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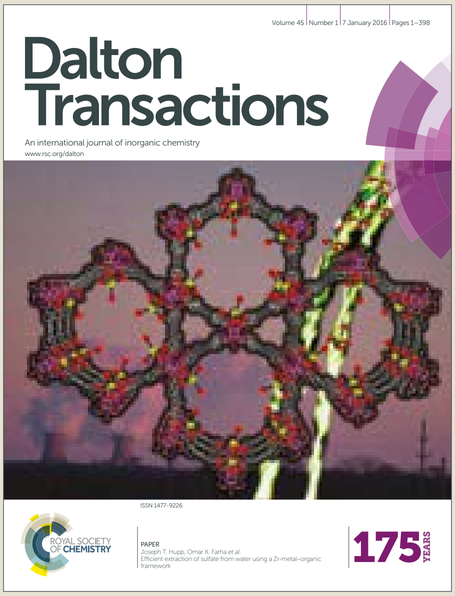

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COMMUNICATION

Synthesis of Hydrogen-Bridged Tetraborane(6): Substituent Effect of Diaminoboryl Group toward B-B Multiple Bond Character

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A hydrogen-bridging tetraborane(6) was synthesized from boryllithium, a boron nucleophile, in three steps. The structural and spectroscopic analysis of the tetraborane(6) revealed σ-donor and π-acceptor effect of diaminoboryl substituents toward the central B–B moiety having multiple bond character. DFT calculations also supported the experimentally observed substituent effect of boryl group.

Recent development of B–B multiple bond species opened a new area of chemistry due to their characteristic structure and reactivity of π-bond(s).[1] Two-electron reduction of diborane(4) led to a formation of the first B=B double bond species with two anionic charge [**A**, Figure 1(a)].[2, 3] The first diborene, a neutral B=B double bond species (**B**), was synthesized by a reduction of NHC-coordinated BBr_3 derivative.[4, 5] After the first discovery, propensities of diborene derivatives were extensively studied by an improvement of their synthesis.[6-28] On the other hand, diboryne, a neutral B≡B triple bond species (**C**),[7, 29-33] has been synthesized by a reduction of Lewis base-stabilized tetrahalodiborane(4) precursor. Related hydrogen-bridging diborane(4) species possessing B-B multiple bond character were synthesized by using a bulky aryl substituent, Eind group (**D**).[34-36] The H-bridged structure of **D** could be considered as a doubly protonated form of dianionic B≡B triple bond compound as supported with DFT study with a remarkably short B-B bond distance in comparison with those observed in diborene derivatives. Recently, an amino-substituted homocatenated triborane(3) compound (**E**), which can be considered as a trimer of aminoborylene, was reported to have a B–B multiple bond character.

In the chemistry of multiply-bonded main group element species, characteristic properties of the multiple bond such as short bond lengths and narrower HOMO-LUMO gap, have been studied. Connection of these species with boryl substituent(s) has been known to be able to alter the electronic properties of these multiple bonds [Figure 1(b)]. Introduction of dialkylboryl substituent to disilene (**F**) provided information about π-accepting character of dialkylboryl group toward Si=Si double bond.[37, 38] We reported synthesis and properties of boryl-substituted diphosphene (**G**), where boryl substituents showed σ-donor and π-acceptor character toward electronic properties of P=P double bond.[39-41] Recently, a boryl-substituted diborene (**H**) was reported to have an effective π-conjugation between B=B double bond and vacant p-orbitals of catecholatoboryl substituents.[23] In this work, we herein report synthesis of boryl-substituted hydrogen-bridged diborane(4), which can be considered as tetraborane(6) species, and the substituent effect of the diaminoboryl substituents toward multiple bond character of the inner B-B moiety.

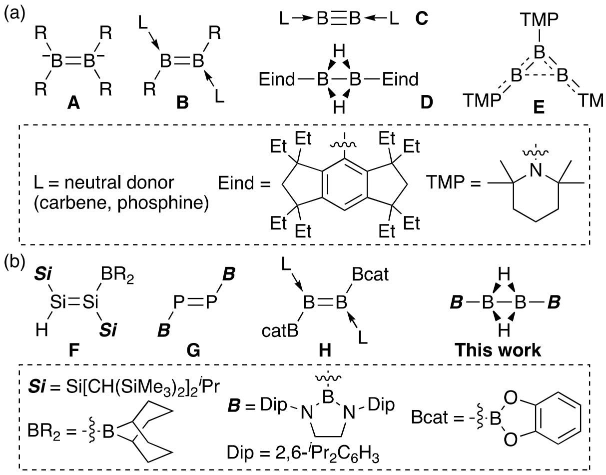

Figure 1. (a) Examples of multiboron compounds having B-B multiple bond character and (b) multiply bonded p-block element species bearing boryl substituent(s)

Reaction of boryllithyum **1**, which was prepared in accordance with our previous contribution,[42, 43] with two equivalents of

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Electronic Supplementary Information (ESI) available: CCDC 1884516-1884518 for **2**-**4**. For ESI and crystallographic data in CIF or other electronic format. See DOI: 10.1039/x0xx00000x

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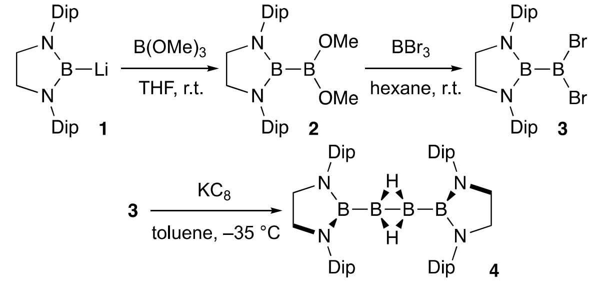
trimethylborate to give an unsymmetrical diborane(4) (**2**) with two amino and two alkoxy substituents in 78% yield (Scheme 1). Treatment of **2** with two equivalents of boron tribromide induced ligand exchange reaction to afford diaminodibromodiborane(4) (**3**) in 53% yield. Reaction of **3** with five equivalents of potassium graphite in toluene at –35 °C generated a hydrogen-bridged tetraborane(6) **4**. Colourless crystals **4** were obtained by recrystallization from its hexane solution in 12% isolated yield. In the ^{1}H NMR spectrum of **4** (C_6D_6), the signal of bridging hydrogen atoms was observed as a broad singlet at –2.25 ppm. This chemical shift is higher-field shifted in comparison with that of the aryl-substituted hydrogen-bridged diborane(4) **D** (2.94 ppm).[34] However, the NMR chemical shift calculations by using GIAO method indicated that the higher field shifted signal of bridging hydrogen atoms in **4** would be their peculiar property of B2H2 core structure (Figure S20) rather than the effect of boryl substituents.[44] In the ^{11}B NMR spectrum, the signals of **4** were observed at 5 and 30 ppm as a broad resonance, in which the former could be assigned as two internal boron atoms in comparison with that in **D**.[34] The IR spectrum of **4** exhibited a series of B–H–B vibrations (1321-1174 cm^{-1}) in the same region to those of **D** (1265-1157 cm^{-1}),[34] confirming the existence of the two bridging hydrogen atoms. Reaction of **3** with KC_8 in toluene-d_8 resulted in an appearance of small signal (–2.30 ppm) in addition to the signal of the bridging hydrogen atoms in **4** (Figure S14). This new signal could be assigned as a bridging hydrogen atom in partially deuterated **4-*d*$_1$**. Although ^{2}H NMR spectrum of partially deuterated **4** did not exhibit any detectable signal probably due to significant broadening of the signal caused by coupling between two quadrupolar nuclei of ^{2}H and $^{11}B/^{10}B$, incorporation of deuterium atoms to **4** was also supported by APCI-TOF MS and IR spectroscopy (Figures S13, 15, 16). This result indicates the origin of the bridging hydrogen atoms in **4** could be attributed to inter- and intra-molecular hydrogen trapping from toluene solvent and backbone or Dip group in **3**.



Scheme 1. Synthesis of hydrogen-bridged tetraborane(6) **4** (Dip = 2,6-$^{i}Pr_2C_6H_3$)

The molecular structure of **4** was unambiguously confirmed by X-ray crystallographic analysis (Figure 2). Two bridging hydrogen atoms were placed as a peaks in a difference Fourier map. It was revealed that the inner B–B bond distance of 1.488(4) Å, which is similar to that in **D** [1.4879(7) Å][34] and lies between the reported B=B double and B≡B triple bonds. On the other hand, the outer B–B distances of 1.666(3), 1.661(3) Å are shorter than B–B covalent bond distance (1.75 Å),[45] and are similar to that of the diboryldiborene **H** (1.645(3) Å-1.676(6) Å),[23] indicating an effective π-conjugation between internal B-B bond possessing a multiple bond character and vacant p-orbitals of diaminoboryl substituents in **4**. These results suggest **4** can be described with resonance structures in Scheme 2.

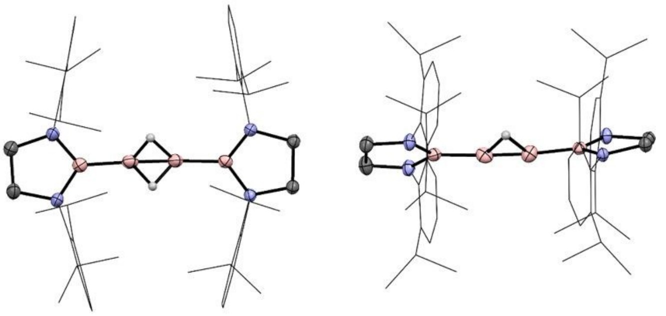
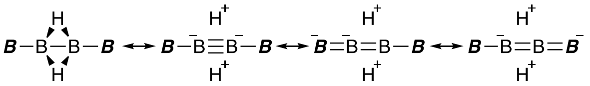


Figure 2. X-ray structure of **4** (left: side view, right: top view); Thermal ellipsoids set at 50% probability. Hydrogen atoms except for the bridging hydrogen atoms are omitted for clarity.



Scheme 2. Possible resonance structures of **4**

DFT calculations were performed to analyse electronic structure of **4**. The experimentally obtained structure of **4** by X-ray analysis was used as an initial structure for optimization at B3LYP/6-31+G(d,p) level of theory. Characteristic molecular orbitals of **4** are illustrated in Figure 3. Two molecular orbitals, HOMO–49 and HOMO–2 would correspond to two π-like orbitals at the central B–B unit. Overlapping of π*-orbitals of the central B-B unit and two vacant p-orbitals in **4** seems to produce LUMO. Two combinations of two π-type N–B–N orbitals construct energetically degenerated HOMO–1 and HOMO. In contrast, aryl-substituted **D** has slightly higher π*-like LUMO and π-like HOMO, and two combinations of π-orbitals of Eind groups consist HOMO-1 and HOMO-2 (Figure S19). This result indicates the boryl substituents in **4** contribute to lower π- and π*-orbital of the central B-B unit through their π-accepting effect. It should be noted that a bonding combination of π-type orbitals of N–B–N unit and the central B–B unit constructs a linear and delocalized π-conjugation over four boron atoms in HOMO-12. This π-conjugation is consistent with resonance structures in Scheme 2. The NPA charges on the central B–B unit in **4** are negative (B1, B2: −0.239), while those of **D** were positive (0.043, 0.074), supporting the σ-donating effect of boryl substituents to increase the electron density at the central B–B unit.

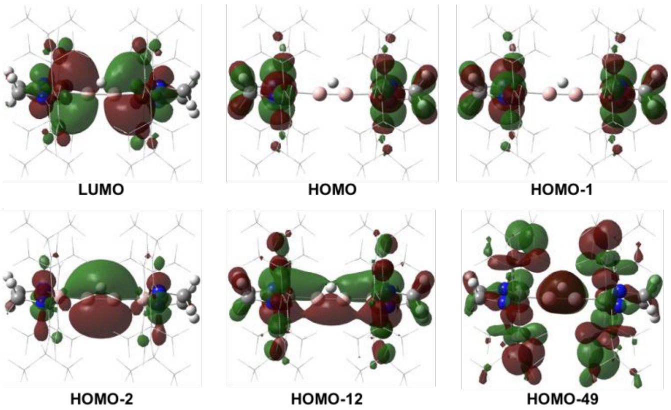


Figure 3. Selected molecular orbitals of **4** calculated at the B3LYP/6-31+G(d,p) level of theory. Hydrogen atoms omitted for clarity except for the bridged hydrogens.

Conclusions

By using boryllithium as a starting material, the hydrogen-bridging tetraborane(6) derivative **4** was synthesized in three steps. The structural and spectroscopic analysis revealed σ-donor and π-acceptor effect of diaminoboryl substituents toward B–B multiple bonding character. DFT calculations further supported the observed substituent effect of boryl groups.

Conflicts of interest

There are no conflicts to declare.

Acknowledgement

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