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Boron compounds tackle dinitrogen

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The high stability of elemental nitrogen (N_2) is reflected in the name that Antoine Lavoisier coined for the element that makes up the seemingly inert component of the atmosphere, *azote*, meaning ‘no life’. Ironically, chemical processes that convert this robust molecule into ammonia (NH_3) – the key component in fertilizer – are essential to keep the billions of people on our planet alive. Both the industrial Haber-Bosch process and the natural nitrogenase enzymes employ the transition metal iron (Fe) to catalyze this challenging chemical transformation. The efforts of synthetic chemists over many decades have shown that complex ions of many metals can interact with N_2 , and detailed studies have led to a relatively mature understanding of metal- N_2 bonding. The ability of transition metals to weaken or break the strong triple bond ($N\equiv N$) is ascribed to the nature of their atomic *d* orbitals, which describe the region in space around an atom where *d* electrons can be found. More specifically, the right combination of empty and filled *d* orbitals can accept electrons from N_2 into one orbital and simultaneously donate electron density into antibonding orbitals of N_2 , an interaction known as π -backdonation that weakens the $N\equiv N$ bond (Figure A). *p*-Block elements such as boron (B) lack accessible *d* orbitals, and because this type of π -back donation cannot occur, they are not expected to weaken N_2 . Despite this “conventional wisdom,” Légaré *et al.* demonstrate that modifying the electronic environment of the B atom enables N_2 binding and reduction at a B center for the first time.

The strategy used by Légaré *et al.* involves the use of a borylene, which is a monovalent B atom with a lone pair of electrons (Figure B). Although most boron compounds have B in the +3 oxidation state, borylenes formally have the +1 oxidation state, making them very electron-rich. In 2011, Bertrand and co-workers demonstrated that these intrinsically reactive boron(I) species can be stabilized by binding cyclic (alkyl)(amino)carbenes or CAACs, which stabilize the extra electrons on B.¹ These borylenes were found to mimic transition metals by binding carbon monoxide (CO),² and releasing it upon irradiation with light.^{3,4} This suggested that borylenes might also bind N_2 , albeit using different orbitals than transition metals do (Figure B). Very recent work demonstrated binding of N_2 to an unstabilized borylene under matrix conditions at 10 K.⁵ However, even at these extremely low temperatures – which are used to observe the most reactive and unstable molecules – N_2 binding was very weak. In this work, Légaré *et al.* show a new method to make a reactive borylene that can bind N_2 to form an adduct that is stable enough to isolate at room temperature (Figure C). The resulting product consists of an N_2 fragment bound by two borylenes. In contrast with the linear M-N-N-M units typically found in transition metal

complexes, the B-N-N-B unit has a zig-zag structure (Figure C). This makes the product somewhat resemble an organic azo compound (C-N=N-C), but quantum mechanical calculations imply an electronic structure where the borylene accepts electron density from N₂ with simultaneous π -backdonation from its filled *p* orbital (Figure B). As a result the triple bond in N₂ is reduced to a bond order of ~1.5 in the borylene adduct, and to an N-N single bond after further reduction and protonation to generate a diborahydrazine in which the N₂ is functionalized (Figure C).

The work by Légaré *et al.* is a remarkable breakthrough, presenting the first isolable example of a nonmetal that can bind and reduce N₂. Showing that borylenes can bind and activate N₂ further underlines the potential of main-group elements for small molecule activation. It also raises the question: “what is next for borylenes?” In addition to binding small molecules in a manner that is analogous to transition metals, can borylenes also catalyze chemical transformations like transition metal complexes? One hindrance is that classical steps in transition metal catalysis typically involve two-electron redox changes on the metal center. However, the borylenes described by Légaré *et al.* undergo one-electron redox changes that could be detrimental. It is possible that binding of cooperative⁶ or redox-active⁷ ligands to a borylene could assist in facilitating multi-electron transformations, a strategy that has met with recent success in complexes of first-row transition metals, enabling systems known for one-electron redox chemistry to achieve two-electron reactions.⁸ Further development also could lead to pathways to use borylenes for the conversion of N₂ into amines and other N-containing organic compounds using Earth-abundant catalysts. Irrespective of the eventual applications, the results are a clear demonstration of the power of molecular design for enabling new and unforeseen reactivity.

References

1. Kinjo R, Donnadiou B, Celik MA, Frenking G, Bertrand G, Science 333, 610–613 (2011). [PubMed: 21798945]
2. Dahcheh F, Martin D, Stephan DW, Bertrand G, Angew. Chem. Int. Ed 53, 13159–13163 (2014).
3. Braunschweig H, Dewhurst RD, Hupp F, Nutz M, Radacki K, Tate CW, Vargas A, Ye Q, Nature 522, 327–330 (2015). [PubMed: 26085273]
4. Braunschweig H, Krummenacher I, Légaré M-A, Matler A, Radacki K, Ye Q, J. Am. Chem. Soc 139, 1802–1805 (2017). [PubMed: 28103028]
5. Edel K, Krieg M, Grote D, Bettinger HF, J. Am. Chem. Soc 139, 15151–15159 (2017). [PubMed: 29016115]
6. Khusnutidnova JR, Milstein D, Angew. Chem. Int. Ed 54, 12236–12273 (2015).
7. Chirik PJ, Wieghardt K, Science 327, 794–795 (2010). [PubMed: 20150476]
8. van der Vlugt JI, Eur. J. Inorg. Chem 3, 363–375 (2012).

Binding N_2 at boron.

(A) Transition metals bind N_2 by accepting and donating electron density with d orbitals. (B) Borylenes have now been shown to have the right electronic structure to do the same with p orbitals. (C) Binding of N_2 is followed by protonation to form a diborahydrazine with new N-H bonds.