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Inorganic chemistry: A reducing role for boron

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Abstract

Carbon monoxide molecules are typically coupled together using metal compounds. The discovery that boron, a non-metal, mediates such a reaction is startling, and raises the prospect of potentially useful carbon-carbon bond-forming processes.

Main text

Ask any chemist about the reactivity of boron, and they will say that it forms strong bonds to carbon and oxygen. But the element is not known for its capacity as a reducing agent. Your chemist friends would therefore be surprised to hear of Braunschweig and colleagues' report¹ in *Nature Chemistry*, which describes the ability of a rather unusual boron compound not only to react and reduce molecules of carbon monoxide, but also to couple them together.

Carbon monoxide (CO) is a particularly reactive molecule, and is used in industry on a million-tonne scale as a source of single carbon atoms. Some of its most useful reactions require catalysts based on transition-metal complexes. The metal centre in these catalysts binds CO through its carbon atom and facilitates the molecule's insertion into adjacent groups also bound to the metal, forging a new carbon-carbon (C-C) bond. The reactions depend on the degree of electron transfer in the bond between the catalytic transition metal and CO. Electron donation from the metal to the CO (known as back-donation) activates the CO for reaction and weakens its carbon-oxygen bond. Such reactions are widely used to make C-C bonds between CO and other substrates, but in general cannot be used to form these bonds between CO molecules themselves.

Non-metallic elements such as boron do not tend to facilitate C-C bond-forming reactions. But the boron-containing compound used by Braunschweig and colleagues in their reactions is highly unusual: it is a

diboryne, a beautifully simple molecule in which two boron atoms are connected through a triple bond² (Fig. 1). Each boron atom is bound to a bulky molecule known as an *N*-heterocyclic carbene, which is characterized by carbon atoms that carry no formal charge, but that can donate a pair of electrons to other molecules. The binding of these carbenes helps to stabilize the diboryne.

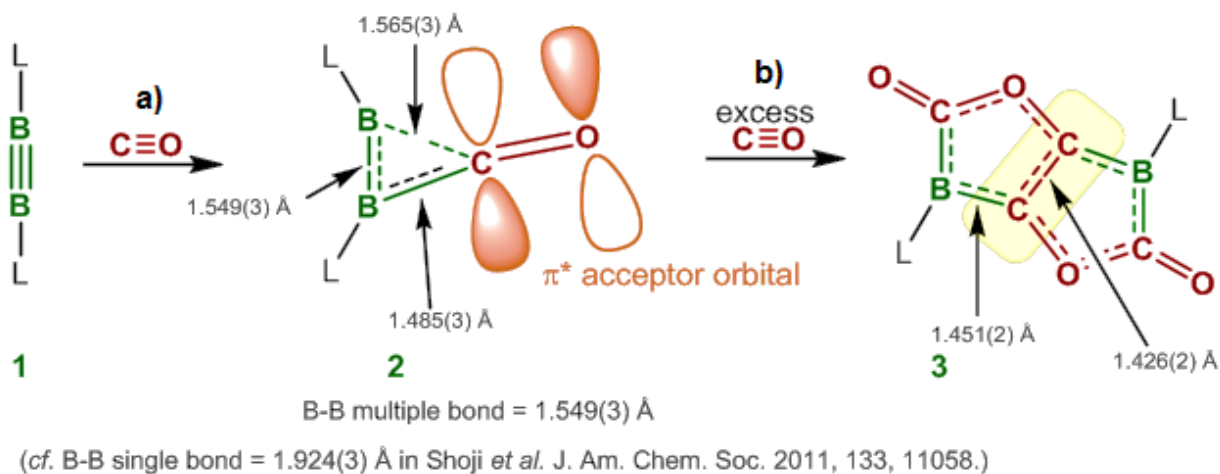


Figure 1. a) Braunschweig *et al.*¹ report that a single molecule of carbon monoxide (red) can be added to a diboryne compound (green) by bridging the diboryne's boron–boron triple bond. L is an *N*-heterocyclic carbene molecule. Dashed lines indicate partial bond formation. **b)** If an excess amount of CO (more than four equivalents) is added to the diboryne, four CO molecules are reduced and coupled together, forming a planar bis(boralactone) molecule that contains a new carbon–carbon bond. This is a rare example of a CO-coupling reaction mediated by a non-metal, and an equally rare example of a boron-mediated reduction reaction.

Braunschweig and co-workers find that either their diboryne binds one CO molecule so that its carbon atom bridges the two boron atoms (Fig. 1a), or that it couples four CO molecules together in a reduction reaction. The latter reaction yields a planar product called a bis(boralactone), in which the boron–boron triple bond is ruptured and a new C–C bond is formed (Fig. 1b). The diboryne binds and activates the first CO molecule through a back-donation of electron density similar to that seen in metal–CO compounds.

Diatomic boron units were originally observed³ in spectroscopy experiments as thermally unstable adducts containing two CO molecules, one bound at either end of the diboryne. In that case, the CO molecules donated two electrons each to the diboryne. By contrast, a single CO molecule binds as an electron acceptor to the thermally stable diboryne studied by Braunschweig *et al.*, bridging the two borons of the diboryne because the carbenes block access to the diboryne's ends. It will be fascinating to learn precisely how the diboryne back-donates electrons to activate the CO, because it does not possess the orbitals used by metal cations for back-donation.

Carbon monoxide can be induced to couple to other CO molecules if it is provided with electrons, allowing up to six molecules to react⁴. Coupling at the carbon atoms is the most common and desirable result⁵, but other bonding patterns are also possible. Braunschweig and colleagues observed that their diboryne can reduce and couple four CO molecules using a total of six electrons, three from each boron atom, in a rare example of a reduction by a boron compound. Intriguingly, all of the bonds in the B–C–C–B system of the product are shorter than equivalent single carbon–boron and C–C bonds, indicating that there is substantial electron delocalization in this molecule.

Braunschweig *et al.* describe the reducing power of their diboryne as strong: its reduction potential is –1.2 volts compared with that of ferrocene, a compound used as a standard for reduction potential. But this is a small value relative to those for uranium systems that also reductively couple CO; all of these have potentials in solution⁶ of about –2 volts, much more strongly reducing than ferrocene. It is exciting to imagine what further reduction chemistry might be possible with the diboryne, and whether simple changes to its carbenes could allow other compounds, formed from different numbers of CO molecules, to be isolated.

The real power of any new reaction for CO reduction depends on whether useful products containing more than one carbon atom can be made. For commercially viable applications, this will undoubtedly require the CO-coupled products to be reacted with hydrogen. Sadly, for the known metal-mediated CO-coupling systems, the only reaction with hydrogen so far reported occurs before any C–C bond formation, and so the resulting hydrogenation-reaction products contain only one carbon atom⁷.

In another coup for boron, it was demonstrated⁸ earlier this year that electron-deficient boron-containing compounds known as boranes can activate both CO molecules and hydrogen (in combination with a suitable base), allowing CO to react with the hydrogen. It will therefore be interesting to see whether Braunschweig and colleagues' bis(boralactone), or analogues of it, will also react with hydrogen, perhaps when pre-activated by one of these electron-deficient boranes. If so, then the crucial question is whether the carbon–carbon bond within it remains intact — that is, whether a product containing two carbon atoms is formed. Also unknown is whether the authors' diboryne reagent can be easily recycled after the reaction, a feature that could open up a new area of boron-catalysed chemistry.

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