Diboryldiborenes: \( \pi \)-Conjugated B\(_4\) Chains Isoelectronic to the Butadiene Dication

Alexander Hermann, Jessica Cid, James D. Mattock, Rian D. Dewhurst, Ivo Krummenacher, Alfredo Vargas,* Michael J. Ingleson,* Holger Braunschweig*

Abstract: \( sp^2–sp^3 \) diborane species based on bis(catecholato) dibor and N-heterocyclic carbenes (NHCs) are subjected to catechol/bromide exchange selectively at the \( sp^3 \) boron atom. The reduction of the resulting 1,1-dibromodiborane adducts led to reductive coupling and isolation of doubly NHC-stabilized 1,2-diboryldiborenes. These compounds are the first examples of molecules exhibiting \( \pi \)-electron delocalization over an all-boron chain.

Molecules featuring two-atom 2\( \pi \)-electron systems (e.g. alkenes, diazo compounds) are well known. However, addition of further \( \pi \) orbitals to a 2\( \pi \)-electron system makes the resulting molecules less stable and consequently much rarer. While aromatic, cyclic three-atom 2\( \pi \)-electron systems such as cyclopentadiene cations (cyclo-[C\( _5 \)R\( _2 \)\( ^\bullet \)]) and borirenes (cyclo-[B\( _5 \)C\( _3 \)R\( _2 \)\( ^\bullet \)]) are relatively stable, acyclic examples such as the allyl cation ([C\( _3 \)R\( _2 \)\( ^\bullet \)])\(^{[1]} \) its trisila analogue ([Si\( _3 \)R\( _2 \)\( ^\bullet \)])\(^{[4]} \) cyclo-(E\( _5 \)R\( _2 \)) diamions (\( E = B, Ga \))\(^{[5]} \) and a triborane(3)\(^{[6]} \) are either transient or highly reactive. Adding a further empty \( \pi \) orbital, resulting in a four-atom 2\( \pi \)-electron system, is even less favorable in terms of stability. Syntheses of cyclobutadiene dications (\( A \), Figure 1) have been reported;\(^{[8]} \) however, despite their nominal aromaticity, their instability has precluded structural authentication. Neutral, Group 13 analogues of cyclobutadiene dications, such as 1,3-diboretes (\( B \), Figure 1)\(^{[8]} \) and a 1,2-dialuminacyclobutene (\( C \))\(^{[9]} \) have been structurally confirmed, although both feature strongly puckered structures suggesting reduced delocalization and aromaticity.

The relative instability of these cyclic, formally aromatic species makes it somewhat unsurprising that acyclic compounds featuring conjugated, four-atom 2\( \pi \)-electron systems are even less well represented. The generation of the butadiene dication ([C\( _4 \)R\( _2 \)\( ^\bullet \)])\(^{[10]} \) – the acyclic derivative of \( A \) – has been inferred by its decomposition products after double photoisomerization of butadiene. However, such a species has thus far not been isolated.\(^{[10]} \) While diboryl olefins such as \( E \) (Figure 1) almost exclusively feature non-coplanar B\(_2\)C\(_2\) units, one example (E-CatBC(H)(C)(H)BCat) has been uncovered with a coplanar B\(_2\)C\(_2\) unit.\(^{[11]} \) A dihydrodiborane species stabilized by two strongly \( \pi \)-withdrawing cyclic (alkyl)(amino)carbene\(^{[12]} \) (CAAC\(^{[13]}\)) donors (\( F \), Figure 1)\(^{[13-15]} \) is a further example of a

---

\(^{[1]} \) A. Hermann, Dr. R. D. Dewhurst, Dr. I. Krummenacher, Prof. Dr. 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. Cid, Dr. M. J. Ingleson
School of Chemistry, University of Manchester
Manchester, United Kingdom
E-Mail: michael.ingleson@manchester.ac.uk

J. D. Mattock, Dr. A. Vargas
Department of Chemistry, School of Life Sciences, University of Sussex, Brighton BN1 9QJ, Sussex, United Kingdom
E-Mail: alfredo.vargas@sussex.ac.uk

Supporting information for this article is given via a link at the end of the document.
four-atom (B₂C₄) 2π-electron system. The extreme rarity of molecules with conjugated four-atomic 2π-electron systems thus makes the isolation of such compounds a worthy synthetic goal.

Chains of sp²-hybridized boron atoms by definition have a contiguous π system comprising the p orbitals of the boron atoms, although the degree to which these orbitals are conjugated will likely be attenuated by steric concerns and the π-donor strength of the atoms attached to the boron atoms. Nevertheless, such compounds present the exciting possibility of filling (or partially filling) their extended π systems with electrons. Such a goal is as yet unrealized, as compounds with B(sp²) chains are exceedingly rare and difficult to prepare. Only five structurally-characterized compounds exist containing a chain (or ring) of four or more tricoordinate boron atoms, the longest being the cyclo-hexaborane B₆(NMe₂)₆.[16] While all of these compounds feature electronic stabilization from π-donor substituents, none of them feature π electrons in the Bπ system or any degree of B-B multiple bonding.

In this work we present the synthesis of doubly carbene-stabilized diboryl diborenes, of the form [Br(BCat)(NHC)₂] (BCat = catecholboryl; NHC = N-heterocyclic carbene; G, Figure 1). In these compounds, the two diborene π electrons are significantly delocalized towards the adjacent boryl groups, leading to a reduced central B-B bond order and increased outer B-B bond orders. The compounds are very rare examples of acyclic compounds featuring conjugated four-atomic 2π-electron systems and the first examples of molecules exhibiting π-electron delocalization over an all-boron chain.

The addition of a single molar equivalent of a strong donor ligand to diboranes(4) has recently become an area of interest in organoboron chemistry, leading in many cases to sp³–sp³ diborane species with nucleophilic boron atoms.[17] In 2015, Ingleson, Radius and Marder reported that reaction of equimolar amounts of bis(catecholato)diboron (B₂Cat₂) with the relatively small and strongly α-donating NHC 1,3,4,5-tetramethylimidazol-2-ylidine (IMeMe) provided the sp²–sp³ diborane 1a (Figure 2).[18] The stability of this species led us to attempt the exchange of one of its catecholyl groups with halides, in order to open up one or both boron atoms for further functionalization. Thereby, equimolar amounts of 1a and BB₃ were combined at −30°C, providing a colorless solid (2a) with ¹¹B NMR spectroscopic signals at δ 36.3 and −13.7. While the position of the low-field signal of 2a is little changed from that of its precursor 1a (δ 38.6, 7.11), the high-field signal has shifted significantly upfield, suggesting that catechol/halide exchange had occurred exclusively at one boron atom.

These synthetic protocols were extended to the synthesis of three further sp²–sp³ diboranes, 1b–d (Figure 2), bearing NHCS 1,3-dimethylimidazol-2-ylidine (Ime), 1,3-diisopropylimidazol-2-ylidine (iPr), and 1,3-dimethylimidazol-2-ylidine (IMes), respectively. The dicatechol sp²–sp³ diboranes 1b–d[19] were subsequently subjected to catechol/halide exchange, forming dibromo sp²–sp³ diboranes 2b–d (Figure 2) in excellent yields (82-99%). The dicatechol sp²–sp³ diboranes 1b–d showed ¹¹B NMR spectral features analogous to those of 1a (1b: δ 37.1, 6.82; 1c: δ 37.6, 7.43; 1d: δ 35.2, 5.90). Likewise, the ¹¹B NMR data of dibromo sp²–sp³ diboranes 2b–d matched those of 2a (2b: δ 36.5, −14.7; 2c: δ 36.0, −14.0; 2d: δ 35.3, −14.7). The crystallographically-derived solid-state structures of 2a–c (Figure 3) confirmed the successful catechol/halide exchange.

The synthesis of dibromocatechol diborane adducts 2a–d provided promising precursors for their chemical reduction. Reduction of NHC-stabilized dihalodiboranes is to date the most reliable method to prepare doubly NHC-stabilized diboranes.[13,14] However, extending this reduction strategy to their diborane analogues, 1,1-dihalo-1-NHC-diboranes, has thus
far only led to C-H activated diborane(5) products with bridging organic and hydride groups.\textsuperscript{[20]} We reasoned that by avoiding the use of IMes bound at or near the B=B site, we may be able to circumvent the C-H activation pathway and generate the hypervalent reduction products, either the doubly NHC-stabilized diborane or perhaps even the corresponding carbene-stabilized borylborylene invoked in previous studies.\textsuperscript{[20]}

Reduction of mesityl-free sp\textsuperscript{2}-sp\textsuperscript{3} diboranes 2a-c provided highly-colored reaction mixtures and orange (3a, Figure 2) or bright yellow (3b,c) solids after filtration and crystallization in modest to good yields (26-76\%). However, it should be noted that all samples contained small amounts of unidentified byproducts originating from the reduction process. These impurities could not be removed by recrystallization (with prolonged storage in solution leading to decomposition of 3a-c) or other methods. The \textsuperscript{11}B NMR spectra of the solids each showed two broad singlets (3a: δ 43.5, 27.1; 3b: δ 41.9, 27.5; 3c: δ 42.1, 27.2). The high-field signal of each compound can be attributed to the diborane boron nuclei, although this signal is found slightly to lower field than those of reported diboranes bearing conventional NHC donors (i.e. with unsaturated backbones; ca. δ 19-25).\textsuperscript{[13,14]} Interestingly, the \textsuperscript{11}B NMR resonances of the -BCat boron nuclei are shifted to low field upon reduction, suggesting depletion of electron density at these centers.

The solid-state structures of 3a-c (Figure 4) confirm the reductive coupling of two diboronic units to form effectively coplanar B\textsubscript{3} chains, with very acute angles between the C1B2B2 and C1B1O2 planes (3a: θ 7.0°; 3b: 13.9°; 3c: 10.5°). The diboranes show short central B-B bonds (3a: 1.582(4) Å; 3b: 1.592(9) Å; 3c: 1.596(4) Å), with longer outer B-B bonds (3a: 1.658(3) Å; 3b: 1.676(6) Å; 3c: 1.645(3) Å). While the B=B distances of 3a-c are indistinguishable with those of other doubly NHC-stabilized diboranes with experimental uncertainty,\textsuperscript{[14]} the outer B-B bonds are slightly shorter than those of precursors 2a-c (2a: 1.681(5) Å; 2b: 1.699(4) Å; 2c: 1.788(4) Å). The B=B distances of 3a-c are, however, significantly shorter than that of a diborane stabilized by two strongly π-withdrawing cyclic (alkyl)(amino)carbene (CAAC) donors and featuring significant delocalization over the B\textsubscript{2}C\textsubscript{2} unit (1.625(2) Å).\textsuperscript{[15]}

In order to quantify the extent of delocalization of B=B π electron density towards the π-withdrawing BCat groups, Kohn-Sham Density Functional Theory (DFT) calculations on 3a-c were undertaken at the OLYP/TZ2P level. The calculated Mayer bond orders of the central B=B bonds of 3a-c (3a: 1.480; 3b: 1.477; 3c: 1.479) lie between those of iso-propyl- and 2-thienyl-substituted diboranes [B\textsubscript{3}Pr\textsubscript{3}(HPr\textsubscript{3})] (I: 1.632) and [B\textsubscript{3}(2-C-H=S)(HPr\textsubscript{3})] (II: 1.424), respectively, calculated for comparison (see Supporting Information). Where the diboryldiboranes 3a-c significantly differ from the non-boryl examples I and II is in the Hirshfeld charge at the B=B atoms (3a: 0.173; 3b: 0.172; 3c: 0.169; I: 0.124; II: 0.116). The much more negative charge on the B atoms of 3a-c can be ascribed to the better η-donating properties of the attached boryl groups.

As a measure of conjugation across the B\textsubscript{3} chain, the outer B-B bonds were calculated to have orders above unity (3a: 1.141; 3b: 1.128; 3c: 1.141), suggesting significant B\textsuperscript{inn}-B\textsuperscript{outer} multiple bonding and/or enhanced η-bonding due to the strongly η-donating BCat units. The calculated HOMO levels of 3a-c effectively comprise the 2π-electron system stretched across the B\textsubscript{3} chain (Figure 5), while the energies of these orbitals (3a: −3.104 eV; 3b: −3.283 eV; 3c: −3.229 eV) are significantly lower than those of NHC-bound alkyl and aryl diboranes (I: −2.094 eV; II: −2.660 eV). The low HOMO energies of 3a-c are also reflected electrochemically, in the fact that 3b (∼0.95 V, see Supporting Information) is substantially more difficult to oxidize than other NHC-bound diboranes (e.g. I: −1.95 V; [B\textsubscript{3}D\textsubscript{3}Me\textsubscript{3}] 1−1.55 V).\textsuperscript{[21]} As boryl units are known to be extremely strong electron-withdrawing donors, one would expect the HOMO levels of 3a-c to be destabilized,
similar to that of the alkyl-substituted diborane I. That the HOMOs of 3a–c are instead strongly stabilized suggests that the π donation from the B–B bond to the outer boron atoms outweighs the σ donation of the latter. Overall, the σ-acceptor / π-donor properties of the B=B unit are in line with the previously-discussed ability of hypovalent boron atoms to act as multismetry (i.e. α/π) charge-flux-mediating centers.[2,22]

As expected, analogous reduction of mesityl-containing sp2–sp3 dibromodiborane 2d led to C–H activation at one of the proximal methyl groups and formation of 4 (Figure 2), as evidenced by the absence of a highly colored reaction mixture, and by 11B NMR spectroscopy, which showed a clear doublet at high field due to B–H coupling (δ = −33.0; 1JBH = 73.4 Hz) along with a broad singlet at low field (δ = 42.1). Interestingly, the former signal is found significantly upfield, and the latter significantly downfield, of the corresponding signals of 2d (δ = 53.1, 1.5 and δ = 55.8, 2.6).[20] The solid-state structure of 4 (Figure 4) confirmed the C–H activation process and the presence of an unbridged B–B unit.

In conclusion, we have presented the synthesis of new sp2–sp3 diborane species based on bis(catecholato)diboron, their catechol/halide exchange products, and the reductive coupling products of the latter: doubly NHC-stabilized 1,2-diboryldiboranes. These compounds are the first examples of molecules exhibiting π-electron delocalization over an all-boron chain. The observed π-delocalization in these B= chains is an exciting discovery which points to the possible future synthesis of extended π-conjugated boron chains and polymers with interesting electronic properties. Furthermore, the presence of two BCat groups in these molecules presents interesting possibilities in terms of their further functionalization, analogous to the extensive use of boronate ester groups in organic chemistry.

**Acknowledgements**

H.B. gratefully acknowledges the European Research Council (ERC) under the European Union Horizon 2020 Research and Innovation Program (grant agreement no. 669054) for funding. A.H. thanks the Fonds der Chemischen Industrie for a PhD fellowship. M.J.I and J.C. gratefully acknowledge the award of a Marie Curie Fellowship to J.C. (703227 – DIBOR). A.V. thanks the University of Sussex for financial support.

**Keywords:** diboranes; diborones; N-heterocyclic carbenes; boron chains; π-conjugation


**Occupy Pi Street**: The reduction of NHC-stabilized 1,1-dibromodiborane adducts leads to reductive coupling and isolation of doubly NHC-stabilized 1,2-diboryldiborenes. These compounds are the first examples of molecules exhibiting π-electron delocalization over an all-boron chain.