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Intramolecular Hydride Transfer Reactions in (Formazanate)Boron Dihydride Complexes

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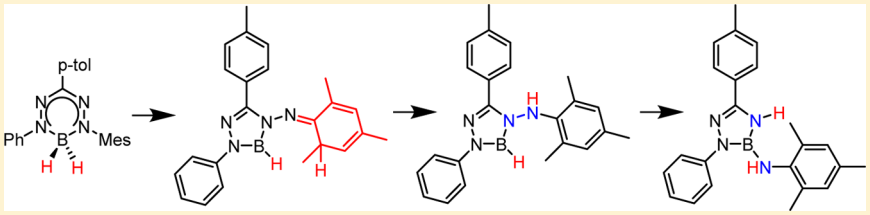
Supporting Information

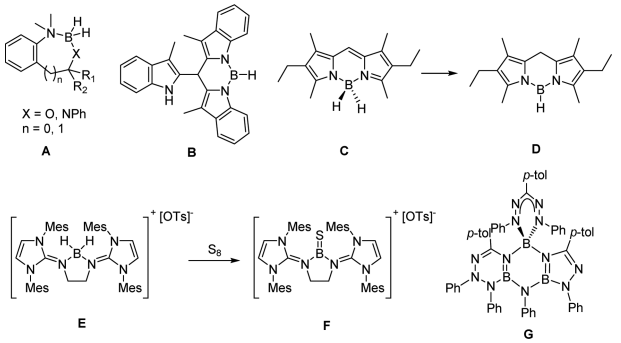


ABSTRACT: The solution-phase thermolysis of (formazanate)boron dihydrides (LBH_2; **2**) results in the formation of aminoborane compounds (**4**) via a series of boron-to-ligand intramolecular hydride transfer reactions. Monitoring the reactions by NMR spectroscopy allowed identification of several intermediates, and a reaction mechanism is proposed. In the case of a ligand with an N-Mes substituent it was possible to characterize an intermediate (**7b-i**) during this transformation that shows an unexpected cyclohexadiene moiety, which results from hydride transfer to the *ortho*-position of the mesityl substituent. Two consecutive boron-to-ligand hydride transfers eventually result in reductive N−N bond cleavage to give triazaboroles as the final product.

INTRODUCTION

Group 13 metal hydrides and their Lewis base adducts have been extensively studied due to their great application potential in the field of organic synthesis and material science. For example, $LiAlH_4$ and $NaBH_4$ are very common reducing agents, and the Lewis base stabilized LMH_3 complexes (M: B, Al, Ga, In; L: Lewis base) show chemo- and stereoselective reduction of unsaturated organic substrates.[1] In the field of material science, aluminum and gallium hydride complexes are used as precursors for metal thin films, nanocrystalline metal, and group 13−15 semiconductors.[2] In recent years, aluminum or boron hydride compounds such as $LiAlH_4$ and $H_3N{\cdot}BH_3$ are investigated as hydrogen storage materials.[3] When we surveyed the literature, we surprisingly noticed that the research of boron hydride compounds bearing bidentate ligands is very limited. Besides the well-known catecholborane (HBcat) and pinacolborane (HBpin), which are commonly used in hydroboration,[4] borylation of C−X bonds[5] and C−H bonds,[6] there are only a few examples that have been synthesized and fully characterized (Chart 1). In 2004, Hey-Hawkins and co-workers reported a series of intramolecularly base-stabilized borane compounds with six- and seven-membered chelate rings (**A**).[7] In 2012, several three-coordinate boron monohydride complexes ligated by the bis(3-methylindolyl)methanes (**B**) were reported by Mason and co-workers.[8] Piers and co-workers indicated the formation of an unstable dipyrrinato boron dihydride complex (**C**) by UV−vis absorption and emission spectroscopy.[9] Complex **C** is too reactive to be isolated, and it decomposes to a dipyrromethane-coordinated borane (**D**) via hydride transfer to the *meso*-position of the ligand. In 2014, a boron dihydride complex bearing a bis(imidazolin-2-imine) ligand (**E**), which can be converted to a thioxoboran salt (**F**), was reported by Inoue and co-workers.[10]

Chart 1



We have been interested in the chemistry of complexes with redox-active formazanate ligands,[11] including boron difluoride derivatives, which have found application as fluorescent dyes in the work of Gilroy and co-workers.[12] Recently, we reported the two-electron reduction chemistry of the boron formazanate compound [PhNNC(*p*-tolyl)NNPh]BF_2, which suggested (transient) formation of a reactive low-valent (formazanate) boron species that ultimately forms BN heterocyclic products (**G**).[13] The heavier group 13 element hydrides (MXH_n, M = Ga or In, X = Cl or Br) are known to give low-valent compounds via reductive dehydrogenation,[14] but to the best of our

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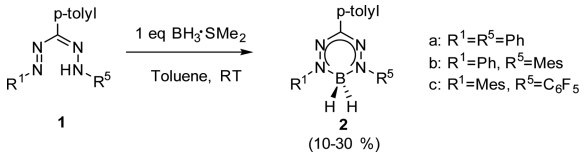
knowledge similar chemistry with B or Al compounds is unknown. We thus hypothesized that dehydrogenation of formazanate boron hydrides could provide an alternative entry into low-valent boron chemistry. Here we describe the synthesis and characterization of three (formazanate)boron hydride (LBH_2, **2**) compounds and evaluate their reactivity.

RESULTS

Monitoring the reaction between formazan **1a** and $BH_3{\cdot}SMe_2$ by ^1H NMR spectroscopy in C_6D_6 shows disappearance of the free ligand and formation of three new products in ca. 1:1:1 ratio (based on the ligand *p*-tolyl CH_3 resonances). On a preparative scale, the synthesis of (formazanate)boron dihydride complexes (**2**) was achieved by reacting free formazans (**1**) with $BH_3{\cdot}SMe_2$ at room temperature in toluene (Scheme 1). The desired formazanate boron dihydride

Scheme 1. Synthesis of Formazanate Boron Hydrides (2)



products were separated from the other (unknown) products by column chromatography to give the pure compounds in a yield of ca. 10−30%. The purity of the products was assessed by NMR spectroscopy and elemental analysis. Both **2a** and **2b** were obtained in pure form, but **2c** was always contaminated with a minor amount of free ligand **1c** (<5%). For **2a**, single crystals suitable for X-ray diffraction were obtained by recrystallization from hexane, and the X-ray analysis confirms the formulation of **2a** as a formazanate boron dihydride (molecular structure and selected bond lengths are shown in Figure 1). The solid-state structure of **2a** shows a four-

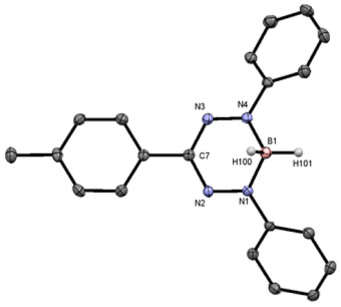


Figure 1. Molecular structure of **2a**. Thermal ellipsoids are shown at 50% probability, and hydrogen atoms are removed for clarity. Selected bond lengths (in Å): N1−N2,1.312(2); N3−N4,1.304(2); C7−N2,1.350(3); C7−N3,1.346(3); N1−B1,1.568(3); N4−B1,1.567(3); B1−H100,1.11(3); B1−H101,1.07(2).

coordinate boron center, which is bound to a formazanate ligand through two terminal N atoms to form a six-membered chelate ring. The C−N and N−N bonds are 1.350(3)/1.346(3) Å and 1.312(2)/1.304(2) Å, respectively, similar to the bond lengths of the reported bis(formazanate)zinc[11a,b] and (formazanate)boron difluoride complexes[12a] and indicative of a delocalized formazanate backbone. The ^1H NMR spectrum of **2a** is very similar to that of the difluoride analogue,[12a] but in addition shows a broad resonance at δ 3.67 ppm, which is assigned to the BH_2 fragment (Figure 2).

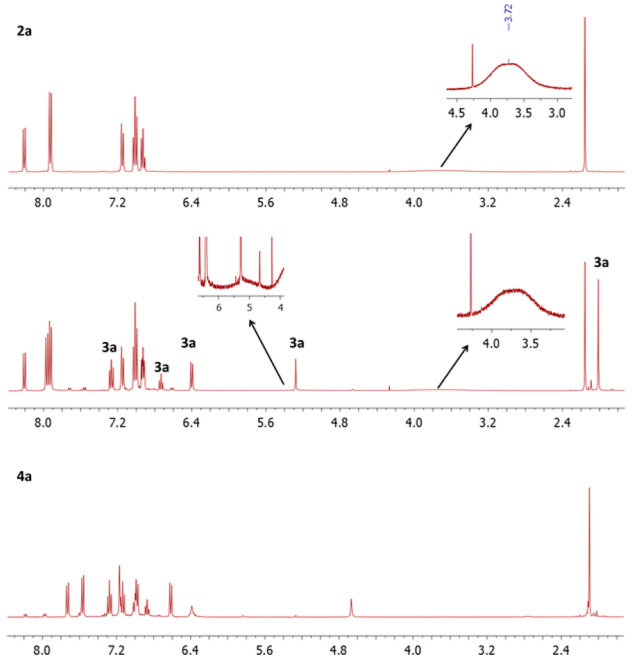
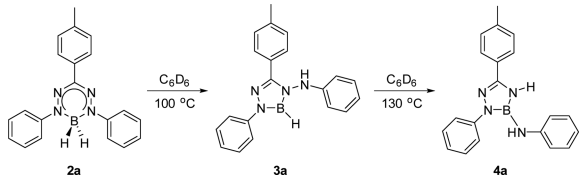


Figure 2. ^1H NMR spectra of the thermolysis reaction of **2a** at 100 °C (400 MHz in C_6D_6). Top: Starting material **2a**; middle: mixture of **2a** and **3a**; bottom: final product **4a**.

In order to test for the possibility of H_2 reductive elimination from a molecular boron complex, thermolysis of [PhNNC(*p*-tolyl)NNPh]BH_2 (**2a**) was monitored by ^1H NMR spectroscopy. After a solution of **2a** was heated in a J. Young NMR tube (C_6D_6, 100 °C, 4 h), the formation of hydrogen gas or B−N heterocyclic products such as those formed upon reduction of the LBF_2 analogues[13] was not observed. Nevertheless, the reaction proceeded cleanly to give two new products (**3a** and **4a**) resulting from hydride transfer, which were identified by NMR spectroscopy (Scheme 2 and Figure 2). It should be

Scheme 2. Synthesis of Compounds 3a and 4a by Thermolysis of 2a



noted that the analogous LBF_2 complexes are stable at this temperature. In the ^1H NMR spectrum of the thermolysis reaction of **2a** taken after 4 h at 100 °C (Figure 2, middle), a new group of resonances belonging to an intact formazanate fragment can be identified in addition to the starting material. The presence of a triplet resonance at δ 6.72 ppm, which integrates as 1H relative to the *p*-tolyl CH_3 group, indicates that the ligand NPh groups become inequivalent in the product **3a**. A new singlet resonance at δ 5.23 ppm (1H) does not correlate with a ^{13}C signal in the HSQC spectrum, which suggests this is due to a NH group in **3a**. In addition, a very broad resonance at around δ 5.08 ppm is observed.

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Measurement of the $^{1}H\{^{11}B\}$ spectrum results in sharpening of this signal (Figure S2), which indicates that this is a B−H functional group. On the basis of these spectroscopic features, we assign **3a** as the diamidoborane [PhNNC(*p*-tol)NNHPh]-BH (Scheme 2). Attempts to obtain **3a** as a pure compound were not successful due to the formation of a subsequent product **4a** (*vide infra*) that occurs simultaneously with conversion of **2a**. According to NMR monitoring, **3a** is always present as a mixture with either the starting material **2a** or the final thermolysis product **4a**, and isolation of pure **3a** from these reaction mixtures was not successful.

An alternative formulation of the initial hydride transfer product that is consistent with the observed NMR data is **3a′** (Figure 3), in which the hydride is transferred to the internal

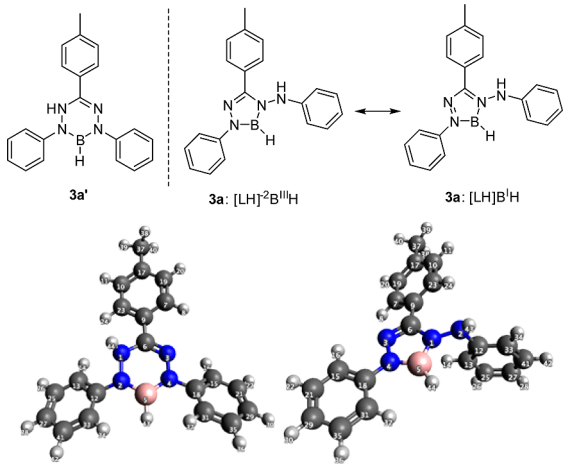


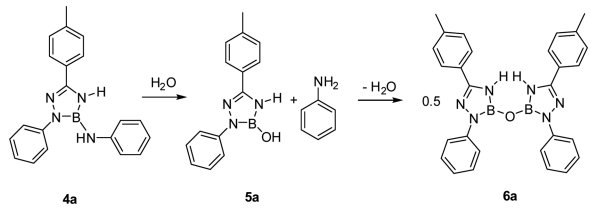
Figure 3. Top: Structure of possible isomers **3a′** and **3a**. Bottom: DFT-optimized structures of **3a′** (left; N1−N2, 1.431; N1−C6, 1.415; C6−N3, 1.285; N3−N4, 1.400) and **3a** (right; N1−N2, 1.401; N1−C6, 1.399; C6−N3, 1.308; N3−N4, 1.391).

nitrogen, resulting in a boron analogue of leuco-verdazyls, which are intermediates in the synthesis of verdazyl radicals and formazans.[15] To evaluate which of the two possibilities is most likely, geometry optimization of both five- (**3a**) and six-membered chelate (**3a′**) isomers was carried out using density functional theory (DFT) calculations at the B3LYP/6-31G(d) level in the gas phase (Figure 3). The calculations show that isomer **3a** is significantly more stable than the six-membered chelate ring **3a′** (ΔG = 11.9 kcal/mol). In the optimized structure of **3a**, the N3−C6 bond (1.308 Å) is shorter than the N1−C6 bond (1.399 Å); in addition, the N−N bond lengths (1.401 and 1.391 Å) are consistent with single bonds. This bond length distribution suggests that **3a** is best described as a boron(III) monohydride complex bearing a two-electron-reduced, dianionic ligand ($[LH]^{-2}B^{III}H$; Figure 3) instead of a boron(I) monohydride complex coordinated by a (neutral) formazan ligand ($[LH]B^{I}H$).

Keeping an NMR tube containing a mixture of **2a**/**3a** at 130 °C for several hours results in the disappearance of both these compounds and appearance of a new set of ^{1}H NMR resonances that belong to compound **4a** (Figure 2, bottom). The ^{1}H NMR spectrum of **4a** shows two broad singlets at δ 6.35 and 4.62 ppm, which do not show correlations in the HSQC spectrum and are therefore assigned to two inequivalent NH groups. No signal is found in the ^{1}H NMR spectrum that can be attributed to a BH resonance. On the basis of these NMR data, compound **4a** was assigned as the triamidoborane [PhNNC(*p*-tol)NH]B(NHPh), containing a triazaborole ring as the central unit (Scheme 2).

Although attempts to isolate **4a** as a pure compound were not successful, its identity was furthermore indirectly confirmed by hydrolysis of the reaction mixture. Hydrolysis of **4a** in the NMR tube resulted in the formation of a new compound (**5a**) and aniline (Scheme 3), as confirmed by comparison to an

Scheme 3. Hydrolysis of 4a Results in Formation of Borinic Acid 5a and Borinic Anhydride 6a

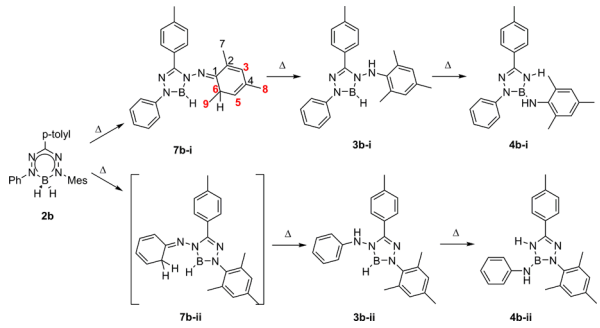


authentic sample. The ^{1}H NMR spectrum of **5a** shows a 1:1 ratio of *p*-tolyl and phenyl groups and contains an N−H resonance at δ 5.85 ppm. These observations indicate that **5a** is a borinic acid derivative,[16] which was further corroborated by the isolation of the crystalline borinic anhydride **6a** upon workup of the reaction mixture.[17] The molecular structure of **6a** is shown in Figure S7.

In order to get more insight into the observed hydride transfer reactivity, two additional formazanate boron dihydride complexes (**2b** and **2c**), with formazanate ligands that have different electronic and steric properties, were heated under similar conditions in an NMR tube. Due to the asymmetric nature of the ligands in these complexes, the formation of two isomers that result from hydride transfer to either the R^1 or R^5 side of the ligand is anticipated.

Monitoring the thermolysis of **2b** by ^{1}H NMR (C_6D_6, 100 °C) shows the expected formation of **3b** after ca. 5 h, which is obtained as two isomers (**3b-i** and **3b-ii**) in a 1:2 ratio (Scheme 4, Figure 4). In addition to **3b**, a new intermediate, **7b-i**, was

Scheme 4. Hydride Transfer Reactions of 2b



observed. The ^{1}H NMR spectrum of **7b-i** features several characteristic resonances: most diagnostic are those at δ 0.83 (q, 3H) and 3.89 (d, 1H) ppm that are mutually coupled with J = 7 Hz. Two additional resonances are observed in the olefinic region at δ 5.25 and 5.83 ppm and originate from the NMes ring. Careful analysis of 2D NMR spectra (Figure S3 for COSY spectrum) for the reaction mixture containing **7b-i** allowed assignment of all the NMR signals. Taken together, the data are consistent with the presence of a mesityl-derived 2,4,6-trimethylcyclohexadiene ring in **7b-i** (Scheme 4).

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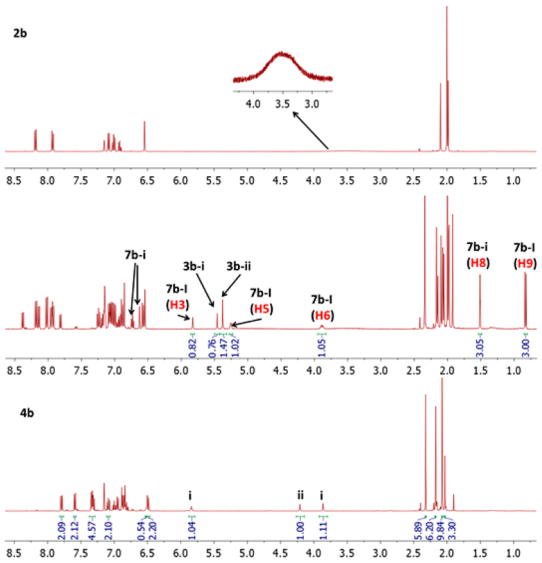


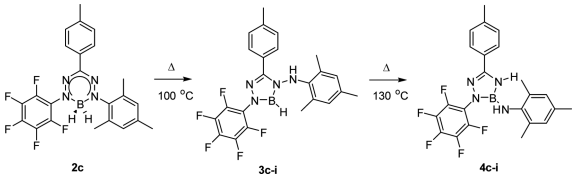
Figure 4. ^{1}H NMR spectra of thermolysis reaction of **2b** (400 MHz in C_6D_6); top: starting material **2b**; middle: mixture of **2b**, **3b-i**, **3b-ii**, and **7b-i**; the red labels correspond to the labeling in Scheme 4; bottom: mixture of **4b-i** and **4b-ii**.

We propose that **7b-i** is formed by hydride transfer from the BH_2 unit to the *ortho*-position of mesityl substituent, resulting in its dearomatization to a cyclohexadiene imine. A related dearomatization reaction was reported by Barclay and co-workers in 1973, who showed intermolecular hydride transfer from vitride ($NaAlH_2(OCH_2CH_2OCH_3)_2$) to 2,4,6-tri-*tert*-butylnitrobenzene to give 2,4,6-tri-*tert*-butyl-2,4-cyclohexadienone oxime at room temperature.[18] To the best of our knowledge, the intramolecular hydride shift from a boron hydride to an aromatic ring such as involved in the formation of **7b-i** is without precedent in the literature.

While compounds **2b** and **3b** remain unchanged at room temperature, **7b-i** is slowly converted to **3b-i** in the course of several days, corroborating that it is an intermediate in the conversion of **2b** to **3b-i**. The isomer **7b-ii**, presumed to be involved in the formation of **3b-ii**, is not observed. Further heating of the reaction mixture containing **2b**/**3b** at 130 °C for several hours shows similar reactivity to that observed for **2a**/**3a**: full conversion to **4b** occurs, which is formed as two isomers, **4b-i** and **4b-ii**. At the end of the thermolysis reaction of **2b**, the ratio of these isomers is approximately 1:1 (Figure 4, bottom).

We next evaluated the thermolysis of **2c**, which contains electronic and steric asymmetry in the formazanate ligand: again two isomers are expected to form. The formazanate ligand in **2c** has both an electron-withdrawing (C_6F_5) and a (sterically demanding) electron-donating substituent (Mes) at the ligand N atoms. Under similar reaction conditions (C_6D_6, 100 °C), the thermolysis of **2c** occurs much faster than that of **2a**/**b**. All starting material was consumed within 1 h, and only a single product was formed (**3c-i**), without any intermediates observable by NMR. Keeping the NMR tube at 130 °C for several hours leads to the formation of compound **4c-i** (Scheme 5). In the 2D NMR spectra of **4c-i**, correlations are observed between an NH resonance at δ 3.53 ppm and the signals of the Mes group, in agreement with the formulation of **4c-i** as the isomer shown in Scheme 5. The introduction of an electron-withdrawing group results in a change in reactivity (faster reaction) and selectivity (formation of a single isomer).

Scheme 5. Thermally Induced Intramolecular Hydride Transfer Reaction of 2c



A study of the kinetics for the transformation from **2a** to **3a** was carried out using two different concentrations (EXP 1: 3.5 mM; EXP 2: 17.2 mM), and the reactions were monitored by ^{1}H NMR spectroscopy in C_6D_6 solution at 100 °C. The disappearance of **2a** was followed to approximately 2 half-lives as shown in Figure 5 (top). The data show that the

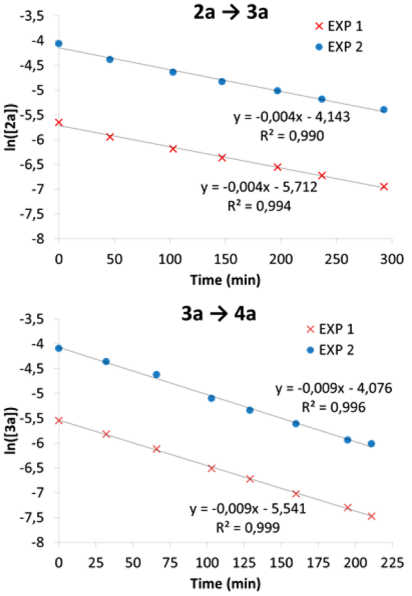


Figure 5. Kinetic study of transformations **2a** → **3a** (top, 100 °C) and **3a** → **4a** (bottom, 130 °C). Exp 1: [**2a**] = 3.5 mM; Exp 2: [**2a**] = 17.2 mM.

transformation from **2a** to **3a** follows first-order kinetics with a rate constant of 0.004 min^{-1} at 100 °C. Thus, formation of **3a** occurs by intramolecular hydride transfer. After following the reaction from **2a** to **3a** for 2 half-lives, the NMR tubes of both EXP 1 and EXP 2 were heated to 130 °C for 30 min to complete the transformation from **2a** to **3a**. The subsequent disappearance of **3a** to form **4a** was monitored at 130 °C for 2 half-lives, as shown in Figure 5 (bottom). These data suggest that also the transformation from **3a** to **4a** is a first-order reaction, with a rate constant of 0.009 min^{-1} at 130 °C. While cleavage of N−N bonds has been reported using a variety of metal-based reducing agents[19] as well as BH_3·THF,[20] the formation of N−N cleavage product **4** is remarkable because it occurs intramolecularly. On the basis of analogy with the N−N cleavage that is observed upon 2e-reduction of the boron difluoride analogue,[13] we speculate that a related reductive cleavage takes place in the conversion of **3** to **4**.

With the assumption that the observed hydride transfer reactions in **2a**−**c** occur through the same pathway for the three

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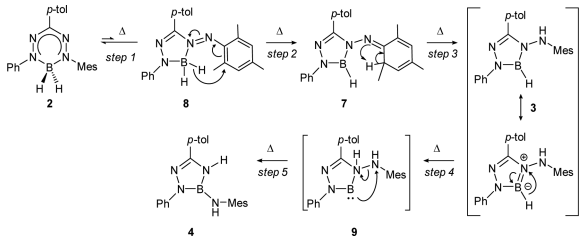
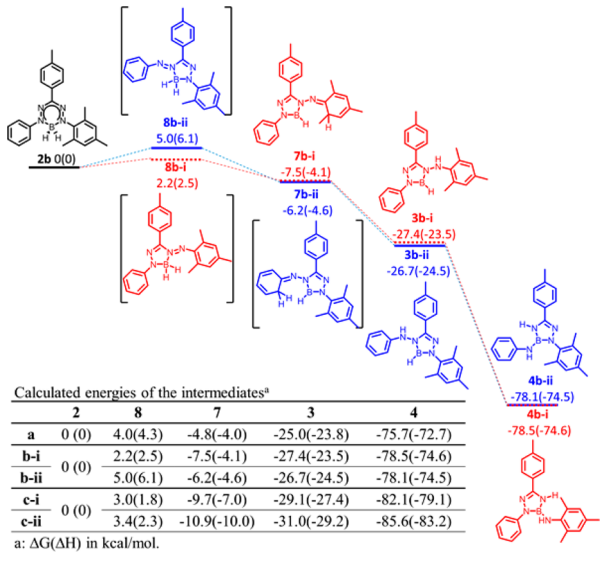
different ligands considered, a mechanism may be proposed that takes into account the identified intermediates and the kinetic data (shown for **2b** → **4b−i** in Scheme 6). A summary

Scheme 6. Proposed Mechanism for the Intramolecular Hydride Transfer Reaction of (Formazanate)boron Dihydride Complex (2b)



of the steps that are proposed to take place in the transformation from **2** to **4** is as follows: step 1 (**2** → **8**), reversible isomerization from a six-membered formazanate chelate to a five-membered chelate ring;[11b] step 2 (**8** → **7**), hydride transfer to the *ortho*-position of the aromatic ring, which results in dearomatization and the formation of a cyclohexadiene imine moiety; step 3 (**7** → **3**), hydrogen migration from the cyclohexadiene group to the terminal nitrogen atom, with rearomatization of the C_6 ring; step 4 (**3** → **9**), transfer of the remaining borohydride to the internal nitrogen atom to form a (formally) low-valent B species; and step 5 (**9** → **4**), reductive N−N bond cleavage forming the final triamidoborane product.[21]

Several of the proposed intermediates in Scheme 6 were subjected to DFT geometry optimization at the B3LYP/6-31G(d) level in the gas phase (Figure 6). The calculated energies of the intermediates reveal that the hydride transfer reaction of compound **2b** is energetically uphill for the first step (to form the five-membered chelate isomers **8b**) and downhill for all the following steps.



Calculated energies of the intermediates[a]

	2	8	7	3	4
a	0 (0)	4.0(4.3)	-4.8(-4.0)	-25.0(-23.8)	-75.7(-72.7)
b-i	0 (0)	2.2(2.5)	-7.5(-4.1)	-27.4(-23.5)	-78.5(-74.6)
b-ii		5.0(6.1)	-6.2(-4.6)	-26.7(-24.5)	-78.1(-74.5)
c-i	0 (0)	3.0(1.8)	-9.7(-7.0)	-29.1(-27.4)	-82.1(-79.1)
c-ii		3.4(2.3)	-10.9(-10.0)	-31.0(-29.2)	-85.6(-83.2)

a: ΔG(ΔH) in kcal/mol.

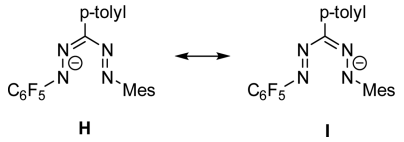
Figure 6. Energy diagram of the thermally induced intramolecular hydride transfer reaction of (formazanate)boron dihydride complex (**2b**) (red: isomer **i**; blue: isomer **ii**).

DISCUSSION

For the thermolysis of **2b**, the intermediates **7b-i** and **7b-ii** have similar calculated Gibbs free energies (−7.5 vs −6.2 kcal/mol relative to **2b**), which suggests that in principle both intermediates could be formed (provided that the reactions are under thermodynamic control). The reason for the experimental observation of only a single isomer (**7b-i**) might be due to a fast subsequent transformation (**7b** → **3b**) in the case of isomer **ii**. Similarly, the lack of an observable intermediate in the formation of **3a** is consistent with the notion that only the dearomatized product that is obtained from hydride transfer to a NMes group (present in **2b** but not in **2a**) is sufficiently kinetically stable to be observed experimentally. However, based on the experimental data the possibility of a direct B to N hydride transfer (bypassing **7**) cannot be completely ruled out.

In the case of **2c**, the calculated energies of the potential intermediates also suggest that formation of isomers **ii** is possible. The reason for the experimental observation of formation of only a single isomer (**3c-i** and **4c-i**) is likely related to the strong electron-withdrawing NC_6F_5 substituent, which localizes the negative charge of the formazanate ligand at that site, resulting in resonance structure **H** being the dominant contributor (Chart 2).[11b] Resonance structure **H** makes the

Chart 2. Resonance Structures of the Formazanate Ligand Present in 2c



isomerization from **H** to **8c-i** more facile than the isomerization from **I** to **8c-ii**. As a consequence, products arsing from hydride transfer to the NC_6F_5 side of the ligand (isomers **ii**) are not formed and thermolysis leads to only a single product (isomer **4c-i** in this case).

The thermally induced boron to ligand hydride transfer reaction of compounds **2** presented here is shown to take place in two steps. A first hydride transfer from the boron center to the ligand backbone forms the (LH)BH intermediate **3**. Subsequently, this is converted to the final product **4**, in which transfer of the remaining borohydride is accompanied by N−N bond cleavage to form a boron tri(amido) complex. For the initial hydride transfer, an intermediate can be intercepted in which a borohydride has reacted with the N−Ar ring to result in dearomatization, a reaction that has little precedent in the literature. Most of the reported examples of (homogeneous) hydride transfer to aromatic rings are based on mononuclear transition metal hydride complexes, such as Nb,[22] W,[23] Ta,[24] Zr,[25] Co,[26] and Fe.[27] In these examples, an anionic cyclohexadienyl moiety is formed upon hydride transfer, which is stabilized by coordination to the metal center. In 2014, examples of C−C bond cleavage and rearrangement of benzene and toluene by a trinuclear titanium hydride were reported by Hou and co-workers.[28] These reactions are promoted by highly reactive multinuclear metal-hydride clusters.[29] The only nontransition metal example we were able to find in the literature is based on an aluminum hydride complex, which was reported by Barclay and co-workers in 1973.[18] To the best of our knowledge, the

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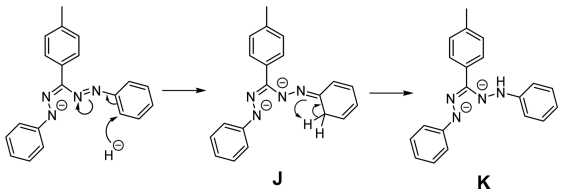
transformation from compound **2b** to **7b-i** is the first example of the dearomatization of an arene by using a molecular boron hydride species. A potential factor involved in the feasibility of this reaction is related to the (redox-active) formazanate ligand being able to function as an electron reservoir.[11,12] Hydride migration to the N−Ar *ortho*-position is accompanied by formation of a neutral cyclohexadiene imine moiety (**J** in Scheme 7), with the negative charge positioned on a ligand N

Scheme 7. Hydride Reduction of the Formazanate Ligand[a]

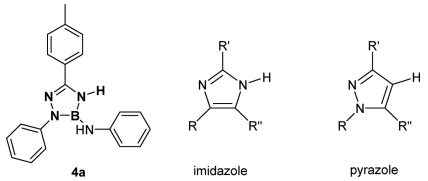


[a]The $[BH]^{+2}$ moiety was omitted for clarity.

atom that is bound to the B center. The cyclohexadiene imine **J** can subsequently tautomerize (rearomatize),[30] resulting in the formation of structure **K**. **K** is related to the monoanionic formazanate ligand (L^-) in the starting material via $2e/H^+$ transfer and is thus formally equivalent to a 2e-reduced formazan (LH^{2-}).

Finally, the formation of the products **4** is thermodynamically very favorable, with calculated changes in the Gibbs free energy relative to the starting materials **2** in excess of −75 kcal/mol. The experimental observation of the intermediates **3** in all cases suggests that the conversion of **3** to **4** has the highest barrier along the reaction coordinate, making the formation of **4** irreversible. Compounds **4** are the result of cleavage of a N−N bond in the ligand backbone to form a triazaborole (BN_3C) core, with an additional anilido substituent on the boron atom. There is considerable interest in the synthesis and properties of such compounds due to the isoelectronic and isosteric relationship between C═C and B−N bonds, which can greatly increase diversity in organic chemistry.[31] In particular, azaboroles possess unique electronic structures and reactivity[32] and are considered potential candidates for bioisosteric replacement of ubiquitous nitrogen heterocycles such as imidazoles and pyrazoles (Chart 3).[33] Although triazaboroles

Chart 3



were first prepared by Dewar in 1971,[34] the synthetic methodology to obtain triazaboroles is still in its infancy. The most common synthetic procedure for preparing triazaboroles is based on reactions of amidrazones and boronic acid derivatives (RBX_2; X = Cl, Br, OMe, OEt, OH, and NMe_2).[35] Therefore, the formation of triazaborole compounds **4** from (formazanate)boron dihydride (**2**) presents a novel route toward triazaboroles.

CONCLUSION

Three (formazanate)boron dihydride complexes LBH_2 (**2**) have been synthesized from the free formazans and $BH_3{\cdot}SMe_2$. Thermolysis of these compounds is shown to result in intramolecular hydride transfer from boron to the ligand backbone in two steps to give triamido boranes as the final products. NMR spectroscopic studies allowed the identification of several intermediates. The first hydride is transferred to the terminal N atom of the ligand (**3**), which in the case of **2b** was shown to involve initial hydride attack at the mesityl ring to give an unusual cyclohexadiene imine species (**7**). Prolonged thermolysis results in transfer of the remaining borohydride to the ligand and is accompanied by ligand N−N bond cleavage to give the final triamido boranes (**4**). These thermally induced boron-to-formazanate hydride transfer reactions show a new type of reactivity for formazanate ligands that is relevant when considering their application as redox-active ligands because they represent sequential two-electron reductions (each hydride corresponds to $2e/H^+$). The intermediates identified here expand our understanding of the reactivity of boron hydrides and provide a starting point for further investigations on the chemistry of complexes bearing redox-active formazanate ligands.

EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out under a nitrogen atmosphere using standard glovebox, Schlenk, and vacuum-line techniques. Toluene, hexane, and pentane (Aldrich, anhydrous, 99.8%) were passed over columns of Al_2O_3 (Fluka), BASF R3-11-supported Cu oxygen scavenger, and molecular sieves (Aldrich, 4 Å). Deuterated solvent (C_6D_6) was vacuum transferred from Na/K alloy and stored under nitrogen. $BH_3(SMe_2)$ was purchased from Aldrich and used as received. Formazan ligands (**1a−c**) were prepared by following reported procedures.[11b] NMR spectra were recorded on Varian Mercury 400, Inova 500, or Agilent 400 MR spectrometers. The ^1H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances and reported in ppm relative to TMS (0 ppm); *J* is reported in Hz. Assignment of NMR resonances was aided by gradient-selected gCOSY, NOESY, gHSQCAD, and/or gHMBCAD experiments using standard pulse sequences. ^{11}B NMR spectra were recorded in quartz (or normal glass) NMR tubes using a OneNMR probe on an Agilent 400 MR system. Elemental analyses were performed at the Microanalytical Departement of the University of Groningen.

Kinetic Studies. *EXP 1.* An NMR young tube was charged with [PhNNC(*p*-tolyl)NNPh]BH_2 (**2a**, 4.4 mg), hexane (1.6 μL), and C_6D_6 (0.45 mL).

EXP 2. An NMR young tube was charged with [PhNNC(*p*-tolyl)NNPh]BH_2 (**2a**, 20.3 mg), hexane (8.0 μL), and C_6D_6 (0.45 mL).

In order to follow the transformation from **2a** to **3a**, the tubes of both EXP1 and EXP 2 were heated at 100 °C and monitored by NMR spectroscopy at regular time intervals. The concentration of **2a** in each ^1H NMR spectrum was determined by the integrations of the resonance located at 8.18 ppm (2H of **2a**) and 0.87 ppm (6H of hexane).

After following the transformation from **2a** to **3a** for 2 half-lives, the NMR tubes were heated at 130 °C for 30 min to convert all of the **2a** to **3a**. Subsequently, the transformation from **3a** to **4a** was monitored at 130 °C by NMR spectroscopy every 15 to 40 min. The concentration of **3a** in each ^1H NMR spectrum was determined by the integrations of the resonance located at 7.95 ppm (2H of **3a**) relative to that at 0.87 ppm (6H of hexane).

DFT Calculations. Calculations were performed with the Gaussian09 program using density functional theory. Geometries were fully optimized starting from the X-ray structures using the

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B3LYP exchange−correlation functional with the 6-31G(d) basis set. Geometry optimizations were performed without (symmetry) constraints, and the resulting structures were confirmed to be minima on the potential energy surface by frequency calculations (number of imaginary frequencies = 0).

X-ray Crystallography. Suitable crystals of **2a** and **6a** were mounted on a cryo-loop in a drybox and transferred, using inert-atmosphere handling techniques, into the cold nitrogen stream of a Bruker D8 Venture diffractometer. The final unit cell was obtained from the *xyz* centroids of 9915 (**2a**) and 9974 (**6a**) reflections after integration. Intensity data were corrected for Lorentz and polarization effects, scale variation, and decay and absorption: a multiscan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (SADABS).[36] The structures were solved by direct methods using the program SHLXS.[37] The hydrogen atoms were generated by geometrical considerations and constrained to idealized geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. Structure refinement was performed with the program package SHELXL.[36] Crystal data and details on data collection and refinement are presented in Table S1.

Synthesis of (Formazanate)boron Dihydride Complexes. *[PhNNC(p-tol)NNPh]BH$_2$, **2a**.* A Schlenk flask was charged with [PhNNC(*p*-tolyl)NNHPh] (**1a**) (601.2 mg, 1.91 mmol), $BH_3(SMe_2)$ (0.18 mL, 1.90 mmol), and dry toluene. The reaction mixture was stirred overnight at RT, and then all volatiles were removed under vacuum. The product was purified by chromatography (DCM/hexane = 1/2, silica gel, R_f = 0.71), after which 178.2 mg (0.46 mmol, 28.6%) of **2a** was obtained. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): 8.16 (d, 2H, *J* = 8.2, *p*-tolyl CH), 7.88 (d, 4H, *J* = 8.1, Ph *o*-CH), 7.10 (d, 2H, *p*-tolyl CH, overlapped with C_6D_6), 6.97 (t, 4H, *J* = 8.3, Ph *m*-CH), 6.88 (tt, 2H, *J* = 7.3, 1.8 Hz, Ph *p*-CH), 3.67 (bs, 2H, BH_2), 2.11 (s, 3H, *p*-tolyl CH_3). ^{11}B NMR (128.3 MHz, C_6D_6, 25 °C): −10.8. ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C): 153.3 (NCN), 145.9 (Ph *i*-C), 138.7 (*p*-tolyl *p*-C), 131.7 (*p*-tolyl *i*-C), 129.3 (*p*-tolyl CH), 128.9 (Ph *m*-CH), 128.2 (Ph *p*-CH), 125.4 (*p*-tolyl CH), 122.4 (Ph *o*-CH), 20.9 (*p*-tolyl CH_3). Anal. Calcd for $C_{20}H_{19}BN_4$: C, 73.64; H, 5.87; N, 17.18. Found: C, 73.16; H, 5.89; N, 16.88.

*[PhNNC(p-tol)NNMes]BH$_2$, **2b**.* The procedure is similar to that of **2a**. [PhNNC(*p*-tolyl)NNHMes] (**1b**) (302.0 mg, 0.85 mmol) and $BH_3(SMe_2)$ (0.08 mL, 0.85 mmol) were used as starting materials. The product was purified by chromatography (DCM/hexane = 1/2, silica gel, R_f = 0.68), after which 64.8 mg (0.18 mmol, 20.7%) of **2b** was obtained. ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): 8.18 (d, *J* = 8.5 Hz, 2H, *p*-tolyl CH), 7.92 (d, *J* = 8.8 Hz, 2H, Ph *o*-CH), 7.08 (d, *J* = 8.0 Hz, 2H, *p*-tolyl CH), 7.01 (t, *J* = 8.1 Hz, 2H, Ph *m*-CH), 6.91 (tt, *J* = 7.4, 1.7 Hz, 1H, Ph *p*-CH), 6.54 (s, 2H, Mes *m*-CH), 3.53 (bs, 2H, BH_2), 2.10 (s, 3H, *p*-tolyl CH_3), 2.00 (s, 6H, Mes *o*-CH_3), 1.98 (s, 3H, Mes *p*-CH_3). ^{13}C NMR (C_6D_6, 125 MHz, 25 °C): 153.1(NCN), 145.8 (Ph *i*-C), 144.0 (Mes *i*-C), 138.6 (*p*-tolyl *i*-C), 137.9 (Mes *p*-C), 134.2 (Mes *o*-C), 131.6 (*p*-tolyl *p*-C), 129.3 (*p*-tolyl CH), 129.1 (Ph *m*-CH), 129.0 (Mes *m*-CH), 128. (Ph *p*-CH), 125.3 (*p*-tolyl CH), 122.5 (Ph *o*-CH), 20.9 (*p*-tolyl CH_3), 20.5 (Mes *p*-CH_3), 17.9 (Mes *o*-CH_3). ^{11}B NMR (C_6D_6, 128 MHz, 25 °C): −8.42 (295 Hz). Anal. Calcd for $C_{23}H_{25}BN_4$: C, 75.01; H, 6.84; N, 15.21. Found: C, 75.24; H, 6.92; N, 15.06.

*[MesNNC(p-tol)NNC$_6$F$_5$]BH$_2$, **2c**.* The procedure is similar to that of **2a**. [MesNNC(*p*-tolyl)NNHC$_6$F$_5$] (**1c**) (324.5 mg, 0.73 mmol) and $BH_3(SMe_2)$ (0.07 mL, 0.74 mmol) were used as starting materials. The product was purified by chromatography (DCM/hexane = 1/2, silica gel, R_f = 0.74), after which 40.9 mg (0.09 mmol, 12.3%) of **2c** was obtained. The isolated product cointains 5% of the free ligand **1c**. ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): 8.10 (d, *J* = 8.0 Hz, 2H, *p*-tolyl *o*-CH), 7.05 (d, *J* = 8.0 Hz, 2H, *p*-tolyl *o*-CH), 6.60 (s, 2H, Mes *m*-CH), 3.31 (bs, 2H, BH_2), 2.16 (s, 6H, Mes *o*-CH_3), 2.08 (s, 3H, *p*-tolyl CH_3), 1.97 (s, 3H, Mes *p*-CH_3). ^{13}C NMR (C_6D_6, 125 MHz, 25 °C): 153.8 (NCN), 143.6 (Mes *i*-C), 143.3 (dm, *J* = 251.4 Hz, C_6F_5 CF), 140.2 (dm, *J* = 251.5 Hz, C_6F_5 CF), 139.4 (*p*-tolyl *i*-C), 139.2 (Mes *p*-C), 137.5 (dm, *J* = 254.3 Hz, C_6F_5 CF), 134.2 (Mes *o*-C), 130.6 (*p*-tolyl *p*-C), 129.5 (Mes *m*-CH), 129.5 (*p*-tolyl CH), 125.3 (*p*-tolyl CH), 122.2 (td, *J* = 12.0, 4.5 Hz, C_6F_5 *i*-C), 20.9 (*p*-tolyl CH_3), 20.5 (Mes *p*-CH_3), 18.0 (Mes *o*-CH_3). ^{19}F NMR (C_6D_6, 375 MHz, 25 °C): −148.3 (d, *J* = 19.7 Hz, 2F, C_6F_5 *o*-CF), −155.5 (t, *J* = 22.1 Hz, 1F, C_6F_5 *p*-CF), −162.3 (td, *J* = 22.4, 5.4 Hz, 2F, C_6F_5 *m*-CF). ^{11}B NMR (C_6D_6, 128 MHz, 25 °C): −7.11 (442 Hz).

NMR Data of Thermolysis Products and Intermediates. *[PhNNC(p-tolyl)NNHPh]BH, **3a**.* ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): 7.96−7.94 (m, 4H, *p*-tolyl CH, Ph *o*-CH), 7.25 (t, *J* = 8.0 Hz, 2H, Ph *m*-CH), 7.02−6.97 (m, 3H, Ph *m*-CH, Ph *p*-CH, overlapped with Ph *m*-CH of **2a**), 6.94−6.89 (m, 2H, *p*-tolyl CH, overlapped with Ph *p*-CH of 10a), 6.72 (t, *J* = 7.4 Hz, 1H, Ph *p*-CH), 6.39 (d, *J* = 7.9 Hz, 2H, Ph *o*-CH), 5.26 (s, 1H, NH), 5.08 (bs, 1H, BH), 2.00 (s, 3H, *p*-tolyl CH_3). ^{13}C NMR (C_6D_6, 125 MHz, 25 °C): 151.7 (NCN), 148.4 (Ph *i*-C), 143.5 (Ph *i*-C), 139.0 (*p*-tolyl *i*-C), 129.3 (Ph *m*-C), 129.2 (Ph *m*-C), 128.9 (*p*-tolyl CH), 128.4 (*p*-tolyl CH), 128.0 (*p*-tolyl *p*-C), 124.0 (Ph *p*-C), 120.7 (Ph *p*-C), 117.7 (Ph *o*-C), 112.8 (Ph *o*-C), 20.9 (*p*-tolyl CH_3). ^{11}B NMR (C_6D_6, 128 MHz, 25 °C): 23.82.

*[PhNNC(p-tolyl)NH]BNHPh, **4a**.* ^{1}H NMR (C_6D_6, 400 MHz, 25 °C): 7.68 (d, *J* = 8.0 Hz, 2H, Ph *o*-CH), 7.52 (d, *J* = 8.0 Hz, 2H, *p*-tolyl CH), 7.23 (t, *J* = 8.1 Hz, 2H, Ph *m*-CH), 7.08 (t, *J* = 7.6 Hz, 2H, Ph *m*-CH), 6.95 (t, *J* = 7.6 Hz, 1H, Ph *p*-CH), 6.93 (d, *J* = 8.0 Hz, 2H, *p*-tolyl CH), 6.82 (t, *J* = 7.6 Hz, 1H, Ph *p*-CH), 6.57 (d, *J* = 7.6 Hz, 2H, Ph *o*-CH), 6.34 (bs, NH), 4.62 (bs, NH), 2.05 (s, 3H, *p*-tolyl CH_3). ^{13}C NMR (C_6D_6, 100 MHz, 25 °C): 147.0 (*p*-tolyl *i*-C), 144.4 (Ph *i*-C), 144.3 (Ph *i*-C), 138.5 (*p*-tolyl *p*-C), 129.4 (Ph *m*-C), 129.2 (Ph *m*-C), 129.2 (*p*-tolyl CH), 125.0 (*p*-tolyl CH), 123.0 (Ph *p*-C), 120.7 (Ph *p*-C), 119.5 (Ph *o*-C), 118.3 (Ph *p*-C), 112.8 (NCN), 20.9 (*p*-tolyl CH_3). ^{11}B NMR (C_6D_6, 128 MHz, 25 °C): 23.06.

*[PhNNC(p-tolyl)NH]BOH (**5a**) + Aniline.* ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): 8.15 (dd, *J* = 8.6, 1.0 Hz, 2H, Ph *o*-CH), 7.58 (d, *J* = 8.3 Hz, 2H, *p*-tolyl CH), 7.30 (dd, *J* = 8.5, 7.0 Hz, 2H, Ph *m*-CH), 6.99 (d, *J* = 8.5 Hz, 2H, *p*-tolyl CH), 6.98 (tt, *J* = 7.5, 1.0 Hz, 1H, Ph *p*-CH), 2.09 (s, 3H, *p*-tolyl CH_3); aniline: 7.06 (dd, *J* = 8.5, 7.5 Hz, 2H, Ph *m*-CH), 6.71 (tt, *J* = 7.4, 0.9 Hz, 1H, Ph *p*-CH), 6.34 (dd, *J* = 8.4, 1.0 Hz, 2H, Ph *o*-CH), 2.75 (bs, 2H, NH_2).

*[PhNNC(p-tolyl)NNHMes]BH, **3b-i**.* ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): 8.22 (d, *J* = 8.4 Hz, 2H, *p*-tolyl CH), 8.37 (dm, *J* = 8.2 Hz, 2H, Ph *o*-CH), 7.17 (dd, *J* = 8.6, 7.4 Hz, 2H, Ph *m*-CH), 7.15 (2H, *p*-tolyl CH, overlapped with C_6D_6), 6.21 (tt, *J* = 6.2, 1.1 Hz, 2H, Ph *p*-CH), 6.62 (s, 2H, Mes *m*-CH), 5.46 (s, 1H, NH), 2.14 (s, 3H, *p*-tolyl CH_3), 2.05 (s, 3H, Mes *p*-CH_3), 1.92 (s, 6H, Mes *o*-CH_3). ^{13}C NMR (C_6D_6, 125 MHz, 25 °C): 129.9 (Mes *m*-CH), 128.9 (*p*-tolyl CH), 123.8 (Ph *p*-CH), 117.6 (Ph *o*-CH), 21.0 (*p*-tolyl CH_3), 20.9 (Mes *p*-CH_3), 17.9 (Mes *o*-CH_3).

*[MesNNC(p-tolyl)NNHPh]BH, **3b-ii**.* ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): 8.01 (d, *J* = 8.2 Hz, 2H, *p*-tolyl CH), 7.05 (d, *J* = 7.3 Hz, 2H, *p*-tolyl CH), 7.04 (m, 2H, Ph *m*-CH), 6.85 (s, 2H, Mes *m*-CH), 6.73 (tt, *J* = 7.4, 1.1 Hz, 1H, Ph *p*-CH), 6.57 (dd, *J* = 7.7, 0.9 Hz, 2H, Ph *o*-CH), 5.38 (s, 1H, NH), 2.34 (s, 6H, Mes *o*-CH_3), 2.16 (s, 3H, Mes *p*-CH_3), 1.97 (s, 3H, *p*-tolyl CH_3). ^{13}C NMR (C_6D_6, 125 MHz, 25 °C): 129.0 (*p*-tolyl CH), 129.0 (Mes *m*-CH), 128.2 (*p*-tolyl CH), 120.6 (Ph *p*-CH), 112.7 (Ph *o*-CH), 20.8 (*p*-tolyl CH_3), 20.7 (Mes *p*-CH_3), 18.3 (Mes *o*-CH_3).

*[PhNNC(p-tolyl)NH]BNHMes, **4b-i**.* ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): 7.79 (dm, *J* = 8.8 Hz, 2H, Ph *o*-CH), 7.33 (d, *J* = 8.2 Hz, 2H, *p*-tolyl CH), 7.31 (dd, *J* = 8.4, 7.4 Hz, 2H, Ph *m*-CH), 6.99 (tt, *J* = 7.3, 1.1 Hz, 1H, Ph *p*-CH), 6.89 (d, *J* = 8.0 Hz, 2H, *p*-tolyl CH), 6.83 (s, 2H, Mes *m*-CH), 5.84 (s, 1H, NH), 3.86 (s, 1H, NH), 2.16 (s, 3H, Mes *p*-CH_3), 2.07 (s, 6H, Mes *o*-CH_3), 2.03 (s, 3H, *p*-tolyl CH_3). ^{13}C NMR (C_6D_6, 125 MHz, 25 °C): 147.1 (NCN), 145.1 (Ph *i*-C), 138.2 (*p*-tolyl *p*-C), 133.8 (Mes *o*-C),129.2 (Ph *m*-CH), 124.9 (*p*-tolyl CH), 122.4 (Ph *p*-CH), 118.6 (Ph *o*-CH), 20.8 (*p*-tolyl CH_3), 18.5 (Mes *o*-CH).

*[MesNNC(p-tolyl)NH]BNHPh, **4b-ii**.* ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): 7.58 (dm, *J* = 8.2 Hz, 2H, *p*-tolyl CH), 7.08 (dd, *J* = 7.8, 7.4 Hz, 1H, Ph *m*-CH), 6.94 (d, *J* = 8.1 Hz, 2H, *p*-tolyl CH), 6.88 (s, 2H, Mes *m*-CH), 6.81 (tt, *J* = 7.4, 1.0 Hz, 1H, Ph *p*-CH), 6.51 (s, 1H, NH), 6.48 (dd, *J* = 7.5, 1.1 Hz, 2H, Ph *o*-CH), 4.21 (s, 1H, NH), 2.32 (s, 6H, Mes *o*-CH_3), 2.16 (s, 3H, Mes *p*-CH_3), 2.07 (s, 3H, *p*-tolyl CH_3). ^{13}C

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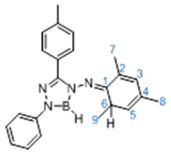
NMR (C_6D_6, 125 MHz, 25 °C): 146.7 (NCN), 144.5(Ph *i*-C), 138.0 (*p*-tolyl *i*-C), 137.7 (Mes *o*-C), 133.8 (*p*-tolyl *p*-C), 124.8 (*p*-tolyl CH), 120.0 (Ph *p*-CH), 117.5 (Ph *o*-CH), 20.7 (*p*-tolyl CH_3), 18.1 (Mes *o*-CH).

7b-i. ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): 8.13 (d, *J* = 8.2 Hz, 2H, *p*-tolyl CH), 7.95 (dm, *J* = 8.7 Hz, 2H, Ph *o*-CH), 7.24 (dd, *J* = 8.6, 7.4 Hz, 2H, Ph *m*-CH), 7.03 (d, *J* = 8.6 Hz, 2H, *p*-tolyl CH), 6.98 (m, 1H, Ph *p*-CH), 5.83 (quintet, *J* = 1.5 Hz, 1H, H3), 5.26 (d, *J* = 5.4 Hz, 1H, H5), 3.89 (quintet, *J* = 6.6 Hz, 1H, H6), 2.07 (bs, 6H, *p*-tolyl CH_3 + H7), 1.51 (t, *J* = 1.4 Hz, 3H, H8), 0.83 (d, *J* = 7.2 Hz, 3H, H9). ^{13}C NMR (C_6D_6, 125 MHz, 25 °C): 171.7 (C1), 117.9 (Ph *o*-CH), 32.94 (C6), 134.2 (C3), 129.0 (C5), 20.6(C8), 20.3 (*p*-tolyl), 17.9 (C7), 17.1 (C9).



[C_6F_5NNC(p-tolyl)NNHMes]BH, ***3c-i.*** ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): 8.28 (d, *J* = 8.4 Hz, 2H, *p*-tolyl *o*-CH), 7.10 (d, *J* = 8.0 Hz, 2H, *p*-tolyl *o*-CH), 6.63 (s, 2H, Mes *m*-CH), 5.51 (s, 1H, NH), 4.65 (bs, 1H, BH), 2.12 (s, 3H, *p*-tolyl CH_3), 2.05 (s, 3H, Mes *p*-CH_3), 1.95 (s, 6H, Mes *o*-CH_3). ^{13}C NMR (C_6D_6, 125 MHz, 25 °C): 152.4 (NCN), 142.6 (dm, *J* = 250.2 Hz, C_6F_5 CF), 141.9 (Mes *o*-C), 139.4 (*p*-tolyl *p*-C), 139.2 (dm, *J* = 252.3 Hz, C_6F_5 CF), 137.6 (dm, *J* = 252.0 Hz, C_6F_5 CF), 133.4 (Mes *p*-C), 129.9 (Mes *m*-C), 129.0 (*p*-tolyl CH), 128.9 (Mes *i*-C), 128.8 (*p*-tolyl CH), 126.4 (*p*-tolyl *i*-C), 119.3 (td, *J* = 12.5, 4.5 Hz, C_6F_5 *i*-C), 20.9 (*p*-tolyl CH_3), 20.3 (Mes *p*-CH_3), 17.8 (Mes *o*-CH_3). ^{19}F NMR (C_6D_6, 375 MHz, 25 °C): −149.7 (dm, *J* = 23.7 Hz, 2F, C_6F_5 *o*-CF), −159.0 (t, *J* = 22.0 Hz, 1F, C_6F_5 *p*-CF), −163.5 (tdm, *J* = 22.2, 5.5 Hz, 2F, C_6F_5 *m*-CF). ^{11}B NMR (C_6D_6, 128 MHz, 25 °C): 23.4 (546 Hz).

[C_6F_5NNC(p-tolyl)NH]BNHMes, ***4c-i.*** ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): 7.33 (d, *J* = 8.2 Hz, 2H, *p*-tolyl *o*-CH), 6.86 (d, *J* = 7.9 Hz, 2H, *p*-tolyl *o*-CH), 6.77 (s, 2H, Mes *m*-CH), 5.77 (s, 1H, NH), 3.54 (s, 1H, NH), 2.19 (s, 6H, Mes *o*-CH_3), 2.14 (s, 6H, Mes *p*-CH_3), 2.03 (s, 3H, *p*-tolyl CH_3). ^{13}C NMR (C_6D_6, 125 MHz, 25 °C): 149.2 (NCN), 143.1 (dm, *J* = 251.8 Hz, C_6F_5 CF), 138.9 (*p*-tolyl *p*-C), 136.4 (Mes *o*-C), 134.2 (Mes *i*-C), 129.1 (*p*-tolyl CH), 128.9 (Mes *m*-C), 128.9 (Mes *p*-C), 126.9 (*p*-tolyl *i*-C), 125.0 (*p*-tolyl CH), 119.0 (m, C_6F_5 *i*-C), 20.8 (*p*-tolyl CH_3), 20.4 (Mes *p*-CH_3), 18.3 (Mes *o*-CH_3). ^{19}F NMR (C_6D_6, 375 MHz, 25 °C): −147.7 (dd, *J* = 22.9, 5.7 Hz, 2F, C_6F_5 *o*-CF), −160.4 (t, *J* = 22.1 Hz, 1F, C_6F_5 *p*-CF), −163.9 (td, *J* = 22.5, 5.5 Hz, 2F, C_6F_5 *m*-CF). ^{11}B NMR (C_6D_6, 128 MHz, 25 °C): 22.9 (422 Hz).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00968.

Crystallograhpic data for **2a** and **6a** (CIF)

Coordinates of DFT-optimized structures (XYZ)

NMR spectra and additional experimental data (PDF)

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Notes

The authors declare no competing financial interest.

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