trans-Selective Insertional Dihydroboration of a *cis*-Diborene: Synthesis of Linear sp³-sp²-sp³-Triboranes and Subsequent Cationization

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Abstract: *The reaction of aryl- and amino(dihydro)boranes with dibora[2]ferrocenophane **1** leads to the formation 1,3-trans-dihydrotriboranes by formal hydrogenation and insertion of a borylene unit into the B=B bond. The aryltriborane derivatives undergo reversible photoisomerization to the cis-1,2-μ-H-3-hydrotriboranes, while hydride abstraction affords cationic triboranes, which represent the first doubly base-stabilized $B_3H_4^+$ analogues.*

Unlike carbon, whose ability to form long and stable homonuclear chains is the basis of organic polymer chemistry, electron-deficient boron has a strong tendency to oligomerize in the form of stable non-classical clusters, in which three-center-two-electron bonding predominates, especially within oligoboron hydrides.[1] In contrast, classical oligoboranes of the form B_nR_{n+2}, in which each boron atom is sp²-hybridized, are particularly prone to ligand scrambling and hydrolysis unless stabilized by electron-donating amino or alkoxy substituents,[2] as exemplified by the commercially available diboranes(4) $B_2(NMe_2)_4$, B_2Pin_2 (Pin = pinacolato), B_2Cat_2 (Cat = catecholato), and B_2Neop_2 (Neop = neopentyl glycolato). In order to enforce electron-precise B−B bonding in oligoboranes, therefore, Lewis bases are commonly used to electronically saturate the boron centers.[3]

The ubiquity of hydroborane and diborane reagents in organic synthesis[4,5] has fueled the search for new synthetic routes to a greater variety of electron-precise di- and oligoboron hydrides. The reductive coupling of N-heterocyclic carbene (NHC)-stabilized $(NHC)BX_2R$ (R = Br, Ph) precursors, for example, provided access to neutral di- and tetrahydrodiboranes of the form $[(NHC)R'HB-BHR'(NHC)]$ (R' = H, Ph),[6] whereas that of $[ArBH_2]_2$ diborane(6) precursors yielded $[ArH_2B-BH_2Ar]^{2-}$ dianions which were in turn converted via double hydride abstraction to neutral dihydrodiboranes(4).[7] Milder routes to diboranes with terminal B−H bonds include the dehydrocoupling of boranes,[8] selective dimethylamino-hydride exchange at $B_2N_2C_2$ heterocycles,[9] the spontaneous transfer hydrogenation of diborenes with $Me_2NH·BH_3$,[10] or the insertion of a borylene into a B−H bond at a boron cluster.[11]

Electron-precise 1-hydrotriboranes were obtained via the uncatalyzed hydroboration of 1,2-diheteroaryldiborenes with HBCat (Scheme 1 a).[12] Use of 9-borabicyclo[3.3.1]nonane (9-BBN) instead of HBCat led to a B_3 *arachno* cluster, presumably due to the greater electron deficiency at boron in 9-BBN.[13] More recently, the double hydroboration of a diboryne to a 2,3-dihydrotetraborane, followed by hydride abstraction, yielded the first cationic 2,3-μ-hydrotetraborane (Scheme 1 b).[14] In this work we report a new strategy for the selective formation of doubly base-stabilized *trans*-1,3-dihydrotriboranes by dihydroboration of a strained *cis*-diborene, resulting in the formal hydrogenation of, and insertion of

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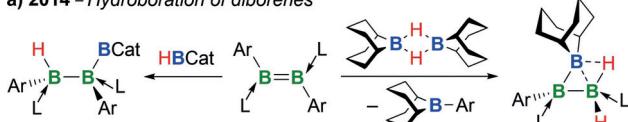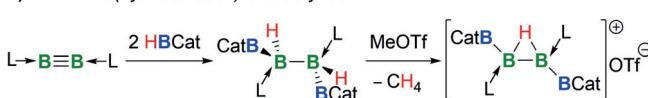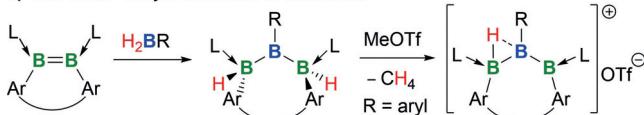
Scheme 1. Atom-efficient methods for the synthesis of electron-precise oligoboron hydrides.

a borylene moiety into, the B=B bond. Furthermore, we study the photoisomerization and cationization of these species (Scheme 1c).

While studying the stoichiometric transfer hydrogenation of the ferrocene-bridged diborene **1**[15] with $Me_2NH·BH_3$, we observed, beside the expected 1,2-dihydrodiborane (δ_{11B} = −18.0 ppm), a second product (δ_{11B} = 88.6, −29.6 ppm, 1:2 ratio), which we deemed to result from the reaction of **1** with the dehydrocoupling byproduct $Me_2N=BH_2$.[10] Similarly, the reaction of **1** with 1 equiv pyrrolidinoborane ($PyrBH_2$) in C_6D_6 at 60 °C overnight resulted in quantitative formation of the triborane **2-Pyr** (Scheme 2), which shows two broad ^{11}B NMR resonances at δ_{11B} = 87.8 (sp^2-*B*) and −28.8 (sp^3-*B*) ppm in a 1:2 ratio and a $^1H\{^{11}B\}$ NMR B*H* resonance (2H) at δ_{1H} = 2.23 ppm.
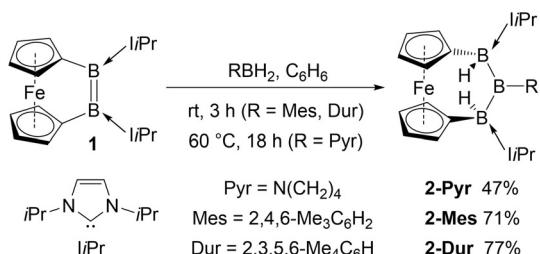
Scheme 2. Addition of dihydroboranes to dibora[2]ferrocenophane **1**.

The analogous reactions of **1** with $MesBH_2$ and $DurBH_2$ (Mes = 2,4,6-$Me_3C_6H_2$; Dur = 2,3,5,6-Me_4C_6H) yielded the triboranes **2-Mes** and **2-Dur** within three hours at room temperature (Scheme 2).[16] **2-Mes** presents two ^{11}B NMR resonances in a 1:2 ratio at δ_{11B} = 100.6 and −13.6 ppm, similarly to **2-Dur** at δ_{11B} = 107.6 and −14.7 ppm. These are significantly downfield-shifted from **2-Pyr** owing to the electron-withdrawing nature of the aryl versus the electron-donating nature of the amino substituent. Comparison with other literature-known amino- and aryl(diboryl)boranes ($\delta(R_2NB(BX_2)_2) \approx 50$–62 ppm,[2,17] $\delta(ArB(BX_2)_2) \approx 70$–85 ppm)[18] shows that the central boron nuclei of **2-R** are unusually deshielded, that is, particularly electron-poor. This was confirmed by density functional theory (DFT) calculations at the OLYP/TZ2P level of theory on **2-Mes** in the gas phase, which gave negative Hirshfeld charges of −0.093 for B1 and B3 and a positive charge of 0.050 for B2 (Figure 3).

X-ray crystallographic analyses of **2-R** show a 1,3-*trans*-dihydro-2-R-tribora[3]ferrocenophane structure (Figure 1 a, Figure S31 in the Supporting Information).[19] With only one diastereomer present in their NMR spectra, we conclude that the addition of RBH_2 to **1** is 100% diastereoselective for the 1,3-*trans*-dihydrotriboranes. The presence of the two boron-bound hydrogen atoms was confirmed by IR bands attributable to terminal B-H vibrations in the 2160 to 2200 cm^{-1} region. These are the first examples of sp^3-sp^2-sp^3-hybridized triboranes, previous examples of electron-precise triboranes being limited to sp^2-sp^2-sp^2 [2,17,18] or sp^2-sp^3-sp^2 hybridization patterns.[11,13] Unlike Nöth's tris(aminoboryl)-[3]ferrocenophane, in which the central B2 atom is tilted out of the B1B3Fe plane,[20] the iron center and all three boron
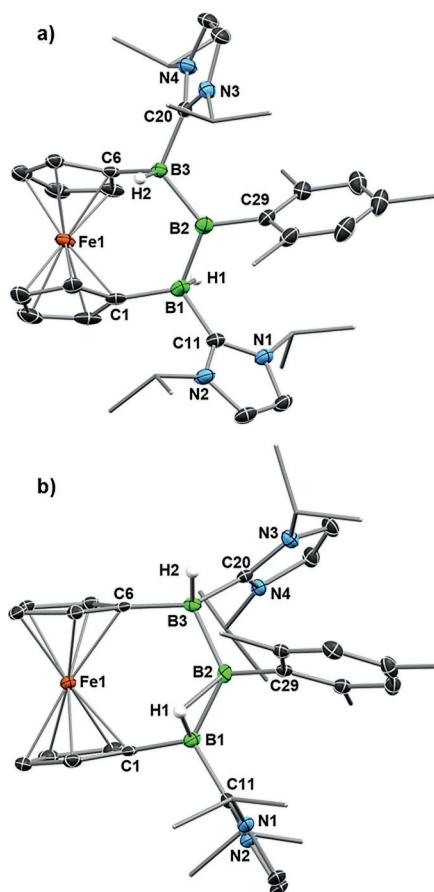

Figure 1. Crystallographically derived molecular structures of a) **2-Mes** and b) **2′-Mes**. Atomic displacement ellipsoids are set at 50% probability. Ellipsoids of Me and *i*Pr groups and hydrogen atoms omitted for clarity except for boron-bound hydrides.[19,30]

atoms of **2-R** lie in the same plane. Owing to the release of strain from the insertion of the third boron atom, the tilt angle between the two Cp ligands (α **2-Pyr** 2.3°; **2-Mes** 7.7°; **2-Dur** 7.3°) is noticeably smaller than in diborene **1** (α 16.1°).[15] In **2-Pyr** the electron-donating pyrrolidino substituent leads to an elongation of the B1−B2 bond (1.756(4) Å) and widening of the B1-B2-B1′ bond angle (127.0(3)°) compared to **2-Mes** (Avg(B1−B2/3) 1.729(3) Å; B1-B2-B3 118.72(17)°) and **2-Dur** (B1−B2 1.724(2) Å; B1-B2-B1′ 119.78(17)°).

Formally, the formation of **2-R** involves the hydrogenation of and the insertion of the RB borylene unit into the B=B double bond of **1**. In contrast, the hydroboration of diborenes with HBCat proceeds by end-on addition of the BCat unit to the diborene (Scheme 1 a).[11] These new reactions therefore provide a complementary method of boron chain growth. Based on literature precedent, the reaction mechanism is likely to proceed via initial *syn*-hydroboration of the diborene.[12,14] This would be followed by insertion of the RB fragment into the remaining B−B bond with concomitant migration of the second hydride to the terminal boron atom. DFT calculations show that the resulting *trans*-1,3-dihydro-triborane **2-Mes** is favored over its *cis*-isomer, **2′-Mes**,[21] by 2.35 kcal mol^{-1}, accounting for the *trans*-selectivity.

Solutions of **2-Ar** in C_6D_6 were stable at 60°C for 24 hours but when irradiated at room temperature for 18 hours two new ^{11}B resonances appeared at $\delta_{11B} = 78.9$ and -11.3 ppm (Ar = Mes) and $\delta_{11B} = 88.8$ and -12.5 ppm (Ar = Dur), respectively (Scheme 3). Even with longer irradiation a max-
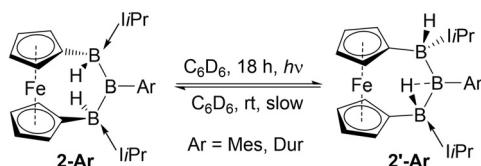
Scheme 3. Reversible photoisomerization of **2-Mes** and **2-Dur**.

imum conversion of 75% to the new species was achieved. The mixtures reverted back to **2-Mes** and **2-Dur** over several days at room temperature or overnight at 60°C under the exclusion of light.[22] In contrast, **2-Pyr**, bearing an electronically stabilizing amino group, remained unchanged under irradiation.

X-ray diffraction analysis of single crystals obtained from a freshly irradiated solution of **2-Mes** (Figure 1 b)[23] revealed the structure of the *cis*-isomer **2'-Mes**, in which H1 has shifted from a terminal position *trans* to H2 to a bridging position *cis* to the terminal H2.[19] This is accompanied by a shortening of the B1−B2 bond from 1.720(3) to 1.650(3) Å, a lengthening of the B2−B3 bond from 1.738(3) to 1.774(3) Å and a slight widening of the B1-B2-B3 angle from 118.72(17) to 122.69-(16)°. Furthermore, the Fe atom no longer lies in the B_3 plane.

Despite their unsymmetrical solid-state structure, **2'-Mes** and **2'-Dur** show only one ^{11}B NMR resonance and a single $^1H\{^{11}B\}$ NMR BH resonance integrating for 2H around 2.6 ppm in solution. Since a *cis*-isomer with two terminal B−H bonds can be ruled out by computations, we propose that in solution H1 and H2 undergo rapid bridging/terminal exchange, leading to the apparent symmetry.

Optimization of a low-lying excited state of **2-Mes** provides insight into a possible mechanism for the tautomerization. Indeed, starting from the *trans*-geometry of **2-Mes**, the system smoothly adopts the same structural characteristics as **2'-Mes**, that is, one bridging and one terminal hydride, albeit in a *trans* configuration. Migration of the bridging hydride to the *cis* position then proceeds with transient breaking and reforming of the B1−B2 bond (see the Supporting Information for details).

DFT calculations on **2'-Mes** yield Hirshfeld charges of -0.059 for B1, -0.018 for B2, and -0.090 for B3 (Figure 3), which reflect the charge flux established between B1 and B2 through the bridging of H1. Furthermore, H1 has lost its hydridic character (-0.005), whereas the terminal H2 has become more hydridic (-0.074).

The increased hydricity of H2 prompted us to attempt its selective abstraction. The addition of methyl triflate (MeOTf) to **2-Ar** resulted in the abstraction of one hydride and quantitative formation of the cationic triboranes **3-Ar** (Scheme 4).[24] The ^{11}B NMR spectra of **3-Mes** and **3-Dur** display three distinct, broad 1:1:1 resonances around 80, 46 and 20 ppm. The complex ^1H NMR spectra are indicative of
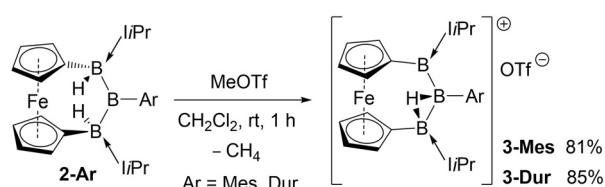
Scheme 4. Cationization of **2-Mes** and **2-Dur** by hydride abstraction.

highly unsymmetrical and/or geometrically constrained compounds. The broad $^1H\{^{11}B\}$ NMR BH resonances at 0.63 (**3-Mes**) and 0.81 ppm (**3-Dur**) are significantly upfield-shifted from those of **2-Ar** (ca. 2.9 ppm) and **2'-Ar** (ca. 2.6 ppm). Furthermore, the IR spectra of **3-Ar** are free of the terminal B-H vibration bands displayed by **2-Ar**, but show bands in the 1560–1570 cm^{-1} region attributable to bridging hydrides.[25] Unlike **2'-Ar**, **3-Ar** show no fluxionality in solution up to 80°C and remain unchanged under UV irradiation.

Single-crystal X-ray diffraction analyses of **3-Mes** (Figure 2) and **3-Dur** (see Figure S33 in the Supporting Information) confirmed their cationic 1,2-μ-hydro-2-
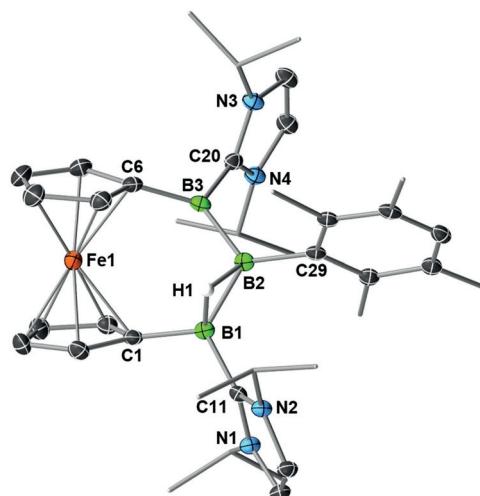
Figure 2. Crystallographically derived molecular structure of the **3-Dur** cation. Thermal ellipsoids are set at 50% probability. Thermal ellipsoids of Me and *i*Pr groups, the OTf⁻ counteranion and hydrogen atoms omitted for clarity except for boron-bound hydrides.[19,30]

aryltribora[3]ferrocenophane structures.[19] While there have been recent reports of linear $B_3H_6^-$ anions,[26] and of cyclic doubly base-stabilized $B_3H_6^+$ cations,[25] these are, to our knowledge, the first examples of linear triborane cations. As doubly base-stabilized analogues of the $B_3H_4^+$ cation they are also structurally related to the $B_3H_6^-$ anion, for which ab initio studies predict a similar C_1 symmetry, with a linear B_3 unit containing a μ-bridging hydride as the structural minimum.[27] Interestingly, the B−B bonds lengths in **3-Ar** are all near-identical (1.658(2)–1.667(4) Å) and significantly shorter than those in **2-Ar** (1.720(3)–1.738(3) Å), as is expected upon cationization. The B1-B2-B3 angle also narrows considerably from 122.69(16)° in **2'-Mes** to ca. 111° in **3-Ar**. Furthermore, the dip angle of the B3 moiety (ca. 17°) is significantly larger

than that of the B1 moiety (ca. 7°). This leads to the B3···Fe distance (**3-Mes** 2.910(2), **3-Dur** 2.920(2) Å) being much shorter than the B1···Fe distance (**3-Mes** 3.163(3), **3-Dur** 3.149(2) Å) and is indicative of a through-space interaction between the cationic B3 and electron-rich Fe^{II} centers (Figure 3).[28]
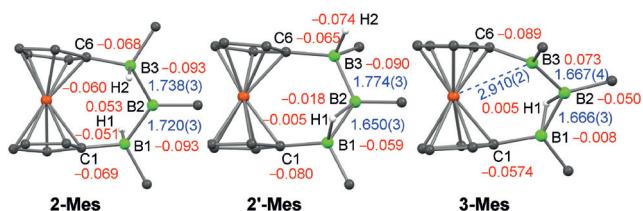

Figure 3. Solid-state structures of **2-Mes**, **2′-Mes** and **3-Mes** (I*i*Pr and Mes ligands omitted for clarity). Experimental bond lengths [Å] in blue, calculated Hirshfeld charges in red.

DFT calculations on **3-Mes** give calculated Hirshfeld charges of −0.008 for B1, −0.050 for B2 and 0.073 for B3 (Figure 3). This enables the attribution of the three ^{11}B NMR resonances as follows: δ(B1) = 46, δ(B2) = 20 and δ(B3) = 80 ppm. A comparison with the partial charges calculated for **2′-Mes** reveals a considerable change in charge density distribution upon abstraction of the terminal hydride at B3. Moreover, the bridging hydrogen H1 has now acquired a very small positive charge (+0.005), suggesting a slightly acidic character.

In conclusion, we have shown that the addition of dihydroboranes to a strained *cis*-diborene provides a complementary method to the addition of monohydroboranes to diborenes for the formation of electron-precise triboranes. The *trans*-1,3-dihydro-2-aryltriboranes undergo fully reversible phototautomerization as well as facile hydride abstraction to yield the first stable, doubly base-stabilized analogues of the $B_3H_4^+$ cation. X-ray structural and DFT analyses reveal significant geometry and charge distribution fluctuations between the various B_3 species. The flexibility of the ferrocenediyl-bridged B_3 core in easily accommodating (and giving up) charge should make these compounds particularly interesting for further reactivity studies.[29]

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

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[21] No energy minimum was found for a *cis*-isomer of **2-Mes** with two terminal hydrides. Instead calculations converged towards **2'-Mes**, in which H1 bridges B1 and B2, while H2 remains terminal.

[22] The isomerization of **2'-Mes** back to **2-Mes** was monitored by ¹H NMR spectroscopy over a period of 3 h at 60 °C. The data could be fitted to a 0.5-order rate law, indicating a complex, multistep process. See Figures S22–S24 in the Supporting Information for NMR kinetics data.

[23] Although an X-ray crystallographic analysis of **2'-Dur** also provided proof of connectivity, the data were not suitable for discussing bond lengths and angles (see Figure S32 in the Supporting Information).

[24] NMR spectra of the reaction of **2-Pyr** with MeOTf also showed the formation of a triborane cation (**3-Pyr**, see NMR spectra in Figure S25 in the Supporting Information). However, the shielded ¹¹B NMR resonance at −18.9 ppm for B1 indicates a terminal rather than a bridging H1, as expected due to the electronic saturation of B2 by the amino substituent. Unlike **3-Ar**, **3-Pyr** decomposed in solution under argon and eluded clean isolation.

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[29] Preliminary experiments adding alkenes, alkynes and ketones to **2-Mes** showed no reactivity up to 80 °C. Further reactivity will be reported in a follow-up study.

[30] CCDC 1947884 (**2-Pyr**), 1947885 (**2'-Dur**), 1947886 (**2-Dur**), 1947887 (**3-Dur**), 1947888 (**3-Mes**), 1947889 (**2-Mes**) und 1947890 (**2'-Mes**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.