

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

- Title: Phosphine-Stabilized Diiododiborenes: Isolable Diborenes with Six Labile Bonds
- Authors: Jonas Muessig, Melanie Thaler, Rian Dewhurst, Valerie Paprocki, Jens Seufert, James Mattock, Alfredo Vargas, and Holger Braunschweig

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201814230 Angew. Chem. 10.1002/ange.201814230

Link to VoR: http://dx.doi.org/10.1002/anie.201814230 http://dx.doi.org/10.1002/ange.201814230

WILEY-VCH

Phosphine-Stabilized Diiododiborenes: Isolable Diborenes with Six Labile Bonds

Jonas H. Muessig, Melanie Thaler, Rian D. Dewhurst, Valerie Paprocki, Jens Seufert, James D. Mattock, Alfredo Vargas,* Holger Braunschweig*

Abstract: The lability of B=B, B-P and B-halide bonds is combined in the syntheses of the first diiododiborenes. In a series of reactivity tests, these diiododiborenes demonstrate cleavage of all six of their central bonds in different ways, leading to products of B=Bhydrogenation and dihalogenation as well as halide exchange.

One of the oldest and most compelling techniques of chemical research is to make molecules "unhappy" (i.e. reactive) - either electronically, photolytically or through strain - and see how they behave. Throughout chemistry, it is an imperative of fundamental curiosity, not to mention old-fashioned bravado, to see just how unhappy we can make a certain class of compounds. In main-group chemistry, as in other fields, the synthesis of a new class of reactive, low-valent molecule inevitably leads to attempts to further destabilize the compounds by the inclusion of increasingly labile bonds. Disilenes [R₂Si=SiR₂] are an archetypal example of these chemical instincts. The first isolated disilenes bore bulky, kineticallystabilizing mesityl groups bound through relatively non-labile Sibonds.^[1] Later, however, the C(sp²) synthesis of dibromodisilenes [RBrSi=SiBrR] provided further points of reactivity for these already reactive molecules, leading to a range of interesting reactions such as reduction to form disilynes [RSi=SiR], their use as synthons for halosilylene fragments of the form [:SiXR], and even as precursors to transition-metal silylidyne complexes [LnM=SiR].^[2]

The chemistry of B-B multiple bonds has seen much activity recently,^[3] however, the inclusion of boron-halide bonds in such compounds is far less well-explored. The first dihalodiborene^[4] to be reported was the doubly NHC-stabilized example [B₂Br₂(IDip)₂] (IDip = 1,3-bis(2,6-di/sopropylphenyl)imidazol-2-ylidene), which was prepared by two-electron reduction of the tetrabromo derivative [B₂Br₄(IDip)₂]. In the same communication, the dibromodiborene was shown to undergo two-electron reduction to form the diboryne [B₂(IDip)₂] (**A**, Figure 1), from which the dibromodiborene could be regenerated by a comproportionation reaction with the tetrabromo derivative

-	
[*]	J. H. Muessig, M. Thaler, Dr. R. D. Dewhurst, V. Paprocki, Dr. J.
	Seufert, Prof. Dr. H. Braunschweig
	Institute for Inorganic Chemistry
	Julius-Maximilians-Universität Würzburg
	Am Hubland, 97074 Würzburg (Germany)
	E-Mail: h.braunschweig@uni-wuerzburg.de
	and
	Institute for Sustainable Chemistry & Catalysis with Boron
	Julius-Maximilians-Universität Würzburg
	Am Hubland, 97074 Würzburg (Germany)
	Dr. J. D. Mattock, Dr. A. Vargas
	Department of Chemistry, School of Life Sciences
	University of Sussex
	Brighton BN1 9QJ, Sussex, UK

E-Mail: alfredo.vargas@sussex.ac.uk

Supporting information for this article is given via a link at the end of the document.

 $[B_2Br_4(IDip)_2].^{[4a]}$ In 2017, Kinjo et al. prepared an interesting unsymmetrical dibromodiborene stabilized by one N-heterocyclic carbene and one cyclic (alkyl)(amino)carbene (CAAC),^[5] which underwent facile B=B bond cleavage and isonitrile insertion (**B**, Figure 1).^[4b] Most recently, we reported the cycloaddition and cleavage of CO₂ at dibromodiborene $[B_2Br_2(IDip)_2]$ (**C**, Figure 1).^[4c]



Figure 1. Currently known reactivity of dihalodiborenes.

The use of phosphine donors in place of carbenes is a more well-established method to enhance the reactivity of diborenes; phosphine-stabilized diborenes^[6] have shown quite diverse reactivity at different positions since their discovery in 2014. Unlike carbene-stabilized diborenes, phosphine-stabilized diborenes offer the additional opportunity (or hindrance) of labile B-P bonds, as demonstrated by a number of rearrangement processes both in the presence and absence of other reagents.^[6g,h,i] However, the B=B bond is also labile, and a number of reactions involving its cleavage have been presented, some of which are followed (or preceded) by B-P bond cleavage. These include the insertion and complete C=C bond cleavage of an alkyne,^[6c] one-electron oxidation with a tropylium cation^[6a] and two-electron oxidation with selenium,[6d] coordination to Cu(I),^[6e] Zn(II)^[6f] and Cd(II)^[6f] (the former being followed by hydroarylation of the B=B bond), inverse-electron-demand Diels-Alder reactions with dienes,[6h] and 1,1- and 1,2-diboration of the B=B bond.[6i]

Given the fascinating reactivity of both phosphine-stabilized diborenes and dihalodiborenes, we have for some time sought to combine the potential lability of B-P and B-X (X = halide)

bonds into a single diborene, i.e. $[B_2X_2(PR_3)_2]$. Several years ago we were able to obtain a single-crystal X-ray structure of a phosphine-stabilized dibromodiborene, however, the compound was highly reactive, could not be reliably isolated, and the diffraction data were poor. We have recently reported simple solution-phase syntheses of the tetrahalodiboranes B_2X_4 (X = F, Cl, I),^[7] and our recent work with B_2I_4 has shown in a number of cases that it reacts differently to the other tetrahalodiboranes.^[8] As our extensive attempts to prepare stable phosphinestabilized dichloro- and dibromodiborenes were unsuccessful, we set our sights on the diiodo variants, which we considered may show different behavior and perhaps allow isolation.

In this work, we report the successful synthesis of three phosphine-stabilized diiododiborenes, the first examples of iodocontaining species with B-B multiple bonding. In a number of reactions, a diborene is shown to undergo 1,2-addition, B-B cleavage, and halide exchange with dihydrogen and halogens, demonstrating the lability of all six of the central bonds of the molecule (B=B, B-I and B-P).



Figure 2. Synthesis and reactivity of diiododiborenes 2a-c.

Reactions of tetrahalodiborane B₂I₄ with 2 equiv of PR₃ (R = Me, Cy or CH₂Cy) led to isolation of colorless solids **1a-c** (Figure 2) in good yield (73–97%), showing ¹¹B NMR and ³¹P NMR signals in very narrow ranges (δ_B –26 to –28; δ_P –5 to –11). The ¹¹B NMR signal of the only known double Lewis base adduct of

tetraiododiborane, $[B_2I_4(SMe_2)_2]$ ($\delta_B -20$) is in agreement with the formation of the tetraiododiborane adducts **1a-c**. The crystallographically-derived structures of **1a-c** show the expected doubly base-stabilized diborane structures, with phosphine ligands bound in *anti* conformation, and only slight differences in their B-B bond distances (**1a**: 1.727(7); **1b**: 1.765(5); **1c**: 1.759(4) Å).

The reduction of the phosphine-stabilized diiododiboranes 1a-c with excess potassium graphite (KC8) led to yellow reaction mixtures and new ¹¹B NMR spectroscopic signals (δ_B 5–6). While these signals are significantly downfield of those of the precursors **1a-c**, they are ca. 10-14 ppm upfield of those of both phosphine-stabilized diaryldiborenes ([B2Mes2(PMe3)2]: δB 16.7; [B₂Mes₂(PEt₃)₂]: δ_B 16.3; [B₂An₂(PMe₃)₂]: δ_B 22; Mes = 2,4,6trimethylphenyl; An = 9-anthryl) and NHC-stabilized dibromodiborenes (δ_B ca. 20). The relatively upfield nature of the ¹¹B NMR signals of **2a-c** is presumably a result of the relatively low electronegativities of the atoms bound to the B=B core (P and I) and suggest a high electron density at this unit thanks to a combination of good σ -donor and poor π -acceptor substituents. Interestingly, the ³¹P NMR signal of 2a (PMe₃) is found to higher field (δ_P -18) than that of precursor **1a** (δ_P -11), while the signals of the diborenes with sterically more demanding phosphines are found to lower field (**2b**: δ_P 8: **2c**: δ_P -4) than their corresponding starting material (**1b**: δ_P –9; **1c**: δ_P –5).

The diborenes 2a-c were isolated as yellow solids in varying yields (2a: 76%; 2b: 84%; 2c: 27%), and while 2b and 2c were indefinitely stable at room temperature under inert conditions, the sterically unencumbered trimethylphosphine derivative 2a was found to be very temperature sensitive, decomposing within 30 mins at RT and within a few hours at -30 °C. The instability of 2a precluded its structural authentication, however, the solidstate structures of 2b/2c confirmed their identity as diborenes, with B=B distances (2b: 1.539(8) Å; 2c: 1.546(5) Å) only marginally shorter than those observed in other phosphinestabilized diborenes (1.57-1.59 Å).[3] Interestingly, the average B-P distances of the diborenes 2b,c are significantly shorter than their corresponding tetraiodo precursors (by 4.4% and 3.5%, respectively). The average B-I distances of the diborenes are also shorter than those of their precursors, but to a lesser extent (1.1% for 2b and 1.9% for 2c).

Heating benzene or toluene solutions of 2b for 2 h at 60 °C or 1 h at 80 °C provided no evidence for decomposition by NMR spectroscopy. Longer heating (12 h at 60 °C) induced decomposition to phosphonium salts of the type [Cy₃PH][I] or [Cy₃PH][I₃] as well as free phosphine (among other unidentified products), as detected by ³¹P NMR spectroscopy. The ¹¹B NMR spectrum of this mixture showed new signals corresponding to unknown decomposition products (δ_B = -26 (s), -37 (br s), -43 (br s), -73 (s)). Full decomposition of the diborene can be observed after 48 h at 80 °C. Diborene 2c is even more thermally stable than 2b, showing no signs of decomposition after 24 h at 80 °C. Diborenes 2b,c were also found to remain unchanged after one week in solution in direct sunlight, and 2b requires longer than 2 h under a UV lamp to show discernible decomposition. Overall, aside from the highly unstable (but sterically unprotected) diborene 2a, the diborenes 2b,c show surprising stability given the observed instability of the dibromo analogues, and their presumably reactive B=B, B-P and B-I bonds.



Figure 3. Crystallographically-derived structures of diborane adducts 1a-c, diborenes 2b,c, and diborene reaction products 3-5. Ellipsoids shown at the 50% probability level. Some ellipsoids, all carbon-bound hydrogen atoms and solvent molecules (if present) have been removed for clarity. Selected bond lengths (Å) and angles (°) for 1a: B1-B1' 1.727(7), B1-I1 2.290(5), B1-I2 2.298(5), B1-P1 1.958(5), For 1b: B1-B2 1.766(6), B1-I1 2.293(4), B1-I2 2.304(4), B2-I3 2.294(4), B2-I3 2.304(4), B2-I3 2.294(4), B2-I3 2.294(4), B1-P1 2.013(4), B2-P2 2.027(4). For 1c: B1-B2 1.759(5), B1-I1 2.302(3), B1-I2 2.281(3), B2-I3 2.306(3), B2-I4 2.289(3), B1-P1 1.980(4), B2-P2 1.981(4). For 2b: B1-B2 1.539(7), B1-I1 2.276(5), B2-I2 2.277(5), B1-P1 1.935(6), B2-P2 1.934(6). For 2c: B1-B1' 1.545(4), B1-I1 2.251(3), B1-P1 1.913(3). For 3: B1-B2 1.746(7), B1-B1 2.051(4), B1-B2 2.073(5), B2-B3 2.063(4), B2-B4 2.063(4). For 4: B1-B1' 1.733(4), B1-I1 2.338(4), B1-H2 1.04(3). For 5: B1-2.273(3), B1-H2 1.09(3), B1-H3 1.10(3).

The good yield and ease of handling of 2b led us to use this compound as representative for the class of compounds in reactivity studies. As an initial test, 2b was treated with a slightly sub-stoichiometric amount of iodine, which, after being left for 24 h in an ultrasound bath, showed complete conversion back to the tetraiododiborane adduct 1b (Figure 2; 73% isolated yield), indicating the 1,2-addition of I₂ to the B=B double bond. Addition of a large excess of bromine to 2b provided a new compound with a high-field ¹¹B NMR signal (δ_B –3) and a ³¹P NMR signal $(\delta_P - 8)$ matching those of **1a-c**. NMR spectroscopy, elemental analysis and single-crystal X-ray diffraction allowed identification of the new compound as the tetrabromodiborane adduct $[B_2Br_4(PCy_3)_2]$ (3, Figures 2 and 3), presumably a product of both iodide/bromide exchange and the bromination of the B=B double bond of 2b. Notably, to our knowledge, the reactions of 2b with Br₂/l₂ are the first reported halogenations of B-B double bonds.

Heating a benzene solution of diborene **2b** (δ_B 6; δ_P 8) to 80 °C under 1 atm of H₂ for 1 h led to full conversion to a new product with a ¹¹B NMR signal at δ_B –26. The ³¹P NMR spectrum showed multiple signals indicative of phosphonium salts. The ¹H NMR of the mixture spectra showed a broad signal at δ_H 3.53, which sharpened upon ¹¹B decoupling, indicating the presence of boron-bound hydrogen atoms. The upfield shift of the ¹¹B NMR signal into the typical region of Lewis-base-stabilized tetraiododiboranes ([B₂I₄(PR₃)₂] (R = Me, Cy, CH₂Cy): δ_B –25 to –27), together with the aforementioned signal in the ¹H NMR spectrum led us to assume a 1,2-addition of H₂ across the B=B double bond of **2b**. Removal of the solvent and extraction of the residue with hexane provided a solution from which single crystals of 1,2-dihydro-1,2-diiododiborane adduct [B₂H₂I₂(PCy₃)₂] (**4**, Figures 2 and 3) grew at –30 °C.

Despite the formation of a small batch of crystals of 4, we were unable to reliably isolate the compound due to its instability, precluding its full characterization. All attempts to obtain substantial amounts of the compound by workup under an Ar atmosphere led instead to isolation of its decomposition product, the known monoborane adduct [BH₂I(PCy₃)] (5, Figures 2 and 3; $\delta_{\rm B}$ -37; $\delta_{\rm P}$ 5; isolated yield 54%). The ¹¹B NMR signal at $\delta_{\rm B}$ -37 matches that observed after heating 2b in benzene for 12 h at 60 °C (as described above), thus, the hydrogenation experiment was repeated with D₂ to confirm that the diborene is indeed reacting with dihydrogen and to exclude reaction with the solvent. Heating **2b** for 1 h at 80 °C under one atmosphere of D₂ resulted in a broad signal in the ²H{¹¹B} NMR at δ_D = 3.50 (δ_H = 3.53), confirming reaction with H₂/D₂. It should be noted here that diborynes [LB=BL],^[9] diboracumulenes [L=B=B=L]^[9] and even diboranes(4)^[10] have shown the ability to undergo hydrogenation with H₂, leaving diborenes as the missing link in the hydrogenation chemistry of B-B bonds.

DFT calculations were performed on **2b** and its hypothetical dibromo variant $[B_2Br_2(PCy_3)_2]$ (**2b**') at the OLYP/ZORA/TZ2P level, in an attempt to rationalize the apparent, and surprising, stability of diiododiborenes relative to dibromodiborenes. Despite the differences in the nature of the halides in **2b** and **2b**', almost all key metrics of the two molecules are very similar, including the B-B and B-P distances, the interaction energies concerning fragmentation at the B=B bond, the Hirshfeld charges at B and P, and the HOMO-LUMO gaps. The Hirshfeld charges at I (**2b**; -0.079) and Br (**2b**'; -0.107) are significantly different, however. Such a difference is somewhat to be expected with different elements, however, the lower negative charge at the iodo groups could indicate increased electron donation from I to B in **2b**. While the Mayer bond orders (MBOs) of the B-X interactions

in **2b** (0.89) and **2b'** (0.75) are by no means indicative of strong multiple bonding, the B-X MBO of the iodo variant is significantly (19%) higher than that of the bromo variant. That the B-I bonds of **2b** are significantly stronger than the B-Br bonds of **2b'** – while metrics related to the rest of the molecules remain effectively constant – suggests a rationale for the higher stability of diiododiborenes than dibromodiborenes.



Figure 4. Calculated frontier orbitals of hypothetical dibromodiborene 2b' and isolated diiododiborene 2b.

Inspection of the frontier orbitals of **2b** shows that the HOMO consists of the conventional B-B π interaction, the HOMO-3

represents out-of-phase p orbitals at the iodide groups, and the HOMO–4 is a combination of the in-phase iodide p orbitals with smaller contributions from the boron atoms, making up a delocalized, fully in-phase π system across the I-B-B-I unit (Figure 4). While this π bonding interaction could in principle rationalize the higher stability of **2b** relative to diborenes with the lighter halides, an entirely analogous interaction is found in the HOMO–4 of hypothetical dibromodiborene **2b'**. Interestingly, preliminary calculations suggest that similar fully in-phase X-C-C-X π interactions also exist in the organic analogues *E*-dibromo- and *E*-diiodoethene.

Closer inspection of 2b and 2b' in terms of conceptual DFT (the branch of the discipline that formalizes the extraction of chemically meaningful properties from electron density^[11]) and calculations based on the atoms-in-molecules (AIM)^[12] approach suggests that differences between the two species lie in diiododiborene 2b being 'softer' in the Pearson sense. Indeed, the value of the atomic Fukui function for nucleophilic attack f⁺ of the boron centres is higher in 2b (0.1402) than 2b' (0.111) while for electrophilic attack both have the same reactivity (2b: 0.2919: 2b': 0.2889). Overall, the two diborenes present nucleophilic character as the values of their dual descriptors are both negative, but more so for 2b' (-0.1777) than 2b (-0.1519). This suggests that 2b is more able to accommodate additional negative charge, and conversely there is a higher incentive for 2b' to give away electrons. These points are supported by the Shannon entropy values at the boron atomic basins, which indicate that 2b' (4.641) has a more structured and localized density than 2b (5.364), that is, given the augmented electron flow towards the B-B core in **2b**, higher disorder and entropy are induced. Further descriptors such as Jenkins metallicity indices and the so-called localization $\lambda(A)$ and delocalization $\delta(A, B)$ indices (LI/DI) are all in line with the points discussed above (see Supporting Information). Overall, the results suggest that a BB core like those of 2b and 2b' can impart hardness (or softness) all over a large part of a molecule, which in turn confers additional stability. Given that diborene 2b was experimentally isolated, one can deduce that such stabilization is higher in this diborene given the higher polarizability of the halide centres compared to those of 2b', which is less stable.

Our successful syntheses of phosphine-stabilized diiododiborenes – including even a relatively unprotected PMe₃ derivative – stands in stark contrast to our work with the dibromo analogues, which have thus far resisted isolation even with strong steric shielding. Computational results point to stronger B-X bonding with iodide groups, due likely to their higher polarizability, and the ensuing lower reactivity leading to the observed stabilization of the diiododiborenes. The presented reactivity tests demonstrate the value of maximizing the number of labile bonds in small, low-valent molecules, and showcase a handful of unique compounds able to be deconstructed in a range of different ways, including both their B-B σ and π bonds, as well as the sets of B-P and B-I bonds.

Acknowledgements

Financial support from the European Research Council (ERC) under the European Union Horizon 2020 Research and Innovation Program (grant agreement no. 669054) is gratefully

acknowledged. A.V. thanks the University of Sussex for financial support.

Keywords: boron; low-valent main-group species; iodine; multiple bonding; 1,2-additions

- a) R. Okazaki, R. West, Adv. Organomet. Chem. 1996, 39, 231–273; b)
 M. Kira, J. Organomet. Chem. 2004, 689, 4475–4488; c) M. Kira, T. Iwamoto, Adv. Organomet. Chem. 2006, 54, 73–148; d) A. Rammo, D. Scheschkewitz, Chem. Eur. J. 2018, 24, 6866–6885.
- [2] a) N. Wiberg, W. Niedermayer, G. Fischer, H. Nöth, M. Suter, *Eur. J. Inorg. Chem.* 2002, 1066–1070; b) N. Wiberg, S. K. Vasisht, G. Fischer, P. Mayer, *Z. Anorg. Allg. Chem.* 2004, 630, 1823–1828; c) K. Suzuki, T. Matsuo, D. Hashizume, K. Tamao, *J. Am. Chem. Soc.* 2011, *133*, 19710–19713; d) T. Agou, N. Hayakawa, T. Sasamori, T. Matsuo, D. Hashizume, N. Tokitoh, *Chem. Eur. J.* 2014, *20*, 9246–9249; e) P. Ghana, M. I. Arz, U. Das, G. Schnakenburg, A. C. Filippou, *Angew. Chem. Int. Ed.* 2015, *54*, 9980–9985; f) T. Sugahara, J.–D. Guo, D. Hashizume, T. Sasamori, S. Nagase, N. Tokitoh, *Dalton Trans.* 2018, *47*, 13318–13322; g) P. Ghana, M. I. Arz, U. Chakraborty, G. Schnakenburg, A. C. Filippou, *J. Am. Chem. Soc.* 2018, *140*, 7187–7198.
- a) H. Braunschweig, R. D. Dewhurst, *Angew. Chem. Int. Ed.* 2013, *52*, 3574–3583; b) H. Braunschweig, I. Krummenacher, M.–A. Légaré, A. Matler, K. Radacki, Q. Ye, *J. Am. Chem. Soc.* 2017, *139*, 1802–1805.
- [4] a) H. Braunschweig, R. D. Dewhurst, K. Hammond, J. Mies, K. Radacki, A. Vargas, *Science* **2012**, 336, 1420–1422; b) W. Lu, Y. Li, R. Ganguly, R. Kinjo, *J. Am. Chem. Soc.* **2017**, *139*, 5047–5050; c) A. Stoy, J. Böhnke, J.O.C. Jimenéz-Halla, R. D. Dewhurst, T. Thiess, H. Braunschweig, *Angew. Chem. Int. Ed.* **2018**, *57*, 5947–5951.
- [5] a) M. Soleilhavoup, G. Bertrand, *Acc. Chem. Res.* 2015, *48*, 256–266;
 b) M. Melaimi, R. Jazzar, M. Soleilhavoup, G. Bertrand, *Angew. Chem. Int. Ed.* 2017, *56*, 10046–10068.

- a) H. Braunschweig, P. Bissinger, A. Damme, T. Kupfer, I. [6] Krummenacher, A. Vargas, Angew. Chem. Int. Ed. 2014, 53, 5689-5693; b) 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; c) M. Arrowsmith, J. Böhnke, H. Braunschweig, M. A. Celik, C. Claes, W. C. Ewing, I. Krummenacher, K. Lubitz, C. Schneider, Angew. Chem. Int. Ed. 2016, 55, 11271-11275; d) S. R. Wang, M. Arrowsmith, J. Böhnke, H. Braunschweig, T. Dellermann, R. D. Dewhurst, H. Kelch, I. Krummenacher, J. D. Mattock, J. H. Müssig, T. Thiess, A. Vargas, J. Zhang, Angew. Chem. Int. Ed. 2017, 56, 8009-8013; e) S. R. Wang, M. Arrowsmith, H. Braunschweig, R. D. Dewhurst, V. Paprocki, L. Winner, Chem. Commun. 2017, 53, 11945-11947; f) S. R. Wang, M. Arrowsmith, H. Braunschweig, R. D. Dewhurst, M. Dömling, J. D. C. Pranckevicius, A. Vargas, J. Am. Mattock. Chem. Soc. 2017, 139, 10661-10664; g) T. E. Stennett, J. D. Mattock, I. Vollert, A. Vargas, H. Braunschweig, Angew. Chem. Int. Ed. 2018, 57, 4098-4102; h) T. E. Stennett, J. D. Mattock, L. Pentecost, A. Vargas, H. Braunschweig, Angew. Chem. Int. Ed. online contents, DOI: 10.1002/anie.201809217; i) T. E. Stennett, R. Bertermann, H. Braunschweig, Angew. Chem. Int. Ed. accepted for publication.
- [7] M. Arrowsmith, J. Böhnke, H. Braunschweig, A. Deißenberger, R. D. Dewhurst, W. C. Ewing, C. Hörl, J. Mies, J. H. Müssig, *Chem. Commun.* 2017, 53, 8265–8267.
- [8] H. Braunschweig, R. D. Dewhurst, J. O. C. Jiménez–Halla, E. Matito, J.
 H. Müssig, Angew. Chem. Int. Ed. 2018, 57, 412–416.
- [9] M. Arrowsmith, J. Böhnke, H. Braunschweig, M. A. Celik, T. Dellermann, K. Hammond, *Chem. Eur. J.* 2016, 22, 17169–17172.
- [10] N. Tsukahara, H. Asakawa, K.-H. Lee, Z. Lin, M. Yamashita, J. Am. Chem. Soc. 2017, 139, 2593–2596
- a) R. G. Parr, W. Yang, *Annu. Rev. Phys. Chem.* **1995**, *46*, 701-728; b)
 P. Geerlings, F. de Proft, W. Langenaeker, *Chem. Rev.* **2003**, *103*, 1793-1873.
- a) J. I. Rodriguez, R. F. W. Bader, P. W. Ayers, C. Michel, A. W. Götz,
 C. Bo, *Chem. Phys. Lett.* **2009** 472, 149-152; b) V. Tognetti, L. Joubert,
 Phys. Chem. Chem. Phys. **2014**, *16*, 14539-14550

Entry for the Table of Contents

FULL PAPER



The lability of B=B, B-P and B-halide bonds is combined in the syntheses of the first diiododiborenes. In a series of reactivity tests, these diiododiborenes demonstrate cleavage of all six of their central bonds in different ways.

Jonas H. Muessig, Melanie Thaler, Rian D. Dewhurst, Valerie Paprocki, Jens Seufert, James Mattock, Alfredo Vargas, Holger Braunschweig

Page No. – Page No.

Phosphine-Stabilized Diiododiborenes: Isolable Diborenes with Six Labile Bonds