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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 electronprecise (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, reactions likely only possible making these with diorganylamino-substituted borane precursors. Nöth's boron chains have recently been supplemented by syntheses of B₄ chains using low-valent boron precursors. In 2012 we reported the unexpected transition-metal-templated catenation of four borylene ligands into a B₄ chain (Fig. 1B).⁵ In the absence of transition metal templation, Kinjo and coworkers found that diboration of a geminally-base-stabilized B₂ species with

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

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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.

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

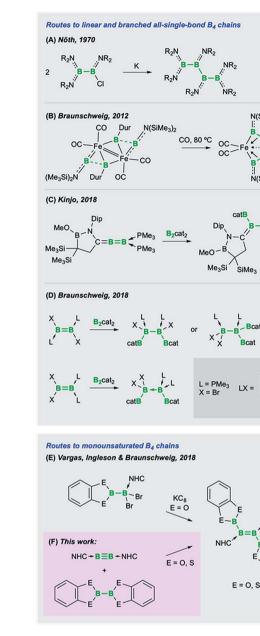
Another goal of short boron chain chemistry is the synthesis of chains with partially filled π orbitals. In an attempt to prepare such species, in joint work with the groups of Vargas and Ingleson, we recently reported the reductive coupling of boryl-substituted dihaloborane Lewis adducts to form diboryldiborenes featuring significantly conjugated B4 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 1,2addition chemistry of σ -bound E–E species across the B \equiv B triple bonds. While both doubly base-stabilized diborenes (LRB=BRL) and diborynes (LB \equiv BL) have shown diverse reactivity with unsaturated species and elemental chalcogens,² they have shown only limited propensity to undergo simple 1,2addition 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

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N(SiMe₃)₂

R

N(SiMe₃)₂

PMe₃

Bcat

NHC

Fig. 1 Synthetic routes to saturated (A–D) and monounsaturated (E and F) B_4 chains (NHC = N-heterocyclic carbene).

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-C₆H₄F) to a diboryne resulted in addition of only one "TeAr" fragment to the B₂ 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 We present herein convergent syntheses of monounsaturated B_4 chains, doubly base-stabilized diboryldiborenes, by simple, uncatalyzed, room-temperature diboration of boronboron triple bonds. The products feature linear chains of four sp²-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 B₂cat₂ or bis(dithiocatecholato)diboron (B₂Scat₂), and stirring in benzene, led to a color change to blue and the emergence of pairs of new ¹¹B NMR spectral signals. Drying of the solution and washing with hexane provided blue solids 2a,b (Fig. 2), which displayed ¹¹B NMR signals (2a: δ 43.0, 27.7; 2b: δ 69.1, 29.6) differing from those of the precursors **1a** (δ 56), B₂cat₂ (δ 31), and B₂Scat₂ (δ 59). The upfield ¹¹B 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 ¹H and ¹³C NMR spectral resonances for the CH₃ 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_2cat_2 or B_2Scat_2 led to a color change from red to brown and the precipitation of orange and red crystals, respectively (**2c,d**; Fig. 2). Highresolution 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 ¹H and ¹¹B NMR spectroscopy and precluding solution NMR spectroscopy for **2d**. Diborene **2c** showed a broad ¹¹B NMR signal at δ 26, but the remaining signal could not be identified

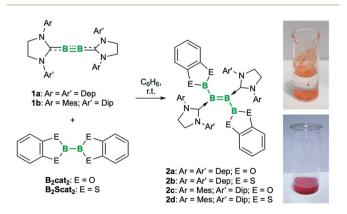


Fig. 2 Catalyst-free diboration of diborynes. Inset photos: suspensions of diborenes 2c (top) and 2d (bottom) in water under ambient atmosphere. Dip = 2,6-diisopropyl-phenyl; Dep = 2,6-diethylphenyl.

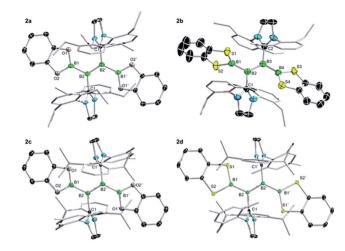


Fig. 3 Crystallographically derived structures of **2a–d**. Ellipsoids shown at the 50% probability level. Some ellipsoids and all hydrogen atoms and solvent molecules (one molecule of C_6H_6 in **2c**) have been removed for clarity. Selected bond lengths (Å) and angles (°) for **2a**: B1–B2 1.650(3), 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 SIDepsubstituted 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 ¹¹B NMR spectra after approximately one week in D₂O. 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 solidstate 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 previouslyreported yellow diboryldiborene⁸ [(IMe)(catB)B=B(Bcat)(IMe)] (IMe = 1,3-dimethylimidazol-2-ylidene; $\lambda_{max} = 435$ 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

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