Formazanate as redox-active, structurally versatile ligand platform
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Chapter 7

Intramolecular Hydride Transfer Reactions in (Formazanate)Boron Dihydride Complexes

The thermolysis reaction of (formazanate)boron dihydrides (LBH$_2$; 10) results in the formation of aminoborane compounds (18) via a series of intramolecular hydride transfer reactions. Based on the NMR analysis, several intermediates of the hydride transfer reaction were identified, and a mechanism of the reaction was proposed. The key steps of the proposed mechanism include the isomerization from the six-membered chelate ring to the five-membered chelate ring followed by hydride transfer to the formazanate ligand and N-N bond cleavage. Importantly, in case of a ligand with an N-Mes substituent it was possible to characterize an intermediate (21c-i) in this transformation that shows an unexpected cyclohexadiene moiety, which results from hydride transfer to the ortho position of the mesityl substituent. The results presented here show a new type of ligand-based 2e-reduction of the formazanate ligand.

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M.-C. Chang and E. Otten*, submitted
Chapter 7 Intramolecular Hydride Transfer Reactions in (Formazanate)Boron Dihydride Complexes

7.1 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, LiAlH₄ and NaBH₄ are very common reducing agents, and the Lewis base stabilized LMH₃ complexes (M: B, Al, Ga, In; L: Lewis base) show chemo- and stereo-selective 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 LiAlH₄ and H₃N-BH₃ are investigated as hydrogen storage materials.³ When we surveyed the literature, we surprisingly noticed that the research of boron hydride compounds bearing multidentate ligands is very limited. Besides the well-known catecholborane (HBcat) and pinacolborane (HBpin), which are commonly used in hydroboration⁴, borylation of arylhalides⁵ and catalytic C-H activation of hydrocarbons⁶, there are only a few examples that have been synthesized and fully characterized (Chart 7.1). 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 dipyrronium-coordinated borane (D) via hydride transfer to the meso position of the ligand. In 2014, a boron dihydride complex bearing bis(imidazolin-2-imine) ligand (E), which can be converted to a thioxoboran salt (F), was reported by Inoue and co-workers.¹⁰

In Chapter 6, we reported the 2-electron reduction chemistry of the boron formazanate compound [PhNNC(p-tolyl)NNPh]BF₂, which suggested (transient) formation of a reactive low-valent (formazanate)boron species that ultimately forms BN heterocyclic products (compounds 11-14 in Chapter 6). The heavier group 13 element hydrides (MXHₙ, M = Ga or In, X = Cl or Br) are known to give low-valent compounds via reductive dehydrogenation,¹¹ but to the best of our 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 (LBH₂, 2) compounds and evaluate their reactivity.

**Chart 7.1**

**7.2 Synthesis of Formazanate Boron Dihydride Complexes**
The synthesis of (formazanate)boron dihydride complexes (10a,c,f) was achieved by reacting free formazan with borane dimethylsulfide complex (BH₃·SMe₂) at room temperature (Scheme 7.1). The products were purified by column chromatography to give the pure compounds in a yield of around 10-30%. The purity of the products was assessed by NMR spectroscopy and elemental analysis.

**Scheme 7.1 Synthetic procedure of LBH₂ (10)**

**7.3 Thermally Induced Intramolecular Hydride Transfer**

**7.3.1 [PhNNC(p-tolyl)NNPh]BH₂ (10a)**

In order to test the possibility to promote H₂ reductive elimination from a molecular boron complex, the thermolysis of [PhNNC(p-tolyl)NNPh]BH₂ (10a) was monitored by ¹H NMR. After a solution of 10a was heated in an NMR tube (C₆D₆, 100 °C, 4 hours), the formation of hydrogen gas or B-N heterocyclic products such as those formed upon reduction of the LBF₂
analogues (see Chapter 5) was not observed. Nevertheless, the reaction proceeded cleanly to give two new products (17a and 18a) resulting from hydride transfer, which were identified by the $^1$H NMR spectra (Scheme 7.2 and Figure 7.1). It is worth mentioning that the analogous LBF$_2$ (6) and LBPh$_2$ (9) complexes are stable at high temperature.

![Scheme 7.2](image)

**Scheme 7.2** Thermally induced intramolecular hydride transfer reaction of 10a (C$_6$D$_6$, 100 °C).

In the $^1$H NMR spectrum of the thermolysis experiment taken after 4 hours at 100 °C (Figure 7.1, middle), a new group of resonances containing all the resonances of the formazanate ligand ([1a$^-$]) can be identified in addition to starting material. The triplet resonance, which has the integration corresponding to one proton at $\delta$ 6.72 ppm, indicates that the two phenyl substituents of the formazanate ligand are no longer equivalent. The most likely explanation for the asymmetry of the formazanate ligand is that it coordinates to the boron center with one internal and one terminal nitrogen atom forming a five-membered chelate ring. The singlet located at $\delta$ 5.23 ppm has the integration corresponding to one proton and does not link to any carbon atoms, which was confirmed by the gHSQCAD spectrum. This singlet resonance indicates that the new compound has an NH functional group. In addition, a very broad resonance at around $\delta$ 5.08 ppm is observed. Measurement of the $^1$H{$^1$B} spectrum results in sharpening of this signal, which indicates that this is a B-H functional group. Based on all the information collected from the NMR experiments, the formation of the new complex 17a is postulated (Scheme 7.2). Attempts to obtain 17a as a pure compound were not successful due to the formation of a subsequent product 18a that occurs simultaneously with conversion of 10a. The $^1$H NMR spectrum of 17a is always mixed with either the starting material 10a or the final thermolysis product 18a. In addition, the attempt to isolate complex 17a from the reaction mixture was also not successful. Even though we never got a spectrum of pure 17a in any of the NMR experiments, all the NMR characterizations support the structure of 17a.
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Figure 7.1 $^1$H NMR spectra of thermolysis reaction of 10a (400 MHz in C$_6$D$_6$); top: starting material 10a; middle: mixture of 10a and 17a; bottom: final product of thermolysis reaction 18a

An alternative formulation of the initial hydride transfer product that is consistent with the observed NMR data is 17a', in which the hydride is transferred to the internal nitrogen resulting in a boron-analogue of leuco-verdazyls (Chart 7.2), which are often involved in synthesis of verdazyl radicals and formazans.$^{12}$ To evaluate which of the two possibilities is most likely, DFT calculation of both five- (17a) and six-membered chelate (17a') isomers were carried out at the B3LYP/6-31G(d) level in the gas phase (Figure 7.2). The calculations show that isomer 17a is more stable than the six-membered chelate ring 17a' ($\Delta G = 11.9$
In the optimized structure of 17a, 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 Å and 1.391 Å) of the optimized structure of 17a are close to bond lengths of N-N single bonds. This bond length distribution of 17a suggests that it is better described as a boron(III) monohydride complex bearing a doubly reduced formazanate ligand ([1a]⁻²BIIIH; Chart 7.2) instead of a boron(I) monohydride complex coordinated by a (neutral) formazan ligand ([1a]B¹H). In other words, the formation of 17a can be treated as a 2e-reduction of the formazanate ligand. To the best of our knowledge, this is the first reported 2e-reduction of formazanate ligands by a chemical method (hydride reduction in this case).

Chart 7.2 Structure of 17a’ (left), and 17 showing the possible resonance structures of [1a]⁻²BIIIH and [1a]B¹H (right)

Figure 7.2 Optimized structures of 17a (left; N1-N2: 1.401; N1-C6: 1.399; C6-N3: 1.308; N3-N4: 1.391) and 17a’ (right; N1-N2: 1.431; N1-C6: 1.415; C6-N3: 1.285; N3-N4: 1.400).

Keeping the same NMR tube at 100 °C for several hours results in the disappearance of 10a and 17a with the appearance of a new compound 18a (Figure 7.1: bottom). The ¹H NMR spectrum of 18a shows two broad singlets at δ 6.35 and 4.62 ppm, which do not show any
crosspeaks in the gHSQCAD spectrum. These two broad singlets indicate that the new compound has two inequivalent NH functional groups. In the NOESY spectrum of 18a, the resonances at δ 6.35 and 4.62 ppm show crosspeaks with the o-CH resonance of the p-tolyl substituent and the o-CH resonances of two phenyl substituents, respectively. In addition, the rest of the resonances of 18a indicate that the formazanate ligand does not have $C_2$ symmetry. Based on the full NMR analysis of 18a, the new compound was assigned as an aminoborane complex (Scheme 7.2).

Even though the isolation of 18a as a pure product was not successful, the formation of 18a was indirectly confirmed by hydrolysis of the reaction mixture. Hydrolysis of 18a in the NMR tube results in the formation of a new compound (19a) and aniline (Scheme 7.3). The formation of aniline was confirmed by overlapping a $^1$H NMR spectrum of pure aniline with the $^1$H NMR spectrum of the reaction mixture. The $^1$H NMR spectrum of 19a shows a 1:1 ratio of the p-tolyl group and the phenyl group. In addition, an N-H resonance having an integration corresponding to one proton can be located at 5.85 ppm. Based on the NMR features mentioned above, we postulate that compound 19a is a borinic acid derivative. While we were unable to obtain 19a as a pure compound and characterize it directly, attempted workup of the reaction mixture afforded crystals of the borinic anhydride 20a (Figure 7.3), the formation of which likely goes through 19a.14

![Scheme 7.3](image-url)

Scheme 7.3 Hydrolysis of 18a and the formation of borinic acid (19a), and borinic acid anhydride (20a)
Figure 7.3 Molecular structure of borinic acid anhydride (20a) showing 50% probability ellipsoids. All hydrogen atoms (except for H100) are omitted for clarity. Selected bond length: B1-N1: 1.439(2); N1-N2: 1.401(2); N2-C7: 1.308(2); C7-N3: 1.384(2); N3-B1: 1.430(2); N3-H100: 0.91(2); O1-B1: 1.366.

In order to get more mechanistic insights of the hydride transfer reaction, two LBH₂ complexes (10c and 10f), of which the formazanate ligands have different electronic and steric properties of the substituents, were heated under similar conditions in an NMR tube. The R¹ and R⁵ substituents of 10c and 10f are different; therefore, two isomers, which result from hydride transfer to either the R¹ or R⁵ sides of the ligand, can be expected for the intermediate 17 and the product 18 of the reaction.

7.3.2 [PhNNC(p-tolyl)NMMes]BH₂ (10c)

The initial result of the thermolysis study (C₆D₆, 100 °C, 5 hours) of 10c shows the formation of the expected intermediate 17c, which is formed as two isomers 17c-i and 17c-ii with a ratio of 1:2 (Scheme 7.4, Figure 7.4). Besides the expected intermediates 17c, a new intermediate 21c-i was observed in the ¹H NMR spectrum. The ¹H NMR spectrum of 21c-i features several characteristic resonances: a quintet at δ 5.83 ppm, a doublet at δ 5.25 ppm, a quintet at δ 3.89 ppm, a resonance at δ 2.07 ppm (overlapped), a triplet at δ 1.51 ppm and a doublet at δ 0.83 ppm with the integration ratio of 1:1:1:3:3:3 (Figure 7.4, middle). Even though the ¹H NMR spectrum of reaction mixture contains at least four species (10c, 17c-i, 17c-ii, and 21c-i), the full ¹H NMR assignment of 21c-i is still achieved by the help of 2D NMR spectra such as gCOSY (Figure 7.5) and gHSQCAD. In the gHSQCAD spectrum, the six resonances mentioned above show crosspeaks, which means that all protons connect to carbon atoms directly, and none of them is an N-H group. The integration ratio of these six resonances suggests that two methyl groups at ortho positions and two hydrogen at meta positions of mesityl substituent are no longer equivalent in 21c-i.
Scheme 7.4 The intermediates and products of the thermolysis reaction of 10c

Figure 7.4 $^1$H NMR spectra of thermolysis reaction of 10c (400 MHz in C$_6$D$_6$); top: starting material 10c; middle: mixture of 10c, 17c-i, 17c-ii, and 21c-i; bottom: mixture of 17c-i and 17c-ii.
The most characteristic resonances of 21c-i are those at 0.83 (3H), 3.89 (1H) and 5.25 (1H) ppm. The three protons doublet at 0.83 ppm is coupling with the quintet at 3.89 ppm with a coupling constant of 7 Hz, which is in the normal range of a $^3J_{H-H}$ coupling. This feature indicates a (CH$_3$)CH fragment in the structure of 21c-i; therefore, the resonances at 0.83 ppm and 3.89 ppm are assigned to H9 and H6 (Figure 7.5), respectively. The gCOSY spectrum shows the coupling between H6 and the resonance at 5.25 ppm, which is in a typical range of a C-C double bond which allows its assignment as H5.

**Figure 7.5** gCOSY spectrum of a mixture of 10c, 17c-i, 17c-ii, 21c-i, (500 MHz, C$_6$D$_6$)

These NMR features suggest that 21c-i has a mesityl-derived 2,4,6-trimethylcyclohexadiene substituent. Based on these NMR features of 21c-i, we can conclude that one of the hydrides of the BH$_2$ unit shifts to the ortho position of mesityl substituent resulting in dearomatization of the mesityl substituent to a cyclohexadiene substituent. A similar dearomatization reaction was reported by Barclay and co-workers in 1973, who showed intermolecular hydride transfer from vitride, which is a comparable hydride reducing agent with LiAlH$_4$, to 2,4,6-tri-t-butylnitrobenzene to give 2,4,6-tri-t-butyl-2,4-cyclohexadienone oxime at room
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The 2,4,6-tri-t-butyl-2,4-cyclohexadienone oxime was further transformed to 2,4,6-tri-t-butylaniline and 2,4,6-tri-t-butyl nitrosobenzene at 170°C. To the best of our knowledge, the intramolecular hydride shift from a boron hydride to an aromatic ring to form compound 21c-i is without precedent in the literature.

![Scheme 7.5](image)

**Scheme 7.5** Hydride reduction of 2,4,6-tri-t-butyl nitrobenzene by vitride at room temperature

Keeping the same NMR tube at room temperature for several days, the intensity of 21c-i decreased, the intensity of the ¹H NMR signal 17c-i increased while the intensity of 10c and 17c-ii remained unchanged. The change of the intensities suggests that compound 21c-i is an intermediate in the conversion of 10c to 17c-i. It is also reasonable to assume that complex 21c-ii, which is not observed in the NMR experiment, is the intermediate from 10c to 17c-ii.

Heating the same NMR tube at 100 °C for several hours shows similar reactivity as observed for 17a: the disappearance of 17c and the appearance of 18c, which is formed as two isomers 18c-i and 18c-ii. At the end of the thermolysis reaction of 10c, the ratio of two isomers (18c-i:18c-ii) is close to 1:1 (Figure 7.4, bottom).

### 7.3.3 \(\text{[C}_6\text{F}_5\text{NNC}(\text{p-toly})\text{NNMes}]\text{BH}_2\) (10f)

Complex 10f is an interesting subject for the thermolysis experiment due to its electronic and steric asymmetry in the formazanate ligand ([1f]⁻), from which both isomer i and ii are expected to form. The formazanate ligand [1f]⁻ has one –C₆F₅ substituent, which is a strong electron-withdrawing group, and one mesityl substituent, which is an electron-donating group with steric hindrance. The result of the thermolysis of 10f can give us some hint about the influence from the –C₆F₅ substituent on reactivity and selectivity of the intramolecular hydride transfer reaction. Applying similar reaction conditions (C₆D₆, 100 °C) of 10a/c to 10f, the thermolysis of 10f is much faster than 10a/c. At 100 °C, all starting material 10f was consumed within 1 hour, and only a single product was formed (17f-i), without any intermediates observable by NMR. Keeping the NMR tube at 130 °C for few hours leads to the formation of compound 18f-i. This example shows that introducing an electron-
withdrawing group results in a change in reactivity (faster reaction) and selectivity (single isomer formation) of the reaction (Scheme 7.6).

Scheme 7.6 Thermolysis reaction of 10f

7.4 Kinetic Study and Proposed Mechanism

7.4.1 Kinetic Study of the Thermolysis of [PhNNC(p-tolyl)NNPh]BH2 (10a)

The kinetic study of the transformation from 10a to 17a was carried out in NMR tubes at 100 °C with two different concentrations (EXP 1: 3.5 mM; EXP 2: 17.2 mM). The kinetic data of both EXP 1 and EXP 2 were followed to 2 half-lifes as shown in Figure 7.5 (left). The data show that the transformation from 10a to 17a is first-order in 10a with a rate constant of 0.004 min⁻¹ at 100 °C. The first-order transformation from 10a to 17a suggests that the hydride transfer reaction is an intramolecular reaction. After following the reaction from 10a to 17a for 2 half-lifes, the NMR tubes of both EXP 1 and EXP 2 were heated up to 130 °C for 30 minutes to complete the transformation from 10a to 17a. When all 10a is consumed, the subsequent disappearance of 17a to form 18a was monitored at 130 °C for 2 half-lifes as shown in Figure 7.5 (right). These data suggest that also the transformation from 17a to 18a is a first-order reaction with a rate constant of 0.009 min⁻¹ at 130 °C.

Figure 7.5 Kinetic study of transformations 10a→17a (left, 100 °C) and 17a→18a (right, 130 °C). Exp 1: [10a] = 3.5 mM; Exp 2: [10a] = 17.2 mM.
7.4.2 Proposed Mechanism and DFT Calculations

Based on the information mentioned above, which include the identified intermediates and results from kinetic studies, a mechanism for the thermally induced hydride transfer reaction is proposed in Scheme 7.7. A summary of the steps that are proposed to take place in the transformation from $10$ to $18$ is as follows:

**Step 1 ($10 \rightarrow 22$):** Reversible isomerization from six-membered chelate ring to five-membered chelate ring. The similar reversible isomerization of formazanate ligand was shown to occur in formazanate Zn complexes (*Chapter 3*).

**Step 2 ($22 \rightarrow 21$):** Hydride transfers to the ortho position of the aromatic ring, which results in the dearomatization of the aromatic ring and the formation of a cyclohexadiene substituent.

**Step 3 ($21 \rightarrow 17$):** Hydride shifts from the cyclohexadiene substituent to the terminal nitrogen and the cyclohexadiene substituent is aromatized back to an aromatic ring.

**Step 4 ($17 \rightarrow 18$):** N-N bond cleavage and formation of an aminoborane product.

All the proposed intermediates were subjected to DFT calculations at the B3LYP/6-31G(d) level in the gas phase (Figure 7.6). The calculated energies of the intermediates reveal that the hydride transfer reaction of compound $10$ is energetically uphill for the first step and downhill for all the following steps.
Figure 7.6 Energy diagram of the thermally induced intramolecular hydride transfer reaction of (formazanate)boron dihydride complex (10c). (Red: isomer i; blue: isomer ii)

For the thermolysis of 10c, the intermediate 21c-i and 21c-ii have similar calculated energies (-7.5 vs. -6.2 kcal/mol), which suggest that both intermediates are possible to form. The reason for the formation of only a single isomer (21c-i) might due to a fast subsequent transformation (21→17) in the case of isomer ii. In other words, the consumption of 21c-ii is faster than its generation. The fast transformation from 21 to 17 might also the reason why we don’t see intermediate 21a in the thermolysis reaction of 10a. It is worth pointing out that based on the experimental data we have, the possibility of a direct hydride transfer resulting in the formation from 10 to 17, in which the intermediate 21 is not involved, can not be completely ruled out.
In the case of 10f, the calculated energies of all possible intermediates also suggest that formation of isomers ii is possible. The reason for single isomers (17f-i, and 18f-i) formation is likely due to the strong electron-withdrawing –C₆F₅ substituent, which localizes the negative charge of formazanate ligand [1f] at the terminal nitrogen close to the –C₆F₅ substituent resulting in resonance structure G being the dominant contributor (Chart 7.3, see also the structure of 5f in Chapter 3). The resonance structure G makes the isomerization from G to 22f-i is more favorable than the isomerization from H to 22f-ii and leads to a single product (isomer 18f-i in this case). In addition, the resonance structure G also favors the hydride transfer to the terminal nitrogen close to the mesityl substituent due to the less electron density at that nitrogen in the case of the direct hydride transfer pathway.

**Chart 7.3** Resonance structures of 10f, the [BH₂]⁺ unit was omitted for clarity.

![Chart 7.3](image)

### 7.5 Discussion

The thermally induced boron to ligand hydride transfer reaction of compounds 10 presented here is shown to take place in two steps. A first hydride (2e/H⁺) transfer from the boron center to the ligand backbone forms the (LH)BH intermediate 17. Subsequently, this is converted to the final product 18, 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, which is very rare in the literature. Most of the reported examples of metal to arenes hydride transfer are based on mononuclear transition metal hydride complexes, such as Nb, W, Ta, Zr, Co, and Fe. In these examples, an anionic cyclohexadienyl moiety is formed upon hydride shifts from the metal center to an arene, which is further stabilized by coordination to a 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. These reactions are promoted by highly reactive multinuclear metal-hydride clusters. The only non-transition metal example we were able to find in the literature is based on an aluminum hydride complex (Scheme 7.5), which was reported by Barclay and co-workers in 1973. To the best of our knowledge, the
transformation from compound 10c to 21c-i is the first example of the dearomatization of an arene by using boron hydride species. In general, boron hydride reagents are not sufficient enough to dearomatize an arene via hydride transfer. The major reason for the observation of an intramolecular boron to arene hydride transfer reactions in compounds 10 is due to the redox-active nature of formazanate ligands: they behave as good electron reservoirs. Once the hydride shifts to an ortho position of an N-Ar substituent, the electron density introduced by the hydride can be released into the ligand backbone instead of being accumulated at the C₆ ring resulting in a formation of a neutral cyclohexadiene imine moiety (I in Scheme 7.8) and two anionic N-donor groups bound to the boron center. The cyclohexadiene moiety of structure I will then rearomatize back to an aromatic ring resulting in formation of structure J. J is related to the monoanionic formazanate ligand in the starting material via 2e/H⁺ transfer and is thus equivalent to a 2e-reduced neutral formazan.

Scheme 7.8 Hydride reduction of formazanate ligand; the [BH]⁺₂ moiety was omitted for clarity

The second half of the hydride transfer reaction is a N-N bond cleavage of the formazanate backbone resulting in an aminoborane product (compounds 18). The structure of 18 is similar to the imidoborane described in Chapter 6 (fragment X, in Chart 7.4), both of which are boron-containing heterocycles having a very rare BN₃C core structure. The BN₃C core of compounds 18 is a triazaborole, which makes compounds 18 a potential candidate for bioisosteric replacement of imidazoles and pyrazoles due to the isoelectronic relationships between the B-N and C=C units. It is worth pointing out that since the first triazaborole has been prepared by Dewar and co-worker in 1971, the synthetic methods of triazaboroles are still very limited. The most common synthetic procedure for preparing triazaboroles is based on reactions of amidrazones and boronic acid derivatives (RBX₂; X= Cl, Br, OMe, OEt, OH and NMe₂) (Chart 7.4). Therefore, the formation of compounds 18 from (formazanate)boron dihydride (10) opens a potential route for preparing triazaboroles.
7.6 Conclusion

The formation of the complexes 17, 18 and 21, which resulted from the thermally induced boron to formazanate hydride transfer reaction, shows a new type of formazanate-based 2e-reduction. The results of the thermolysis reaction of three different starting materials (10a, 10c, and 10f) suggests that the reactivity and selectivity of the hydride transfer reaction are tunable by different substituents on the formazanate ligands. The intermediates identified here expand our understanding of the reactivity of boron hydrides and form a starting point for further investigations on 2-electron reduction chemistry of complexes bearing formazanate ligands.

7.7 Experimental Section

General Considerations. All manipulations were carried out under nitrogen atmosphere using standard glovebox, Schlenk, and vacuum-line techniques. Toluene, hexane, and pentane (Aldrich, anhydrous, 99.8%) were passed over columns of Al₂O₃ (Fluka), BASF R3-11-supported Cu oxygen scavenger, and molecular sieves (Aldrich, 4 Å). Deuterated solvent (C₆D₆) was vacuum transferred from Na/K alloy and stored under nitrogen. NMR spectra were recorded on Mercury 400, Inova 500 or Agilent 400 MR spectrometers. The ¹H and ¹³C 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, gHSQC and/or gHMBC experiments using standard pulse sequences. ¹¹B 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 study

EXP 1: A NMR young tube was charged with [PhNNC(p-tolyl)NNPh]BH₂ (10a) 4.4 mg, hexane (1.6 μL), and C₆D₆ 0.45 mL.
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**EXP 2:** A NMR young tube was charged with [PhNNC(p-toly]NNPh]BH₂ (10a) 20.3 mg, hexane (8.0 µL), and C₆D₆ 0.45 mL.

In order to follow the transformation from 10a to 17a, the tubes of both EXP 1 and EXP 2 were heated at 100 °C and monitored by NMR spectroscopy for every 40 to 60 mins. The concentration of 10a in each ¹H NMR spectra was determined by the integrations of the resonance located at 8.18 ppm (2H of 10a) and 0.87 ppm (6H of hexane).

After followed the transformation from 10a to 17a for 2 half-lifes, the NMR tubes were heated at 130 °C for 30 mins to convert all of the 10a to 17a. After which, the transformation from 17a to 18a was promoted at 130 °C and followed by NMR spectroscopy for every 15 to 40 mins. The concentration of 17a in each ¹H NMR spectra was determined by the integrations of the resonance located at 7.95 ppm (2H of 17a) and 0.87 ppm (6H of hexane).

**DFT Calculation**

Calculations were performed with the Gaussian09 program using density functional theory (DFT). Geometries were fully optimised starting from the X-ray structures using the B3LYP exchange-correlation functional with the 6-31G(d) basis set. Geometry optimisations 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).

**Synthesis of LBH₂**

[PhNNC(p-toly]NNPh]BH₂ 10a. A schlenk flask was charged with [PhNNC(p-toly]NNHPh] (1a) (601.2 mg, 1.91 mmol), BH₃(SMe₂) (0.18 mL, 1.90 mmol) and dry toluene. The reaction mixture was stirred overnight at RT, and then all volatile were removed under vacuum. The product was purified by chromatography (DCM/hexane = 1/2, silica gel, Rf = 0.71). After which 178.2 mg (0.46 mmol, 29 %) of 10a was obtained.

[PhNNC(p-toly]NNMes]BH₂ 10c. The procedure is similar with 10a. [PhNNC(p-toly]NNHMes] (1c) (302.0 mg, 0.85 mmol) and BH₃(SMe₂) (0.08 mL, 0.85 mmol) was used. The product was purified by chromatography (DCM/hexane = 1/2, silica gel, Rf = 0.68). After which 64.8 mg (0.18 mmol, 21 %) of 10c was obtained.

[MesNNC(p-toly]NNC₆F₅]BH₂ 10f. The procedure is similar with 10a. [MesNNC(p-toly]NNHC₆F₅] (1f) (324.5 mg, 0.73 mmol) and BH₃(SMe₂) (0.07 mL, 0.74 mmol) was used.
The product was purified by chromatography (DCM/hexane = 1/2, silica gel). After which 40.9 mg (0.09 mmol, 12 %) of 10f was obtained.

**Characterization Data of products and intermediates**

**[PhNNC(p-tolyl)NPh]BH₂ 10a.** $^1$H NMR (400 MHz, C$_6$D$_6$, 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, overlap with C$_6$D$_6$), 6.97 (t, 4H, $J = 8.3$, Ph m-CH), 6.88 (tt, 4H, $J = 7.3$, 1.8, Ph p-CH), 3.67 (bs, 2H, BH₂), 2.11 (p-tolyl CH$_3$). $^{11}$B NMR (128.3 MHz, C$_6$D$_6$, 25 °C): -10.8. $^{13}$C NMR (100.6 MHz, C$_6$D$_6$, 25 °C): 153.3 (N-CN), 145.9 (Ph i-C), 138.7 (p-tolyl p-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$_3$).

**[PhNNC(p-tolyl)NNHPh]BH 17a.** $^1$H NMR (C$_6$D$_6$, 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, overlap with Ph m-CH of 10a), 6.94-6.89 (m, 2H, p-Tolyl CH, overlap with Ph p-CH of 10a), 6.72 (t, 7.4 Hz, 1H, Ph p-CH), 6.39 (d, 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$_6$D$_6$, 125 MHz, 25 °C): 151.7 (N-CN), 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$_6$D$_6$, 128 MHz, 25 °C): 23.82

**[PhNNC(p-tolyl)NH]BNHPh 18a.** $^1$H NMR (C$_6$D$_6$, 400 MHz, 25 °C): 7.68 (d, 8.0 Hz, 2H ,Ph o-CH), 7.52 (d, 8.0 Hz, 2H , p-tolyl CH), 7.23 (t, 8.1 Hz, 2H ,Ph m-CH), 7.08 (t, 7.6 Hz, 2H ,Ph m-CH), 6.95 (t, 7.6 Hz, 1H ,Ph p-CH), 6.93 (d, 8.0 Hz, 2H , p-tolyl CH), 6.82 (t, 7.6 Hz, 1H ,Ph p-CH), 6.57 (d, 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$_6$D$_6$, 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 (Ph o-C), 20.9 (p-Tolyl CH$_3$). $^{11}$B NMR (C$_6$D$_6$, 128 MHz, 25 °C): 23.06

**[PhNNC(p-tolyl)NH]BOH 19a + aniline.** $^1$H NMR (C$_6$D$_6$, 500 MHz, 25 °C): 8.15 (dd, 8.6, 1.0 Hz, 2H ,Ph o-CH), 7.58 (dd, 8.3 Hz, 2H , p-tolyl CH), 7.30 (dd, 8.5, 7.0 Hz, 2H ,Ph m-CH), 6.99 (d, 8.5 Hz, 2H , p-tolyl CH), 6.98 (tt, 7.5, 1.0 Hz, 1H ,Ph p-CH), 2.09 (s, 3H, p-Tolyl CH$_3$), aniline: 7.06 (dd, 8.5, 7.5 Hz, 2H ,Ph m-CH), 6.71 (tt, 7.4, 0.9 Hz, 1H ,Ph p-CH), 6.34 (dd, 8.4, 1.0 Hz, 2H ,Ph o-CH), 2.75 (bs, 2H, NH$_2$)

**[PhNNC(p-tolyl)NMes]BH$_2$ 10c.** $^1$H NMR (C$_6$D$_6$, 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, BH2), 2.10 (s, 3H, p-toly1 CH3), 2.00 (s, 6H, Mes o-CH3), 1.98 (s, 3H, Mes p-CH3). $^{13}$C NMR (C6D6, 125 MHz, 25 °C): 153.1 (NCN), 145.8 (Ph i-C), 144.0 (Mes i-C), 138.6 (p-toly1 i-C), 137.9 (Mes p-C), 134.2 (Mes o-C), 131.6 (p-toly1 p-C), 129.3 (p-toly1 CH), 129.1 (Ph m-CH), 129.0 (Mes m-CH), 128. (Ph p-CH), 125.3 (p-toly1 CH), 122.5 (Ph o-CH), 20.9 (p-toly1 CH3), 20.5 (Mes p-CH3), 17.9 (Mes o-CH3). $^{11}$B NMR (C6D6, 128 MHz, 25 °C): -8.42 (295 Hz). Anal. Calcd for C23H25BN4: C, 75.01; H, 6.84; N, 15.21. Found: C, 75.24; H, 6.92; N, 15.06.

[PhNCC(p-toly1)NNHMes]BH 17c-i. $^1$H NMR (C6D6, 500 MHz, 25 °C): 8.22 (d, J = 8.4 Hz, 2H, p-toly1 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-toly1 CH, overlap with C6D6), 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-toly1 CH3), 2.05 (s, 3H, Mes p-CH3), 1.92 (s, 6H, Mes o-CH3). $^{13}$C NMR (C6D6, 125 MHz, 25 °C): 129.9 (Mes m-CH), 128.9 (p-toly1 CH), 123.8 (Ph p-CH), 117.6 (Ph o-CH), 21.0 (p-toly1 CH3), 20.9 (Mes p-CH3), 17.9 (Mes o-CH3).

[MesNNC(p-toly1)NNHPh]BH 17c-ii. $^1$H NMR (C6D6, 500 MHz, 25 °C): 8.01 (d, J = 8.2 Hz, 2H, p-toly1 CH), 7.05 (d, J = 7.3 Hz, 2H, p-toly1 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-CH3), 2.16 (s, 3H, Mes p-CH3), 1.97 (s, 3H, p-toly1 CH3). $^{13}$C NMR (C6D6, 125 MHz, 25 °C): 129.0 (p-toly1 CH), 128.0 (Mes m-CH), 128.2 (p-toly1 CH), 120.6 (Ph p-CH), 112.7 (Ph o-CH), 20.8 (p-toly1 CH3), 20.7 (Mes p-CH3), 18.3 (Mes o-CH3).

[PhNNC(p-toly1)NH]BNHMes 18c-i. $^1$H NMR (C6D6, 500 MHz, 25 °C): 7.79 (dm, J = 8.8 Hz, 2H, Ph o-CH), 7.33 (d, J = 8.2 Hz, 2H, p-toly1 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-toly1 CH), 6.83 (s, 2H, Mes m-CH), 5.84 (s, 1H, NH), 3.86 (s, 1H, NH), 2.16 (s, 3H, Mes p-CH3), 2.07 (s, 6H, Mes o-CH3), 2.03 (s, 3H, p-toly1 CH3). $^{13}$C NMR (C6D6, 125 MHz, 25 °C): 147.1 (NCN), 145.1 (Ph i-C), 138.2 (p-toly1 p-C), 133.8 (Mes o-C), 129.2 (Ph m-CH), 124.9 (p-toly1 CH), 122.4 (Ph p-CH), 118.6 (Ph o-CH), 20.8 (p-toly1 CH3), 18.5 (Mes o-CH).

[MesNNC(p-toly1)NH]BNHPh 18c-ii. $^1$H NMR (C6D6, 500 MHz, 25 °C): 7.58 (dm, J = 8.2 Hz, 2H, p-toly1 CH), 7.08 (dd, J = 7.8, 7.4 Hz, 1H, Ph m-CH), 6.94 (d, J = 8.1 Hz, 2H, p-toly1 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-CH3), 2.16 (s, 3H, Mes p-CH3), 2.07 (s, 3H, p-toly1 CH3). $^{13}$C NMR (C6D6, 125 MHz, 25 °C): 146.7 (NCN),
Intramolecular Hydride Transfer Reactions in (Formazanate)Boron Dihydride Complexes

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 CH3), 18.1 (Mes o-CH).

1H NMR (C6D6, 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 Hz, 2H, p-tolyl CH), 6.98 (m, 1H, Ph p-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 CH3 + H7), 1.51 (t, J = 1.4 Hz, 3H, H8), 0.83 (d, J = 7.2 Hz, 3H, H9).

13C NMR (C6D6, 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 CH3), 17.9 (C7), 17.1 (C9).

[C6F5NNC(p-tolyl)NNMes]BH2 10f.

1H NMR (C6D6, 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, BH2), 2.16 (s, 6H, Mes o-CH3), 2.08 (s, 3H, p-tolyl CH3), 1.97 (s, 3H, Mes p-CH3).

13C NMR (C6D6, 125 MHz, 25 °C): 153.8 (NCN), 143.6 (Mes i-C), 143.3 (dm, J = 250.2 Hz, C6F5 CF), 140.2 (dm, J = 251.5 Hz, C6F5 CF), 139.4 (p-tolyl i-C), 139.2 (Mes p-C), 137.5 (dm, J = 254.3 Hz, C6F5 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, C6F5 i-C), 20.9 (p-tolyl CH3), 20.5 (Mes p-CH3), 18.0 (Mes o-CH3).

19F NMR (C6D6, 375 MHz, 25 °C): -148.3 (d, J = 19.7 Hz, 2F, C6F5 o-CF), -159.0 (t, J = 22.1 Hz, 1F, C6F5 p-CF), -162.3 (td, J = 22.4, 5.4 Hz, 2F, C6F5 m-CF).

11B NMR (C6D6, 128 MHz, 25 °C): -7.11 (442 Hz).

[C6F5NNC(p-tolyl)NH]BNHMes 17f-i.

1H NMR (C6D6, 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 CH3), 2.05 (s, 3H, Mes p-CH3), 1.95 (s, 6H, Mes o-CH3).

13C NMR (C6D6, 125 MHz, 25 °C): 152.4 (NCN), 142.6 (dm, J = 250.2 Hz, C6F5 CF), 141.9 (Mes o-C), 139.4 (p-tolyl p-C), 139.2 (dm, J = 252.3 Hz, C6F5 CF), 137.6 (dm, J = 252.0 Hz, C6F5 CF), 133.4 (Mes p-C), 129.9 (Mes m-CH), 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, C6F5 i-C), 20.9 (p-tolyl CH3), 20.3 (Mes p-CH3), 17.8 (Mes o-CH3).

19F NMR (C6D6, 375 MHz, 25 °C): -149.7 (dm, J = 23.7 Hz, 2F, C6F5 o-CF), -159.0 (t, J = 22.0 Hz, 1F, C6F5 p-CF), -163.5 (td, J = 22.2, 5.5 Hz, 2F, C6F5 m-CF).

11B NMR (C6D6, 128 MHz, 25 °C): -7.11 (442 Hz).
13C NMR (CD6, 125 MHz, 25 °C): 149.2 (NCN), 143.1 (dm, J = 251.8 Hz, C6F5 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, C6F5 i-C), 20.8 (p-tolyl CH3), 20.4 (Mes p-CH3), 18.3 (Mes o-CH3). 19F NMR (CD6, 375 MHz, 25 °C): -147.7 (dd, J = 22.9, 5.7 Hz, 2F, C6F5 o-CF), -160.4 (t, J = 22.1 Hz, 1F, C6F5 p-CF), -163.9 (td, J = 22.5, 5.5 Hz, 2F, C6F5 m-CF). 11B NMR (CD6, 128 MHz, 25 °C): 22.9 (222 Hz).

Crystallographic Data

Suitable crystals of 20a was 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 9974 (20a) reflections after integration. Intensity data were corrected for Lorentz and polarisation effects, scale variation, for decay and absorption: a multiscan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (SADABS).27 The structures were solved by direct methods using the program SHELXS.28 The hydrogen atoms were generated by geometrical considerations and constrained to idealised 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.28 Crystal data and details on data collection and refinement are presented in following table.

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### 7.8 Reference


