

Unprecedented formation of a boron-boron covalent bond opens a new corner of chemistry

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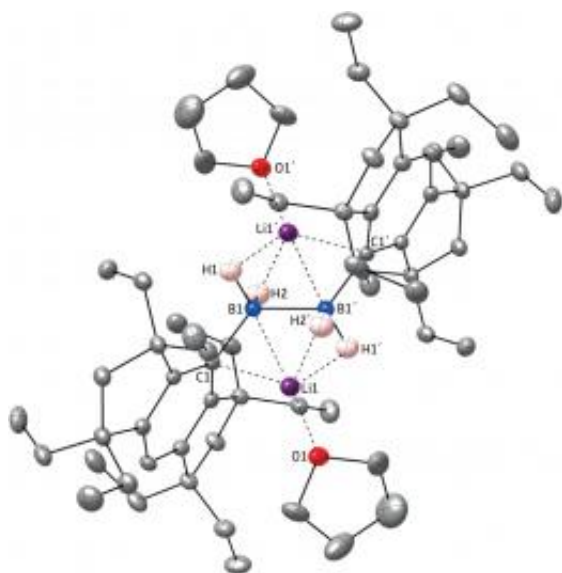


Figure 1: In the dilithium diborane(6) dianion, bulky side-groups (grey) protect the delicate boron-boron bond (blue). Credit: Ref. 1 © 2011 Y. Shoji et al.

Boron-based chemical compounds rarely form simple structures. Boron is an electron-deficient element; and, as electrons are the glue that hold compounds together, this leads to some unusual bonding behavior. Using a new method developed in Japan to link two boron atoms together by a regular, single covalent bond, the element can be forced into more conventional behavior. The method was developed by a team of researchers including Yoshiaki Shoji, Tsukasa Matsuo, and Kohei Tamao at the RIKEN Advanced Science Institute, Wako.

The compound that the researchers made features two [boron atoms](#) held together by a shared pair of [electrons](#). For other elements-carbon, for example-that would be a typical bond, but electron-poor boron tends to prefer a more complex

arrangement. In the boron compound diborane (B_2H_6), for example, two boron atoms are bridged by hydrogen atoms, with each boron - hydrogen - boron bond sharing a single pair of electrons across three atoms rather than the usual two.

Theory has long predicted that by pumping extra electrons into a compound such as diborane, the boron - hydrogen - boron structure should break down to form a boron - boron single bond. Until now, however, all such attempts to make and isolate such a structure had failed, instead generating clusters or single boron species.

Matsuo and Tamao's strategy for generating the boron - boron bond was to start with a borane precursor where each boron atom was fitted with a bulky side-group known as an Eind group. The researchers suspected that previous attempts probably succeeded in generating the boron - boron single bond but failed to protect that structure from quickly falling apart through over-reaction. Using the bulky side-groups, they were able to block these over-reaction processes, and successfully isolate the desired boron - boron single bond (Fig. 1).

Having discovered a new way to make the boron - boron bond, the next step will be to assess its chemistry and reactivity, and to explore related structures, says Shoji. The bond has already proved to be relatively stable: the team has shown that if protected from air and moisture, the boron - boron compound can be stored for months at ambient temperature. It can also be converted into a three-membered ring, in which a bridging hydrogen atom is the third member, forming a molecule with potentially useful properties. "We think that the hydrogen-bridged boron - boron bond has a double-bond character," says Matsuo. "We would like to explore the new reaction chemistry of

multiply bonded boron species."

More information: Shoji, Y., et al. Boron - boron π -bond formation by two-electron reduction of a H-bridged dimer of monoborane. [Journal of the American Chemical Society](#) 133, 11058 - 11061 (2011).

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