

Electronic Transmutation: A Modern Twist on Alchemy

Alexander Kurzhals

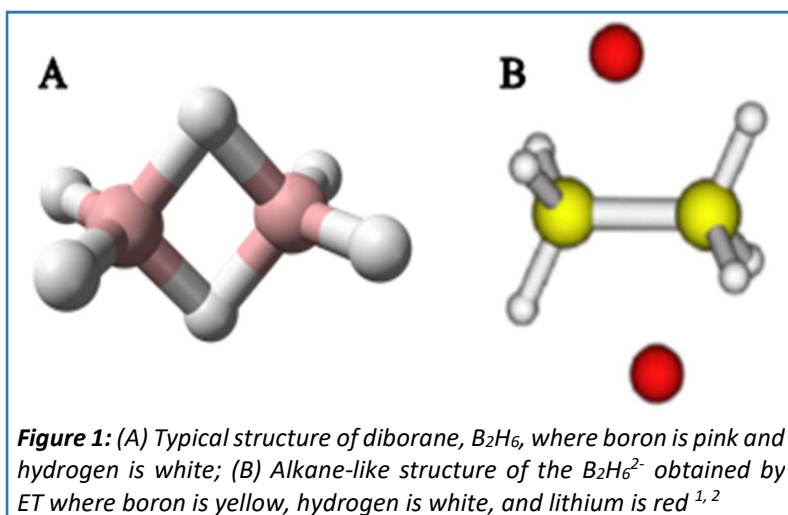
Literature Seminar

November 6, 2018

For thousands of years, alchemists attempted to transform lead and other inferior metals into those of higher quality such as gold and silver. Of course, it is now known that this process would require nuclear reactions which, at least as of yet, cannot be facilitated by chemistry alone. Nonetheless, there is evidence in current literature showing that some elements can be coerced into assuming the behavior of others through electronic transmutation (ET).^{1, 2} While this is by no means actual alchemy, ET is capable of stabilizing novel compounds which exhibit unique characteristics and may be utilized in the future for the design of advanced materials.

Originally proposed in 2012 by Jared Olson and Alexander Boldyrev,¹ ET occurs when a donor atom sacrifices one of its electrons to a neighboring element of atomic number Z which, thereby, starts to exhibit the properties of an element with atomic number $Z+1$.² Consequently, Group 13 elements, which normally possess an electron configuration of the form Ns^2Np^1 , become isoelectronic with Group 14 elements (Ns^2Np^2) and adopt the bonding properties of the new configuration. There is also evidence for transmutations of Group 14 and 15 elements,² but it remains to be determined if this is a universal principle across the periodic table. Even so, the possible implications of ET on traditional synthetic methods are worthy of investigation.

With their first publication on the topic, Olson and Boldyrev computationally investigated several boron analogues of alkanes and determined their global energy minima.¹ The structures of borohydrides are unique because elemental boron is notoriously electron deficient and is stabilized by forming $3c-2e$ bonds (three centers, two electrons). Molecularly, these manifest as polyhedral clusters with numerous bridging boron-hydrogen-boron (B-H-B) bonds according to the Wade-Mingos rules.^{3, 4} Contrarily, these structural modes are not observed with carbon because it readily forms $2c-2e$ bonds (two centers, two electrons) which result in the extended, chain-like structure of alkanes. One example from Olson and Boldyrev is B_2H_6 . As a neutral molecule, the dimeric structure has two B-H-B bonds (Figure 1A); however, by the addition of two electron-donating lithium atoms, $B_2H_6^{2-}$ preferentially adopts the staggered conformation of ethane with a $2c-2e$ boron-boron single bond and ionically-coordinated lithium atoms (Figure 1B).¹

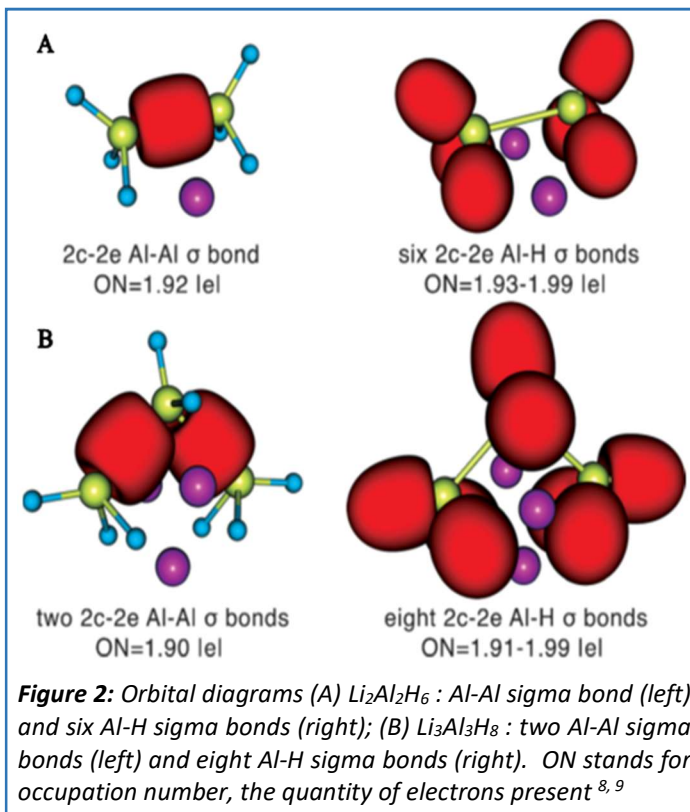


Further analysis of higher order $Li_nB_nH_{2n+2}$ ($n = 3, 4$) suggests comparable $(B_nH_{2n+2})^{n-}$ units have local energy minima for alkane structures, but global minima were too expansive to compute.^{1, 2}

Computational predictions by Alexandrova, et al, have predicted that boron may also form planar, aromatic structures through ET.⁵ Interestingly, there is synthetic evidence of this as well. In 2001, Nagamatsu and coworkers reported

a high temperature superconductor made from magnesium diboride in which X-ray diffraction confirmed graphene-like sheets of boron were separated by planes of Mg^{2+} ions.⁶ As stated by Zhang, complete charge transfer from each magnesium atom to neighboring boron atoms is expected because of the large difference in electronegativity between the two.² This means that MgB_2 exists as $\text{Mg}^{2+}(\text{B}^-)_2$ and ET has caused boron to assume the two-dimensional, aromatic properties that are typical of carbon. Additionally, in 2018, Li, et al, reported the synthesis of a honeycomb-structured monolayer of borophene on an aluminum (1 1 1) surface where each boron atom accepts one additional electron from the Al substrate.⁷ Given the precedent of Nagamatsu,⁶ the group is excited to investigate and optimize the electronic properties of their novel material.

Other than boron, ET has been utilized to alter the properties of aluminum, gallium, silicon, nitrogen, and phosphorous.² Research in this field with aluminum is of particular interest because it transmutes to silicon, which is widely used in electronics as a semiconductor. In 2015, Gish and coworkers computationally investigated the stability of two chain-like structures of aluminum that silicon is known to form⁸ using the same method as Olson and Boldyrev.¹ Silanes are known to be stable in the form $\text{Si}_n\text{H}_{2n+2}$ ($n = 1-8$) and the counterparts considered are $\text{Li}_n\text{Al}_n\text{H}_{2n+2}$ ($n = 2, 3$) which possess the transmuted molecular cores $(\text{Al}_n\text{H}_{2n+2})^{n-}$ that are isoelectronic with their silicon analogues.⁸ Aside from a few structural oddities, such as a preference for the eclipsed conformation, the group concluded that $\text{Li}_n\text{Al}_n\text{H}_{2n+2}$ ($n = 2, 3$) are energetically stable and possess aluminum-aluminum sigma bonds which had been previously unreported (Figure 2, A&B).⁸ Later that same year, Popov, et al, managed to observe $\text{Li}_2\text{Al}_3\text{H}_8^-$ (the anion variant of $\text{Li}_3\text{Al}_3\text{H}_8$) by photoelectron spectroscopy (PES).⁹ These results are exciting because the aluminum-hydrogen bond is heavily polarized toward hydrogen which makes compounds such as $\text{Li}_n\text{Al}_n\text{H}_{2n+2}$ viable candidates for hydrogen storage that is easily reversible.^{8, 9} Future work will hopefully be targeted at isolating these compounds so they may be tested for usability in these and other materials.



Notably, ET has also been used in the synthesis of designer clusters exhibiting main-group multiple bonding that are often difficult to obtain. For example, in 2017, Lundell and coworkers used the method of Popov⁹ to observe $\text{LiAl}_2\text{H}_4^-$ which contains the aluminum-aluminum double bond equivalent of Si_2H_4 without the need for steric effects from bulky ligands like previously reported examples.¹⁰ Furthermore, in 2018, Zhang, et al, expanded the concepts and applicability of ET to Double Electronic Transmutation (DET) when they discovered an aluminum-aluminum triple bond in the gas-phase cluster Na_3Al_2^- .¹¹ This is the first reported instance of DET in which

aluminum was effectively transmuted to phosphorous and the corresponding bond has taken the effective form of diphosphorous (P_2). The results for both clusters containing $Al=Al$ and $Al\equiv Al$ were extensively reinforced by computational support for PES spectra as well as comparison of bond lengths, dissociation energies, and bond angles.^{10, 11} While these compounds were designed for proof of concept, they also hold potential as building blocks for novel solid-state materials similar to the examples of boron presented earlier^{6, 7} or otherwise unprecedented chemical solids.

Electron transmutation may not match the classic conception of alchemy that scientists and philosophers once had; however, it remains a fascinating way to chemically alter the properties of an element to mirror another. There is evidence of ET being applicable to several different main group elements² and applying it across the periodic table could yield limitless possibilities for discovery. In fact, other literature suggests that gallium forms a polyethylene structure with the stoichiometry $Rb_n(GaH_2)_n$ making it a functional metallopolymer.¹² With the addition of DET, one may also ponder if electronic transmutation can work in higher orders of magnitude such as Triple Electronic Transmutation? Oppositely, can carbon be transmuted to adopt the properties of boron? The field of ET has many intriguing questions that will inspire chemists for years to come.

References

- (1) Olson, J. K.; Boldyrev, A. I. Electronic Transmutation: Boron Acquiring an Extra Electron Becomes “Carbon.” *Chem. Phys. Lett.* **2012**, *523*, 83-6.
- (2) Zhang, X.; *et al.* Electronic Transmutation (ET): Chemically Turning One Element into Another. *Chem. Eur. J.* **2018**, *24*, 9200-10.
- (3) Wade, K. The Structural Significance of the Number of Skeletal Bonding Electron-Pairs in Carboranes, the Higher Boranes and Borane Anions, and Various Transition-Metal Carbonyl Cluster Compounds. *J. Chem. Soc. D: Chem. Commun.* **1971**, *15*, 792–3.
- (4) Mingos, D. M. P. A General Theory for Cluster and Ring Compounds of the Main Group and Transition Elements. *Nature Physical Science.* **1972**, *236*, 99–102.
- (5) Alexandrova, A. N.; *et al.* Flattening the $B_6H_6^-$ Octahedron. Ab Initio Prediction of a New Family of Planar All-Boron Aromatic Molecules. *J. Am. Chem. Soc.* **2003**, *125*, 10786–87.
- (6) Nagamatsu, J.; Nakagawa, N.; Murankaka, T.; Zenitani, Y.; Akimitsu, J. Superconductivity at 39 K in Magnesium Diboride. *Nature* **2001**, *410*, 63-4.
- (7) Li, W.; *et al.* Experiment Realization of Honeycomb Borophene. *Sci. Bull.* **2018**, *63*, 282-6.
- (8) Gish, J. T.; Popov, I. A.; Boldyrev, A. I. Homocatenation of Aluminum: Alkane-like Structures of $Li_2Al_2H_6$ and $Li_3Al_3H_8$. *Chem. Eur. J.* **2015**, *21*, 5307-10.
- (9) Popov, I. A.; *et al.* Aluminum Chain in $Li_2Al_3H_8^-$ as Suggested by Photoelectron Spectroscopy and Ab Initio Calculations. *Phys. Chem. Chem. Phys.* **2015**, *17*, 26079-83.
- (10) Lundell, K. A.; *et al.* The Existence of a Designer $Al=Al$ Double Bond in the $LiAl_2H_4^-$ Cluster Formed by Electronic Transmutation. *Angew. Chem. Int. Ed.* **2017**, *56*, 16593-96.
- (11) Zhang, X.; *et al.* Realization of an $Al\equiv Al$ Triple Bond in the Gas-Phase $Na_3Al_2^-$ Cluster via Double Electronic Transmutation. *Angew. Chem. Int. Ed.* **2018**, *57*, 14060-4.
- (12) Fahlquist, H.; *et al.* Two New Cluster Ions, $Ga[GaH_3]_4^{5-}$ with a Neopentane Structure in $Rb_8Ga_5H_{15}$ and $[GaH_2]_n^{n-}$ with a Polyethylene Structure in $Rb_n(GaH_2)_n$, Represent a New Class of Compounds with Direct Ga-Ga Bonds Mimicking Common Hydrocarbons. *J. Am. Chem. Soc.* **2011**, *133*, 14574–77.