,N′*-di-*tert*-alkylimidazolin-2-ylidenes, including the carbene **1h** as the dimethyl derivative of **1a**. NMR spectroscopic pK_a measurements revealed that **1h** is the strongest imidazolin-2-ylidene base known to date (pK_a = 24.8).[33,35] Thus, the use of **1h** together with B(C_6F_5)$_3$ should afford an FLP with an even higher reactivity than that of **1a**/B(C_6F_5)$_3$ and should additionally prevent deactivation by abnormal carbene binding. As previously described,[34] **1h** was isolated in a multistep synthesis as a colorless liquid, which solidifies when stored at −30 °C. Single crystals of **1h** could be obtained from pentane solution at −30 °C, and X-ray diffraction analysis provided the molecular structure (approximate symmetry C_{2v} with rms deviation 0.2 Å) shown in Figure 6. The structural parameters within the imidazole ring [N1−C1 = 1.3638(16) Å, N2−C1 = 1.3643(16) Å, N1−C1−N2 = 103.40(10)°] compare well with those established for **1a**[36] and **1g** (vide supra); the N−C−N angle of 103.40(19)° lies between the values of 102.2(5)° and 104.52(7)° found in **1a** and **1g**, respectively. In a similar fashion as observed for the solid state structure of **1g** and for that of the corresponding 1,3-di-*tert*-butyl-4,5-dimethylimidazolium triflate [**1h**·H][CF_3SO_3],[34] steric interaction with the methyl groups in the 4,5-positions in **1h** enforces a staggered conformation of the *tert*-butyl groups that results in a particularly efficient shielding of the carbene carbon atom. A further symptom of strain in **1h** is furnished by the out-of-plane deviations of the substituents at N1 and N2, by about 0.2 Å to opposite sides of the ring plane.

In view of the steric and electronic properties of **1h**, clean THF activation was anticipated upon addition of **1h** to a THF solution of B(C_6F_5)$_3$, and indeed, instantaneous formation of the ring-opened product **11** was observed, which could be isolated in 91% yield by crystallization from THF/pentane solution (Scheme 7). The ^{11}B NMR resonance at −2.4 ppm is in agreement with the presence of an sp^3-hybridized B−O moiety; characteristic multiplets for the $(CH_2)_4O$ chain are found at 1.61, 1.76−1.82, 3.21, and 3.54 ppm together with two singlets at 1.79 and 2.43 ppm for the CMe_3 and 4,5-Me groups, respectively. X-ray diffraction analysis confirmed the formation of zwitterionic **11**; the molecular structure features a B−O bond of 1.4592(18) Å and C−N

Scheme 7



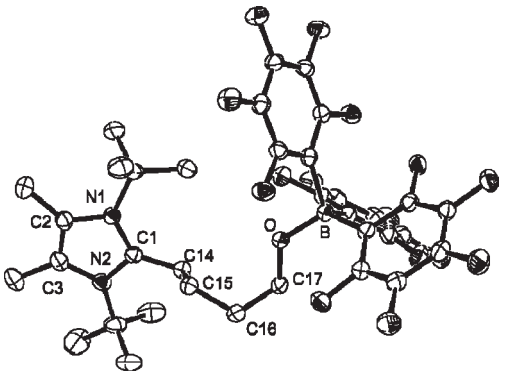


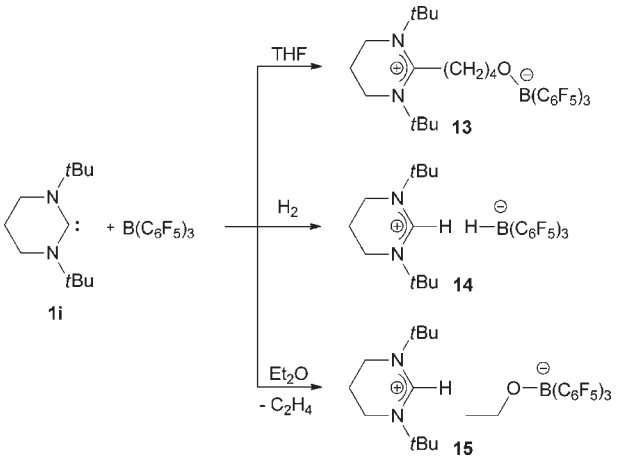
Figure 7. ORTEP diagram of **11** with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å] and angles [deg]: C1−N1 1.3505(18), C1−N2 1.3553(19), C2−C3 1.356(2), C1−C14 1.4971(19), B−O 1.4592(18), C17−O 1.4094(17); N1−C1−N2 108.57(12), O−B−C30 104.42(11), O−B−C18 109.34(11), O−B−C24 113.81(12).

bonds of 1.3505(18) (C1−N1) and 1.3553(19) Å (C1−N2) together with an N1−C1−N2 angle of 108.57(12)° that are typical of imidazolium salts (Figure 7).[15] One of the "protective" *tert*-butyl groups retains its position, with C5−C4−N1−C1 13.8(2)°, but the other rotates to a position with steric crowding between C9 and C11; C1−N2−C10−C13 −53.3(2)° but C3−N2−C10−C11 6.8(3)°. The atom C14 lies 0.28 Å out of the ring plane.

In line with the reactivity observed above, **1h**/B(C_6F_5)$_3$ is a viable FLP for heterolytic dihydrogen cleavage; purging an equimolar toluene solution of the carbene and the borane with H_2 resulted in quantitative formation of the imidazolium-hydroborate **12**, which, in contrast to other hydroborate salts, did not precipitate from solution, but was isolated as a white solid in 94% yield after evaporation of toluene, suspension in pentane, and filtration. The B−H unit of the hydroborate anion gives rise to a doublet at −25.1 ppm in the ^{11}B NMR spectrum with $^1J(^1H,^{11}B)$ = 93 Hz and consequently to a broad quartet at 3.58 ppm in the ^{1}H NMR spectrum, which also exhibits singlets at 1.67, 2.41, and 7.99 ppm for the CMe_3, Me, and CH hydrogen atoms of the imidazolium cation. Unfortunately, single crystals of **12** isolated from a saturated CH_2Cl_2/hexane solution at −30 °C suffered from severe disorder of the [HB(C_6F_5)$_3$]$^-$ ion, and determination of an X-ray crystal structure was not possible.

Again, attempts to isolate a normal carbene-borane adduct proved unsuccessful, despite the blocking of the 4,5-positions. In contrast to **1a**/B(C_6F_5)$_3$ mixtures,[18,19] toluene solutions of **1h** and B(C_6F_5)$_3$ can be stored at −30 °C for prolonged periods of

Scheme 8



time without marked decomposition, and these solutions retained the capability of H_2 cleavage even after two weeks. An adduct, however, could not be isolated from these solutions, and fractional crystallization of the borane as a fluffy white solid was observed instead. In contrast, yellowish toluene solutions of **1h**/$B(C_6F_5)_3$ quickly darkened at room temperature, and a dark red oil separated. After washing with pentane, a dark red solid was isolated, the NMR spectroscopic characterization of which indicated the formation of various species. On one occasion, we were able to isolate red single crystals from a diffusion reaction in pentane at room temperature, and X-ray diffraction analysis revealed the formation of the imidazolium-fluoroborate [**1h**·H][$FB(C_6F_5)_3$], indicating that C−F activation reactions might be involved in mutual carbene-borane deactivation (vide infra, see Supporting Information for a presentation of the X-ray crystal structure). The $[FB(C_6F_5)_3]^-$ ion can also be detected spectroscopically as the main fluorine-containing compound, and the ^{11}B NMR resonance at −2.1 ppm (in THF-d_8) with a $^1J(^{11}B,^{19}F,)$ coupling constant of 65 Hz and also the ^{19}F NMR resonances are in good agreement with those previously established.[37] Nonetheless, the complexity of the NMR spectra suggested the interference of several competing reactions and precluded us from assigning a conclusive deactivation path.

Lewis Pair 1,3-Di-*tert*-butyltetrahydropyrimidin-2-ylidene (1i)/B(C_6F_5)$_3$. Recently, six-membered NHCs of the tetrahydropyrimidin-2-ylidene type have received considerable interest as ligands in organotransition metal chemistry,[38−40] since these so-called ring-expanded *N*-heterocyclic carbenes[40,41] exhibit higher basicities than their five-membered counterparts.[33] It has been suggested that, in the absence of other influences such as electron-donating or -withdrawing substitutents, the widening of the NCN angle has the strongest impact on the increase of the basicity, rather than electron delocalization. At the same time, six-membered NHCs can be considered as sterically more demanding ligands than five-membered NHCs for simple geometric reasons. Thus, we aimed at the synthesis of the previously unknown 1,3-bis-*tert*-butyltetrahydropyrimidin-2-ylidene (**1i**) to obtain a bulkier and more basic analogue of **1a** (Scheme 8). The corresponding pyrimidinium bromide was prepared according to the procedure published by Buchmeiser et al.,[39] and the free carbene could be isolated as a colorless oil in good yield by deprotonation with sodium hexamethyldisilazide, $NaN(SiMe_3)_2$.

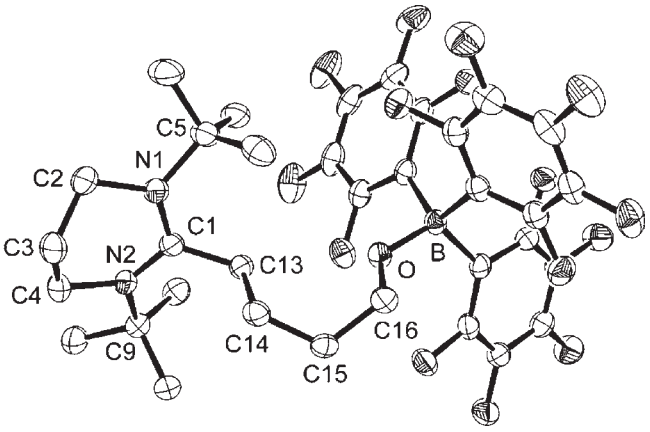


Figure 8. ORTEP diagram of **13** with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å] and angles [deg]: N1−C1 1.3365(16), N1−C2 1.4774(16), N2−C1 1.3483(16), N2−C4 1.4815(15), B−O 1.4544(15), O−C16 1.4139(14), C1−C13 1.5059(16), C2−C3 1.5077(19), C3−C4 1.501(2), N1−C1−N2 121.22(11), O−B−C23 108.97(9), O−B−C17 104.11(9), O−B−C29 114.51(10).

The oil solidifies to a colorless crystalline solid in the refrigerator at −30 °C, and its ^{13}C NMR spectrum exhibits the signal for the carbene carbon atom at 237.5 ppm, which falls in the expected range.[40,41]

FLP reactivity of the **1i**/$B(C_6F_5)_3$ pair was initially checked by dissolution of both components in THF, and the zwitterion **13** was obtained in satisfactory yield (67%) as a white solid (Scheme 8). The ^{11}B NMR resonance at −2.8 ppm is in good agreement with the chemical shifts observed for the related imidazolium-borates obtained by ring-opening of THF (vide supra). Single-crystals suitable for an X-ray diffraction study were obtained from CH_2Cl_2/pentane solution at −30 °C, and the molecular structure is shown in Figure 8. The six-membered pyrimidine ring displays a 1,3-diplanar conformation whereby the four atoms N1, N2, C1, C2 are approximately coplanar (mean deviation 0.03 Å), and C3 and C4 lie 0.99 and 0.43 Å respectively out of the plane in the same direction. The atom C1 and its three direct substituents are coplanar (mean deviation 0.02 Å). The C1−N1 and C1−N2 bond lengths of 1.3365(16) and 1.3483(16) Å are very similar to those in the corresponding 1,3-di-*tert*-butylimidazolium species **2a** and **2b**,[18,20] whereas the N1−C1−N2 angle of 121.22(11)° is significantly more obtuse. The bridging THF fragment exhibits an O−B bond length of 1.4544(15) Å and a C1−C13 bond length of 1.5059(16) Å.

Since the ring-opening of THF provided evidence for the presence of an FLP system, heterolytic dihydrogen cleavage with **1i**/$B(C_6F_5)_3$ was performed. A solution of $B(C_6F_5)_3$ in toluene was cooled to −78 °C, purged with H_2 for some minutes, and a toluene solution of carbene **1i** was subsequently added. The reaction mixture was kept under one atm of H_2 and quickly brought to room temperature. After 1 h, the pyrimidinium hydroborate **14** was isolated in 70% yield (Scheme 8). We noticed that the FLP **1i**/$B(C_6F_5)_3$ showed a particularly high propensity to form the corresponding hydroxyborate salt containing the $[(HO)B(C_6F_5)_3]^-$ anion. Therefore, it is mandatory to carry out these reactions in silylated glassware and to employ solvents dried over potassium−sodium alloy; without these precautions, the pyrimidinium hydroxyborate was formed as the predominant species. The hydroborate salt **14** shows the

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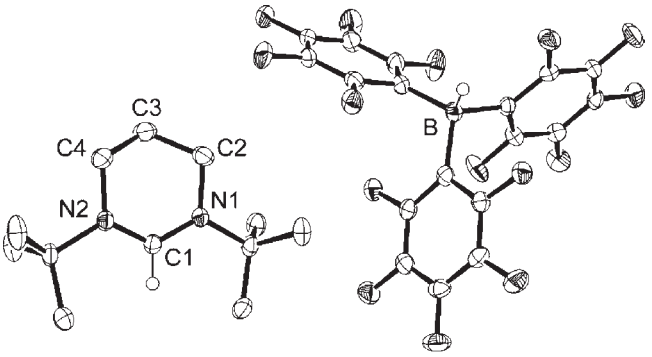


Figure 9. ORTEP diagram of **14** with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å] and angles [deg]: N1−C1 1.3164(19), N2−C1 1.3165(19), N1−C2 1.4758(19), N2−C4 1.475(2), C2−C3 1.512(2), C3−C4 1.511(2), N1−C1−N2 126.02(14), C13−B−C25 114.82(12), C13−B−C19 112.52(12), C25−B−C19 107.40(12).

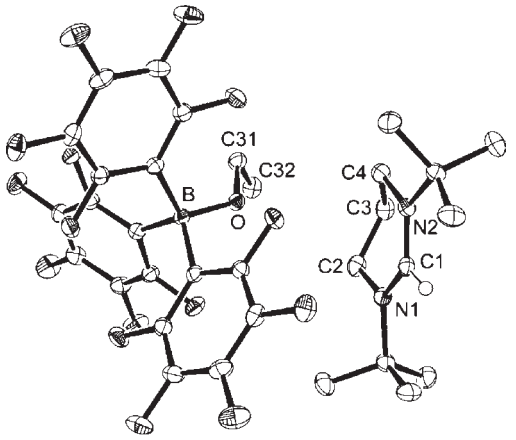


Figure 10. ORTEP diagram of **15** with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å] and angles [deg]: N1−C1 1.3187(14), N2−C1 1.3173(15), B−O 1.4617(14), O−C31 1.4197(13), N1−C2 1.4740(14), N2−C4 1.4771(14), C2−C3 1.5179(17), C3−C4 1.5161(16), C31−C32 1.5207(16), O−B−C19 108.46(8), O−B−C13 106.24(8), O−B−C25 114.38(9), N2−C1−N1 125.75(10).

characteristic doublet at −25.2 ppm in the ^{11}B NMR spectrum with a $^{1}J(^{1}H,^{11}B)$ coupling constant of 90 Hz, together with a broad quartet at 3.59 ppm in the ^{1}H NMR spectrum. The resonance for N_2CH hydrogen atom is observed at 7.82 ppm. **14** was additionally characterized by X-ray diffraction analysis (Figure 9), confirming the presence of a pyrimidinium cation and a tetrahedral $[HB(C_6F_5)_3]^-$ anion, in which the C−B−C angles range between 107.40(12)° and 114.82(12)°. The six-membered pyrimidinium ring now displays a 1,2-diplanar ("sofa") conformation, in which C3 lies 0.68 Å out of the plane of the other five atoms (mean deviation 0.02 Å), and thus has approximate mirror symmetry (rms deviation 0.12 Å). In the cation, the C1−N1 and C1−N2 bond lengths and the N1−C1−N2 angle of 126.02(14)° are in agreement with those established for other pyrimidinium salts.[38a,40,41e,42] Similar to **3a** and **3b**[18,20] and unlike the BH···HP contact of 2.75 Å observed for the salt $[(t\mathrm{Bu})_3\mathrm{PH}][HB(C_6F_5)_3]$,[4] the B−H and C−H units in **14** are not oriented toward each other. Instead, both ions display numerous interionic C−H···F contacts ranging from 2.25 to 2.63 Å. In contrast to **3a** and **3b**, no intermolecular contacts involving the B−H moiety are observed.

As mentioned above, the combinations **1a**/$B(C_6F_5)_3$ and **1b**/$B(C_6F_5)_3$ do not afford stable Lewis adducts, but formation of the abnormal adduct **4** and, in case of **1b**, dehydrogenation is observed instead.[18,20] To investigate whether the pair **1i**/$B(C_6F_5)_3$ exhibits similar reactivity, equimolar amounts of both compounds were dissolved in toluene. Within minutes, a yellow oil formed, and the reaction mixture was stirred for 1 h. After evaporation, the residue was examined by NMR spectroscopy, revealing that the pyrimidinium hydroborate **14** had formed as the main product, presumably by self-dehydrogenation. Unfortunately, we were able to identify neither any dehydro species nor any other byproduct, since the ^{1}H, ^{19}F and ^{11}B NMR spectra indicated the presence of an intractable mixture of compounds.

Therefore, we chose to perform the reaction in a different solvent; **1i** and $B(C_6F_5)_3$ were dissolved in diethyl ether. Within 30 min, a white precipitate had formed, which was collected by filtration. The ^{1}H NMR spectrum indicated the presence of a pyrimidinium cation, with an N_2CH resonance at 7.83 ppm, and of an OCH_2CH_3 moiety with a triplet at 1.02 ppm ($^{3}J_{HH}$ = 6.8 Hz) together with a broad quartet at 3.14 ppm. The latter two signals are shifted to higher field compared to the Et_2O solvent. The ^{11}B NMR does not display the characteristic doublet at about −25 ppm, and a resonance at −2.9 ppm is observed instead, which can be assigned to a tetrahedral $[(CH_3CH_2O)B(C_6F_5)_3]^-$ anion. The formation of the pyrimidinium ethoxyborate **15** (Scheme 8) was also confirmed by X-ray diffraction analysis. The molecular structure is shown in Figure 10; the structural parameters of the cation in **15** are similar to those established for the cation in **14**. The borate anion exhibits O−B−C bond angles in the range from 106.2° to 114.3°. In addition to various C−H···F contacts, the oxygen atom of the ethoxy group displays O···H−C contacts to hydrogen atoms at C2 and C4 of 2.33 and 2.71 Å, respectively. Since **15** was isolated in 71% yield from diethyl ether solution, we propose that its formation proceeds via deprotonation of the etherate $[(Et_2O)B(C_6F_5)_3]$ by **1i** in the β-position, followed by release of ethylene. In principle, ethylene could also be captured by the FLP; however, the large excess of the solvent diethyl ether prevents the formation of a CH_2CH_2-bridged zwitterion as was previously observed for P−B Lewis pairs.[7a]

Lewis Pair 1,3-Bis(2,6-diisopropylphenyl)tetrahydropyrimidin-2-ylidene (1j)/B(C$_6$F$_5$)$_3$. The Dipp-substituted imidazolin-2-ylidene **1d** was shown to form the normal adduct **9** with $B(C_6F_5)_3$, despite its ability to activate the C−O bond in $[(THF)B(C_6F_5)_3]$ (vide supra, Scheme 4). Since the corresponding six-membered pyrimidin-2-ylidene **1j** can be expected to confer a higher steric impact toward the Lewis acid, this carbene was also employed for THF and H_2 activation. **1j** was prepared from the corresponding pyrimidinium tetrafluoroborate by deprotonation with KO*t*Bu, whereas previous protocols involve $KN(SiMe_3)_2$ or $LiN(SiMe_3)_2$ as bases.[40,41a] The free carbene was crystallized from a saturated solution in THF at −35 °C to obtain crystals suitable for an X-ray diffraction analysis. The molecule displays crystallographic mirror symmetry, whereby, for example, the N1−C1−N2 moiety and the *ipso*- and *para*-carbon atoms of the Dipp-substituents (Figure 11) lie in the mirror plane. However, the methylene groups at C2, C3, and C4 are disordered and located either below or above the crystallographic mirror plane, leading to two alternative sofa conformations of the ring. The phenyl groups adopt a perfectly perpendicular orientation toward the N−C−N plane. The

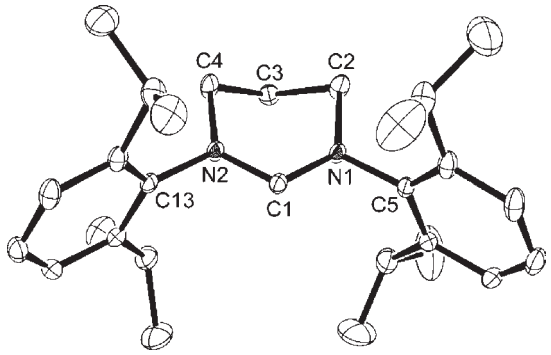


Figure 11. ORTEP diagram of **1j** with thermal displacement parameters drawn at 30% probability. Selected bond lengths [Å] and angles [deg]: N1−C1 1.338(3), N1−C2 1.488(4), C2−C3 1.531(13), C3−C4 1.528(14), N2−C4 1.478(3), N2−C1 1.347(3), N1−C1−N2 115.48(19). The carbon atoms C2, C3, and C4 are disordered across a mirror plane; only one conformation is displayed.

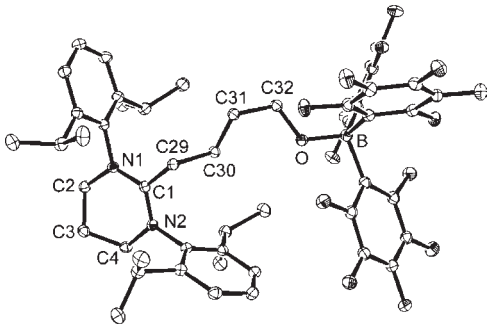
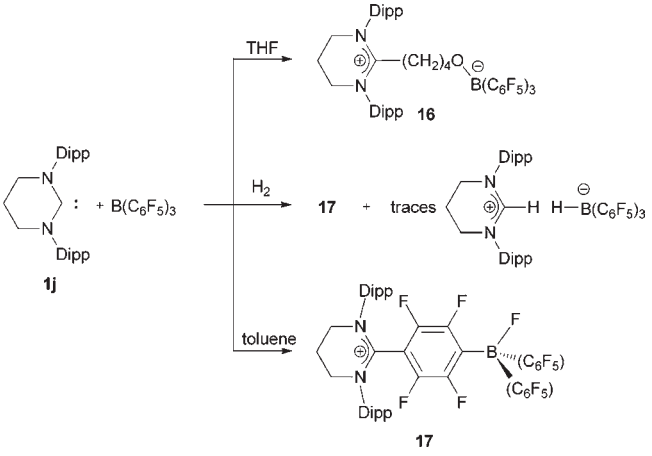


Figure 12. ORTEP diagram of **16** with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å] and angles [deg]: N1−C1 1.3255(18), N1−C2 1.4780(18), N2−C1 1.3314(18), N2−C4 1.4817(18), B−O 1.4581(19), O−C32 1.4078(17), C1−C29 1.5040(19), C2−C3 1.508(2), C3−C4 1.509(2), N1−C1−N2 120.99(13), O−B−C33 105.02(12), O−B−C39 108.71(12), O−B−C45 114.83(12).

Scheme 9



corresponding N1−C1−N2 angle of 115.48(19)° and the C1−N1 and C1−N2 bond lengths of 1.338(3) and 1.347(3) Å are in good agreement with the structures of related free six-membered carbenes,[41] but the dimensions of disordered structures should be interpreted with caution.

As expected, the reaction of **1j** with $B(C_6F_5)_3$ in THF led to the formation of the zwitterionic compound **16**, which was isolated in 76% yield (Scheme 9). The NMR spectroscopic data and also the structural parameters of **16** that were established by X-ray diffraction analysis of the dichloromethane hemisolvate (Figure 12) are consistent with those of **13**, even though the presence of sterically less demanding Dipp-substituents affords a significantly more acute N1−C1−N2 angle of 120.99(13) Å. The ring again displays a sofa conformation.

In contrast to THF activation, ambiguous reactivity of **1j**/$B(C_6F_5)_3$ toward dihydrogen was observed. Purging a toluene solution of this Lewis pair with H_2 produced the corresponding pyrimidinium hydroborate in only small amounts as indicated by a characteristic doublet in the ^{11}B NMR spectrum at −25.2 ppm ($^1J(^{11}B,^1H)$ = 90 Hz) together with a N_2CH ^1H NMR resonance at 7.63 ppm. Although the yield of this product could be increased by performing the reaction at −78 °C, the NMR spectra are dominated by resonances pertaining to the zwitterionic pyrimidinium fluoroborate **17**. In addition, contamination with $[(HO)B(C_6F_5)_3]^-$ salts was observed, despite careful silylation of the glassware.

In absence of H_2, the formation of a gel-like precipitate was observed, and **17** could be isolated in 75% yield by filtration and subsequent extraction of byproduct with Et_2O and hexane (Scheme 9). The ^1H NMR spectrum displays relatively broad resonances, indicating hindered rotation, presumably around the $N_2C-C_6F_4$ bond. In the ^{13}C NMR spectrum, the resonance for the N_2C carbon atom is found at 158.0 ppm and, as expected, shifted to significantly higher field compared to the free carbene **1j** (244.9 ppm). The ^{19}F NMR spectrum exhibits two signals for the bridging C_6F_4 unit at −133.0 and −135.3 ppm, partially overlapping with the resonance assigned to the *ortho*-C_6F_5 fluorine atoms, whereas the *meta*- and *para*-C_6F_5 peaks are observed at −166.4 and −161.9 ppm. The broad resonances for the B−F moiety appear at −193.0 and −0.7 ppm in the ^{19}F and ^{11}B NMR spectra, respectively. The latter resonances are in good agreement with those reported for related phosphonium borates that have been isolated from the reactions of $B(C_6F_5)_3$ with sterically encumbered phosphines PR_3 (R = Et, *n*Bu, *i*Pr, Cy, Ph, FC_6H_4, $MeOC_6H_4$) and R_2PH (R = *t*Bu, Cp, Cy, Ph $C_6H_2Me_3$-2,4,6).[1,21,28a] In a similar fashion as described for these species, the formation of **17** can be rationalized by nucleophilic attack of the carbene at the *para*-position of a C_6F_5 ring, followed by fluoride migration to boron.

The molecular structure of **17** was also confirmed by X-ray diffraction (Figure 13); the pyrimidinium ring again displays the sofa conformation, and the B−F1 and B−C32 bond lengths of 1.4185(15) and 1.6579(18) Å fall in the expected range compared to related phosphonium fluoroborates.[1,21,28a] The angle between the planes N1,C1,N2,C29 and C29−34 is 63°, corresponding to a more perpendicular rather than a coplanar orientation between the carbene moiety and the C_6F_4 ring.

Lewis Pair Bis(diisopropylamino)methylene (1k)/B(C$_6$F$_5$)$_3$. According to theoretical calculations,[33] acyclic diaminocarbenes such as **1k** are among the most basic *N*,*N*-substituted carbenes, and therefore, the reactivity of this so-called Alder-carbene toward $B(C_6F_5)_3$ was also studied.[45] Mixing of **1k** and $B(C_6F_5)_3$ in toluene afforded the normal adduct $[(\mathbf{1k})B(C_6F_5)_3]$ (**18**) as an air-stable white solid (Scheme 10). The ^{11}B NMR resoance at −14.1 ppm is in good agreement with the chemical shift (−15.6 ppm) found for

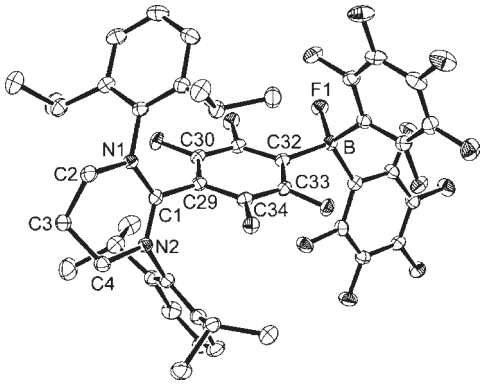
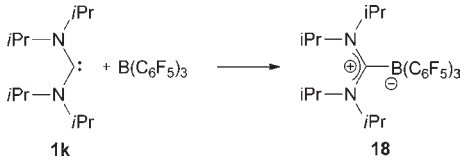


Figure 13. ORTEP diagram of **17** with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å] and angles [deg]: B−F1 1.4185(15), B−C32 1.6579(18), N1−C1 1.3307(15), N2−C1 1.3324(16), C1−C29 1.4942(16), N1−C1−N2 122.68(11), N1−C1−C29−C30 −65.18(16), N2−C1−C29−C34 −62.36(15).

Scheme 10



the normal adduct [(**1d**)B(C_6F_5)$_3$] (**9**). At room temperature, however, the ^{1}H, ^{13}C, and ^{19}F NMR spectra exhibit broad resonances, indicating fluxional behavior on the NMR time scale, which could be ascribed to hindered rotation around the C−N and C−B bonds. A variable-temperature NMR study revealed that sharp spectra can be recorded at −30 °C, and for instance, the ^{1}H NMR spectrum displays eight individual doublets for the eight methyl groups, two of which show additional through-space coupling to one ^{19}F nucleus. In a similar fashion, 15 well-separated signals are observed in the ^{19}F NMR spectrum for the fluorine atoms of the three C_6F_5 rings (see Supporting Information for a presentation of these spectra).

Recrystallization of **18** from a CH_2Cl_2/Et_2O/pentane solution at 3 °C afforded single-crystals suitable for an X-ray diffraction analysis. The carbene carbon atom C1 resides in an almost perfectly trigonal-planar environment with an N1−C1−N2 angle of 120.69(12)°, which together with the C1−N bond distances of 1.3585(17) and 1.3736(16) Å only slightly deviates from the structural parameters found for the free carbene **1k** [121.0(5)°, 1.363(6) Å, 1.381(6) Å].[45a] In contrast, the boron atom is coordinated in a strongly distorted tetrahedral fashion (Figure 14). Strikingly, a very long C1−B bond length of 1.711(2) Å is observed, which significantly exceeds the $C_{carbene}$−B distances found for the adducts [(**1d**)B(C_6F_5)$_3$] [1.684(2) Å] and [(**1f**)B(C_6F_5)$_3$] [1.6407(16) Å] and falls in the same range as the C−B distance calculated for the elusive normal adduct [(**1a**)B(C_6F_5)$_3$].[18] These structural features suggested that the formation of the adduct **18** might be reversible and that sufficient amounts of the carbene and the borane might be present in solution to observe FLP reactivity. However, various attempts to effect dihydrogen cleavage by a solution of **18** proved unsuccessful, and this observation is in line with its calculated stability (vide infra, Table 1).

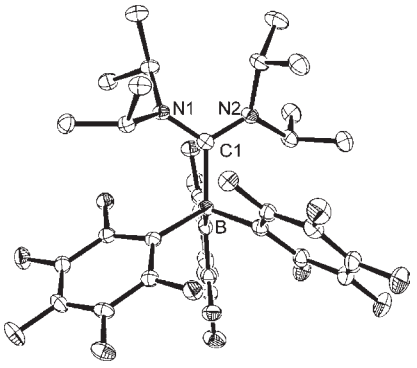


Figure 14. ORTEP diagram of **18** with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å] and angles [deg]: B−C1 1.711(2), C1−N1 1.3585(17), C1−N2 1.3736(16); N1−C1−N2 120.69(12), N1−C1−B, N2−C1−B, C1−B−C14 104.47(11), C1−B−C20 114.61(11), C1−B−C26 114.67(11).

Table 1. Selected Energies [kcal·mol^{-1}], Bond Lengths [Å], and Angles [deg] for the Formation of the Normal Carbene-Borane Adducts [(1)B(C_6F_5)$_3$]^a

	ΔE_{el}	ΔE_{0K}	ΔH_{298K}	ΔG_{298K}	d(C−B)	∠(NCN)
1a	−23.8	−20.2	−21.1	−2.5	1.714	105.0
1b	−20.1	−16.4	−17.3	1.7	1.727	108.4
1c	−25.1	−21.1	−21.7	−2.2	1.720	104.9
1d	−51.5	−47.8	−48.8	−26.2	1.682	104.6
1e	−59.3	−55.9	−56.5	−40.6	1.646	105.3
1g	−10.6	−7.5	−8.4	10.6	1.714	106.7
1h	−18.6	−14.4	−15.4	3.5	1.708	105.9
1i	−11.5	−8.1	−8.9	10.6	1.711	113.3
1j	−36.9	−32.5	−33.7	−9.4	1.734	116.5
1k	−57.6	−53.6	−54.6	−35.1	1.708	116.7

^{a} ΔE_{el} = zero-point uncorrected M05-2X/6-311G(d,p) electronic energies, ΔE_{0K} = energies at 0 K, ΔH_{298K} = enthalpies at 298 K, ΔG_{298K} = Gibbs free energies at 298 K.

Theoretical Calculations of Carbene-Borane Adduct Formation. To rationalize the reactivity of the carbene-borane Lewis pairs, the thermodynamics of adduct formation with B(C_6F_5)$_3$ were calculated for all carbenes that have been previously employed (**1a**, **1b**)[18−21] or were used in this study (**1c**, **1d**, **1g**−**1k**). In addition, adduct formation was also calculated for the sterically least demanding carbene **1e**, for which normal adduct formation can be expected, since the analogous adduct [(**1f**)B(C_6F_5)$_3$] is known (Figure 1). For all calculations, the M05-2X functional developed by Zhao and Truhlar was applied, which conveniently describes noncovalent interactions that can be expected to significantly contribute to the overall binding energies in these sterically encumbered systems.[46] Table 1 summarizes the zero-point uncorrected energies (ΔE_{el}) and also the values for the energies at 0 K (ΔE_{0K}) and for the enthalpies (ΔH_{298K}) and Gibbs free energies at 298 K (ΔG_{298K}) calculated by statistical thermodynamics. Since the energetic differences between the carbene-borane adducts is reproduced in a similar fashion for all these energies, the following discussion will focus on the ΔH_{298K} and ΔG_{298K} values only, and for clarity, a bar diagram of these values is shown in Figure 15. Presentations of all structures together with their Cartesian coordinates can be found in the Supporting Information.

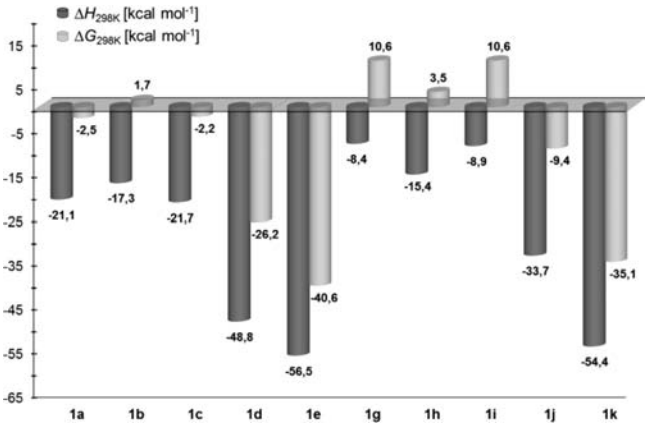


Figure 15. Bar diagram showing the enthalpies at 298 K (ΔH_{298K}) and Gibbs free energies at 298 K (ΔG_{298K}) for the formation of the normal carbene-borane adducts $[(\mathbf{1})B(C_6F_5)_3]$.

As previously reported, normal adduct formation for the *t*Bu-substituted NHCs **1a** and **1b** is calculated to be exothermic by −21.1 and −17.3 kcal mol^{-1}, and our inability to isolate the adducts $[(\mathbf{1a})B(C_6F_5)_3]$ and $[(\mathbf{1b})B(C_6F_5)_3]$ could be ascribed not only to their thermodynamic instability, but to the higher stability of the abnormal adduct **4**, which is formed in both cases. Given that adduct formation is reversible, the small absolute values of ΔG_{298K} (−2.5 and 1.7 kcal mol^{-1}) indicate that sufficient amounts of free carbene and borane are present in solution to observe FLP reactivity, for example, THF and H_2 activation. As expected from very similar spatial requirements, the values calculated for the diadamant-1-yl-substituted carbene **1c** are almost identical with those of **1a**. In contrast, adduct formation is calculated to be significantly more strongly exothermic and exergonic (−48.8/−26.2 kcal mol^{-1}) for the Dipp-derivative **1d**, and consequently, the adduct $[(\mathbf{1d})B(C_6F_5)_3]$ can be isolated and structurally characterized (vide supra).[19,21] The $C_{carbene}$−B bond length of 1.684(2) Å established in this publication is also nicely reproduced (1.682 Å). This trend is followed upon further reduction of the steric requirements, as is the case for **1e**, and $[(\mathbf{1e})B(C_6F_5)_3]$ represents the most stable adduct in this series (−56.5/−40.6 kcal mol^{-1}) and exhibits the shortest $C_{carbene}$−B bond distance (1.646 Å), which is also in excellent agreement with the experimental value of 1.6407(16) Å in $[(\mathbf{1f})B(C_6F_5)_3]$.[27]

The structural characterization of the carbenes **1g** and **1h** bearing chlorine or methyl groups in the 4,5-positions indicated that these carbenes can be regarded as sterically more demanding ligands in comparison with **1a** and should therefore furnish less stable adducts. This is theoretically confirmed for $[(\mathbf{1g})B(C_6F_5)_3]$ (−8.4, +10.6 kcal mol^{-1}) and $[(\mathbf{1h})B(C_6F_5)_3]$ (−15.4, +3.5 kcal mol^{-1}), and the differences between these two adducts can be easiliy ascribed to the smaller basicitiy and nucleophilicity of **1g** as a result of the electron-withdrawing chlorine substituents. Consequently, the combination $\mathbf{1g}/B(C_6F_5)_3$ showed an inferior perfomance in THF and H_2 activation compared to $\mathbf{1h}/B(C_6F_5)_3$.

Although the six-membered *t*Bu- and Dipp-substituted NHCs **1i** and **1j** can be regarded as being more basic and more strongly nucleophilic than their five-membered counterparts **1a** and **1d**, the ring enlargement affords sterically more demanding Lewis bases, resulting in thermodynamically less stable adducts $[(\mathbf{1i})B(C_6F_5)_3]$ (−8.9, +10.6 kcal mol^{-1}) and $[(\mathbf{1j})B(C_6F_5)_3]$ (−33.7, −9.4 kcal mol^{-1}). Adduct $[(\mathbf{1i})B(C_6F_5)_3]$ exhibits a particularly high degree of frustration, since the adduct is unstable for steric reasons, allowing full exploitation of the high reactivity of the FLP combination $B(C_6F_5)_3$ and **1i**, which represents the most basic *N*-heterocyclic carbene in this study. Therefore, $\mathbf{1i}/B(C_6F_5)_3$ showed a particularly high propensity for THF, H_2, and even Et_2O activation, whereas in the absence of substrates fast and uncontrolled decomposition was observed. In contrast, the only moderately frustrated Lewis pair $\mathbf{1j}/B(C_6F_5)_3$ seems to undergo self-deactivation in a more orderly fashion, allowing unambigous identification of a C−F activation process, which might, inter alia, also be relevant for other carbene-borane Lewis pairs.

Finally, the structurally characterized adduct $[(\mathbf{1k})B(C_6F_5)_3]$ containing the acyclic diaminomethylene **1k** is confirmed to be thermodynamically stable (−54.6, −35.1 kcal mol^{-1}). It is interesting to note that the formation of this adduct is almost as exothermic as calculated for the adduct of the sterically least hindered carbene **1e**, although a significantly longer $C_{carbene}$−B bond length of 1.708 Å is obtained, which nicely matches the experimental value of 1.711(2) Å (Figure 14).

CONCLUSIONS

This study confirmed the potential of frustrated carbene-borane Lewis pairs for metal-free small molecule activation, and various combinations containing *N*-heterocyclic carbenes (NHCs) and $B(C_6F_5)_3$ were shown to effect C−O and H−H bond cleavage. The degree of "frustration" and the ensuing reactivity of these Lewis pairs can be efficiently tuned by variation of the NHC type and its respective steric and electronic properties. For most of these FLP systems, however, the cumulative Lewis acid−base strength leads to self-destruction in the absence of substrates, and possible decomposition pathways involving C−H and C−F bond activation were discovered. This behavior might be regarded as a drawback, but particularly reactive combinations might nonetheless become useful stoichiometric reagents, for example, for dehydrogenation. Furthermore, the reactivity of carbene-borane Lewis pairs could be moderated by employing less Lewis acidic boranes or other Lewis acids,[22,51] and such combinations are currently under investigation in our laboratories.

EXPERIMENTAL SECTION

Synthetic Details. *Chemicals and Instrumentation.* All operations with air and moisture-sensitive compounds were performed in a glovebox under a dry argon atmosphere (MBraun 200B) or on a high vacuum line using Schlenk techniques. Hydrogen gas was purchased from Westfalen AG and passed through a P_4O_{10} column prior to use. All solvents were purified by a solvent purification system from MBraun and stored over molecular sieve (4 Å) prior to use. The ^{1}H, ^{13}C, ^{11}B, ^{19}F and ^{31}P NMR spectra were recorded on Bruker DPX 200 (200 MHz), Bruker AV 300 (300 MHz), Bruker DRX 400 (400 MHz), and Bruker DPX 600 (600 MHz) devices. The chemical shifts are expressed in parts per million (ppm) using tetramethylsilane (TMS) as internal standard. Coupling constants (*J*) are reported in Hertz (Hz), and splitting patterns are indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), sept (septet) and br (broad). Elemental analysis (C, H, N) succeeded by combustion MS on a Finnigan MAT 95 (EI), Finnigan MAT 95 XL (ESI), respectively and HR-MS from Bruker-Demo QTOF micro.

Synthesis and Characterization. Unless otherwise indicated, all starting materials were obtained from Sigma-Aldrich and were used without further purification. 1,3-Di-*tert*-butylimidazolin-2-ylidene (**1a**),[36] 1,3-di-*tert*-butylimidazolidin-2-ylidene (**1b**),[43] 1,3-di-1-adamantylimidazolin-2-ylidene

(**1c**),[44] 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (**1d**),[32b] 1,3-di-*tert*-butyl-4,5-dimethylimidazolin-2-ylidene (**1h**),[34] bis(diisopropylamino) carbene (**1i**),[45] 1,3-di-*tert*-butylhexahydropyrimidine[42] and $B(C_6F_5)_3$[47] were prepared according to literature procedures.

*1,3-Di-tert-butyl-4,5-dichloroimidazol-2-ylidene (**1g**).* To a solution of 1,3-di-*tert*-butylimidazolin-2-ylidene **1a** (30.0 mmol, 5.40 g) in THF (100 mL) was added CCl_4 (80.0 mmol; 7.60 mL) under an inert atmosphere. The reaction is slightly exothermic and was stirred for 6 h at 40 °C. Subsequent removal of the volatiles under reduced pressure at 10 °C gave a violet solid. Sublimation of the solid at 50 °C and 0.02 atm afforded a white oily raw product, which was dissolved in 5 mL of pentane. The solvent was removed in vacuo. Sublimation of the remaining solid gave **1g** in 43% (3.20 g) yield. Crystals suitable for X-ray diffraction analysis were obtained by sublimation. Note: **1g** is a light and air-sensitive solid. **^{1}H NMR** (200 MHz, C_6D_6): δ/ppm 1.57 (s, 18H, $C(CH_3)_3$); **^{13}C NMR** (50 MHz, C_6D_6): δ/ppm 30.3 (CH_3), 59.5 ($C(CH_3)_3$), 115.2 (NCCl), 213.0 (NCN), **melting point**: 60 °C.

*1,3-Di-tert-butyltetrahydropyrimidin-2-ylidene (**1i**).* 1,3-Di-*tert*-butyltetrahydropyrimidinium bromide (18.0 mmol, 5.00 g) was suspended in THF (100 mL), and a solution of $NaN(SiMe_3)_2$ (18.0 mmol, 3.18 g) in THF (50 mL) was added at −78 °C. The reaction mixture was stirred for 3 h at −78 °C and then allowed to warm to room temperature. The solvent was then reduced to 100 mL, and the suspension was filtered through Celite. The solvent was removed in vacuo to yield the free carbene as a colorless oil (2.46 g, 72%). **^{1}H NMR** (200 MHz, C_6D_6): δ/ppm 1.27 (br s, 18H, $C(CH_3)_3$), 1.36 (m, CH_2), 2.61 (br t, $^3J_{HH}$ = 6.0 Hz, 4H, $N_2(CH_2)_2$); **^{13}C NMR** (50 MHz, C_6D_6): δ/ppm 23.4 (CH_2), 29.6 ($C(CH_3)_3$), 36.1 ($N_2(CH_2)_2$), 58.5 ($C(CH_3)_3$), 237.5 (N_2C).

1,3-Di-tert-butyltetrahydropyrimidinium Bromide. To a solution of 1,3-di-*tert*-butylhexahydropyrimidine[42] (223 mmol, 44.2 g) in 100 mL of abs. dimethoxyethane was slowly added solid *N*-bromosuccinimide. The suspension was stirred for 3 h at room temperature. The white precipitate was filtered off, washed with pentane, and dried in vacuo to yield the product as a white powder (34.3 g, 55%). **^{1}H NMR** (200 MHz, $CDCl_3$): δ/ppm 1.54 (s, 18H, $C(CH_3)_3$), 2.16 (m, 2H, CH_2), 3.59 (br t, $^3J_{HH}$ = 5.8 Hz, 4H, $N_2(CH_2)_2$), 8.04 (s, N_2CH); **^{13}C NMR** (50 MHz, $CDCl_3$): δ/ppm 20.2 (CH_2), 28.1 ($C(CH_3)_3$), 40.5 ($N_2(CH_2)_2$), 61.5 ($C(CH_3)_3$), 147.0 (N_2CH); **^{1}H NMR** (400 MHz, DMSO): δ/ppm 1.38 (s, 18H, $C(CH_3)_3$), 2.50 (m, 2H, CH_2), 3.41 (br t, $^3J_{HH}$ = 5.7 Hz, 4H, $N_2(CH_2)_2$), 7.82 (s, 1H, N_2CH); **^{13}C NMR** (100 MHz, DMSO): δ/ppm 19.4 (CH_2), 27.0 ($C(CH_3)_3$), 40.1 ($N_2(CH_2)_2$), 60.3 ($C(CH_3)_3$), 146.5 (N_2CH).

*[(**1c**)(CH$_2$)$_4$OB(C$_6$F$_5$)$_3$] (**5**).* A 1:1 mixture of $B(C_6F_5)_3$ (0.98 mmol, 500 mg) and **1c** (0.98 mmol, 328 mg) was dissolved in 20 mL of THF. The yellow solution was stirred for 12 h at room temperature, resulting in the formation of a colorless solution. The solvent was removed in vacuo, and the remaining solid was stirred for 10 min with 20 mL of pentane. The white precipitate was isolated by filtration, immediately washed three times with 10 mL of pentane, and dried in vacuo yielding the product as a white solid (0.77 g, 93%). Crystals suitable for X-ray analysis of **5** were obtained from a mixture of CH_2Cl_2 and Et_2O at 0 °C. **^{1}H NMR** (300 MHz, acetone-d_6): δ/ppm 1.68 (m, 2H, $N_2CCH_2CH_2$), 1.78 (br s, 12 H, Ad), 1.95 (m, 2H, CH_2CH_2O), 2.26 (br s, 6H, Ad) 2.40 (m, 12H, Ad), 3.23 (t, $^3J_{HH}$ = 5.3 Hz, 2H, N_2CCH_2), 3.54 (m, 2H, CH_2O), 7.85 (s, 2H, N_2CH); **^{11}B NMR** (96 MHz, acetone-d_6): δ/ppm −1.7 (s); **^{13}C NMR** (75 MHz, acetone-d_6): δ/ppm 27.6 ($N_2CCH_2CH_2$), 28.6 (OCH_2CH_2), 29.8 (CH, Ad), 31.6 (N_2CCH_2), 34.7 (CH_2, Ad), 41.7 (CH_2, Ad), 62.7 (CH_2O), 65.6 (*C*, Ad), 119.8 ($N_2(CH)_2$), 137.1 (dm, $^1J_{CF}$ = 251.9 Hz, *m*-C_6F_5), 138.9 (dm, $^1J_{CF}$ = 247.2 Hz, *p*-C_6F_5), 149.0 (dm, $^1J_{CF}$ = 242.5 Hz, *o*-C_6F_5), 149.5 (N_2C); **^{19}F NMR** (178 MHz, acetone-d_6): δ/ppm −132.8 (m, $^3J_{FF}$ = 22.35 Hz, 6F, *o*-C_6F_5), −163.7 (m, $^3J_{FF}$ = 20.23 Hz, 3F, *p*-C_6F_5), −167.1 (m, $^3J_{FF}$ = 19.24 Hz 6F, *m*-C_6F_5); **elemental analysis** (%) calcd. for $C_{45}H_{40}BF_{15}N_2O$: N 3.04, C 58.71, H 4.38, found: N 2.92, C 59.16, H 5.07.

*[**1c**·H][HB(C$_6$F$_5$)$_3$] (**6**).* A 1:1 mixture of $B(C_6F_5)_3$ (0.78 mmol, 400 mg) and **1c** (0.78 mmol, 263 mg) was dissolved in 20 mL of toluene at −30 °C under an atmosphere of H_2. The yellow solution was purged with H_2 for 10 min, resulting in the formation of a milky white suspension. The reaction was stirred under a static atmosphere of H_2 for 8 h at room temperature. The solvent was removed in vacuo, and the remaining solid was stirred for 10 min with 20 mL of a 1:10 toluene/pentane mixture. The white precipitate was isolated by filtration, immediately washed three times with 10 mL of pentane and dried in vacuo. The product **6** was collected as a white solid in 89% yield (603 mg). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ/ppm 1.78 (dd, $J_{AA'BB'}$ = 42.93 Hz, $^3J_{HH}$ = 12.8 Hz, 12 H, Ad), 2.10 (d, J_{HH} = 2.6 Hz, 12H, Ad), 2.30 (br s, 6H, Ad), 3.58 (q, $^1J_{HB}$ = 90 Hz, 1H, B*H*), 7.47 (d, J_{HH} = 1.8 Hz, 2H, *CH*), 8.29 (t, J_{HH} = 1.7 Hz, 1H, N_2CH); **^{11}B NMR** (96 MHz, CD_2Cl_2): δ/ppm −25.2 (s); **^{13}C NMR** (100 MHz, CD_2Cl_2): δ/ppm 29.9 (*C*H, Ad), 35.5 (CH_2, Ad), 43.2 (CH_2, Ad), 61.5 (*C*, Ad), 119.7 ($N_2(CH)_2$); **^{19}F NMR** (376 MHz, CD_2Cl_2): δ/ppm −133.8 (m, $^3J_{FF}$ = 21.8 Hz, 6F, *o*-C_6F_5), −164.5 (m, $^3J_{FF}$ = 20.0 Hz, 3F, *p*-C_6F_5), −167.5 (m, 6F, *m*-C_6F_5); **Elemental analysis** (%) calcd. for $C_{41}H_{34}BF_{15}N_2$: N 3.29, C 57.90, H 4.03, found: N 3.20, C 57.08, H 4.23; **MS** (ESI, MeOH), *m*/*z* (%): positive 373.2 (100, [*Ad*ImH]$^+$), negative 512.9 (100, [H−B(C_6F_5)$_3$]$^-$).

*Abnormal Adduct **7**.* A 1:1 mixture of $B(C_6F_5)_3$ (0.98 mmol, 500 mg) and **1c** (0.98 mmol, 328 mg) was dissolved in 40 mL of toluene. The yellow solution was stirred for 24 h at room temperature, resulting in the formation of a yellowish solution with some precipitation. The solvent was removed in vacuo, and the remaining solid was stirred for 10 min with 20 mL of pentane. The white precipitate was isolated by filtration, immediately washed several times with 10 mL of pentane and recrystallized from $CHCl_3$ at −35 °C. The product was dried in vacuo and collected as a white solid in 79% yield (523 mg). Note: **7** decomposes at room temperature in chlorinated solvents and THF. **^{1}H NMR** (300 MHz, $CDCl_3$): δ/ppm 1.34−2.24 (m, 30H, Ad), 6.84 (br m, 1H, *CH*CB), 8.07 (d, $^4J_{HH}$ = 1.9 Hz, 1H, N_2CH); **^{11}B NMR** (96 MHz CD_2Cl_2): δ/ppm −15.4 (s); **^{13}C NMR** (75 MHz, $CDCl_3$): δ/ppm 29.2 (CH) 29.7 (CH), 35.1 (CH_2), 35.4 (CH_2), 42.1 (CH_2), 42.8 (CH_2), 30.7 (CH_3), 58.4 (*C*), 63.5 (*C*), 123.7 (CH), 128.2 (CH), the C_6F_5 resonances were too broad for assignment; **^{19}F NMR** (178 MHz, $CDCl_3$): δ/ppm −124.7 (br s, 1F, *o*-C_6F_5), −129.0 (br s, 1F, *o*-C_6F_5), −130.2 (m, 1F *o*-C_6F_5), −134.1 (m, 1F *o*-C_6F_5), −135.3 (m, 2F, *o*-C_6F_5), −160.0 (m, 1F, *p*-C_6F_5), −160.2 (m, 1F, *p*-C_6F_5), 161.1 (m, 1F, *p*-C_6F_5), −164.1 (m, 1F, *m*-C_6F_5), −164.7 (m, 1F, *m*-C_6F_5), −165.0 (m, 1F, *m*-C_6F_5), −165.9 (m, 1F, *m*-C_6F_5), −166.3 (m, 2F, *m*-C_6F_5); **elemental analysis** (%) calcd. for $C_{41}H_{32}BF_{15}N_2$: N 3.30, C 58.04, H 3.80, found: N 3.12, C 58.64, H 3.94.

*[(**1d**)(CH$_2$)$_4$OB(C$_6$F$_5$)$_3$] (**8**).* Compound **8** was prepared according to the procedure described for **5**. $B(C_6F_5)_3$ (0.98 mmol, 500 mg) and **1d** (0.98 mmol, 381 mg); yield 0.77 g (93%). Crystals suitable for X-ray analysis of **8** were obtained from a mixture of THF, toluene and pentane at 20 °C; **^{1}H NMR** (400 MHz, THF-d_8): δ/ppm 1.19 (m, 2H, $N_2CCH_2CH_2$), 1.21 (d, $^3J_{HH}$ = 6.7 Hz, 12H, $CH(CH_3)_2$), 1.26 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.41 (m, 2H, CH_2CH_2O), 2.34 (sept, 4H, $CH(CH_3)_2$), 2.62 (m, 2H, N_2CCH_2), 2.84 (m, 2H, CH_2O), 7.49 (m, 4H, *m*-CH_{Dipp}), 7.60 (m, 2H, *p*-CH_{Dipp}), 8.00 (s, 2H, $N_2(CH)_2$); **^{13}C NMR** (100 MHz, THF-d_8): δ/ppm 22.7 ($CH(CH_3)_2$), 25.1 ($N_2CCH_2CH_2$), 25.3 ($CH(CH_3)_2$), 25.7 (CH_2CH_2O), 30.2 ($CH(CH_3)_2$), 33.0 (N_2CCH_2), 63.9 (CH_2O), 125.8 ($N_2(CH)_2$), 125.9 (*m*-CH_{Dipp}), 130.4 (*i*-C_{Dipp}) 133.1 (*p*-CH_{Dipp}), 137.1 (dm $^1J_{CF}$ = 244.2 Hz, *m*-C_6F_5), 138.9 (dm $^1J_{CF}$ = 240.7 Hz, *p*-C_6F_5), 146.0 (*o*-C_{Dipp}), 148.8 (dm $^1J_{CF}$ = 242.5 Hz, *o*-C_6F_5), 151.6 (N_2C); **^{19}F NMR** (178 MHz, THF-d_8): δ/ppm −132.6 (m, $^3J_{FF}$ = 22.0 Hz, 6F, *o*-C_6F_5), −164.5 (m, $^3J_{FF}$ = 20.0 Hz, 3F, *p*-C_6F_5), −167.3 (m, $^3J_{FF}$ = 19.5 Hz 6F, *m*-C_6F_5); **^{11}B NMR** (96 MHz, THF-d_8): δ/ppm −2.6 (s); **elemental analysis** (%) calcd. for $C_{49}H_{44}BF_{15}N_2O$: C 60.51, H 4.50, N 2.88, found: C 59.85, H 4.36, N 2.82.

*[(**1d**)B(C$_6$F$_5$)$_3$] (**9**).* A 1:1 mixture of $B(C_6F_5)_3$ (0.98 mmol, 500 mg) and **1d** (0.98 mmol, 379 mg) was dissolved in 10 mL of toluene. The

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reaction was stirred for 6 h at room temperature. Further addition of 30 mL pentane resulted in the formation of a white precipitate, which was isolated by filtration and dried in vacuo. Yield 0.75 g (86%). Crystals of **9** were obtained from a toluene/pentane mixture at −35 °C. Note: Compound **9** decomposes at room temperature. NMR data are consistent with those previously established.[19] **Elemental analysis** (%) calcd. for $C_{45}H_{36}BF_{15}N_2$: C 60.02, H 4.03, N 3.11, found: C 60.85, H 4.21, N 2.97.

*[**1g**·H][HB(C$_6$F$_5$)$_3$] (**10**).* A 1:1 mixture of B(C$_6$F$_5$)$_3$ (0.85 mmol, 436 mg) and **1g** (0.85 mmol, 212 mg) was dissolved in 20 mL of toluene at −30 °C under an atmosphere of H_2. The yellow solution was purged with H_2 for 10 min, resulting in the formation of a milky white suspension. The reaction was stirred under a static atmosphere of H_2 for 1 h at room temperature. The solvent was then removed in vacuo, and the remaining solid was stirred for 10 min with 20 mL of a 1:10 toluene/pentane mixture. The white precipitate was isolated by filtration, immediately washed three times with 10 mL of pentane and dried in vacuo. The raw product contains the hydroxyborate anion as an impurity, which could be partially removed by recrystallization from CH_2Cl_2/pentane. Yield: 40% based on the ^{19}F NMR spectra of the raw product. Note: A combination of **1g**/B(C$_6$F$_5$)$_3$ is extremely hygroscopic. **^{1}H NMR** (600 MHz, toluene-d_8): δ/ppm 1.01 (s, 18H, C(CH_3)$_3$), 3.70 (q, 1H, $^1J_{HB}$ = 93 Hz, BH), 8.14 (s, 1H, N$_2$CH); **^{11}B NMR** (96 MHz, toluene-d_8): δ/ppm −24.4 (s); **^{13}C NMR** (150 MHz, toluene-d_8): δ/ppm 27.3 (C(CH_3)$_3$), 65.8 (C(CH$_3$)$_3$), 120.7 (N$_2$(CCl)$_2$), 131.0 (N$_2$CH), the C$_6$F$_5$ resonances were too broad for assignment; **^{19}F NMR** (178 MHz, toluene-d_8): δ/ppm −133.1 (m, $^3J_{FF}$ = 21.4 Hz, 6F, *o*-C$_6$F$_5$), −163.0 (m, $^3J_{FF}$ = 20.4 Hz, 3F, *p*-C$_6$F$_5$), −166.4 (m, 6F, *m*-C$_6$F$_5$); **elemental analysis** (%) calcd. for $C_{29}H_{20}BCl_2F_{15}N_2$: N 3.67, C 45.64, H 2.64, found: N 3.70, C 46.06, H 2.90.

*[(**1**·h)(CH$_2$)$_4$OB(C$_6$F$_5$)$_3$] (**11**).* Compound **11** was prepared according to the procedure described for **5**. B(C$_6$F$_5$)$_3$ (0.58 mmol, 300 mg) and **1h** (0.58 mmol); yield 0.42 g (91%); crystals suitable for X-ray analysis of **12** were obtained from a mixture of THF/pentane at 5 °C; **^{1}H NMR** (400 MHz, THF-d_8): δ/ppm 1.61 (m, 2H, N$_2$CCH$_2$CH_2), 1.76−1.82 (m, 18H, C(CH_3)$_3$ + 2H, CH_2CH$_2$O), 2.43 (s, 6H, CH$_3$), 3.21 (br t, $^3J_{HH}$ = 4.8 Hz, 2H, N$_2$CCH_2CH$_2$) 3.54 (m, 2H, OCH_2CH$_2$); **^{11}B NMR** (128 MHz, THF-d_8): δ/ppm −2.4 (s); **^{13}C NMR** (100 MHz, THF-d_8): δ/ppm 14.1 (CH$_3$), 29.7 (N$_2$CCH$_2$CH$_2$), 29.9 (OCH$_2$CH$_2$), 31.6 (C(CH$_3$)$_3$), 35.1 (N$_2$CCH$_2$CH$_2$), 63.2 (OCH$_2$CH$_2$), 65.68 (C(CH$_3$)$_3$), 125.8 (br s, *i*-C$_6$F$_5$), 129.5 (NCC(CH$_3$)); 137.0 (dm, $^1J_{CF}$ = 248.0 Hz, *m*-C$_6$F$_5$), 138.8 (dm, $^1J_{CF}$ = 248.5 Hz, *p*-C$_6$F$_5$), 148.9 (dm, $^1J_{CF}$ = 242.5 Hz, *o*-C$_6$F$_5$), 151.0 (N$_2$C), **^{19}F NMR** (376 MHz, THF-d_8): δ/ppm −132.5 (br d, $^3J_{FF}$ = 22.6, 6F, *o*-C$_6$F$_5$), −164.4 (t, 3F, $^3J_{FF}$ = 20.2, *p*-C$_6$F$_5$), −167.2 (m, 6F, *m*-C$_6$F$_5$); **elemental analysis** (%) calcd. for $C_{35}H_{33}BF_{15}N_2O$: N 3.53, C 52.98, H 4.19, found: N 3.15, C 52.47, H 4.12.

*[**1h**·H][HB(C$_6$F$_5$)$_3$] (**12**).* The experiment was carried out in silylated glassware using toluene that had been dried over sodium−potassium alloy. A solution of B(C$_6$F$_5$)$_3$ (0.976 mmol, 500 mg) in 10 mL of toluene was cooled to −78 °C. To the cooled solution was added via a syringe **1h** (0.976 mmol, 203 mg) dissolved in 5 mL of toluene. After addition, hydrogen was immediately purged through the mixture for 10 min. The reaction mixture was brought to room temperature and stirred for an additional 1.5 h under H_2 atmosphere at room temperature. After removal of the solvent in vacuo the residue was washed with 3 mL of pentane and dried in vacuo, giving 0.662 g (94%) of a white solid. **^{1}H NMR** (400 MHz, CD_2Cl_2): δ/ppm 1.67 (s, 18H, CH_3), 2.41 (s, 6H, CH_3) 3.58 (q, 1H, $^1J_{HB}$ = 93 Hz, BH), 7.99 (s, 1H, N$_2$CH); **^{11}B NMR** (128 MHz, CD_2Cl_2): δ/ppm −25.1 (d, J_{H-B} = 93 Hz); **^{13}C NMR** (100 MHz, CD_2Cl_2): δ/ppm 11.7 (CH$_3$), 29.42 (C(CH$_3$)$_3$), 61.84 (C(CH$_3$)$_3$), 128.7 (N$_2$CH), 129.9 (N$_2$CC(CH$_3$)), 136.9 (dm, $^1J_{CF}$ = 245.0 Hz, *m*-C$_6$F$_5$), 138.0 (dm, $^1J_{CF}$ = 242.0 Hz, *p*-C$_6$F$_5$), 148.5 (dm, $^1J_{CF}$ = 239.4 Hz, *o*-C$_6$F$_5$); **^{19}F NMR** (376 MHz, CD_2Cl_2): δ/ppm −133.81 (m, $^3J_{FF}$ = 21.69 Hz, 6F, *o*-C$_6$F$_5$), −164.54 (m, $^3J_{FF}$ = 19.86 Hz, 3F, *p*-C$_6$F$_5$), −167.51 (m, 6F, *m*-C$_6$F$_5$); **Elemental analysis** (%) calcd. for $C_{13}H_{27}BF_{15}N_2$: N 3.87, C 51.47, H 3.76, found: N 3.55, C 51.29, H 3.55.

*[(**1i**)(CH$_2$)$_4$OB(C$_6$F$_5$)$_3$] (**13**).* Compound **13** was prepared according to the procedure described for **5**. B(C$_6$F$_5$)$_3$ (0.39 mmol, 200 mg) and **1i** (0.39 mmol); yield 0.20 g (67%); crystals suitable for X-ray analysis of **11** were obtained from a mixture of CH_2Cl_2/pentane at −35 °C; **^{1}H NMR** (300 MHz, CD_2Cl_2): δ/ppm 1.52 (s, 18H, C(CH_3)$_3$), 1.60 (m, $^3J_{HH}$ = 5.8 Hz, 2H, N$_2$(CH$_2$)$_2$CH_2), 1.76 (m, 2H, N$_2$CCH$_2$CH_2), 1.88−2.20 (br m, 2H, OCH$_2$CH_2), 3.19 (br t, $^3J_{HH}$ = 5.4, N$_2$CCH_2CH$_2$), 3.27−3.41 (br m, 6H, OCH_2CH$_2$, N$_2$(CH_2)$_2$); **^{11}B NMR** (96 MHz, CD_2Cl_2): δ/ppm −2.8 (s); **^{13}C NMR** (75 MHz, CD_2Cl_2): δ/ppm 25.6 (N$_2$(CH$_2$)$_2$CH$_2$), 30.5 (C(CH_3)$_3$), 31.3 (N$_2$CCH$_2$CH$_2$), 36.6 (OCH$_2$CH$_2$), 40.1 (N$_2$CCH$_2$CH$_2$), 46.4 (OCH$_2$CH_2), 63.3 (OCH$_2$CH$_2$), 64.6 (C(CH$_3$)$_3$), 177.1 (N$_2$C), the C$_6$F$_5$ resonances were too broad for assignment; **^{19}F NMR** (376 MHz, acetone-d_6): δ/ppm −132.6 (br d, $^3J_{FF}$ = 21.8 Hz, 6F, *o*-C$_6$F$_5$), −163.60 (t, 3F, $^3J_{FF}$ = 20.1 Hz, *p*-C$_6$F$_5$), −167.0 (m, 6F, *m*-C$_6$F$_5$); **elemental analysis** (%) calcd. for $C_{34}H_{32}BF_{15}N_2O$: N 3.59, C 52.33, H 4.13, found: N 3.71, C 52.33, H 4.27.

*[**1i**·H][HB(C$_6$F$_5$)$_3$] (**14**).* The glassware was silylated with hexamethyldisiloxane prior to use, and toluene was dried over sodium−potassium alloy! A solution of B(C$_6$F$_5$)$_3$ (0.39 mmol, 200 mg) in 3 mL of toluene was cooled to −78 °C under an atmosphere of H_2. **1i** (0.39 mmol, 77.0 mg) was added as a solution in 2 mL of toluene, and the reaction was quickly brought to room temperature. The reaction was stirred under a static atmosphere of H_2 at room temperature for 1 h. The solvent was removed in vacuo, and the remaining solid was stirred for 10 min in 10 mL of pentane. The white precipitate was isolated by filtration, immediately washed three times with 10 mL of pentane and dried in vacuo. The product was collected as a white solid (0.19 g, 70%). Crystals suitable for X-ray analysis of **12** were obtained from a mixture of CH_2Cl_2/pentane at −35 °C. **^{1}H NMR** (400 MHz, CD_2Cl_2): δ/ppm 1.39 (s, 18H, C(CH_3)$_3$), 2.04 (m, CH_2), 3.40 (br t, $^3J_{HH}$ = 6.0 Hz, 4H, N$_2$(CH_2)$_2$), 3.58 (br q, $^1J_{HB}$ = 90 Hz, 1H, BH), 7.82 (s, N$_2$CH); **^{11}B NMR** (128 MHz, CD_2Cl_2): δ/ppm −25.2 (d, J_{HB} = 90 Hz); **^{13}C NMR** (100 MHz, CD_2Cl_2): δ/ppm 19.9 (CH$_2$), 27.5 (C(CH$_3$)$_3$), 40.1 (N$_2$(CH$_2$)$_2$), 61.9 (C(CH$_3$)$_3$), 136.9 (dm, $^1J_{CF}$ = 245 Hz, *m*-C$_6$F$_5$), 138.1 (dm, $^1J_{CF}$ = 228 Hz, *p*-C$_6$F$_5$), 148.7 (dm, $^1J_{CF}$ = 232 Hz, *o*-C$_6$F$_5$), 146.1 (N$_2$CH); **^{19}F NMR** (376 MHz, CD_2Cl_2): δ/ppm −133.8 (br d, $^3J_{FF}$ = 22.0 Hz, 6F, *o*-C$_6$F$_5$), −164.4 (t, 3F, $^3J_{FF}$ = 20.3 Hz, *p*-C$_6$F$_5$), −167.4 (m, 6F, *m*-C$_6$F$_5$); **elemental analysis** (%) calcd. for $C_{30}H_{26}BF_{15}N_2$: N 3.94, C 50.73, H 3.69, found: N 4.02, C 50.24, H 3.72.

*[**1i**·H][CH$_3$CH$_2$OB(C$_6$F$_5$)$_3$] (**15**).* To a solution of B(C$_6$F$_5$)$_3$ (0.39 mmol, 200 mg) in 2 mL of Et$_2$O was added a solution of **1i** (0.39 mmol, 77.0 mg) in 3 mL of Et$_2$O. After 30 min, a white precipitate had formed, which was collected by filtration, washed with pentane, and dried in vacuo to yield the product as a white solid (0.21 g, 71%). Crystals suitable for X-ray analysis of **15** were obtained from a mixture of CH_2Cl_2/pentane at −35 °C. **^{1}H NMR** (400 MHz, CD_2Cl_2): δ/ppm 1.02 (t, $^3J_{HH}$ = 6.8 Hz, 3H, OCH$_2$CH_3), 1.41 (s, 18H, C(CH_3)$_3$), 2.05 (m, 2H, CH_2), 3.14 (br q, $^3J_{HH}$ = 6.8 Hz, 2H, OCH_2CH$_3$), 3.41 (br t, $^3J_{HH}$ = 5.8 Hz, 4H, N$_2$(CH_2)$_2$), 7.83 (s, N$_2$CH); **^{11}B NMR** (96 MHz, CD_2Cl_2): δ/ppm −2.8 (s); **^{13}C NMR** (100 MHz, CD_2Cl_2): δ/ppm 18.3 (br s, OCH$_2$CH$_3$), 19.9 (CH$_2$), 27.6 (C(CH$_3$)$_3$), 40.1 (N$_2$(CH$_2$)$_2$), 59.6 (OCH$_2$CH$_3$), 61.9 (C(CH$_3$)$_3$), 136.5 (dm, $^1J_{CF}$ = 245 Hz, *m*-C$_6$F$_5$), 138.6 (dm, $^1J_{CF}$ = 248 Hz, *p*-C$_6$F$_5$), 148.4 (dm, $^1J_{CF}$ = 241 Hz, *o*-C$_6$F$_5$), 146.1 (N$_2$CH); **^{19}F NMR** (376 MHz, CD_2Cl_2): δ/ppm −133.9 (br d, $^3J_{FF}$ = 22.8 Hz, 6F, *o*-C$_6$F$_5$), −163.9 (t, 3F, $^3J_{FF}$ = 20.2 Hz, *p*-C$_6$F$_5$), −167.3 (m, 6F, *m*-C$_6$F$_5$); **elemental analysis** (%) calcd. for $C_{34}H_{34}BF_{15}N_2O$: N 3.56, C 51.58, H 4.20, found: N 3.86, C 51.41, H 4.27.

*[(**1j**)(CH$_2$)$_4$OB(C$_6$F$_5$)$_3$] (**16**).* Compound **16** was prepared according to the procedure described for **5**. B(C$_6$F$_5$)$_3$ (0.19 mmol, 100 mg) and **1j**

Table 2. Crystallographic Data

	1g	1h	1j	5	8	9	11
empirical formula	$C_{11}H_{18}Cl_2N_2$	$C_{13}H_{24}N_2$	$C_{28}H_{40}N_2$	$C_{45}H_{40}BF_{15}N_2O$	$C_{49}H_{44}BF_{15}N_2O$	$C_{45}H_{36}BF_{15}N_2$	$C_{35}H_{32}BF_{15}N_2O$
a (Å)	9.2303(3)	5.8979(6)	6.141(2)	7.5356(2)	14.2587(6)	12.0311(16)	10.3406(4)
b (Å)	11.7158(4)	6.4251(8)	19.031(7)	21.3544(6)	14.9988(8)	18.5858(8)	21.7522(8)
c (Å)	12.0991(3)	17.3670(2)	11.164(4)	24.8512(6)	21.4354(14)	18.8956(8)	15.2061(6)
α (deg)	90	84.434(10)	90	90	90	90	90
β (deg)	90	80.802(10)	103.73(6)	90.533(2)	91.215(4)	107.195(9)	94.775(4)
γ (deg)	90	82.488(8)	90	90	90	90	90
V (Å^3)	1308.40(7)	642.12(13)	1267.6(8)	3998.84(18)	4583.2(4)	4036.3(6)	3408.4(2)
Z	4	2	2	4	4	4	4
formula weight	249.17	208.34	404.62	920.60	972.67	900.57	792.44
space group	$P2_12_12_1$	$P\bar{1}$	$P2_1/m$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/n$
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
λ (Å)	0.71073	1.54184	0.71073	0.71073	0.71073	0.71073	1.54184
D_{calcd} (g cm^{-3})	1.265	1.078	1.060	1.529	1.410	1.482	1.544
μ (mm^{-1})	0.469	0.477	0.061	0.139	0.126	0.135	1.330
reflection collected	38844	5887	37120	103670	68169	55754	29655
independent reflections	3994 R_{int} = 0.0220	2655 R_{int} = 0.0376	2483 R_{int} = 0.0873	8183 R_{int} = 0.0635	9325 R_{int} = 0.0812	10015 R_{int} = 0.0633	7025 R_{int} = 0.0212
goodness of fit on F^2	1.017	1.027	1.050	0.907	0.991	0.830	1.033
$R(F_o)$, $[I > 2\sigma(I)]$	0.0192	0.0454	0.0565	0.0348	0.0623	0.0377	0.0387
$R_w(F_o^2)$	0.0531	0.1227	0.1166	0.0488	0.1556	0.0729	0.1046
$\Delta\rho$ [e Å^{-3}]	0.286/−0.129	0.239/−0.191	0.169/−0.168	0.237/−0.194	0.412/−0.363	0.309/−0.236	0.409/−0.374

(0.19 mmol); yield 0.14 g (76%); crystals suitable for X-ray analysis of **16** were obtained from a mixture of CH_2Cl_2/pentane at −35 °C; **^{1}H NMR** (300 MHz, acetone-d_6): δ/ppm 0.85 (m, 2H, $N_2(CH_2)_2CH_2$), 1.24 (m, 2H, $N_2CCH_2CH_2$), 1.29 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.33 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $CH(CH_3)_2$), 2.12 (m, 2H, OCH_2CH_2), 2.64 (m, 4H, $N_2CCH_2CH_2$, OCH_2CH_2), 3.07 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, $CH(CH_3)_2$), 4.11 (m, 4H, $N_2(CH_2)_2$), 7.39−7.42 (m, 4H, m-CH_{Dipp}), 7.47−7.52 (m, 2H, p-CH_{Dipp}); **^{11}B NMR** (96 MHz, acetone-d_6): δ/ppm −1.9 (s); **^{13}C NMR** (75 MHz, acetone-d_6): δ/ppm 19.6 ($N_2(CH_2)_2CH_2$), 22.4 ($N_2CCH_2CH_2$), 23.1 ($CH(CH_3)_2$), 26.4 ($CH(CH_3)_2$), 29.6 ($CH(CH_3)_2$), 32.2 (OCH_2CH_2), 33.2 ($N_2CCH_2CH_2$), 52.1 ($N_2(CH_2)_2CH_2$), 63.4 (OCH_2CH_2), 126.4 (m-CH_{Dipp}), 131.7 (p-CH_{Dipp}), 137.1 (i-C_{Dipp}), 145.4 (o-C_{Dipp}), 167.2 (N_2C), the C_6F_5 resonances were too broad for assignment; **^{19}F NMR** (188 MHz, acetone-d_6): δ/ppm −132.6 (br d, $^3J_{FF}$ = 21.4 Hz, 6F, o-C_6F_5), −163.6 (t, 3F, $^3J_{FF}$ = 20.0 Hz, p-C_6F_5), −167.24 (m, 6F, m-C_6F_5); **elemental analysis** (%) calcd. for $C_{50}H_{48}BF_{15}N_2O \cdot 1.5$THF: N 2.73, C 60.95, H 5.11, found: N 2.58, C 60.49, H 5.41.

*[(**1j**)C_6F_4{$FB(C_6F_5)_2$}] (**17**).* To a solution of **1j** (0.15 mmol, 60.0 mg) in 5 mL of toluene a solution of $B(C_6F_5)_3$ (0.15 mmol, 79.0 mg) in 5 mL of toluene was added, which resulted in the formation of a gel-like, voluminous precipitate within a couple of minutes. After 1 h, the solvent was reduced to 5 mL, and the white solid was filtered off, washed with Et_2O (small portion) and hexane, and dried in vacuo to yield the raw product as a white solid. To obtain an analytically pure sample, **17** was recrystallized from CH_2Cl_2/pentane solutions. (0.11 g, 75%). Crystals suitable for X-ray analysis were obtained from a saturated solution of **17** in CH_2Cl_2 at room temperature. **^{1}H NMR** (300 MHz, CD_2Cl_2): δ/ppm 1.20 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.24 (br d, $^3J_{HH}$ = 6.6 Hz, 12H, $CH(CH_3)_2$), 2.60 (br m, 2H, $N_2(CH_2)_2CH_2$), 2.99 (br sept, $^3J_{HH}$ = 6.6 Hz, 4H, $CH(CH_3)_2$), 4.07 (br m, 4H, $N_2(CH_2)_2$), 7.16−7.18 (m, 4 H m-CH_{Dipp}), 7.33−7.38 (m, 2H, p-CH_{Dipp}); **^{13}C NMR** (75 MHz, CD_2Cl_2): δ/ppm 19.1 ($N_2(CH_2)_2CH_2$), 22.4 (br, $CH(CH_3)_2$), 27.3 ($CH(CH_3)_2$), 29.5 (br, $CH(CH_3)_2$), 52.5 ($N_2(CH_2)_2CH_2$), 125.5 (m-CH_{Dipp}), 131.6 (p-CH_{Dipp}), 135.9 (i-C_{Dipp}), 145.6 (o-C_{Dipp}), 158.0 (N_2C), the $C_6F_{4,5}$ resonances were too broad for assignment; **^{19}F NMR** (188 MHz, CD_2Cl_2): δ/ppm −133.0 (br m, 2F, C_6F_4), −135.3, (m, 2F, C_6F_4), −135.4 (m, 6F, o-C_6F_5), −161.9 (t, $^3J_{FF}$ = 20.0 Hz, 2F, p-C_6F_5), −166.4 (m, 4F, m-C_6F_5), −193.0 (br s, 1F, $FB(C_6F_5)_2$); **^{11}B NMR** (96 MHz, CD_2Cl_2): δ/ppm −0.7 (br s); **elemental analysis** (%) calcd. for $C_{46}H_{40}BF_{15}N_2 \cdot 1/2CH_2Cl_2$: C 58.57, H 4.55, N 2.88, found: C 58.68, H 4.41, N 2.74.

*(**1k**)$B(C_6F_5)_3$] (**18**).* A 1:1 mixture of $B(C_6F_5)_3$ (0.98 mmol, 500 mg) and **1j** (0.98 mmol, 206 mg) was dissolved in 10 mL of toluene. The reaction was stirred for 30 min at room temperature. The solvent was removed in vacuo, and the remaining solid was washed with pentane. Recrystallization from a saturated solution in CH_2Cl_2/pentane at 3 °C afforded a white, air-stable solid, which was dried in vacuo. Yield 97% (686 mg). Crystals suitable for X-ray analysis of **16** were obtained from a mixture of CH_2Cl_2/Et_2O/pentane at 3 °C. Note: broad NMR resonances at room temperature. **^{1}H NMR** (400 MHz, −30 °C, CD_2Cl_2): δ/ppm 0.68 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH_3), 1.06 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH_3), 1.18 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3), 1.27 (m, 3H, CH_3), 1.35 (m, 3H, CH_3), 1.50 (d, $^3J_{HH}$ = 7.2 Hz, 3H, CH_3), 1.57 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH_3), 1.65 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH_3), 4.05 (sept, $^3J_{HH}$ = 6.6 Hz, 1H, CH), 4.27 (sept, $^3J_{HH}$ = 6.4 Hz, 2H, CH), 4.59 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH); **^{11}B NMR** (96 MHz, −30 °C, CD_2Cl_2): δ/ppm −14.1 (s); **^{13}C NMR** (150 MHz, −30 °C, CD_2Cl_2): δ/ppm 20.5 (CH_3), 21.3 (CH_3), 22.0 (CH_3), 22.9 (m, CH_3), 23.0 (CH_3), 24.9 (m, CH_3), 25.0 (CH_3), 25.7 (m, CH_3), 53.3 (m, CH), 59.6 (CH), 63.2 (CH), the NCN resonance was not observed; **^{19}F NMR** (178 MHz, −30 °C, CD_2Cl_2): δ/ppm −121.8 (m, $^3J_{FF}$ = 25.7 Hz, 1F, o-C_6F_5), −126.7 (m, $^3J_{FF}$ = 25.4 Hz, 1F, o-C_6F_5), −128.7 (m, 1F, o-C_6F_5), −129.5 (m, 1F, o-C_6F_5), −134.7 (m, $^3J_{FF}$ = 23.6 Hz, 1F, o-C_6F_5), −134.9 (m, 1F, o-C_6F_5), −158.4 (m, $^3J_{FF}$ = 20.9 Hz, 1F, p-C_6F_5), −159.3 (m, $^3J_{FF}$ = 21.0 Hz, 1F, p-C_6F_5), −159.93 (m, $^3J_{FF}$ = 20.7 Hz, 1F, p-C_6F_5), −163.52 (m, 1F, m-C_6F_5), −164.2 (m, 1F, m-C_6F_5), −164.5 (m, 1F, m-C_6F_5), −165.3 (m, 1F, m-C_6F_5), −165.8 (m, 1F, m-C_6F_5), −166.3 (m, 1F, m-C_6F_5); **elemental analysis** (%) calcd. for $C_{31}H_{28}BF_{15}N_2$: N 3.87, C 51.80, H 3.90, found: N 3.78, C 52.29, H 4.22.

Theoretical Calculations. All computations were performed using the density functional method M05-2X as implemented in the Gaussian09 program.[46,48] For all main-group elements (C, H, N, B, F,

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Table 3. Crystallographic data

	13	14	15	16·0.5CH_2Cl_2	17	18	[1h·H][FB(C_6F_5)$_3$][a]
empirical formula	$C_{34}H_{32}BF_{15}N_2O$	$C_{30}H_{26}BF_{15}N_2$	$C_{32}H_{30}BF_{15}N_2O$	$C_{50.50}H_{49}BClF_{15}N_2O$	$C_{46}H_{40}BF_{15}N_2$	$C_{31}H_{28}BF_{15}N_2$	$C_{31}H_{25}BF_{16}N_2$
a (Å)	12.5752(2)	10.1143(2)	8.0521(2)	9.5340(4)	11.6425(8)	10.5602(6)	16.7801(2)
b (Å)	15.5632(2)	14.0410(2)	18.2928(4)	14.5959(6)	12.3525(10)	10.7479(8)	10.1136(2)
c (Å)	16.9021(2)	21.5565(2)	22.2546(4)	17.6549(8)	14.7161(8)	14.5654(8)	18.1876(4)
α (deg)	90	90	90	94.969(2)	82.343(6)	93.988(4)	90
β (deg)	91.345(2)	98.729(2)	95.965(2)	96.389(2)	81.076(4)	97.676(4)	97.464(2)
γ (deg)	90	90	90	99.508(2)	81.820(6)	109.782(6)	90
V (Å^3)	3307.00(8)	3025.89(8)	3260.25(12)	2394.15(18)	2056.1(2)	1529.96(17)	3060.41(10)
Z	4	4	4	2	2	2	4
formula weight	780.43	710.34	754.39	1031.18	916.61	724.36	740.34
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
λ (Å)	1.54184	1.54184	1.54184	1.54184	1.54184	0.17073	1.54184
D_{calcd} (g cm^{-3})	1.567	1.559	1.537	1.430	1.481	1.572	1.607
μ (mm^{-1})	1.359	1.397	1.357	1.585	1.169	0.156	1.458
reflection collected	50872	39634	47250	35103	33761	37026	55661
independent reflections	6866 R_{int} = 0.0211	6284 R_{int} = 0.0254	6769 R_{int} = 0.0297	9896 R_{int} = 0.0318	8407 R_{int} = 0.0295	6732 R_{int} = 0.0426	6360 R_{int} = 0.0219
goodness of fit on F^2	1.042	1.072	1.030	1.034	1.050	0.857	1.028
$R(F_o)$, $[I > 2\sigma(I)]$	0.0314	0.0407	0.0312	0.0377	0.0352	0.0327	0.0372
$R_w(F_o^2)$	0.0826	0.1090	0.0845	0.0985	0.0938	0.0665	0.1052
$\Delta\rho$ [e Å^{-3}]	0.272/−0.208	0.617/−0.222	0.273/−0.237	0.488/−0.367	0.337/−0.246	0.256/−0.212	0.298/−0.228

[a] An ORTEP diagram of this structure can be found in the Supporting Information.

and Cl) the all-electron triple-ζ basis set (6-311G**) was used.[49] All geometry optimizations were performed without any imposed symmetry constraints. After the relevant stationary points were localized on the energy surface, they were further characterized as minima by normal-mode analysis based on the analytical energy second derivatives. Enthalpic and entropic contributions were calculated by statistical thermodynamics as implemented in the Gaussian09 set of programs. Presentations together with Cartesian coordinates can be found in the Supporting Information.

Single-Crystal X-ray Structure Determinations. Crystals were mounted in inert oil on glass fibres. Intensity measurements were performed at low temperature on Oxford Diffraction Xcalibur diffractometers using monochromated Mo K_α or mirror-focused Cu K_α radiation. Absorption corrections were based on multiscans. Structures were refined anisotropically on F^2 using the program SHELXL-97.[50] Carbenium hydrogen atoms were refined freely; other hydrogens were included using idealized rigid methyl groups or a riding model. Crystallographic data are summarized in Tables 2 and 3. *Exceptions and special features*: Compound **1g** was refined as a racemic twin, with minor component 0.10(3). The structure of compound **1j** is disordered in $P2_1/m$, with atoms C2, C3, C4 occupying alternative positions on both sides of the mirror plane. The structure can also be refined without disorder in space group $P2_1$, but the refinement is not satisfactory (e.g., it displays larger and more irregular thermal ellipsoids). It is unlikely that X-ray methods alone can determine which model is correct, and the quantitative results should be interpreted with caution, although the qualitative nature of the compound has been established. For compound **5**, the atoms C16 and C17 are disordered over two positions with occupancy 3:1. Despite the use of similarity restraints, dimensions of the minor component are not entirely satisfactory. It is possible that C15 is also slightly disordered. Data for **8** were weak, and 300 restraints to anisotropic displacement parameters were employed to improve stability of refinement. In **14** the hydrogen at boron was refined freely. The dichloromethane molecule in **16** is disordered over an inversion center; appropriate similarity restraints were used to ensure stability of refinement.

■ ASSOCIATED CONTENT

Supporting Information. Details of the electronic structure calculations, presentations of all calculated structures together with Cartesian coordinates of their atomic positions and selected NMR spectra of **18** are provided. See DOI: 10.1039/b000000x/. This material is available free of charge via the Internet at http://pubs.acs.org.

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