Spontaneous *trans*-Selective Transfer Hydrogenation of Apolar B=B Double Bonds

Merle Arrowsmith,[a] Michael Dömling,[a] Uwe Schmidt,[a] Luis Werner,[a] Abril C. Castro,[b] J. Oscar C. Jiménez-Halla,[b] Jonas Müssig,[a] Dominic Prieschl,[a] H. Braunschweig*[a]

Abstract: *The transfer hydrogenation of NHC-supported diborenes with dimethylamine borane proceeds with high selectivity for the trans-1,2-dihydrodiboranes(6). DFT calculations suggest a stepwise proton-first-hydride-second reaction mechanism via an intermediate μ-hydrodiboronium dimethylaminoborate ion pair.*

Since the 1925 landmark discovery by Meerwein and Verley of the aluminium alkoxide-promoted hydrogenation of ketones using alcohols as sacrificial hydrogen donors,[1] transfer hydrogenation has become an attractively mild and selective alternative to direct hydrogenation.[2] Being easy-to-handle hydrogen storage materials,[3] ammonia borane (AB = $H_3N{\cdot}BH_3$) and amine boranes ($R_2NH{\cdot}BH_3$) have also demonstrated their usefulness in catalytic transfer hydrogenation reactions.[4]

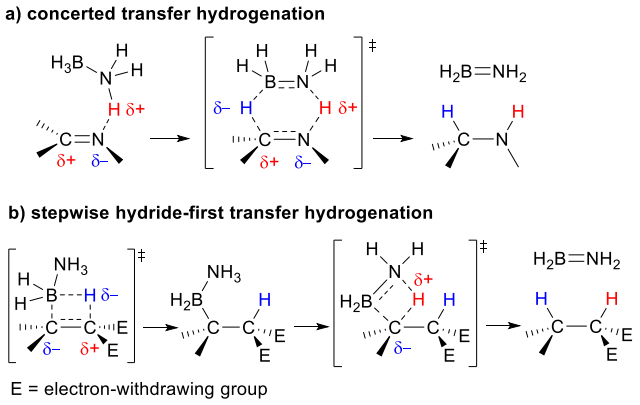
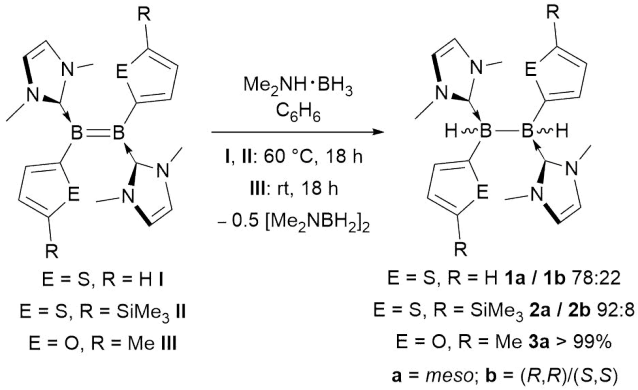


Figure 1. Mechanisms of spontaneous transfer hydrogenation with AB.

While the majority of these reactions are applied to polar substrates, such as imines and ketones,[5] there are several examples of transition-metal- and main-group-catalyzed transfer hydrogenations of apolar N=N,[6] C=C[7] and C≡C bonds[8] using AB or dimethylamine borane (DMAB) as the hydrogen source. Spontaneous, uncatalyzed transfer hydrogenation reactions with AB or DMAB have only been reported for imines,[9] highly polarized olefins,[10] aminoboranes[11] and, most recently, iminoboranes.[12]

Detailed experimental and theoretical studies have shown that, in the case of imines and iminoboranes, the reaction proceeds via pre-coordination of the protic amine hydrogen to the more electronegative nitrogen atom, followed by concerted delivery of both the protic and hydridic hydrogen atoms to the unsaturated bond, via the six-membered transition state depicted in Fig. 1a.[9,12] In contrast, the catalyst-free transfer hydrogenation of 1,1-dicyanoolefins was shown to proceed via a stepwise mechanism, involving initial hydroboration of the polar C=C bond, followed by proton transfer to the borylated carbon atom and liberation of the aminoborane by-product (Fig. 1b).[10]

Our research has focused on the functionalization of B-B multiple bonds.[13] We have thus demonstrated that N-heterocyclic carbene (NHC)-stabilized diheteroaryldiborenes undergo spontaneous *syn*-hydroboration with catecholborane[14] and 9-borabicyclo[3.3.1]nonane (9-BBN).[15] We have also shown that a saturated NHC-stabilized diboryne featuring a formal B≡B triple bond and a diboracumulene stabilized by π-acidic cyclic (alkyl)(amino)carbene (CAAC) ligands undergo facile uncatalyzed hydrogenation to the corresponding *trans*-dihydrodiborenes.[16] In contrast, the direct hydrogenation of diborenes has eluded our efforts, with the exception of our recently reported diiododiborene, $(PCy_3)_2B_2I_2$, which undergoes stepwise hydrogenation, first to the rather unstable 1,2-dihydrodiborane(6), $(Cy_3P)_2B_2H_2I_2$, and then to the (dihydro)iodoborane $(Cy_3P)BH_2I$ with concomitant B-B bond cleavage.[17] Herein we report the catalyst-free transfer hydrogenation of apolar diborenes with DMAB and propose a new mechanism for the observed *trans*-selectivity.



Scheme 1. Transfer hydrogenation of NHC-stabilized bis(heteroaryl)diborenes.

The reaction of the IMe-stabilized dithienyldiborene **I** (IMe

[a] Dr. M. Arrowsmith, M. Dömling, U. Schmidt, L. Werner, J. Müssig, D. Prieschl, Prof. Dr. H. Braunschweig
Institut für Anorganische Chemie & the Institute for Sustainable Chemistry & Catalysis with Boron, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany.
E-mail: h.braunschweig@uni-wuerzburg.de.

[b] Dr. A. C. Castro, Prof. J. O. C. Jiménez-Halla
Departamento de Química, División de Ciencias Naturales y Exactas, Universidad de Guanajuato, Noria Alta S/N, 36050, Guanajuato, México.

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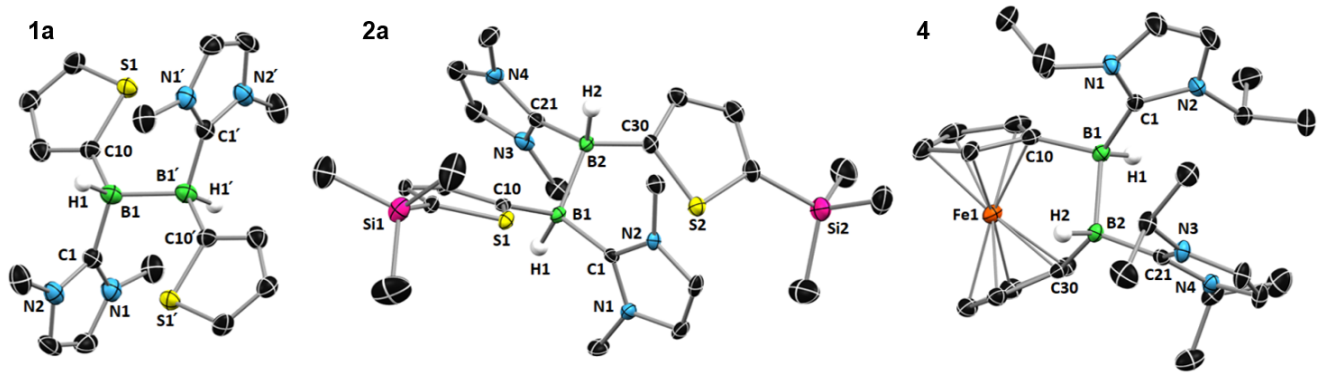
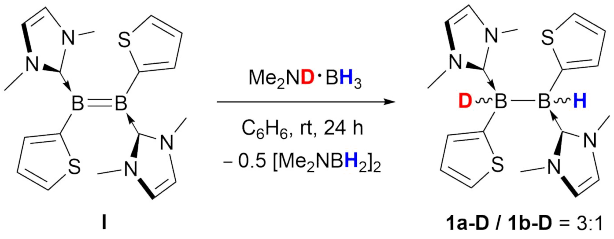


Figure 2. Crystallographically-derived molecular structure of **1a**, **2a** and **4**. Thermal ellipsoids drawn at 50% probability level. Hydrogen atoms omitted for clarity except the boron-bound hydrides. Selected bond lengths (Å) and dihedral angles (°) for **1**: B1-B1' 1.793(6), (H1,B1,B1',H1') 180.0; for **2**: B1-B2 1.817(4), (H1,B1,B2,H2) 163(2); for **4**: B1-B1' 1.8171(19), (H1,B1,B2,H2) 177(1).

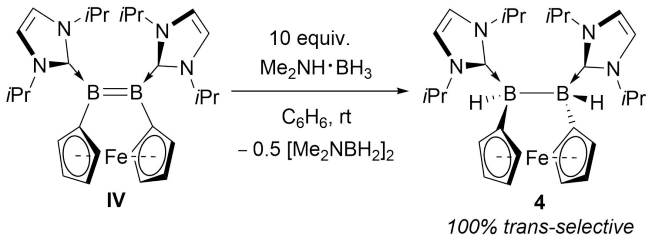
= 1,3-dimethylimidazol-2-ylidene, Scheme 1) with one equivalent of DMAB at 60 °C in benzene over 18 hours resulted in complete consumption of the reagents and the formation of two products, **1a** and **1b**, presenting upfield ^{11}B NMR doublets at –22.7 and –23.9 ppm ($^{1}J_{11B\text{-}1H}$ = 72 Hz), alongside the cyclic dimer $[Me_2NBH_2]_2$ as the only byproduct (δ_{11B} = 5.6 ppm, t, $^{1}J_{11B\text{-}1H}$ = 114 Hz). After isolation by precipitation with pentane and removal of any residual $[Me_2NBH_2]_2$ *in vacuo*, **1a** and **1b** were identified by NMR spectroscopic analysis as two diastereomeric 1,2-dihydrodiborane(6) compounds, presumably resulting from the formal *syn*- and *trans*-hydrogenation of **I**. Integration of the ^{1}H{^{11}B} NMR spectrum of the product mixture provided a 78:22 ratio of the two species, which present distinct B*H* resonances at 3.20 and 3.24 ppm, respectively, integrating for 2H with respect to the corresponding ligand set. **1a** and **1b** did not interconvert on the NMR time scale even upon heating and presented near-identical diffusion coefficients as determined by a DOSY experiment (**1a**: 7.06 10^{-10} m^2 s^{-1}, **1b**: 6.85 10^{-10} m^2 s^{-1}), thus confirming their identity as diastereomers.



Scheme 2. HD-transfer hydrogenation with $Me_2ND{\cdot}BH_3$.

The same reaction performed using *N*-deuterated $Me_2ND{\cdot}BH_3$ at room temperature yielded a 3:1 mixture of **1a-D** and **1b-D** (Scheme 2), which displayed broad ^{11}B NMR resonances centered at –22.8 and –24.1 ppm, respectively, rather than doublets. The ^{1}H{^{11}B} NMR spectrum showed two B*H* resonances at 3.21 and 3.18 ppm, integrating for only 1H with respect to the ligands, while the ^{2}H{^{11}B} NMR spectrum showed two broad, overlapping B*D* resonances in the 3.16-3.22 ppm range, confirming that both a hydrogen and a deuterium have been transferred to the diborene.

The transfer hydrogenation of the thienyl and furanyl derivatives **II** and **III** with DMAB at 60 °C and room temperature, respectively, provided quantitative conversion to the corresponding 1,2-dihydrodiborane(6) diastereomeric pair **2a/b** (**2a**, 92%, δ_{11B} = –22.7, d, $^{1}J_{B\text{-}H}$ = 72 Hz; **2b**, 8%, δ_{11B} = –23.9, d, $^{1}J_{B\text{-}H}$ = 68 Hz) and the single diastereomer **3a** (δ_{11B} = –25.6, d, $^{1}J_{B\text{-}H}$ = 70.7 Hz), respectively (Scheme 1). For the dibora[2]ferrocenophane **IV**, the reaction with one equivalent of DMAB proceeded rapidly at room temperature but yielded several products, including the desired 1,2-dihydrodiborane(6), compound **4**. Complete selectivity for **4** was achieved by employing ten equivalents of DMAB, the excess being removed *in vacuo* upon workup (Scheme 3). NMR spectra of **4** showed a single diastereomer, displaying an ^{11}B NMR *B*H doublet at –18.0 ppm ($^{1}J_{B\text{-}H}$ = 72 Hz) and a ^{1}H{^{11}B} NMR B*H* singlet at 3.40 ppm. Attempts to apply the transfer hydrogenation procedure to the phosphine-stabilized diborenes $(R_3P)B_2Mes_2$ (R = Me, Et; Mes = 2,4,6-$Me_3C_6H_2$)[18] failed, as the phosphine ligands were abstracted to form the phosphine borane adducts $R_3P{\cdot}BH_3$. In contrast, $(IMe)_2B_2Mes_2$[19] did not react with DMAB even at 100 °C in toluene, which may be ascribed to the excessive steric hindrance provided by the mesityl substituents.



Scheme 3. *Trans*-selective transfer hydrogenation of dibora[2]ferrocenophane **IV**.

X-ray crystallographic analysis of single crystals of compounds **1**, **2** and **4** revealed in all three cases the 1,2-dihydrodiboranes(6) resulting from a formal *trans*-addition of H_2 to the B=B double bond, i.e. the *meso* forms for **1** and **2** and the (*R*,*R*)/(*S*,*S*) form for **4** (Fig. 2). The B-B bond distance in **1a** (1.793(6) Å) is similar to that reported by Robinson for

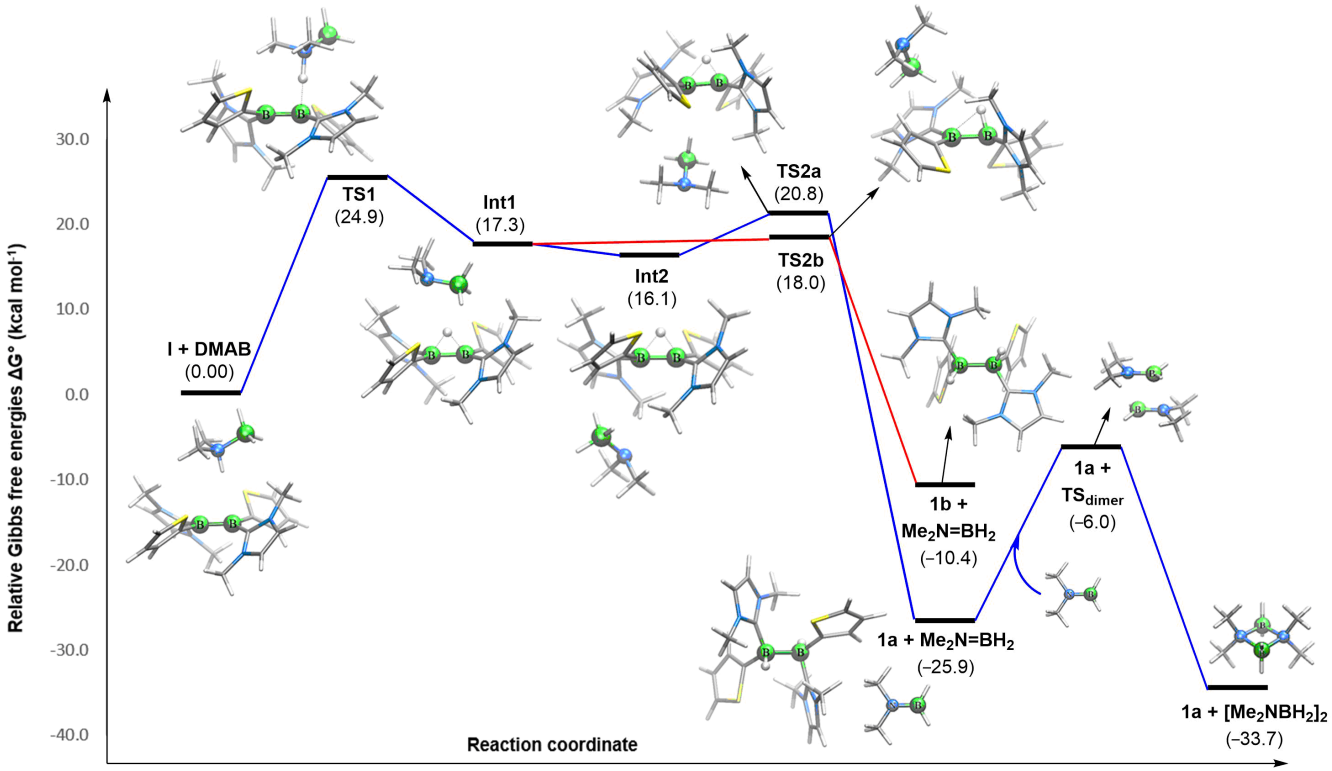


Figure 3. Mechanism of the transfer hydrogenation of **I** with DMAB calculated at the (PCM:benzene)M06-2X/6-311+G(2d,p)//M06-2X/6-31+G(d) level of theory. Relative Gibbs free energies in brackets (kcal mol^{-1}). Blue: reaction coordinates for the *trans*-addition pathway leading to **1a** and dimerization of the aminoborane byproduct: Red: reaction coordinates for the *syn*-addition pathway leading to **1b**.

(I*i*Pr^{Me})$_2$B$_2$H$_2$Ph$_2$ (1.796(3) Å, I*i*Pr^{Me} = 1,3-di*iso*propyl-4,5-dimethylimidazol-2-ylidene).[20] Those in **2a** (1.817(4) Å) and **4** (1.8171(19) Å) are slightly longer, presumably due to the increased steric bulk provided by the 5-trimethylsilyl-2-thienyl ligands and the strain of the ferrocenediyl chelate, respectively. The boron-bound hydrogen atoms, which were located in the Fourier difference map and freely refined, are positioned *trans* to each other in all three cases (dihedral angles (H1,B1,B2,H2): **1a** 180; **2a** 163(2); **4** 177(1)°), resulting in an eclipsed conformation of the boron substituents. Since repeated crystallizations of **1** and **2** only ever afforded single crystals of the *meso* forms, these were assigned to the major diastereomers formed, **1a** and **2a**, respectively.

The high *trans*-selectivity in these reactions is in stark contrast with literature-known transfer hydrogenations of polar multiple bonds, which typically proceed by concerted *syn*-addition as shown in Fig. 1a.[9,12] The exclusive *trans*-selectivity in the transfer hydrogenation of the 1,2-chelated *cis*-diborene **IV**, in particular, highlights the impossibility of a concerted transfer mechanism. We therefore set out to investigate possible reaction mechanisms for the transfer hydrogenation of **I** with DMAB using DFT calculations at the (PCM:benzene)M06-2X/6-311+G(2d,p)//M06-2X/6-31+G(d) level (see ESI for details). The energy barrier for direct hydrogenation was calculated to be prohibitively high at $\Delta G^{\ddagger}$ = 61.5 kcal mol^{-1}, thus confirming our experimental observation that H_2 does not directly add to these diborenes. The concerted transfer hydrogenation pathway (see Fig. S23 in the Supporting Information), which could account for the small amounts of **1b**, **2b** and **3b** formed at 60 °C, presents a barrier of $\Delta G^{\ddagger}$ = 31.6 kcal mol^{-1}, which, although accessible under these reaction conditions, is not applicable to the formation of **4**.

After testing different pathways, namely B-H bond activations through the assistance of carbene ligands and internal rotations, as well as classical borane 1,2-addition followed by proton transfer, the lowest energy pathway was found to be the stepwise transfer mechanism presented in Fig. 3. In the first step the amine-bound proton is transferred from $Me_2NH{\cdot}BH_3$ to diborene **I** via **TS1** with an energy barrier of $\Delta G^{\ddagger}$ = 24.9 kcal mol^{-1} (hydride-first transfer to diborene **I** was computed to be *ca.* 2.5 kcal mol^{-1} higher in energy). This rate-limiting step results in a high-energy cationic hydrodiborenium intermediate, **Int1** (ΔG^1 = 17.3 kcal mol^{-1} above reactants), in which the transferred proton bridges both boron atoms. The aminoborate counteranion $[Me_2NBH_3]^-$ may then readily transfer a boron-bound hydride via **TS2b** ($\Delta G^{\ddagger}$ = 0.7 kcal mol^{-1}) to yield the *syn*-addition product **1b** and the $Me_2N{=}BH_2$ byproduct (reaction step energy: ΔG^2 = –27.7 kcal mol^{-1}, total reaction energy ΔG_{R1b} = –10.4 kcal mol^{-1}). Alternatively, the $[Me_2NBH_3]^-$ counteranion may rotate around the hydrodiborenium cation to a thermodynamically more stable position, **Int2** (ΔG^3 = –1.2 kcal mol^{-1}), from which hydride migration via **TS2a** ($\Delta G^{\ddagger}$ = 4.7 kcal mol^{-1}) leads to the thermodynamically significantly more stable *trans*-addition product **1a** and $Me_2N{=}BH_2$ (reaction step energy: ΔG^4 = –42.0 kcal mol^{-1}, total reaction energy ΔG_{R1a} = –25.9 kcal mol^{-1}). From there, the dimerization of the aminoborane byproduct $Me_2N{=}BH_2$ occurs via an energy barrier of $\Delta G^{\ddagger}$ = 19.9 kcal mol^{-1} and is exergonic by ΔG_{R3} = –7.8 kcal mol^{-1} (total reaction energy from reactants: ΔG_R = –33.7 kcal mol^{-1}). While **1a** is clearly favoured thermodynamically, the slightly lower

barrier to the formation of **1b** results in a non-negligible amount of *syn*-addition in this case. It is likely that the higher *trans*-selectivity observed in the transfer hydrogenation of **II**–**IV** is caused by an increasingly higher barrier to *syn*-addition.

To conclude, we have demonstrated the facile and highly *trans*-selective transfer hydrogenation of diborenes with DMAB as the hydrogen source. This is, to our knowledge, a unique example of spontaneous transfer hydrogenation of apolar multiple bonds. The unusual *trans*-selectivity can be rationalized by a stepwise proton-first-hydride-second transfer mechanism proceeding via a $[\mu\text{-H-B}_2\text{R}_2\text{L}_2]^+[\text{Me}_2\text{NBH}_3]^-$ ion pair intermediate, which favors the thermodynamic *trans*-dihydrodiborane over the kinetic *syn*-dihydrodiborane product. We are continuing to explore the scope of transfer hydrogenation for B-B multiple bonds.

Acknowledgements

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Keywords: Transfer hydrogenation • Diborene • Amine borane dehydrocoupling • Diborane • DFT mechanism

[1] a) A. Verley, *Bull. Soc. Chim. Fr.* **1925**, *37*, 537-542; b) H. Meerwein, R. Schmidt, *Liebigs Ann. Chem.* **1925**, *444*, 221-238.

[2] Recent reviews: a) D. Wang, D. Astruc, *Chem. Rev.* **2015**, *115*, 6621-6686; b) B. Štefane, F. Požgan, *Top. Curr. Chem. (Z)* **2016**, *374*:18; c) M. Wills, *Top. Curr. Chem. (Z)* **2016**, *374*:14.

[3] Selected reviews: a) U. B. Demirci, *Int. J. Hydr. Eng.* **2017**, *42*, 9978 - 10013; b) N. C. Smythe, J. C. Gordon, *Eur. J. Inorg. Chem.* **2010**, *4*, 509–521; c) A. Staubitz, A. P. M. Robertson, I. Manners, *Chem. Rev.* **2010**, *110*, 4079-4124; d) C. W. Hamilton, R. T. Baker, A. Staubitz, I. Manners, *Chem. Soc. Rev.* **2009**, *38*, 279-293; e) F. H. Stephens, V. Ponsa, R. T. Baker, *Dalton Trans.* **2007**, 2613-2626.

[4] A. Staubitz, A. P. M. Robertson, M. E. Sloan, I. Manners, *Chem. Rev.* **2010**, *110*, 4023-4078.

[5] a) Q. Zhou, W. Meng, J. Yang, H. Du, *Angew. Chem. Int. Ed.* **2018**, *57*, 12111-12115; b) S. Li, G. Li, W. Meng, H. Du, *J. Am. Chem. Soc.* **2016**, *138*, 12956-12962; c) T.-J. Zhao, Y.-N. Zhang, K.-X. Wang, J. Su, X. Wei, X.-H. Li, *RSC Adv.* **2015**, *5*, 102736-102740; d) T. D. Nixon, M. K. Whittlesey, J. M. J. Williams, *Tet. Lett.* **2011**, 52, 6652-6654.

[6] C. C. Chong, H. Hirao, R. Kinjo, *Angew. Chem. Int. Ed.* **2014**, *53*, 3342-3346.

[7] Selected examples: a) E. Korytiaková, N. O. Thiel, F. Pape, J. F. Teichert, *Chem. Commun.* **2017**, *53*, 732-735; b) K. A. Erickson, J. P. W. Stelmach, N. T. Mucha, R. Waterman, *Organometallics* **2015**, *34*, 4693–4699; c) Y. Jiang, H. Berke, *Chem. Commun.* **2007**, 3571-3573.

[8] a) Y.-P. Zhou, Z. Mo, M.-P. Luecke, M. Driess, *Chem. Eur. J.* **2018**, *24*, 4780-4784; b) J. K. Pagano, J. P. W. Stelmach, R. Waterman, *Dalton Trans.* **2015**, *44*, 12074-12077.

[9] X. Yang, L. Zhao, T. Fox, Z.-X. Wang, H. Berke, *Angew. Chem. Int. Ed.* **2010**, *49*, 2058-2062.

[10] X. Yang, T. Fox, H. Berke, *Chem. Commun.* **2011**, *47*, 2053-2055.

[11] A. P. M. Robertson, E. M. Leitao, I. Manners, *J. Am. Chem. Soc.* **2011**, *133*, 19322–19325.

[12] L. Winner, W. C. Ewing, K. Geetharani, T. Dellermann, B. Jouppi, T. Kupfer, M. Schäfer, H. Braunschweig, *Angew. Chem. Int. Ed.* **2018**, *57*, 12275-12279.

[13] M. Arrowsmith, H. Braunschweig, T. E. Stennett, *Angew. Chem. Int. Ed.* **2017**, *56*, 96-115.

[14] H. Braunschweig, R. D. Dewhurst, C. Hörl, A. K. Phukan, F. Pinzner, S. Ullrich, *Angew. Chem. Int. Ed.* **2014**, *53*, 3241-3244.

[15] H. Braunschweig, C. Hörl, *Chem. Commun.* **2014**, *50*, 10983-10985.

[16] M. Arrowsmith, J. Böhnke, H. Braunschweig, M. A. Celik, T. Dellermann, K. Hammond, *Chem. Eur. J.* **2016**, *22*, 17169-17172.

[17] J. H. Muessig, M. Thaler, R. D. Dewhurst, V. Paprocki, J. Seufert, J. D. Mattock, A. Vargas, H. Braunschweig, *Angew. Chem. Int. Ed.* **2019**, *58*, DOI: 10.1002/anie.201814230.

[18] a) P. Bissinger, H. Braunschweig, M. A. Celik, C. Claes, R. D. Dewhurst, S. Endres, H. Kelch, T. Kramer, I. Krummenacher, C. Schneider, *Chem. Commun.* **2015**, *51*, 15917-15920; b) H. Braunschweig, P. Bissinger, A. Damme, T. Kupfer, I. Krummenacher, A. Vargas, *Angew. Chem. Int. Ed.* **2014**, *53*, 5689-5693.

[19] P. Bissinger, H. Braunschweig, A. Damme, T. Kupfer, A. Vargas, *Angew. Chem. Int. Ed.* **2012**, *51*, 9931-9934.

[20] Y. Wang, G. H. Robinson, *Inorg. Chem.* **2011**, *50*, 12326-12337.

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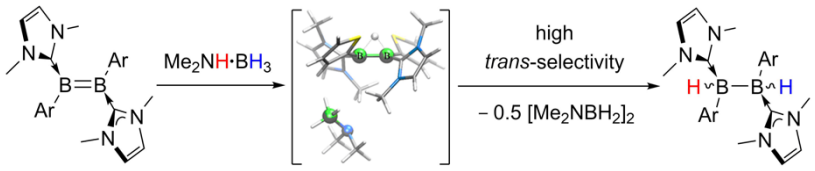

The transfer hydrogenation of apolar *cis*- and *trans*-diborenes with dimethylamine borane as the hydrogen source proceeds with high selectivity for the corresponding *trans*-1,2-dihydrodiboranes(6). DFT calculations reveal a new reaction mechanism proceeding via a proton-first-hydride-second pathway via an intermediate μ-hydrodiboronium aminoborate ion pair.