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Heterocycles

B–B Cleavage and Ring-Expansion of a 1,4,2,3-Diazadiborinine with N-Heterocyclic Carbenes

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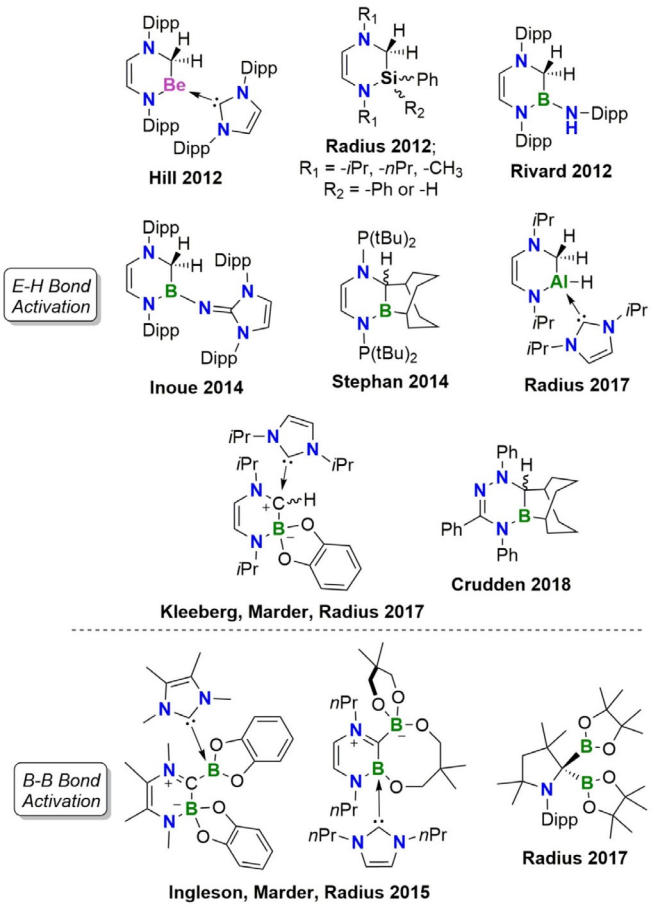
Abstract: A 1,4,2,3-diazadiborinine derivative was found to form Lewis adducts with strong two-electron donors such as N-heterocyclic and cyclic (alkyl)(amino)carbenes. Depending on the donor, some of these Lewis pairs are thermally unstable, converting to sole B,N-embedded products upon gentle heating. The products of these reactions, which have been fully characterized by NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction, were identified as B,N-heterocycles with fused 1,5,2,4-diazadiborepine and 1,4,2-diazaborinine rings. Computational modelling of the reaction mechanism provides insight into the formation of these unique structures, suggesting that a series of B–H, C–N, and B–B bond activation steps are responsible for these "intercalation" reactions between the 1,4,2,3-diazadiborinine and NHCs.

Introduction

The development of stable, isolable carbenes by Bertrand[1] and Arduengo[2] in the early 1990s has revolutionized the modern chemical landscape. N-heterocyclic carbenes (NHCs), for example, have found widespread use in a number of fields such as transition metal chemistry[3–8] and catalysis.[9–12] Additionally, their strong two-electron donating capabilities have proved critical for the isolation of various exotic, low-valent main-group species.[13–15] Although the success of NHCs in these applications is predicated on their robust nature,[16] the susceptibility of these carbenes to C–N bond cleavage has been known for many years.[17,18] It has since become apparent that NHCs readily undergo ring-expansion reactions (RERs) in the presence of various E–H hydrides at elevated temperatures, generating the wide variety of ring-expanded products shown in Scheme 1. Early reports by the groups of Hill[19] and Radius[20] established that beryllium and silicon hydrides could insert into the C–N bonds of both bulky and non-bulky NHCs, with concomitant hydride migration to the carbene C atom. Later work by the research groups of Crudden,[21] Inoue,[22]



Scheme 1. NHC-ring expanded products from E–H activation (E = Be, B, Al, and Si; top), as well as B–B activation (bottom). Dipp = 2,6-diisopropylphenyl.

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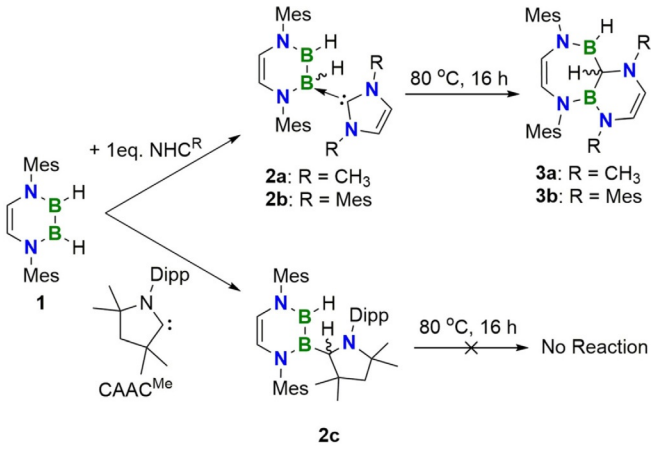
Marder,[23,24] Radius,[25–27] Rivard,[28] and Stephan[29] were able to extend this reactivity pattern to other E–H substrates (E = Al and B) and NHCs,[25,28] as well as demonstrate that diboron(4) reagents such as bis(catecholato)diboron(4) can participate in a related B–B bond activation/B insertion reaction.[23,24,27,30] Despite the growing number of RERs reported in the literature, to the best of our knowledge, C–N bond activation of NHCs with heterocycles containing endocyclic E–H functionalities remains completely unknown.

As part of our ongoing efforts to access novel diboranes, we recently reported the facile and quantitative synthesis of the first *cis*-1,2-dihydrodiborane(4) (**1**), shown in Scheme 2.[31] This



Scheme 2. Synthesis of carbene-diazadiborinine adducts **2a**–**2c** and the RER products **3a**/**3b**. Mes = 2,4,6-trimethylphenyl.

$B_2N_2C_2$ heterocycle, a derivative of 1,4,2,3-diazadiborinine, is a B,N isostere of benzene, in which two of the C=C bonds have been replaced by isoelectronic and isostructural B–N units. Unlike mono-substituted azaborines, which are aromatic,[32] the $^1H/^{11}B$ nuclear magnetic resonance (NMR) data of **1** indicates that the B–N units possess more localized B=N character. As such, we postulated that the boron centers in **1** should retain some of their Lewis acidity and thus be able to form adducts with strong donors such as carbenes (**2a**–**2c**; Scheme 2). Given the proximity of B–H and NHC groups in **2a**/**2b**, thermal RERs should be accessible to these systems, yielding a new class of bicyclic B,N-heterocycles. Indeed, heating **2a**/**2b** in solution overnight results in the clean formation of diazadiborepines **3a**/**3b** shown in Scheme 2, which represent the very first examples of NHC RERs with an endocyclic B–H substrate. In the case of **2c**, insertion of the cyclic (alkyl)(amino)carbene cAAC^{Me} (see Scheme 2 for structure) into the B–H bond of **1** is observed without the accompanying RER. The synthetic, spectroscopic, and mechanistic details of this new NHC-azaborinine ring fusion reaction are presented herein.

Results and Discussion

The carbene-diazadiborinine adducts **2a** and **2b** were synthesized in good yields (70–80%; >95% purity) according to the reaction shown in Scheme 2. Regardless of the reaction conditions, combining cAAC^{Me} and **1** resulted in the formation of **2c** as well as a variety of unidentifiable side-products. Therefore, **2c** could only be isolated in low yield (12%) following recrystallization from pentane at −30 °C. All three compounds were fully characterized by multinuclear NMR spectroscopy (^1H, ^{13}C, and ^{11}B) and elemental analysis (EA). At room temperature, the NMR resonances of **2b** are all significantly broadened. Therefore, the ^1H and ^{13}C NMR spectroscopic data of **2b** were collected at −20 °C, whereas its ^{11}B NMR spectrum was recorded at 20 °C to prevent quadrupolar line broadening.[33] The ^{11}B NMR spectra of **2a** and **2b** both showed two signals at 54 and −16 ppm, indicative of distinct chemical environments around each boron atom. The ^1H NMR spectra of **2a** showed two separate resonances for the vinylene hydrogens on the ligand (doublets at 5.65 and 5.02 ppm; $^3J_{HH} = 5.8$ Hz) and hydrides attached to boron (broad singlets at 5.75 and 3.61 ppm), consistent with its unsymmetrical structure (see Supporting Information for details). Despite its bulky mesityl groups, the diazadiborinine **2a** experiences minimal steric crowding, as evidenced by the N–CH_3 substituents of NHC^{Me}, which resonate as a broad singlet at 3.3 ppm. Compound **2b** possesses many of the same NMR spectroscopic features as **2a**, except for the *o*-methyl signals of the four mesityl substituents in **2b**, which all appear as broad, resolved singlets in the upfield ^1H NMR region due to considerable steric hindrance. Unlike **2a**/**2b**, compound **2c** only shows a single ^{11}B NMR spectroscopic resonance at 47 ppm, as this B–H activation product still contains two trigonal planar boron atoms. Once again, **2c** is mildly encumbered, as suggested by the resolved -*CH*$(CH_3)_2$ isopropyl resonances at 4.58 and 3.15 ppm, respectively (septets; $^3J_{HH} = 6.9$ Hz).

Single crystals of **2b** and **2c** suitable for X-ray diffraction were obtained by slow evaporation of saturated Et_2O solutions at −30 °C and their X-ray structures are shown in Figure 1. Similar to compound **1**, both **2b** and **2c** are quasi-planar, with N1-B1-B2-N2 and N1-C1-C2-N2 torsion angles of <5°. In fact, the bonding parameters of **1** and **2c** are very similar since cAAC^{Me} insertion into the B–H bond barely impacts the overall molecular structure.

Conversely, **2b** exhibits significantly different B–N bond lengths due to sp^3-hybridization at the carbene-bound B atom (B1–N1 = 1.408 vs. B2–N2 = 1.570 Å), which can no longer accept electron density from the lone pair on N2. Notably, the B2–N2 bond length in **2b** is still in the range expected for a B–N bond with some π-bonding character,[34] possibly due to the weaker B2–C1 bond resulting from steric constraints. Despite its congested structure, the central six-membered ring in **2b** retains its nearly planar orientation. Single crystals of **2a** could not be obtained, as each attempted recrystallization of **2a** yielded single crystals of **3a** after several weeks at −30 °C.

Compounds **2a**/**2b** were found to be thermally unstable at room temperature, and slowly convert to the bicyclic B,N-heterocycles **3a**/**3b** shown in Scheme 2 over the course of several weeks. This process can be dramatically accelerated using heat, with full conversion observed after 16 hours at 80 °C in C_6D_6 and an isolated yield of 75%. The fused-ring products **3a**/

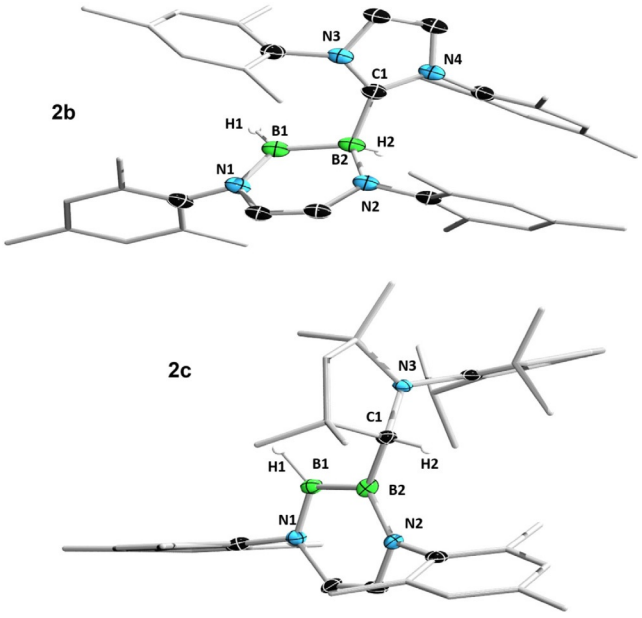


Figure 1. Single-crystal X-ray crystallographic structures of **2b** and **2c**. Atomic displacement ellipsoids are depicted at 50% probability and omitted at the ligand periphery. Hydrogen atoms are omitted for clarity, except for those bound to boron. Selected bond lengths [Å] and angles [°]: for **2b** B2–B1 1.699(2), B1–N1 1.408(2), B2–N2 1.570(2), B2–C1 1.633(2), B1–H1 1.12(2), N1-B1-B2 119.0(1), N2-B2-B1 110.4(1), N2-B2-C1 114.1(1), B1-B2-C1 114.6(1), B1-B2-C1-N3 33.5(2); for **2c**: B1–H1 1.18(2), N1–B1 1.419(4), B1–B2 1.678(5), B2–N2 1.434(3), B2–C1 1.599(4), N1-B1-B2 117.2(2), B1-B2-N2 112.7(2), N2-B2-C1 120.1(2), B2-C1-N3 112.8(2), N1-B1-B2-N2 2.0(3), B1-B2-C1-N3 −48.5(3), N2-B2-C1-N3 138.0(2).

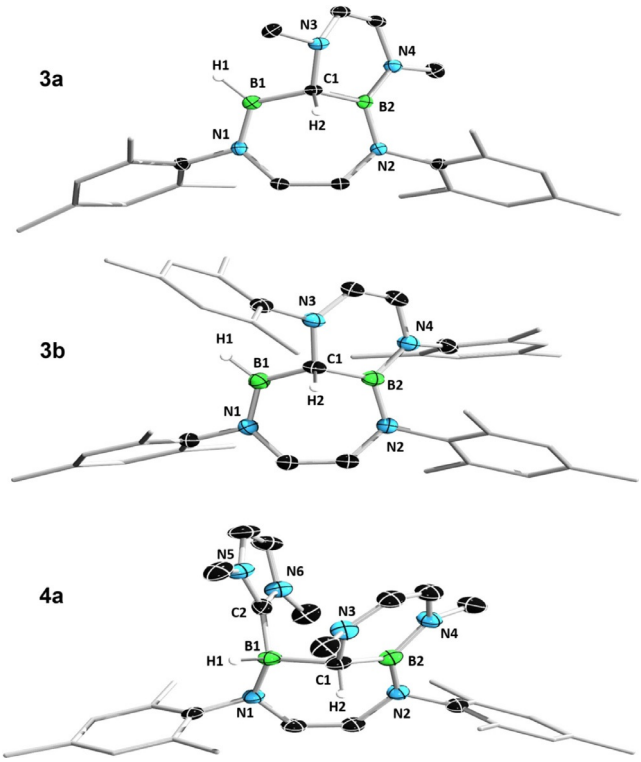
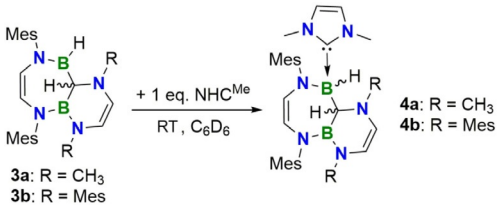


Figure 2. Single-crystal X-ray crystallographic structures of **3a**, **3b**, and **4a**. Atomic displacement ellipsoids are depicted at 50% probability and omitted at the ligand periphery. Most hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: for **3a**: N2–B2 1.443(2), B2–N4 1.411(2), N1–B1 1.403(2), B1–C1 1.574(2), C1–B2 1.588(2), C1–N3 1.474(2), B1–H1 1.11(2), N2-B2-C1 116.6(1), B2-C1-B1 105.36(9), B1-C1-N3 116.5(1), N3-C1-B2 111.72(9), C1-B2-N4 118.9(1), N4-B2-N2 124.5(1), C1-B1-N1 118.7(1), N2-B2-C1-N3 157.0(1), B1-C1-B2-N4 104.1(1), N1-B1-C1-B2 68.3(1), N1-B1-C1-N3 −167.2(1), N2-B2-C1-B1 −75.5(1), N1-B1-C1-B2 68.3(1), B1-C1-B2-N2 −75.5(1), B2-C1-B1-N1 68.3(1); for **3b**: B1–C1 1.564(4), C1–B2 1.577(4), B2–N4 1.418(4), C1–N3 1.473(3), B1–N1 1.410(3), N2–B2 1.446(3), N2-B2-C1 116.9(2), B2-C1-B1 106.3(2), B2-C1-N3 113.5(2), N3-C1-B1 114.1(2), C1-B2-N4 120.1(2), N4-B2-N2 123.0(2), N1-B1-C1 120.1(2), N2-B2-C1-B1 −71.2(3), B2-C1-B1-N1 68.0(3), N1-B1-C1-N3 −166.1(2), B1-C1-B2-N4 109.7(3), N2-B2-C1-N3 162.6(2); for **4a**: N1–B1 1.539(3), B1–C1 1.648(4), C1–B2 1.577(4), B2–N2 1.443(4), B2–N4 1.426(3), C1–N3 1.494(4), B1–C2 1.641(3), N1-B1-C1 112.8(2), N1-B1-C2 115.6(2), C2-B1-C1 107.4(2), N2-B2-C1 119.7(2), N2-B2-N4 120.7(2), N4-B2-C1 119.6(2), B2-C1-N3 113.3(2), N3-C1-B1 107.7(2), N1-B1-C1-B2 64.6(3), N1-B1-C1-B2 64.6(3), N1-B1-C1-N3 −167.9(2), B1-C1-B2-N2 −67.7(3), B1-C1-B2-N4 112.3(3), N2-B2-C1-N3 167.8(2), N1-B1-C2-N5 140.9(3), N6-C2-B1-C1 83.1(3).

3b were fully characterized by NMR spectroscopy and EA, with their connectivity established by single-crystal X-ray diffraction (see Figure 2). As shown in Figure 2, **3a**/**3b** consist of 1,5,2,4-diazadiborepine and 1,4,2-diazaborinine rings that are conjoined at their [2,3-*b*] B–C periphery. Formally, these structures are obtained by "intercalation" of the imidazole and 1,4,2,3-diazadiborinine rings, whereby one B atom inserts into the C–N bond of the NHCs in **2a**/**2b** following hydride transfer from boron to carbon,[28] with subsequent insertion of the carbene C atom into the B–B bond of **1**. Therefore, these thermal rearrangements involve three different bond activations, namely, B–H and B–B on the 1,4,2,3-diazadiborinine and C–N on the NHCs, and represent the first examples of NHC RERs with a cyclic diborane. Based on previous findings and computed mechanisms,[35–41] it is anticipated that the first step in the reaction from **2a**/**2b** to **3a**/**3b** is the transfer of hydride from B to the central carbon of the NHC, which is in agreement with our DFT computed mechanism (vide infra). Due to their 4a*H*-benzo[7]annulene scaffolds and quaternary C1 atoms, the 1,5,2,4-diazadiborepine rings of **3a** and **3b** adopt pseudo-boat conformations (B1-C1-B2 = 106.3°), with quasi-*trans* configurations between the H atoms of B1 and C1 ($\theta_{H\text{-}B1\text{-}C1\text{-}H}$ = 134.9° in **3a** and 131.3° in **3b**). Furthermore, the 1,4,2-diazaborinine rings experience slight distortion from planarity, with N1-C1-B2-N2 torsion angles of −23.3 and −16.5° for **3a** and **3b**, respectively. The ^{11}B NMR spectra of **3a** and **3b** contain two signals which are consistent with an isolated B–N bond (B1 = 44 ppm)[42] and a B atom located between two N atoms in a conjugated system (B2 = 29 ppm).[43] These ^{11}B resonances suggest that the B1 atoms in **3a**/**3b** are more electron-deficient compared to B2, as increasingly electron-deficient boron species tend to appear at higher frequencies. Heating of **2c** under the same conditions does not induce any C–N bond activation/RER, which is analogous to other works on *p*-block element hydride adducts of cAAC^{Me}.[25]

To probe the Lewis acidity of the two unique boron atoms in these new B,N-heterocycles, one additional equivalent of NHC^{Me} was added to **3a** and **3b**, resulting in the formation of adducts **4a** and **4b** in moderate yields (Scheme 3). Monitoring this reaction by ^{11}B NMR, the B1–H1 resonances of **3a**/**3b** disappear, whereas new peaks emerge at −8.8 and −16.8 ppm for **4a** and **4b**, respectively. This assignment is further support-



Scheme 3. Reaction between **3a**/**3b** and NHC^{Me}.

ed by the fact that one-bond ^{1}H-coupling is observed in the new ^{11}B signal of **4a** ($^{1}J_{BH}$ = 78.6 Hz). Single crystals of **4a** were obtained by slow evaporation of a saturated Et_2O solution at −30 °C, with its X-ray structure shown in Figure 3. All attempts to crystallize **4b** failed. The bonding parameters of **4a** are very similar to those of **3a**, with the diazadiborepine retaining a pseudo-boat conformation (B1-C1-B2 = 115.0°). The only major difference is the tetrahedral B1 atom, which changes the quasi-*trans* configuration of H-B1-C1-H to a staggered conformation ($\theta_{H\text{-}B1\text{-}C1\text{-}H}$ = 63.5°). The preferential binding of NHC^{Me} to B1 in **3a**/**3b** confirms that these boron atoms are more electron-deficient than the respective B2 atoms. This is likely because B2 is sandwiched between two N atoms, which are both capable of donating electron density to boron.

To elucidate the reaction mechanism leading to **3a**/**3b** from *cis*-diborane(4) **1** and NHC$^{Me/Mes}$, density functional theory (DFT) calculations were carried out at the PBEPBE/def2-SVP level of theory. The calculated reaction profiles are shown in Figure 3. The initial step of these reactions involve the formation of the adducts **2a**/**2b**, which are both slightly more stable than the starting reagents (−11.2 and −6.8 kcal mol^{-1} for NHC^{Me} and NHC^{Mes}, respectively). Next, the hydride bound to the tetrahedral boron atom migrates to the central carbene C, resulting in the formation of **Int1**. In the case of NHC^{Me}, this step is rate-limiting, with an activation barrier of 28.9 kcal mol^{-1} relative to **2a**. The intermediates **Int1** are close to another transition state, wherein the boron atoms bound to the carbene centers insert into the C–N bonds of the NHCs, resulting in the spiro-structures **Int2**. Due to its bulky Mes groups, this step is rate-limiting for NHC^{Mes} with E_a = 26.9 kcal mol^{-1} relative to **2b**. Finally, the carbene C inserts into the B–B bond of **Int2**, which is almost barrierless for NHC^{Me} and slightly uphill for NHC^{Mes} (12.8 kcal mol^{-1}). This results in the formation of the final products **3a**/**3b**, with the overall reactions being exergonic by ≈40 kcal mol^{-1}.

Conclusions

We have shown that 1,4,2,3-diazadiborinines can form adducts or B–H insertion products with strongly electron donating carbenes. The NHC adducts of 1,4,2,3-diazadiborinines are thermally unstable and undergo ring-expansion reactions upon gentle heating over the course of several hours. This previously unknown reactivity of BN-embedded aromatics provides the first examples of RERs between a cyclic diborane and NHCs. The resulting B,N-heterocycles, which were identified by single-crystal X-ray diffraction, consist of fused 1,5,2,4-diazadiborepine and 1,4,2-diazaborinine rings, and can be thought of as doubly B,N-doped 4a*H*-benzo[7]annulenes. The mechanism of this transformation was determined computationally, suggesting that the initial steps of the reaction are analogous to those of known RERs (B–H/C–N bond activation), with subsequent insertion of the carbene carbon atom into the B–B bond of the diazadiborinine, leading to the novel B,N-heterocyclic products. Consistent with previous findings, the cAAC^{Me} B–H insertion products of the 1,4,2,3-diazadiborinine are thermally stable even at elevated temperatures. Attempts to expand this reactivity pattern to various other B,N aromatics is ongoing in our laboratory, and will be reported in due course.

Experimental Section

NMR spectra of all compounds, crystallographic details, and theoretical details/structures can be found in the Supporting Information. CCDC 1923561, 1923562, 1923563, 1923564, 1923565 (**2c**, **3a**, **3b**, **4a**, **2b**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

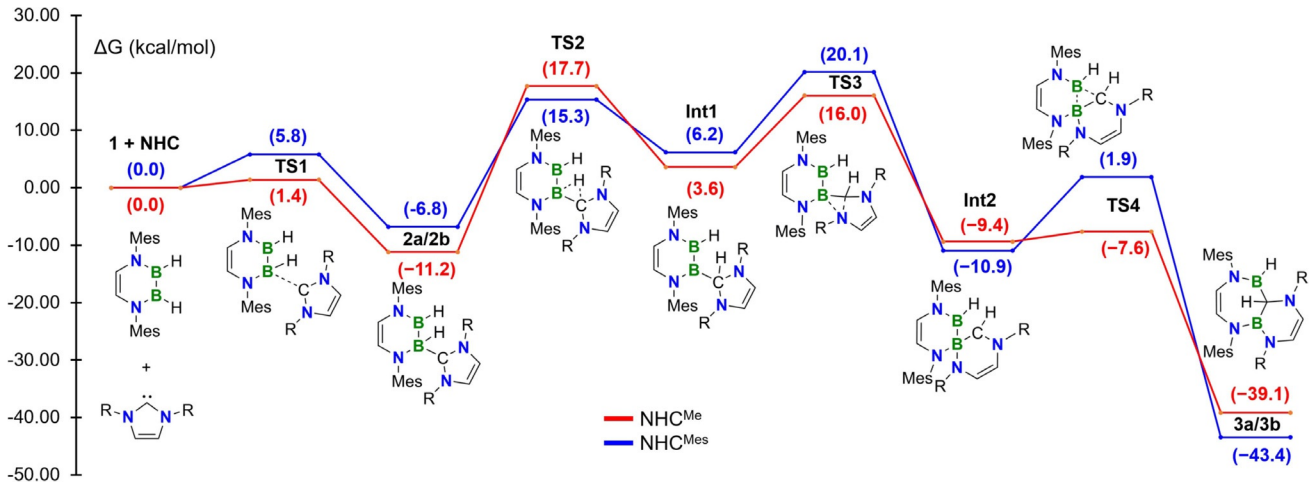


Figure 3. Calculated (DFT) reaction pathways for the reaction of **1** with NHC^{Me} (red) and NHC^{Mes} (blue) at the PBEPBE/def2-SVP level of theory.

All reactions were performed under an atmosphere of dry Ar using standard Schlenk line or glovebox techniques. Deuterated benzene and toluene were degassed by three freeze-pump-thaw cycles and dried over molecular sieves. Other solvents were dried by distillation from potassium (benzene, THF) under an Ar atmosphere and stored under Ar over activated 4 Å molecular sieves. Compounds **1**,[31] NHC^{Me},[44] NHC^{Mes},[44] and $cAAC^{Me}$[45] were synthesized according to literature procedures. NMR spectra were obtained from a Bruker Avance 500 NMR spectrometer (^1H and $^1H\{^{11}B\}$: 500.1 MHz, $^{13}C\{^1H\}$: 125.8 MHz; ^{11}B: 160.5 MHz) at 298 K, if not stated otherwise. Chemical shifts (δ) are given in ppm and internally referenced to the carbon nuclei ($^{13}C\{^1H\}$) or residual protons (^1H) of the solvent. ^{11}B NMR spectra were referenced to external standard $BF_3{\cdot}OEt_2$. Microanalyses (C, H, N) were performed on an Elementar vario MICRO cube elemental analyzer. Low carbon analyses were observed for some of the boron-containing products, likely due to the formation of refractory boron carbide (BC) during analysis.[46]

Synthetic Procedures

Synthesis of ***2a****:* In a J. Young-type NMR tube, a mixture of **1** (38.9 mg, 123 μmol) and NHC^{Me} (11.8 mg, 123 μmol) was dissolved in 0.5 mL of C_6D_6 and a yellow solution was formed. After a few minutes, all volatiles were removed in vacuo and **2a** was obtained as a yellow powder (35.1 mg, 85.0 μmol, 69%). ^1H NMR (500.13 MHz, C_6D_6): δ (ppm) = 7.00 (m, 1H, *meta-CH*), 6.93 (m, 1H, *meta-CH*), 6.92 (m, 1H, *meta-CH*), 6.75 (m, 1H, *meta-CH*), 5.75 (brs, 1H, B*H*), 5.65 (d, 1H, CH=CH, $^3J_{HH}$ = 5.78 Hz), 5.63 (brs, 2H, $C(NCH_3)_2(CH)_2$), 5.02 (d, 1H, CH=*CH*, $^3J_{HH}$ = 5.78 Hz), 3.61 (brs, 1H, B*H*), 3.58–2.97 (br, 6H, $C(NCH_3)_2$), 2.91 (s, 3H, *ortho*-CH_3), 2.73 (s, 3H, *ortho*-CH_3), 2.46 (s, 3H, *ortho*-CH_3), 2.23 (s, 3H, *para*-CH_3), 2.22 (s, 3H, *para*-CH_3), 1.69 (s, 3H, *ortho*-CH_3); $^{13}C\{^1H\}$ NMR (125.76 MHz, C_6D_6): δ (ppm) = 170.9 (brs, N_2CB), 151.1 (s, *ipso*-C_q), 149.6 (s, *ipso*-C_q), 138.4 (s, *ortho*-C_q), 135.2 (s, *ortho*-C_q), 134.8 (s, *ortho*-C_q), 134.0 (s, *para*-C_q), 132.8 (s, *ortho*-C_q), 132.7 (s, *para*-C_q), 130.2 (s, *meta*-CH), 129.6 (s, *meta*-CH), 129.1 (s, *meta*-CH), 128.7 (s, *meta*-CH), 127.1 (s, *CH*=CH), 119.7 (brs, CN_2C=CH), 106.0 (s, CH=CH), 35.6 (s, $C(NCH_3)$), 21.0(6) (s, *para*-CH_3), 21.0(5) (s, *para*-CH_3), 19.3(4) (s, *ortho*-CH_3), 19.3(0) (s, *ortho*-CH_3), 19.1 (s, *ortho*-CH_3), 17.2 (s, *ortho*-CH_3); $^{11}B\{^1H\}$ NMR (160.46 MHz, C_6D_6): δ (ppm) = 54.2 (brs, $h_{1/2}$ = 860 Hz, N*B*HB), −16.8 (brs, $h_{1/2}$ = 308 Hz, NBH*B*C); elemental anal. [%]: calcd. for $C_{25}H_{35}B_2N_4$ (413.2 g mol^{-1}) C: 72.67, H: 8.54, N: 13.56; found: C: 71.76, H: 8.08, N: 13.56.

Synthesis of ***2b****:* In a J. Young-type NMR tube, a mixture of **1** (20.0 mg, 120 μmol) and NHC^{Mes} (19.3 mg, 120 μmol) was dissolved in 0.5 mL of [D_8]toluene and instantly cooled to −40 °C. After removal of all volatiles in vacuo, **2b** was obtained as yellow powder in 82% yield (32.2 mg, 51.8 μmol). ^1H and ^{13}C NMR data were collected at low temperature (−20 and −30 °C respectively) to resolve all peaks in the spectrum, whereas ^{11}B NMR data were collected at 20 °C. ^1H NMR (500.13 MHz, [D_8]toluene, T = 253 K): δ (ppm) = 6.84 (s, 1H, *meta-CH*), 6.72 (s, 1H, *meta*-CH), 6.66 (s, 3H, *meta-CH*), 6.56 (s, 1H, *meta-CH*), 6.48 (s, 2H, *meta-CH*), 5.63 (s, 2H, $C(NMes)_2CH$=CH), 5.24 (brs, 1H, B*H*), 5.22 (d, 1H, $^3J_{HH}$ = 5.93 Hz, (BH)(NMes)CH=CH), 4.67 (d, 1H, $^3J_{HH}$ = 5.93 Hz, (BH)(NMes)CH=*CH*), 3.60 (brs, 1H, B*H*C), 2.47 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 2.13(4) (s, 6H, CH_3), 2.12(9) (s, 3H, CH_3), 2.08 (s, 6H, CH_3), 1.95 (s, 3H, CH_3), 1.76 (brs, 6H, CH_3); $^{13}C\{^1H\}$ NMR (125.76 MHz, [D_8]toluene, T = 263 K): δ (ppm) = 173.0 (brs, N_2CB), 151.1 (*ipso*-C_q), 149.6 (*ipso*-C_q), 138.4 (C_q), 136.7 (C_q), 135.8 (C_q), 135.5 (C_q), 134.9 (C_q), 134.7 (C_q), 133.3 (C_q), 133.0 (C_q), 131.0(9) (C_q), 130.0(7) (*meta*-CH), 129.2(2) (*meta*-CH), 129.1(9) (*meta*-CH), 129.1 (*meta*-CH), 128.9 (*meta*-CH), 128.6 (*meta*-CH), 127.2 (*meta*-CH), 125.5 (*meta*-CH), 127.2 (HC=CH), 121.5 (CN_2C=CH), 107.2 (HC=*CH*), 21.2 (CH_3), 21.1(3) (CH_3), 21.1(2) (CH_3), 21.0(7) (CH_3), 21.0(0) (CH_3), 20.8 (CH_3), 20.7 (CH_3), 19.8 (CH_3), 18.6 (CH_3). $^{11}B\{^1H\}$ NMR (160.46 MHz, C_6D_6): δ (ppm) = 54.1 (brs, $h_{1/2}$ = 1002 Hz, N*B*HB), −16.4 (s, $h_{1/2}$ = 337 Hz, NBH*B*C); elemental anal. [%]: calcd. for $C_{41}H_{50}B_2N_4$ (621.51 g mol^{-1}) C: 79.36, H: 8.12, N: 9.03; found: C: 77.89, H: 7.90, N: 8.74.

Synthesis of ***2c****:* In a J. Young-type NMR tube, a mixture of **1** (33 mg, 104 μmol) and $cAAC^{Me}$ (29.8 mg, 104 μmol) was dissolved in 0.5 mL C_6D_6. Afterwards, all volatiles were removed in vacuo and the residue was dissolved in pentane and stored at −30 °C. After several days, colorless crystals of **2c** were obtained and dried in vacuo. Isolated yield: 12% (8.9 mg, 12.9 μmol). ^1H NMR (500.13 MHz, C_6D_6): δ (ppm) = 7.18 (m, 1H, *para-CH*), 7.09 (m, 2H, *meta-CH*), 6.85 (m, 1H, *meta-CH*), 6.82 (m, 1H, *meta-CH*), 6.72 (m, 1H, *meta-CH*), 6.60 (m, 1H, *meta-CH*), 6.05 (brs, 1H, B*H*), 5.78 (d, 1H, $^3J_{HH}$ = 6.04 Hz, HC=*CH*), 5.55 (d, 1H, $^3J_{HH}$ = 6.04 Hz, CH=CH), 4.58 (sept, 1H, $^3J_{HH}$ = 6.96 Hz, *CH*$(CH_3)_2$), 3.15 (sept, 1H, $^3J_{HH}$ = 6.80 Hz, *CH*$(CH_3)_2$), 3.06 (s, 1H, *CH*B), 2.32 (s, 3H, *ortho*-CH_3), 2.21 (d, 1H, $^2J_{HH}$ = 12.65 Hz, *CH*H), 2.18 (s, 3H, *para*-CH_3), 2.16 (s, 3H, *ortho*-CH_3), 2.12 (s, 6H, *ortho*-CH_3, *para*-CH_3), 1.94 (d, 1H, $^2J_{HH}$ = 12.65 Hz, CH*H*), 1.92 (s, 3H, CHC$(CH_3)(CH_3)$), 1.52 (s, 3H, CHNC$(CH_3)(CH_3)$), 1.25 (s, 3H, *i*PrCH_3), 1.23 (s, 3H, *i*PrCH_3), 1.19 (s, 3H, CHNC$(CH_3)(CH_3)$), 1.15 (s, 3H, *ortho*-CH_3), 1.13 (s, 3H, *i*PrCH_3), 1.03 (s, 3H, CHC$(CH_3)(CH_3)$), 0.75 (s, 3H, *i*PrCH_3). $^{13}C\{^1H\}$ NMR (125.76 MHz, C_6D_6): δ (ppm) = 152.6 (s, $C_q(CH(CH_3)_2)$), 150.3 (s, $C_q(CH(CH_3)_2)$), 147.6 (s, *ipso*-C_q), 146.0 (s, *ipso*-C_q), 144.9 (s, *ipso*-C_q), 135.8 (s, *ortho*-C_q), 135.7 (s, *para*-C_q), 134.3 (s, *ortho*-C_q), 133.7 (s, *ortho*-C_q), 133.7 (s, *para*-C_q), 132.2 (s, *ortho*-C_q), 129.9 (s, *meta*-CH), 129.6 (s, *meta*-CH), 129.3 (s, *meta*-CH), 128.9 (s, *meta*-CH), 126.3 (s, *para*-CH), 125.4 (s, *meta*-CH), 124.0 (s, *meta*-CH), 121.9 (s, HC=CH), 120.3 (s, HC=CH), 70.5 (brs, $(CH_3)_2$CHCH), 64.9 (s, B(CH)$C_q(CH_3)_2$), 60.8 (s, $(CH(CH_3)_2)CH_2$), 42.7 (s, B(CH)$NC_q(CH_3)_2$), 33.4 (s, $(CH_3)C(CH_3)$), 33.3 (s, $(CH_3)C(CH_3)$), 31.2 (s, $(CH_3)C(CH_3)$), 28.6 (s, $(CH_3)C(CH_3)$), 28.1 (s, *CH*$(CH_3)_2$), 27.6 (s, *CH*$(CH_3)_2$), 26.0 (s, *i*Pr-CH_3), 25.9 (s, *i*Pr-CH_3), 25.5 (s, *i*Pr-CH_3), 25.0 (s, *i*Pr-CH_3), 20.9 (s, *para*-CH_3), 20.8 (s, *ortho*-CH_3), 18.8 (s, *ortho*-CH_3), 18.8 (s, *para*-CH_3), 18.7 (s, *ortho*-CH_3), 16.9 (s, *ortho*-CH_3). $^{11}B\{^1H\}$ NMR (160.46 MHz, C_6D_6): δ (ppm) = 46.9 (brs, $h_{1/2}$ = 1402 Hz, *B*H, *B*CH). elemental. anal. [%]: calcd. for $C_{41}H_{51}B_2N_4$ (621.51 g mol^{-1}) C: 79.87, H: 9.55, N: 6.99; found: C: 78.64, H: 9.39, N: 6.89.

Synthesis of ***3a****:* In a J. Young-type NMR tube, a mixture of **1** (38.9 mg, 123 μmol) and NHC^{Me} (11.8 mg, 123 μmol) was dissolved in 0.5 mL of C_6D_6 and heated to 80 °C for 16 hours. After removing all volatiles from the yellow mixture, **3a** was isolated as a yellow powder in 69% yield (35.1 mg, 85 μmol). ^1H NMR (500.13 MHz, C_6D_6): δ (ppm) = 6.86 (m, 0.5H, *meta-CH*), 6.80 (m, 1H, *meta-CH*), 6.77 (m, 1H, *meta-CH*), 6.75 (s, 1.5H, *meta-CH*), 5.38 (brs, 1H, B*H*), 5.27 (dd, 1H, CNC*H*, $^3J_{HH}$ = 6.02 Hz, $^4J_{HH}$ = 0.73 Hz), 5.23 (d, 1H, CBN_2CH, $^3J_{HH}$ = 7.00 Hz), 5.17 (d, 1H, (BH)NC*H*, $^3J_{HH}$ = 7.00 Hz), 4.50 (d, 1H, BNC*H*, $^3J_{HH}$ = 6.02 Hz), 2.81 (brs, B_2NC*H*), 2.79 (s, 3H, (CH)NCH_3), 2.38 (s, 3H, *ortho*-CH_3), 2.27 (s, 3H, *ortho*-CH_3), 2.24 (s, 3H, *ortho*-CH_3), 2.23 (s, 3H, *ortho*-CH_3), 2.14 (s, 3H, *para*-CH_3), 2.13 (s, 3H, *para*-CH_3), 2.08 (s, 3H, BNCH_3); $^{13}C\{^1H\}$ NMR (128.76 MHz, C_6D_6): δ (ppm) = 145.3 (s, *ipso*-C_q), 144.3 (s, *ipso*-C_q), 135.7 (s, C_q), 135.7 (s, C_q), 135.6 (s, C_q), 135.4 (s, C_q), 134.8 (s, C_q), 133.6 (s, C_q), 129.7 (s, *meta*-CH), 129.5 (s, *meta*-CH), 129.4 (s, *meta*-CH), 129.3 (s, *meta*-CH), 124.2 (s, (CBN)NCH), 121.9 (s, (CH)NCH), 116.7 (s, (BH)NCH), 108.2 (s, (NBC)NCH), 53.2 (brs, B_2NCH), 44.4 (s, (CH)NCH_3), 36.7 (s, (BNC)NCH_3), 21.0 (s, *para*-CH_3), 20.9 (s, *para*-CH_3), 19.4 (s, *ortho*-CH_3), 19.3 (s, *ortho*-CH_3), 18.8 (s, *ortho*-CH_3), 18.2 (s, *ortho*-CH_3); $^{11}B\{^1H\}$ NMR (160.46 MHz, C_6D_6): δ (ppm) = 43.9 (brs, $h_{1/2}$ = 817 Hz, *B*H), 28.4 (brs, $h_{1/2}$ = 545 Hz, *B*N); elemental anal. [%]: calcd. for $C_{25}H_{35}B_2N_4$ (413.2 g mol^{-1}) C: 72.67, H: 8.54, N: 13.56; found: C: 72.13, H: 8.54, N: 13.22.

*Synthesis of **3b**:* In a J. Young-type NMR tube, a mixture of **1** (38.9 mg, 120 μmol) and NHC^{Mes} (36.6 mg, 120 μmol) were dissolved in 0.5 mL of C_6D_6 and heated to 80 °C for 16 hours. After removing all volatiles in vacuo, **3b** was isolated as a yellow powder in 83% yield (62.0 mg, 99.6 μmol). ^{1}H NMR (500.13 MHz, C_6D_6): δ (ppm) = 6.86 (m, 1H, *meta-CH*), 6.83 (m, 1H, *meta-CH*), 6.75 (m, 1H, *meta-CH*), 6.68 (m, 1H, *meta-CH*), 6.61 (m, 1H, *meta-CH*), 6.60 (m, 1H, *meta-CH*), 6.40 (m, 1H, *meta-CH*), 6.35 (m, 1H, *meta-CH*), 5.43 (d, 1H, CH=CH, $^3J_{HH}$ = 6.06 Hz), 5.22 (brs, 1H, B*H*), 5.18 (d, 1H, CH=CH, $^3J_{HH}$ = 7.10 Hz), 5.11 (d, 1H, CH=C*H*, $^3J_{HH}$ = 7.10 Hz), 4.60 (d, 1H, CH=C*H*, $^3J_{HH}$ = 6.06 Hz), 3.63 (s, 1H, BC*H*), 2.62 (s, 3H, *ortho*-CH_3), 2.58 (s, 3H, *ortho*-CH_3), 2.54 (s, 3H, *ortho*-CH_3), 2.51 (s, 3H, *ortho*-CH_3), 2.33 (s, 3H, *ortho*-CH_3), 2.20 (s, 3H, *para*-CH_3), 2.09 (m, 6H, *para*-CH_3), 2.08 (s, 3H, *para*-CH_3), 1.92 (s, 3H, *ortho*-CH_3), 1.82 (s, 3H, *ortho*-CH_3), 1.78 (s, 3H, *ortho*-CH_3); ^{13}C{^{1}H} NMR (125.76 MHz, C_6D_6): δ (ppm) = 146.1 (s, *ipso*-C*q*), 144.8 (s, *ipso*-C*q*), 143.8 (s, *ipso*-C*q*), 142.6 (s, *ipso*-C*q*), 137.0 (s, *ortho*-C*q*), 136.6 (s, *ortho*-C*q*), 136.2 (s, *ortho*-C*q*), 135.7 (s, *ortho*-C*q*), 135.1(8) (s, *para*-C*q*), 135.1(7) (s, *para*-C*q*), 134.8 (s, *ortho*-C*q*), 134.7 (s, *ortho*-C*q*), 134.6 (s, *ortho*-C*q*), 134.5 (s, *para*-C*q*), 134.2(6) (s, *para*-C*q*), 134.2(5) (s, *ortho*-C*q*), 130.2 (s, *meta*-C*q*), 129.7 (s, *meta*-C*q*), 129.5 (s, *meta*-C*q*), 129.2(8) (s, *meta*-C*q*), 129.2(6) (s, *meta*-C*q*), 128.8 (s, *meta*-C*q*), 128.7 (s, 2C, *meta*-C*q*), 124.5 (s, CH=CH), 120.3 (s, C=CH), 116.5 (s, C=CH), 105.7 (s, CH=CH), 51.9 (brs, BCH), 21.0(2) (s, *ortho*-CH_3), 21.0 (s, *para*-CH_3), 20.9 (s, *para*-CH_3), 20.8(6) (s, *para*-CH_3), 20.8(5) (s, *para*-CH_3), 20.5 (s, *ortho*-CH_3), 19.9 (s, *ortho*-CH_3), 19.1 (s, *ortho*-CH_3), 18.5(3) (s, *ortho*-CH_3), 18.5(1) (s, *ortho*-CH_3), 18.1(4) (s, *ortho*-CH_3), 18.1 (s, *ortho*-CH_3); ^{11}B{^{1}H} NMR (160.46 MHz, C_6D_6): δ (ppm) = 44.3 (brs, $h_{1/2}$ = 1061 Hz, *B*H), 29.4 (brs, $h_{1/2}$ = 807 Hz, *B*N); elemental anal. [%]: calcd. for $C_{41}H_{51}B_2N_4$ (621.51 g mol^{-1}) C: 79.36, H: 8.12, N: 9.03; found: C: 78.55, H: 8.21, N: 8.83.

*Synthesis of **4a**:* Compound **4a** can be prepared by two different methods. *Method A:* In a J. Young-type NMR tube, a mixture of **1** (30.0 mg, 94.9 μmol) and NHC^{Me} (18.3 mg, 190 μmol, 2 equiv.) was dissolved in 0.5 mL of C_6D_6 and heated to 80 °C for 16 hours. After removing all volatiles in vacuo, **4a** was isolated as a yellow powder in 41% yield (20.1 mg, 39.5 μmol). *Method B:* In a J. Young-type NMR tube, a mixture of **1** (30.0 mg, 94.9 μmol) and NHC^{Me} (9.13 mg, 94.9 μmol) was dissolved in 0.5 mL of C_6D_6 and heated to 80 °C for 16 hours. After full conversion to **3a** was confirmed by ^{1}H and ^{11}B NMR spectroscopy, one additional equivalent of NHC^{Me} (9.13 mg, 94.9 μmol) was added to the yellow solution. After a few minutes, all volatiles were removed in vacuo and **4a** was obtained in about the same yield. The spectroscopic data for each method were found to be identical. ^{1}H NMR (500.13 MHz, C_6D_6): δ (ppm) = 7.01 (s, 1H, *meta-CH*), 6.86 (s, 1H, *meta-CH*), 6.82 (s, 1H, *meta-CH*), 6.79 (s, 1H, *meta-CH*), 5.90–5.78 (m, 2H, C(NMe)$_2$CH=C*H*), 5.40 (d, 1H, $^3J_{HH}$ = 8.35 Hz), 4.86 (d, 1H, $^3J_{HH}$ = 5.80 Hz), 4.46 (d, 1H, $^3J_{HH}$ = 8.35 Hz), 4.25 (d, 1H, $^3J_{HH}$ = 5.80 Hz), 4.07 (m, 3H, (CH_3)-NCBH), 3.56 (brs, 0.5H, B*H*), 3.30 (brs, 0.5H, B*H*), 3.02 (m, 3H, (C_3)-NCBH), 2.85 (s, 3H, CH_3), 2.80 (s, 3H, *ortho*-CH_3), 2.52 (s, 3H, *ortho*-CH_3), 2.48 (s, 3H, *ortho*-CH_3), 2.21 (s, 3H, *para*-CH_3), 2.19 (s, 3H, *para*-CH_3), 2.13 (s, 3H, *ortho*-CH_3), 2.04 (s, 3H, CH_3); ^{13}C{^{1}H} NMR (125.76 MHz, C_6D_6): δ (ppm) = 170.9 (brs, (BH)*C*(N$_2$)), 154.6 (s, *ipso*-C$_q$), 147.0 (s, *ipso*-C$_q$), 137.7 (s, *ortho*-C$_q$), 136.4 (s, *ortho*-C$_q$), 134.8 (s, *ortho*-C$_q$), 134.6 (s, *ortho*-C$_q$), 133.5 (s, *para*-C$_q$), 132.6 (s, *para*-C$_q$), 130.8 (s, *meta*-CH), 130.1 (s, *meta*-CH), 129.5 (s, *meta*-CH), 128.7 (s, *meta*-CH), 125.6 (s, (CH)(BH)NC*H*=CH), 121.3 (brs, (BH)CNC*H*=CH), 120.3 (s, (CH)B(NCH$_3$)CH=CH), 119.6 (brs, (BH)CNCH=CH), 107.8 (s, (CH)B(NCH$_3$)*CH*=CH), 106.8 (s, (CH)(BH)NCH=CH), 51.2 (brs, CH), 43.5 (s, (CH)NCH$_3$), 37.2 (s, (CH)BNCH$_3$), 20.9 (s, *para*-CH_3), 20.9 (s, *para*-CH_3), 20.2 (s, *ortho*-CH_3), 20.1 (s, *ortho*-CH_3), 19.4 (s, *ortho*-CH_3); ^{11}B{^{1}H} NMR (160.46 MHz, C_6D_6): δ (ppm) = 33.1 (brs, $h_{1/2}$ = 399 Hz, N$_2$*B*C), −8.78 (d, $^1J_{BH}$ = 78.6 Hz, $h_{1/2}$ = 129 Hz, *B*H); elemental anal. [%]: calcd. for $C_{30}H_{43}B_2N_6$ (508.33 g mol^{-1}) C: 70.89, H: 8.33, N: 16.53; found: C: 69.97, H: 8.12, N: 16.33.

*Synthesis of **4b**:* In a J. Young-type NMR tube a mixture of **1** (20.0 mg, 63.3 μmol) and NHC^{Mes} (19.3 mg, 63.3 μmol) was dissolved in 0.5 mL of C_6D_6 and heated to 80 °C for 16 hours. After the full conversion to **3b** was confirmed by ^{1}H and ^{11}B NMR spectroscopy, one equivalent of NHC^{Me} (6.08 mg, 63.3 μmol) was added to the yellow reaction solution. After several minutes, all volatiles were removed in vacuo and **4b** was isolated as a yellow powder in a yield of 75% (34.1 mg, 47.6 μmol). ^{1}H NMR (500.13 MHz, C_6D_6): δ (ppm) = 6.69 (m, 1H, *meta-CH*), 6.80 (m, 2H, *meta-CH*), 6.76 (m, 1H, *meta-CH*), 6.57 (m, 1H, *meta-CH*), 6.38 (m, 1H, *meta-CH*), 6.37 (m, 1H, *meta-CH*), 6.34 (m, 1H, *meta-CH*), 5.63 (d, 1H, (NBC)NC=C*H*, $^3J_{HH}$ = 6.65 Hz), 5.33 (d, 1H, (BH)C(NCH$_3$)C=C*H*, $^3J_{HH}$ = 1.59 Hz), 5.29 (d, 1H, (BH)C(NCH$_3$)C=C*H*, $^3J_{HH}$ = 1.59 Hz), 5.21 (dd, 1H, (CH)NC=C*H*, $^3J_{HH}$ = 5.81 Hz, $^4J_{HH}$ = 1.09 Hz), 4.81 (d, 1H, (NBC)NC=C*H*, $^3J_{HH}$ = 5.81 Hz), 4.51 (d, 1H, (BH)NC=C*H*, $^3J_{HH}$ = 6.65 Hz), 4.33 (m, 0.5-1H, B*H*), 4.03 (d, 1H, (CH)B*H*, $^3J_{HH}$ = 8.11 Hz), 3.17 (s, 3H, *ortho*-CH_3), 3.03 (s, 3H, *ortho*-CH_3), 2.95 (s, 3H, (BH)CNCH_3), 2.88 (s, 3H, *ortho*-CH_3), 2.76 (s, 3H, *ortho*-CH_3), 2.72 (s, 3H, (BH)CNCH_3), 2.30 (s, 3H, *ortho*-CH_3), 2.27 (s, 3H, *ortho*-CH_3), 2.18 (s, 3H, *para*-CH_3), 2.17 (s, 3H, *para*-CH_3), 2.16 (s, 3H, *para*-CH_3), 2.15 (s, 3H, *para*-CH_3), 1.61 (s, 3H, *ortho*-CH_3), 1.56 (s, 3H, *ortho*-CH_3); ^{13}C{^{1}H} NMR (125.76 MHz, C_6D_6): δ (ppm) = 166.8 (brs, B*C*(NCH$_3$)$_2$), 147.5 (s, (CBN)*N-ipso*-C$_q$), 146.8 (s, (CH)*N-ipso*-C$_q$), 144.8 (s, (BH)*N-ipso*-C$_q$), 144.1 (s, (NBC)*N-ipso*-C$_q$), 138.9 (s, *ortho*-C$_q$), 137.7 (s, *ortho*-C$_q$), 137.2 (s, *ortho*-C$_q$), 137.1 (s, *ortho*-C$_q$), 136.3 (s, *ortho*-C$_q$), 135.7 (s, *ortho*-C$_q$), 134.6 (s, *ortho*-C$_q$), 134.2 (s, *ortho*-C$_q$), 133.7 (s, *para*-C$_q$), 133.6 (s, *para*-C$_q$), 132.7 (s, *para*-C$_q$), 132.1 (s, *para*-C$_q$), 129.5 (s, *meta*-CH), 129.3 (s, *meta*-CH), 129.1 (s, *meta*-CH), 128.5 (s, *meta*-CH), 128.3 (s, *meta*-CH), 128.2 (s, *meta*-CH), 127.8 (s, *meta*-CH), 127.9 (s, *meta*-CH), 126.5 (s, (BCN)NC*H*=CH), 120.1 (s, C(NCH$_3$)$_2$*C*=C), 119.6 (s, C(NCH$_3$)$_2$*CH*=CH), 117.6 (s, (CH)NC*H*=CH), 112.1 (s, (BH)NC*H*=CH), 109.1 (s, (NBC)NC*H*=CH), 45.7 (brs, B$_2$NCH), 36.5 ((BH)CNCH$_3$), 35.2 ((BH)CNCH$_3$), 21.4 (s, *ortho*-CH_3), 21.1 (s, *para*-CH_3), 21.0 (s, *para*-CH_3), 20.9(6) (s, *para*-CH_3), 20.9(0) (s, *para*-CH_3), 20.6 (s, *ortho*-CH_3), 20.4 (s, *ortho*-CH_3), 20.3 (s, *ortho*-CH_3), 19.3 (s, *ortho*-CH_3), 18.9 (s, *ortho*-CH_3), 17.8 (s, *ortho*-CH_3), 17.2 (s, *ortho*-CH_3); ^{11}B{^{1}H} NMR (160.46 MHz, C_6D_6): δ (ppm) = 32.0 (brs, $h_{1/2}$ = 1076 Hz, N$_2$*B*C), −9.77 (brs, $h_{1/2}$ = 351 Hz, *B*H); elemental anal. [%]: calcd. for $C_{46}H_{58}B_2N_6$ (716.63 g mol^{-1}) C: 77.10, H: 8.16, N: 11.73; found: C: 75.78, H: 7.99, N: 11.33.

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Conflict of interest

The authors declare no conflict of interest.

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