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.

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 hypovalent 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 (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 diorganylamin-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). 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). 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). This strategy would eliminate the need for installing various functional groups directly into the Lewis-base-bound dihaloborane precursor (LB=BRL) (LB = Lewis base; ERn = 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, 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...
We present herein convergent syntheses of mono-unsaturated B₄ chains, doubly base-stabilized diboryldiborenes, by simple, uncatalyzed, room-temperature diboration of boron-boron 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(dithiocatecholate) diboron (B₂Scat₂), 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: $\delta$ 43.0, 27.7; 2b: $\delta$ 69.1, 29.6] differing from those of the precursors 1a ($\delta$ 56), B₂cat₂ ($\delta$ 31), and B₂Scat₂ ($\delta$ 59). The upfield $^{11}$B NMR signals of 2a, b fall at the lower-field end of those of known NHC-stabilized diborenes ($\delta$ 18–30), ²,³ and the pair of signals for 2a match those of the previously-reported diboryldiborenes bearing Bcat groups ($\delta$ 42–44 and 27–28).⁸ The observation of single $^1$H and $^{13}$C 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 B₂cat₂ or B₂Scat₂ 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 $\delta$ 26, but the remaining signal could not be identified.
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 $\pi$ conjugation with the outer boron atoms, the Bcat and BScat groups show a relatively broad range of E–B–B torsion angles ($16^\circ$–$54^\circ$), the larger of which indicate strong non-coplanarity and thus discount the presence of significant $\pi$ 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 diboryldiborennes (1.65–1.68 Å).

We were surprised to observe that while the SIDep-substituted diborennes 2a,b decompose within 15 minutes in air, diborennes 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 diborennes are slowly solubilized and decomposed. As diborennes 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 miniscule amounts, the compounds quickly decompose in the presence of moisture.

The UV-vis spectra of the diboryldiborennes 2 are remarkably different in their features (see ESIT). The spectrum of the orange compound 2c ($\lambda$ 451 nm) resembles that of the previously-reported yellow diboryldiborennes $[(\text{IMe})(\text{catB})B=\text{B}(\text{Bcat})(\text{IMe})]$ (IMe = 1,3-dimethylimidazol-2-ylidene; $\lambda_{\text{max}}$ = 435 nm), both having low-wavelength features and no absorption in the longer wavelength region. However, the other three diborennes 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 $[(\text{IMe})(\text{catB})B=\text{B}(\text{Bcat})(\text{IMe})]$ suggest that the more $\sigma$-donating and $\pi$-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$_2$cat$_2$ and B$_2$Scat$_2$. However, after monitoring conversion to the respective diboryldiborennes 2a,b, no further reaction was observed, even with heating ($100^\circ$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 diboryldiborenne products is very encouraging. The extreme sensitivity generally shown by diborennes is the main practical impediment towards their use as “$\pi$ 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**

Financial support for this project was provided by the European Research Council (ERC) under the European Union Horizon 2020 Research and Innovation Program (Advanced Grant agreement no. 669054). The authors also thank Allychem Co., Ltd. (Dalian, China) for a generous gift of B$_2$cat$_2$ and Mr Dominic Prieschl for photography.

**Notes and references**


