B−H Borylenes

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Trapping the Elusive Parent Borylene**

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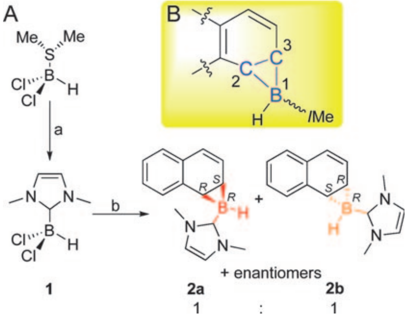
Borylenes BR are a fascinating class of reactive intermediates that have remained rather mysterious to chemists for decades, despite their fundamental importance associated with the close electronic relationship to the well-known carbenoids CR_2. However, in stark contrast to the latter species, conclusive evidence for the existence of free borylenes or a free borylene mechanism has not yet been obtained. Only recently, borylenes have been successfully incorporated into the ligand sphere of transition metals, thus enabling the isolation and structural characterization of stable borylene complexes.[1] While these achievements are an important step towards an improved understanding of the electronic properties of borylenes, all attempts to generate free borylenes selectively have been consistently hampered by their high reactivity. Various more-or-less successful trapping approaches have been developed to substantiate their existence, some of which subsequently having been disputed.[2] These approaches include high-temperature reactions,[3] the photolytic cleavage of B−E bonds,[4] and inter-[5] and intramolecular[6] reductive dehalogenation reactions, which all suffered either from 1) poor analytical data for the resulting species, 2) harsh reaction conditions, and/or 3) low selectivity and yields of isolated products. They all failed to provide the ultimate evidence for the existence of free borylenes. A novel strategy towards the isolation of highly reactive main-group element species has been the use of N-heterocyclic carbenes (NHCs) as stabilizing ligands.[7] Thus, access to several subvalent boron,[8] silicon,[9] phosphorous,[10] and arsenic species[11] has been provided. Following this approach, herein we present the highly selective generation of the elusive parent B−H borylene stabilized by a NHC, and the full characterization of its diastereomeric trapping products.

After due consideration, we reasoned that the NHC adduct $BHCl_2{\cdot}I\mathrm{Me}$ (**1**; *I*Me = 1,3-dimethylimidazol-2-ylidene) might be a suitable candidate for the generation of a NHC-stabilized B−H borylene by the dehalogenation route. Compound **1** was readily isolated in fairly good yields from the Lewis base exchange reaction of commercially available $BHCl_2{\cdot}SMe_2$ with *I*Me (Scheme 1). Conclusive characterization of **1** posed no difficulties, and NMR spectroscopic (^{11}B: $\delta = -37.25$ ppm) and X-ray diffraction parameters (Figure 1) are unremarkable. Subsequent dehalogenation of **1** with two equivalents of sodium naphthalenide, $Na[C_{10}H_8]$, in THF at low temperature cleanly afforded 7,8-($I\mathrm{Me}{\cdot}BH$)-$C_{10}H_8$ (**2**) as a 1:1 mixture of the diastereoisomers **2a** and **2b** (Scheme 1).



Scheme 1. A) Synthesis of diastereoisomers **2a** and **2b**. a) *I*Me, toluene, −78 °C, 68 %; b) 2 $Na[C_{10}H_8]$, THF, −78 °C, 88 %. B) Labeling sequence for the stereogenic centers within the BCC three-membered ring (**2a** *RRS/SSR*, **2b** *RSR/SRS*).

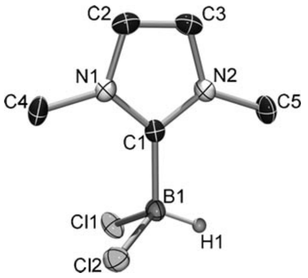


Figure 1. Molecular structure of **1** in the solid state. Only hydrogen atoms attached to boron are shown for clarity.

The formation of only two possible pairs of enantiomers is a result of the *syn*-selective trapping reaction of the NHC-stabilized borylene $I\mathrm{Me}{\cdot}BH$ with naphthalene. Thus, although three stereogenic centers are generated within the BCC three-membered ring, the *syn* selectivity restricts the number of possible enantiomers to two pairs (**2a** *RRS/SSR*, **2b** *RSR/SRS*; Scheme 1). According to ^{1}H and ^{11}B NMR spectroscopy, the reaction proceeded highly selectively and without the formation of any soluble side or degradation products, thus allowing the isolation of **2a** and **2b** as a yellow crystalline material in excellent yields (88 %). Separation of the diastereoisomers was accomplished by repeated crystallizations from toluene at −30 °C. The identity of both species was unequivocally ascertained by NMR spectroscopy, GC/MS,

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and elemental analysis, carried out with both the diastereomeric mixture and the single diastereoisomers. All of the resonances obtained by solution NMR spectroscopy (in C_6D_6; ^1H, ^{11}B, $^{13}C\{^1H\}$) could be assigned without difficulty to the diastereoisomers **2a** and **2b**, respectively. Most importantly, the ^{11}B NMR spectra (Figure 2) are fully consistent with the presence of a four-coordinate boron center (**2a** $\delta = -37.25$ ppm, **2b** $\delta = -33.43$ ppm) featuring one hydrogen substituent (**2a** $^1J_{BH} = 117.57$ Hz, **2b** $^1J_{BH} = 119.34$ Hz).

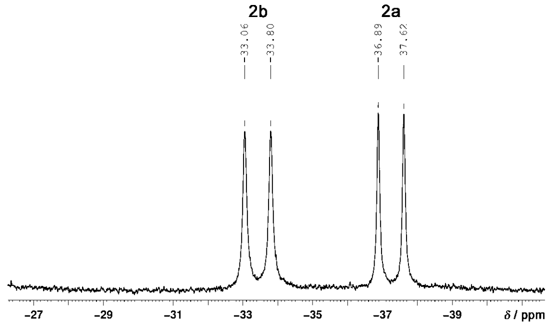

Figure 2. Excerpt of the ^{11}B NMR spectrum of the 1:1 mixture of the diastereoisomers **2a** and **2b** in C_6D_6.

Furthermore, GC/MS analysis of toluene solutions of **2a** and **2b** revealed similar retention times (**2a** 11.84 min, **2b** 12.06 min), each corresponding to the expected molecular weight at m/z 236. As **2a** and **2b** are yellow-colored species, we also acquired UV/Vis spectra of the isolated diastereoisomers in toluene solution. In both cases, a single broad absorption band is observed (**2a** $\lambda_{max} = 336.5$ nm, $\varepsilon = 6917$ mol L^{-1} cm^{-1}; **2b** $\lambda_{max} = 343.5$ nm, $\varepsilon = 10428$ mol L^{-1} cm^{-1}). The color is noteworthy, keeping in mind that related boron-free naphthalene systems are usually colorless,[12] implying a substantial electronic impact of the boron NHC moiety, which is fully supported by time-dependent DFT calculations at the B3LYP level of theory. The experimentally determined excitation energies of the lowest-energy absorption bands of **2a** and **2b** are reproduced fairly well by the theoretical calculations (Table 1). Accordingly, the unexpected yellow color of **2a** and **2b** arises from electronic transitions from the HOMOs, which are located predominately at the central three-membered BCC ring, to predominantly NHC-centered orbitals (Figure 3).

Table 1: Experimentally determined[a] and calculated[b] UV/Vis parameters for the lowest-energy excitation of **2a** and **2b**.

	2a	**2b**
λ_{max} [nm]	336.5	343.5
ε [L mol^{-1} cm^{-1}]	6917	10428
λ_{calcd} [nm]	338.17	372.82
f[c]	0.0365	0.3927
transitions[d]	63*→64 63*→66 63*→67	63*→64 63*→67

[a] Determined in toluene solution. [b] TD-DFT applying the B3LYP functional and 6-311+G(d,p) basis sets. [c] Oscillator strengths. [d] MOs involved in the lowest-energy excitation. The HOMO is indicated with an asterisk.

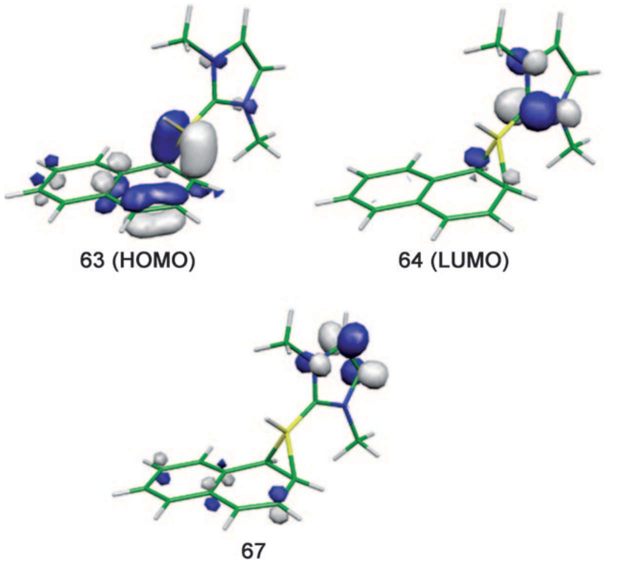

Figure 3. Molecular orbitals involved in the lowest-energy electronic excitation of diastereoisomer **2b**. MOs relevant for the excitation of **2a** are of similar composition.

Single crystals of **2a** and **2b** were studied by X-ray diffraction analysis (Figure 4), which confirms the molecular structure of each species in the solid state. The key feature of the crystal structure determinations is the relative orientations of the NHC ligand with respect to the naphthalene fragment. As illustrated in Figure 4 A and B, the NHC moiety points towards the naphthalene backbone for **2a** and away for **2b**. Both boron atoms are found in a highly distorted tetrahedral environment with C17-B1-C18 angles of 57.76(9)° and 56.57(9)° for **2a** and **2b**, respectively. The bond lengths within the three-membered boracycles are comparable for **2a** (B1–C17 1.602(2), B1–C18 1.618(2), C17–C18 1.556(2) Å) and **2b** (B1–C17 1.624(2), B1–C18 1.621(2), C17–C18 1.538(2) Å), and lie within the typical ranges for B–C and C–C single bonds, while differences are to be ascribed to the steric influence and the relative orientation of the NHC ligand. The carbon atoms of the BCC fragment, that is, C17 and C18, also feature highly distorted tetrahedral geometries, with angles between 114.99–121.55°. As a con-

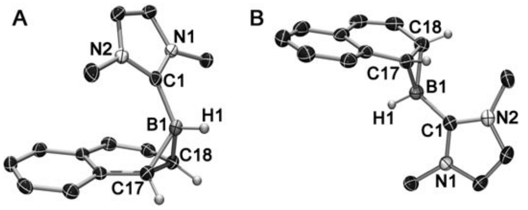

Figure 4. Molecular structures of **2a** (A) and **2b** (B) in the solid state. Only relevant hydrogen atoms are shown for clarity.

sequence, the angles between the calculated planes defined by the BCC moiety and the boron-substituted six-membered ring amount to 71.65° (**2a**) and 73.60° (**2b**). The B1–C1 bond distances are similar for **2a** (1.588(2) Å) and **2b** (1.570(2) Å), and only marginally shorter than that of the precursor species **1** (1.606(3) Å).

This experimental approach thus provides persuasive evidence for the existence of a borylene species. We propose that dehalogenation of **1** initially affords *I*Me•BH, which subsequently undergoes a *syn*-selective [2+1] cycloaddition reaction to afford the trapping products **2a** and **2b**. This assumption is fully supported by the following findings: 1) The cycloaddition pathway is also prevalent in the chemistry of the related carbenes, for which the existence as "free" intermediates is well-established,[13] 2) the energy difference between **2a** and **2b** has been calculated to be only 8 kJ mol^{-1}, and 3) the diastereoisomers are formed selectively in a relative ratio of 1:1, which suggests similar transition states and activation barriers. If in turn dehalogenation of **1** does not involve formation of the borylene, but rather ionic or radical species, the concerted cycloaddition pathway becomes unlikely and a multistep reaction mechanism is then favored. In this case, additional intermediates must be taken into account in which the influence of the boron fragment (electronic/steric) on the product distribution is presumably much more developed. As a consequence, a distinct preference for one of the diastereoisomers is to be expected.

Further evidence for the absence of an ionic/radical mechanism is derived from experimental results. To exclude the participation of radical species in the formation of **2a** and **2b**, we took advantage of the persistency of the boron-centered boryl radical *I*Me•BH$_2^{\bullet}$ described recently by Walton et al.[7b] Thus, *I*Me•BH$_2^{\bullet}$ was generated by irradiation of *I*Me•BH$_3$ in C_6D_6 in the presence of di-*tert*-butyl peroxide and naphthalene. No reaction involving naphthalene took place, and only the characteristic formation of the 1,2-bis-NHC-diborane derivative (*I*Me)•H$_2$B=BH$_2$•(*I*Me) was observed. Furthermore, the fact that not even trace amounts of the NHC-stabilized diborene *I*Me•(H)B=B(H)•*I*Me are detected during reduction of **1** strongly suggests that ionic species are also not involved in the formation of **2a** and **2b**.[8]

Support for the [2+1] cycloaddition pathway is obtained from DFT calculations. Thus, the mechanism for the reaction of the NHC stabilized borylene *I*Me•BH with naphthalene was studied for the *RSR* diastereoisomer **2b** at the B3LYP level of theory employing 6-311+G(d,p) basis sets for all atoms. For this purpose, *I*Me•BH in its singlet electronic state, naphthalene, and **2b** were fully optimized without symmetry restraints. The transition state for the formation of **2b** was subsequently located applying the synchronous guided quasi-Newton method embedded within the Gaussian 03 software package, while the nature of the transition state was further verified by frequency calculations. According to the calculations, the reaction proceeds via an early transition state with a rather small activation barrier of 10.7 kJ mol^{-1} (Figure 5). Thus, the structure of the transition state **TS** strongly resembles those of the reactants, with the borylene *I*Me•BH approaching the double-bond system of the undisturbed naphthalene fragment symmetrically. The separation distances B1–C17 and B1–C18 in the transition-state structure **TS** amount to 3.040 Å and 3.108 Å, respectively, which is fully consistent with the anticipated [2+1] cycloaddition pathway. Successive bond formation to afford **2b** is energetically highly favorable by 204.0 kJ mol^{-1} with respect to the **TS** or by 193.3 kJ mol^{-1} with respect to the reactants. Along with the small energy difference between **2a** and **2b** (8.0 kJ mol^{-1}), and the exothermic nature of this transformation, the low activation barrier inevitably provides a reasonable explanation for the observation of a 1:1 ratio of the diastereoisomers **2a** and **2b**. In conclusion, both experimental findings and the results of the theoretical calculations strongly suggest a mechanism involving the reaction of the NHC-stabilized borylene *I*Me•BH with naphthalene ([2+1] cycloaddition) rather than a mechanism involving ionic or radical species.

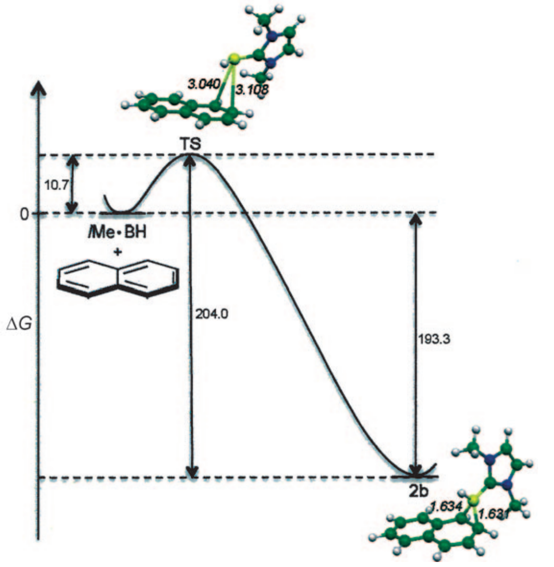

Figure 5. Reaction profile and transition-state structure (**TS**) for the formation of **2b** via the [2+1] cycloaddition pathway. Calculated energy differences are given in kJ mol^{-1} and distances in Å.

Despite their rather fundamental nature, these results offer a unique opportunity to apply **2** as a readily accessible borylene synthon, an aspect that we are currently investigating extensively in our group.

Experimental Section

General considerations regarding the experimental procedures, X-ray diffraction, computational studies, and analytical data of all compounds are provided in the Supporting Information.

1: BHCl$_2$•SMe$_2$ (2.91 g, 20.1 mmol) was added dropwise to a solution of *I*Me (1.93 g, 20.1 mmol) in toluene (40 mL) at −78 °C. The addition was accompanied by the immediate precipitation of an orange-colored solid. The mixture was allowed to warm to room temperature. After 1 h, the solid was collected on a medium-porosity frit and washed with hexanes (3 × 20 mL). Recrystallization from toluene at −30 °C afforded analytically pure colorless crystals of **1** (yield 2.45 g, 13.7 mmol, 68 %).

2: A solution of Na[C$_{10}$H$_8$] (5.86 mL, 1.68 mmol, 0.286 M in THF) was added dropwise to a solution of **1** (150 mg, 839 μmol) in THF (15 mL) at −78 °C, and the color of the solution immediately changed to red. The reaction mixture was allowed to slowly warm to room temperature and was subsequently stirred for 1 h to afford a dark yellow solution. The solvent and free naphthalene were removed in vacuo at 25°C. Crystallization of the yellow residue from toluene at −30°C afforded a 1:1 mixture of the two diastereomers **2a** and **2b** as a yellow crystalline solid (yield 175 mg, 741 μmol, 88%). The diastereomers **2a** and **2b** were separated by repeated recrystallizations from toluene at −30°C.

CCDC-800402 (**1**), 800403 (**2a**), and 800404 (**2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] For selected recent reviews on transition-metal borylene complexes, see: a) H. Braunschweig, D. Rais, *Heteroat. Chem.* **2005**, *16*, 566–571; b) H. Braunschweig, G. R. Whittell, *Chem. Eur. J.* **2005**, *11*, 6128–6133; c) H. Braunschweig, C. Kollann, D. Rais, *Angew. Chem.* **2006**, *118*, 5380–5400; *Angew. Chem. Int. Ed.* **2006**, *45*, 5254–5274; d) C. E. Anderson, H. Braunschweig, R. D. Dewhurst, *Organometallics* **2008**, *27*, 6381–6389; e) H. Braunschweig, C. Kollann, F. Seeler, *Struct. Bonding (Berlin)* **2008**, *130*, 1; f) D. Vidovic, G. A. Pierce, S. Aldridge, *Chem. Commun.* **2009**, 1157–1171; g) H. Braunschweig, R. D. Dewhurst, *Chim. Oggi* **2009**, *27*, 40–42; h) H. Braunschweig, R. D. Dewhurst, A. Schneider, *Chem. Rev.* **2010**, *110*, 3924–3957.

[2] R. Schlögl, B. Wrackmeyer, *Polyhedron* **1985**, *4*, 885–892.

[3] a) P. L. Timms, *J. Am. Chem. Soc.* **1967**, *89*, 1629–1632; b) P. L. Timms, *Acc. Chem. Res.* **1973**, *6*, 118–123.

[4] a) B. Pachaly, R. West, *Angew. Chem.* **1984**, *96*, 444–445; *Angew. Chem. Int. Ed. Engl.Angew. Chem. Int. Ed.* **1984**, *23*, 454–455; b) H. F. Bettinger, *J. Am. Chem. Soc.* **2006**, *128*, 2534–2535.

[5] a) S. M. van der Kerk, J. Boersma, G. J. M. van der Kerk, *Tetrahedron Lett.* **1976**, *17*, 4765–4766; b) S. M. van der Kerk, P. H. M. Budzelaar, A. van der Kerk-van Hoof, G. J. M. van der Kerk, P. von R. Schleyer, *Angew. Chem.* **1983**, *95*, 61; c) A. Meller, U. Seebold, W. Maringgele, M. Noltemeyer, G. M. Sheldrick, *J. Am. Chem. Soc.* **1989**, *111*, 8299–8300; d) A. Meller, D. Bromm, W. Maringgele, A. Heine, D. Stalke, G. M. Sheldrick, *J. Chem. Soc. Chem. Commun.* **1990**, 741–742.

[6] W. J. Grigsby, P. P. Power, *J. Am. Chem. Soc.* **1996**, *118*, 7981–7988.

[7] a) Y. Wang, G. H. Robinson, *Chem. Commun.* **2009**, 5201–5213; b) J. C. Walton, M. M. Brahmi, L. Fensterbank, E. Lacôte, M. Malacria, Q. Chu, S.-H. Ueng, A. Solovyev, D. P. Curran, *J. Am. Chem. Soc.* **2010**, *132*, 2350–2358.

[8] a) Y. Wang, B. Quillian, P. Wei, C. S. Wannere, Y. Xie, R. B. King, H. F. Schaefer III, P. von R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2007**, *129*, 12412–12413; b) Y. Wang, B. Quillian, P. Wei, Y. Xie, C. S. Wannere, R. B. King, H. F. Schaefer III, P. von R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2008**, *130*, 3298–3299.

[9] a) Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer III, P. von R. Schleyer, G. H. Robinson, *Science* **2008**, *321*, 1069–1071; b) R. S. Ghadwal, H. W. Roesky, S. Merkel, J. Henn, D. Stalke, *Angew. Chem.* **2009**, *121*, 5793–5796; *Angew. Chem. Int. Ed.* **2009**, *48*, 5683–5686; c) A. C. Filippou, O. Chernov, G. Schnakenburg, *Angew. Chem.* **2009**, *121*, 5797–5800; *Angew. Chem. Int. Ed.* **2009**, *48*, 5687–5690.

[10] a) Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer III, P. von R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2008**, *130*, 14970–14971; b) O. Back, G. Kuchenbeiser, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2009**, *121*, 5638–5641; *Angew. Chem. Int. Ed.* **2009**, *48*, 5530–5533; c) O. Back, M. A. Celik, G. Frenking, M. Melaimi, B. Donnadieu, G. Bertrand, *J. Am. Chem. Soc.* **2010**, *132*, 10262–10263.

[11] M. Y. Abraham, Y. Wang, Y. Xie, P. Wie, H. F. Schaefer III, P. von R. Schleyer, G. H. Robinson, *Chem. Eur. J.* **2010**, *16*, 432–435.

[12] a) E. Müller, H. Fricke, H. Kessler, *Tetrahedron Lett. Tetrahedr. Let.* **1964**, *5*, 1525–1530; b) K. Villeneuve, W. Tam, *J. Am. Chem. Soc.* **2006**, *128*, 3514–3515.

[13] F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry - Part B: Reactions and Synthesis* Ed. 5, Springer, New York, **2007**, pp. 903.