EDGE ARTICLE

Check for updates

Mild synthesis of diboryldiborenes by diboration of B−B triple bonds†

Tobias Brückner,[ab] Rian D. Dewhurst, [ID] [ab] Theresa Dellermann, [ID] [ab] Marcel Müller[ab] and Holger Braunschweig [ID] *[ab]

A set of diboryldiborenes are prepared by the mild, catalyst-free, room-temperature diboration of the B−B triple bonds of doubly base-stabilized diborynes. Two of the product diboryldiborenes are found to be air- and water-stable in the solid state, an effect that is attributed to their high crystallinity and extreme insolubility in a wide range of solvents.

Introduction

The propensity of polyboron species to form clusters as a way of quenching the natural electron deficiency of boron is now well documented.[1] A consequence of this phenomenon is that networks of hypovalent boron atoms, bound through electron-precise (2e2c, 4e2c or 6e2c) bonds, are extremely difficult to deliberately construct.[2] Thus, a chemistry based on boron chains, analogous to the ubiquitous chain chemistry of carbon, is simply nonexistent. While boranes (BR_3) and diboranes(4) (B_2R_4)[3] are now relatively well studied compounds, even some of the most simple boron analogues of organic species, such as short chains and small cyclic species, are extremely rare and suffer from difficult syntheses. Nöth's syntheses of linear tri-, tetra-, penta- and hexaboranes in 1970 and 1994,[4] which are based on the reductive coupling of haloboranes, still represent some of the only rational synthetic routes to boron chain species, as exemplified in Fig. 1A. However, these synthetic routes rely on somewhat temperamental B–B coupling steps under harsh, functional-group-intolerant reductive conditions, making these reactions likely only possible with diorganylamino-substituted borane precursors. Nöth's boron chains have recently been supplemented by syntheses of B_4 chains using low-valent boron precursors. In 2012 we reported the unexpected transition-metal-templated catenation of four borylene ligands into a B_4 chain (Fig. 1B).[5] In the absence of transition metal templation, Kinjo and coworkers found that diboration of a geminally-base-stabilized B_2 species with

bis(catecholato)diboron (B_2cat_2) provided a highly unusual B_4 chain (Fig. 1C),[6] while in our laboratories, the same reagent led to both 1,1- and 1,2-diborations of doubly base-stabilized diborenes (LRB=BRL) (Fig. 1D).[7]

Another goal of short boron chain chemistry is the synthesis of chains with partially filled π orbitals. In an attempt to prepare such species, in joint work with the groups of Vargas and Ingleson, we recently reported the reductive coupling of boryl-substituted dihaloborane Lewis adducts to form diboryldiborenes featuring significantly conjugated B_4 chains with two π electrons (Fig. 1E).[8] These reactions, while allowing access to these unusual compounds, were hampered by the combination of the relatively labile B–B bond in the precursor and the harsh reductive conditions required. A more convergent and potentially advantageous strategy to prepare diborylated diborenes – as well as other difunctionalized diborenes – would be the direct addition of E–E σ bonds across the B≡B triple bond of diborynes (Fig. 1F).[2] This strategy would eliminate the need for installing various functional groups directly into the Lewis-base-bound dihaloborane precursor $(LB)BX_2(ER_n)$ (LB = Lewis base; ER_n = functional group), as well as circumventing the incompatibility of this functional group with the harsh reduction conditions needed to form the B=B double bond.

The success of such a strategy would require reliable 1,2-addition chemistry of σ-bound E–E species across the B≡B triple bonds. While both doubly base-stabilized diborenes (LRB=BRL) and diborynes (LB≡BL) have shown diverse reactivity with unsaturated species and elemental chalcogens,[2] they have shown only limited propensity to undergo simple 1,2-addition reactions with other σ-bonded species, and often react unpredictably or not at all. In addition to the diboration reactions described above (Fig. 1D), doubly base-stabilized diborenes undergo hydroboration with the hydroborane HBCat; however, application of the more Lewis acidic borane 9-borabicyclo[3.3.1]nonane led instead to disproportionation and

*a*Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany. E-mail: h.braunschweig@uni-wuerzburg.de

*b*Institute for Sustainable Chemistry & Catalysis with Boron, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany
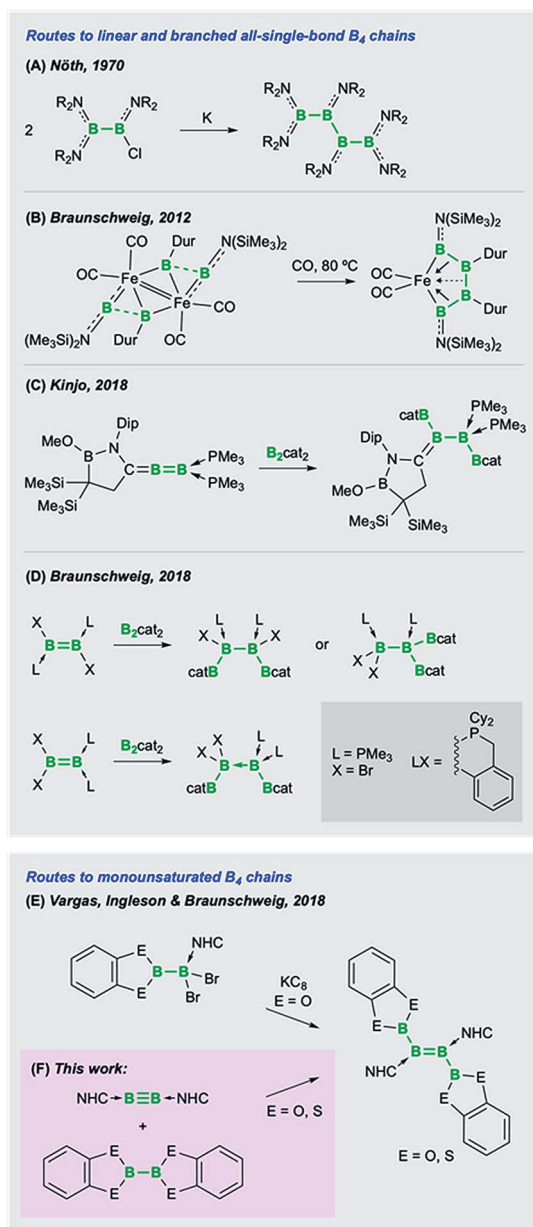
Fig. 1 Synthetic routes to saturated (A–D) and monounsaturated (E and F) B$_4$ chains (NHC = *N*-heterocyclic carbene).

We present herein convergent syntheses of mono-unsaturated B$_4$ chains, doubly base-stabilized diboryldiborenes, by simple, uncatalyzed, room-temperature diboration of boron–boron triple bonds. The products feature linear chains of four sp^2-hybridized boron atoms, with the outer boron atoms possessing varying degrees of coplanarity and conjugation with the central B=B double bonds.

Results and discussion

Combination of the doubly NHC-stabilized diboryne **1a** (Fig. 2) with equimolar amounts of either B$_2$cat$_2$ or bis(dithiocatecholato)diboron (B$_2$Scat$_2$), and stirring in benzene, led to a color change to blue and the emergence of pairs of new ^{11}B NMR spectral signals. Drying of the solution and washing with hexane provided blue solids **2a,b** (Fig. 2), which displayed ^{11}B NMR signals (**2a**: δ 43.0, 27.7; **2b**: δ 69.1, 29.6) differing from those of the precursors **1a** (δ 56), B$_2$cat$_2$ (δ 31), and B$_2$Scat$_2$ (δ 59). The upfield ^{11}B NMR signals of **2a,b** fall at the lower-field end of those of known NHC-stabilized diborenes (δ 18–30),[2,13a] and the pair of signals for **2a** match those of the previously-reported diboryldiborenes bearing Bcat groups (δ 42–44 and 27–28).[8] The observation of single ^{1}H and ^{13}C NMR spectral resonances for the CH$_3$ groups of the NHC donors indicated the symmetry of the molecule in solution. High-resolution LIFDI mass spectrometry confirmed the molecular formulae of **2a,b** corresponding to the 1 : 1 addition of the precursor diborane to diboryne **1a**.

The combination of diboryne **1b**, featuring unsymmetrically substituted NHC donors, with either B$_2$cat$_2$ or B$_2$Scat$_2$ led to a color change from red to brown and the precipitation of orange and red crystals, respectively (**2c,d**; Fig. 2). High-resolution LIFDI mass spectrometry and elemental analysis performed on these crystals again indicated 1 : 1 addition of the diborane to **1b**. The crystals of **2c,d** proved to be highly insoluble, allowing only partial characterization of **2c** by solution ^{1}H and ^{11}B NMR spectroscopy and precluding solution NMR spectroscopy for **2d**. Diborene **2c** showed a broad ^{11}B NMR signal at δ 26, but the remaining signal could not be identified

cluster formation.[9] The only other confirmed 1,2-addition to a diborene consisted of an unexpected intramolecular C–H addition across the B=B bond.[10] Like diborenes, diborynes have also shown a marked reluctance to undergo conventional 1,2-additions with labile σ-bonded species. Hydrogenation of diborynes has been demonstrated with some diborynes but appears not to take place with others.[11] In 2016 we reported that combination of diaryl ditellurides ArTeTeAr (Ar = Ph, 4-C$_6$H$_4$F) to a diboryne resulted in addition of only one "TeAr" fragment to the B$_2$ unit and formation of an aryltelluride salt.[12] However, the lighter diorganyldichalogenides were more recently found to undergo conventional 1,2-additions across diborynes, producing either diborenes or diradical products.[13]
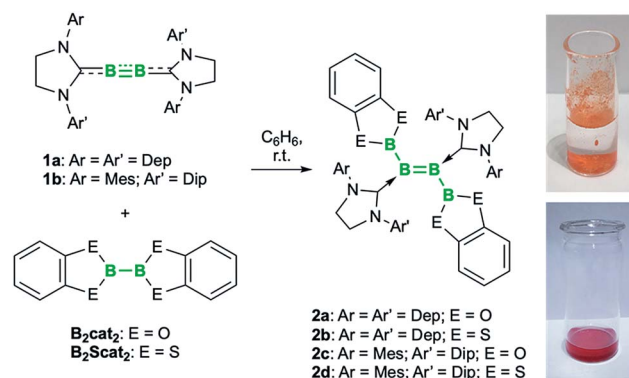

Fig. 2 Catalyst-free diboration of diborynes. Inset photos: suspensions of diborenes **2c** (top) and **2d** (bottom) in water under ambient atmosphere. Dip = 2,6-diisopropyl-phenyl; Dep = 2,6-diethylphenyl.
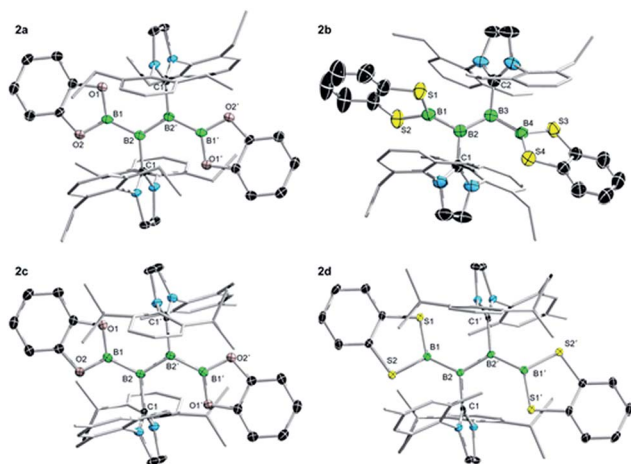
Fig. 3 Crystallographically derived structures of **2a–d**. Ellipsoids shown at the 50% probability level. Some ellipsoids and all hydrogen atoms and solvent molecules (one molecule of C_6H_6 in **2c**) have been removed for clarity. Selected bond lengths (Å) and angles (°) for **2a**: B1–B2 1.650(3), B2–B2′ 1.605(3), O1–B1–B2–B2′ 15.9(3). For **2b** (two molecules in unit cell): B1–B2 1.685(4), 1.691(4), B2–B3 1.617(3), 1.619(3), B3–B4 1.689(4), 1.687(4), S1–B1–B2–B3 48.9(3), 52.9(3), S3–B4–B3–B2 53.6(3), 50.3(3). For **2c**: B1–B2 1.652(2), B2–B2′ 1.608(3), O1–B1–B2–B2′ 19.4(2). For **2d**: B1–B2 1.664(2), B2–B2′ 1.627(2), O1–B1–B2–B2′ 29.8(2).

due to the low concentration of the sample. Unfortunately, attempts to record solid-state MAS NMR spectra of **2d** provided either no signal (without rotation) or resulted in decomposition of the sample under the pressure created by the sample rotation.

Single-crystal X-ray diffraction analysis of **2a–d** provided final confirmation of the structures of the products (Fig. 3). While all four compounds show relatively long B=B double bonds (**2a**: 1.605(3) Å; **2b**: 1.617(3), 1.619(3) Å; **2c**: 1.608(3) Å; **2d**: 1.627(2) Å) that could be indicative of increased π conjugation with the outer boron atoms, the Bcat and BScat groups show a relatively broad range of E–B–B=B torsion angles (16–54°), the larger of which indicate strong non-coplanarity and thus discount the presence of significant π conjugation in the solid state. The outer B–B bond distances of **2a–d** (**2a**: 1.650(3) Å; **2b**: 1.685(4), 1.691(4), 1.689(4), 1.687(4) Å; **2c**: 1.652(2) Å; **2d**: 1.664(2) Å) are in line with those of the previously-reported diboryldiborenes (1.65–1.68 Å).

We were surprised to observe that while the SIDep-substituted diborenes **2a,b** decompose within 15 minutes in air, diborenes **2c,d** are stable for days in the solid state in ambient air and even as a suspension in water (Fig. 2, inset photos). Although the appearance of solid **2c** remains unchanged, a small boronic acid signal can be observed in the ^1H and ^{11}B NMR spectra after approximately one week in D_2O. These suspensions gradually decolorize within one hour upon addition of CH_2Cl_2, into which the diborenes are slowly solubilized and decomposed. As diborenes **2a–d** are relatively similar in terms of electronics and sterics, the remarkable solid-state stability of **2c,d** is likely a consequence of their high crystallinity. Once dissolved, even in miniscule amounts, the compounds quickly decompose in the presence of moisture.

The UV-vis spectra of the diboryldiborenes **2** are remarkably different in their features (see ESI†). The spectrum of the orange compound **2c** (λ 451 nm) resembles that of the previously-reported yellow diboryldiborene[8] [(IMe)(catB)B=B(Bcat)(IMe)] (IMe = 1,3-dimethylimidazol-2-ylidene; $λ_{max}$ = 435 nm), both having low-wavelength features and no absorption in the longer wavelength region. However, the other three diborenes **2a,b,d** have significant absorptions in the region 550–650 nm (**2a**: λ 422, 578 (max.) nm; **2b**: λ 503, 608 (max.) nm; **2d**: λ 543 (max.), 622 nm). Overall the longer wavelength absorptions of **2a–d** relative to those of [(IMe)(catB)B=B(Bcat)(IMe)] suggest that the more σ-donating and π-withdrawing saturated-backbone NHCs in the former lead to significant decreases in the HOMO–LUMO gaps of the molecules.

It should also be noted that, in an attempt to induce double diboration, the diborynes **1a,b** were treated with two molar equivalents of the diboranes B_2cat_2 and B_2Scat_2. However, after monitoring conversion to the respective diboryldiborenes **2a,b**, no further reaction was observed, even with heating (100 °C) or under photolytic conditions.

Conclusions

The diboryne diboration reactions herein provide convergent access to monounsaturated boron chains and provide a new tool in the challenging construction of electron-precise B–B bonds. Moreover, the high stability of the bulky diboryldiborene products is very encouraging. The extreme sensitivity generally shown by diborenes is the main practical impediment towards their use as "π superdonor" units in molecular electronic materials, thus the discovery of derivatives able to withstand air and water – even if only in the solid state – is a significant step forward.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

1 (a) A. Stock, *Hydrides of Boron and Silicon*, Cornell Univ. Press, Ithaca, NY, 1933; (b) W. N. Lipscomb, *Adv. Inorg. Chem.*, 1959, **1**, 117–156; (c) K. Wade, *J. Chem. Soc., Chem. Commun.*, 1971, 792–793; (d) R. E. Williams, *Inorg. Chem.*, 1971, **10**, 210–214; (e) M. A. Fox and K. Wade, *Pure Appl. Chem.*, 2003, **75**, 1315–1323; (f) E. Osorio, J. K. Olson, W. Tiznado and A. I. Boldyrev, *Chem.–Eur. J.*, 2012, **18**, 9677–9681.

2 (a) K. Nozaki, Y. Aramaki, M. Yamashita, S.-H. Ueng, M. Malacria, E. Lacôte and D. P. Curran, *J. Am. Chem. Soc.*, 2010, **132**, 11449–11451; (b) H. Braunschweig and R. D. Dewhurst, *Angew. Chem., Int. Ed.*, 2013, **52**, 3574–3583; (c) M. Arrowsmith, H. Braunschweig and T. E. Stennett, *Angew. Chem., Int. Ed.*, 2017, **56**, 96–115.

3 (a) E. C. Neeve, S. J. Geier, I. A. I. Mkhalid, S. A. Westcott and T. B. Marder, *Chem. Rev.*, 2016, **116**, 9091–9161; (b) D. G. Hall, *Boronic Acids: Preparation, Applications in Organic Synthesis and Medicine*, Wiley-VCH, Weinheim, 2005.

4 (a) K. H. Hermannsdörfer, E. Matejčikova and H. Nöth, *Chem. Ber./Recl.*, 1970, **103**, 516–527; (b) G. Linti, D. Loderer, H. Nöth, K. Polborn and W. Rattay, *Chem. Ber.*, 1994, **127**, 1909–1922.

5 H. Braunschweig, Q. Ye, A. Vargas, R. D. Dewhurst, K. Radacki and A. Damme, *Nat. Chem.*, 2012, **4**, 563–567.

6 W. Lu, Y. Li and R. Kinjo, *Angew. Chem., Int. Ed.*, 2018, **57**, 15691–15695.

7 T. E. Stennett, R. Bertermann and H. Braunschweig, *Angew. Chem., Int. Ed.*, 2018, **57**, 15896–15901.

8 A. Hermann, J. Cid, J. D. Mattock, R. D. Dewhurst, I. Krummenacher, A. Vargas, M. J. Ingleson and H. Braunschweig, *Angew. Chem., Int. Ed.*, 2018, **57**, 10091–10095.

9 (a) H. Braunschweig, R. D. Dewhurst, C. Hörl, A. K. Phukan, F. Pinzner and S. Ullrich, *Angew. Chem., Int. Ed.*, 2014, **53**, 3241–3244; (b) H. Braunschweig and C. Hörl, *Chem. Commun.*, 2014, **50**, 10983–10985.

10 S. R. Wang, M. Arrowsmith, H. Braunschweig, R. D. Dewhurst, V. Paprocki and L. Winner, *Chem. Commun.*, 2017, **53**, 11945–11947.

11 M. Arrowsmith, J. Böhnke, H. Braunschweig, M. A. Celik, T. Dellermann and K. Hammond, *Chem.–Eur. J.*, 2016, **22**, 17169–17172.

12 H. Braunschweig, P. Constantinidis, T. Dellermann, W. C. Ewing, I. Fischer, M. Hess, F. R. Knight, A. Rempel, C. Schneider, S. Ullrich, A. Vargas and J. D. Woollins, *Angew. Chem., Int. Ed.*, 2016, **55**, 5606–5609.

13 (a) J. Böhnke, T. Dellermann, M. A. Celik, I. Krummenacher, R. D. Dewhurst, S. Demeshko, W. C. Ewing, K. Hammond, M. Heß, E. Bill, E. Welz, M. Röhr, R. Mitrić, B. Engels, F. Meyer and H. Braunschweig, *Nat. Commun.*, 2018, **9**, 1197; (b) E. Welz, J. Böhnke, R. D. Dewhurst, H. Braunschweig and B. Engels, *J. Am. Chem. Soc.*, 2018, **140**, 12580–12591.