Introduction

The propensity of polyboron species to form clusters as a way of quenching the natural electron deficiency of boron is now well documented. A consequence of this phenomenon is that networks of hypervalent boron atoms, bound through electron-precise (2e2c, 4e2c or 6e2c) bonds, are extremely difficult to deliberately construct. Thus, a chemistry based on boron chains, analogous to the ubiquitous chain chemistry of carbon, is simply nonexistent. While boranes (BR₃) and diboranes(4) (B₂R₄) 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, 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 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). In the absence of transition metal templation, Kinjo and coworkers found that diboration of a geminally-base-stabilized B₂ species with bis(catecholato)diboron (B₂cat₂) provided a highly unusual B₄ chain (Fig. 1C), while in our laboratories, the same reagent led to both 1,1- and 1,2-diborations of doubly base-stabilized diborynes (LRB=BRL) (Fig. 1D). A set of diboryldiborenes is 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.
We present herein convergent syntheses of mono-unsaturated \( \text{B}_4 \) chains, doubly base-stabilized diboryldiborenes, by simple, uncatalyzed, room-temperature diboration of boron–boron triple bonds. The products feature linear chains of four \( \text{sp}^3 \)-hybridized boron atoms, with the outer boron atoms possessing varying degrees of coplanarity and conjugation with the central \( \text{B}–\text{B} \) double bonds.

## Results and discussion

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

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

![Fig. 1] Synthetic routes to saturated (A–D) and monounsaturated (E and F) \( \text{B}_4 \) chains (NHC = \( N \)-heterocyclic carbene).

![Fig. 2] Catalyst-free diboration of diborynes. Inset photos: suspensions of diborenes \( 2\text{c} \) (top) and \( 2\text{d} \) (bottom) in water under ambient atmosphere. Dip = 2,6-disopropyl-phenyl; Dep = 2,6-diethylphenyl.

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=E 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 $^1$H and $^11$B NMR spectra after approximately one week in D$_2$O. These suspensions gradually decolorize within one hour upon addition of CH$_2$Cl$_2$, into which the diborenes are slowly solubilized and decomposed. As diborenes 2a–d are relatively similar in terms of electronics and steric, the remarkable solid-state stability of 2c,d is likely a consequence of their high crystallinity. Once dissolved, even in minuscule 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 ($\lambda$ 451 nm) resembles that of the previously-reported yellow diboryldiborene$^8$ ([IMe]catB=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: $\lambda$ 422, 578 (max.) nm; 2b: $\lambda$ 503, 608 (max.) nm; 2d: $\lambda$ 543 (max.), 622 nm). Overall the longer wavelength absorptions of 2a–d relative to those of ([IMe]catB=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 diboranes 1a,b,c were treated with two molar equivalents of the diboranes B$_2$cat$_2$ and B$_2$Scat$_2$. However, after monitoring conversion to the respective diboryldiborenes 2a,b,c, no further reaction was observed, even with heating (100 °C) or under photolytic conditions.

Conclusions

The diborone 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 diboryldiborone 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.

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Notes and references


