▍Clusters

Boron-Made N₂: Realization of a B≡B Triple Bond in the B₂Al₃⁻ Cluster

Nikita Fedik+,[b] Chaonan Mu+,[a] Ivan A. Popov,[c] Wei Wang,[a] Jie Wang,[a] Haopeng Wang,[d] Kit H. Bowen,*[d] Alexander I. Boldyrev,*[b] and Xinxing Zhang*[a]

Abstract: Until now, all B≡B triple bonds have been achieved by adopting two ligands in the L→B≡B←L manner. Herein, we report an alternative route of designing the B≡B bonds based on the assumption that by acquiring two extra electrons, an element with the atomic number Z can have properties similar to those of the element with the atomic number $Z+2$. Specifically, we show that due to the electron donation from Al to B, the negatively charged B≡B kernel in the B₂Al₃⁻ cluster mimics a triple N≡N bond. Comprehensive computational searches reveal that the global minimum structure of B₂Al₃⁻ exhibits a direct B–B distance of 1.553 Å, and its calculated electron vertical detachment energies are in excellent agreement with the corresponding values of the experimental photoelectron spectrum. Chemical bonding analysis revealed one σ and two π bonds between the two B atoms, thus confirming a classical textbook B≡B triple bond, similar to that of N₂.

The synthesis of homodinuclear triple bonds of Group 13 elements imposes one of the most challenging frontiers in modern chemistry. Unlike the classical textbook triple bonds found in dinitrogen (N≡N) and acetylene (HC≡CH) that are composed of one σ bond and two π bonds constructed from the p orbitals perpendicular to the σ bond,[1,2] most of the existing Group 13 homodinuclear triple bonds are either non-

classical or controversial. The history of Group 13 triple bonds began with the epic "digallyne debate".[3] In 1997, Robinson and co-workers synthesized the famous "digallyne" molecule Na₂[ArGaGaAr] (Ar = C₆H₃-2,6-(C₆H₂-2,4,6-iPr₃)₂) featuring the shortest Ga–Ga bond.[4] Based on the fact that the [ArGaGaAr]²⁻ core is valence-isoelectronic to acetylene, the Ga–Ga contact was initially considered as a triple bond. However, the nature of this bond caused considerable debates afterwards.[5] The affirmative side described the triple bond as a combination of two dative bonds and one π bond,[5a] or a combination of a σ bond, a π bond, and a non-classical "slipped" π bond.[5b] The opposite side opined that the Ga–Ga bond had substantial nonbonding characters.[5c–e] All these studies have significantly contributed to the understanding of homodinuclear multiple bonding in Group 13 elements. For aluminum, an Al≡Al triple bond was achieved in the example of a stable Na₂[Ar'AlAlAr'] (Ar' = C₆H₃-2,6-(C₆H₂-2,4,6-iPr₃)₂) compound named dialuminyne, as reported by Power and co-workers.[6] However, similarly to the digallyne[4] molecule, it features a trans-bent structure, wherein the Al–Al interaction was also described as a non-traditional triple bond with a "slipped" π bond. More recently, our group reported an Al≡Al triple bond in the Al₂Na₃⁻ cluster in which the Al₂⁴⁻ moiety is both isoelectronic and isostructural to the P≡P molecule.[7]

Compared to the relatively devoid research on the Ga≡Ga and Al≡Al triple bonds, it has been fruitful for B≡B. The first example was a molecule OC→B≡B←CO isolated in an argon matrix at 8 K by Zhou et al.,[8] which further triggered copious theoretical and experimental studies on the B₂ kernel stabilized by other ligands such as NHC (N-heterocyclic carbene), diatomic molecules (CO, CS, N₂, BO⁻), and phosphine derivatives (PCl₃, PMe₃).[9–14] Experimentally synthesized NHC→B≡B←NHC crystal featured the first ambient-temperature isolable diboryne.[15] The lighter B compared to Al and Ga contributes to the linear NHC-stabilized core with very short B–B distances of 1.449 Å, which is in accordance with the B–B triple bond length (1.460 Å) predicted by Pyykkö.[16] However, Köppe and Schnöckel questioned this triple bond based on significant electronic and mechanical interactions between the B–B bond and the two B–(NHC) bonds.[17] Responding to this interpretation, Frenking's calculations[18] and Braunschweig's Raman spectroscopic measurements[19] further supported the existence of the B≡B triple bond in NHC→B≡B←NHC. Alterations of carbenes, including the size, degree of unsaturation, and substitution groups on the backbone of carbenes, as well as the character of the elements adjacent to the carbene carbon

[a] C. Mu,+ W. Wang, J. Wang, Prof. Dr. X. Zhang
Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Renewable Energy Conversion and Storage Center (ReCAST)
College of Chemistry, Nankai University, Tianjin 300071 (P. R. China)
E-mail: zhangxx@nankai.edu.cn

[b] N. Fedik,+ Prof. Dr. A. I. Boldyrev
Department of Chemistry and Biochemistry, Utah State University
0300 Old Main Hill, Logan, UT, 84322-0300 (USA)
E-mail: a.i.boldyrev@usu.edu

[c] Dr. I. A. Popov
Theoretical Division, Los Alamos National Laboratory
Los Alamos, New Mexico 87545 (USA)

[d] Dr. H. Wang, Prof. Dr. K. H. Bowen
Departments of Chemistry and Material Science
Johns Hopkins University, Baltimore, MD 21218 (USA)
E-mail: kbowen@jhu.edu

[+] These authors contributed equally to this work.

📖 Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
https://doi.org/10.1002/chem.202001159.

Chemistry–A European Journal

Communication
doi.org/10.1002/chem.202001159

**Chemistry
Europe**
European Chemical
Societies Publishing

atom will result in remarkable difference in the σ-donating ability and the great capacity to accept π-back-donation. Based on this strategy, cyclic (alkyl)(amino) carbene (cAAC)-stabilized linear diboracumulene (cAAC)$_2$B$_2$ featuring a B≡B triple bond was synthesized by Braunschweig et al.[20] Subsequently, they also synthesized saturated NHC^{Dipp}-stabilized diboryne with a B≡B bond distance of 1.465 Å.[21] In 2017, a DFT study on the stabilization of B≡B triple bonds in metallocene, Zr(η^5-Cp)$_2$, was reported with different bonding situation compared to B$_2$(L)$_2$ complexes.[22] Furthermore, multidentate carbenes were computationally studied to stabilize the diborynes nanostructures by Nascimento's group.[23,24] Similar to NHCs, another "nonclassical" type of carbenes called mesoionic carbenes (MICs) were demonstrated to have the possibility to stabilize B≡B triple bonds.[25]

However, all of the existing B≡B triple bonds were constructed by using two ligands in the L→B≡B←L fashion. The ligands "forced" the three valence electrons of one B atom to bond with the other three electrons of the neighboring B atom so that the whole molecule fulfills the octet rule. Here, we utilize a completely different strategy for designing B≡B. By acquiring two extra electrons, an element with the atomic number Z begins to have properties characteristic of the element with the atomic number $Z+2$. Given that boron is two electrons short than nitrogen, the B^{2-}≡B^{2-} prototype should be similar to the textbook triple bond in N$_2$. Previously, this strategy[26] has been successfully applied for the prediction of many new compounds, which were experimentally observed afterwards. While the enrichment of each Al atom by two extra electrons was previously used to design a triple Al≡Al in Na$_3$Al$_2^-$ cluster,[7] its application to B species has not yet been reported, and remains intriguing especially due to significantly smaller atomic radius.

Due to the ability of Al to form mono-valent Al^I compounds,[27] as well as its lower electronegativity than that of B, this metal is chosen as a potential candidate to form B^{2-}. In principle, Al is anticipated to be a single electron donor instead of providing all of its three valence electrons. It has recently been shown that Al is able to donate one electron to B, making the latter isoelectronic to carbon by forming an unprecedented graphene-like 2D boron sheet.[28] Following the above discussions, a cluster anion, B$_2$Al$_3^-$, is suggested assuming that the three Al atoms could provide three electrons to B atoms, in addition to the forth electron given in form of the negative charge.

In lieu of the neutral B$_2$Al$_4$ molecule, the B$_2$Al$_3^-$ anion is designed in order to facilitate the anion photoelectron spectroscopic (PES) experiments. Details of the experimental methods and the apparatus are given in the Supporting Information. The PES of B$_2$Al$_3^-$ generated in an ion beam is taken with 3.49 eV (355 nm) laser and presented in Figure 1. The spectrum has an electron binding energy (EBE) band starting from ≈2.1 eV and peaks at 2.59 eV. The first experimental vertical detachment energy (VDE) is the photodetachment transition, at which the Franck-Condon overlap between the wave functions of the anion and its neutral counterpart is maximal, corresponding to the peak value of 2.59 eV. The second EBE band
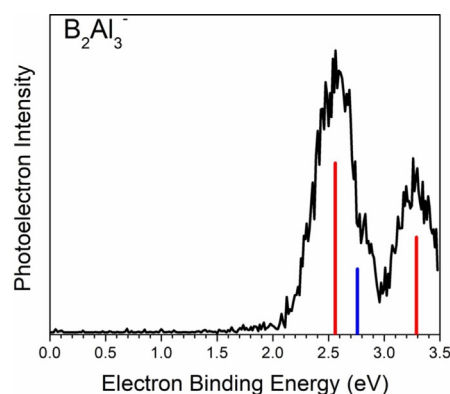

Figure 1. Experimental photoelectron spectrum of B$_2$Al$_3^-$ taken with 355 nm laser (black line) and calculated vertical detachment energies at CCSD(T) for Iso I (red stick) and Iso II (blue stick).

starts from ≈3.0 eV and peaks at 3.26 eV. It corresponds to the vertical transition from the anion to the first excited state of the neutral.

In order to determine the structure of the experimentally observed cluster, which is expected to have lowest energy on the potential energy surface, an unbiased search[29–31] was performed for both singlet and triplet spin state electronic configurations of the B$_2$Al$_3^-$ stoichiometry using the Coalescence Kick method[32] at the PBE0/6–311+G*[33,34] level of theory. All isomers within 20 kcal mol^{-1} were fully reoptimized using more extensive aug-cc-pwCVTZ basis set including full electron correlation.[30] Finally, relative energies were obtained at the CCSD(T)/aug-cc-pwCVTZ[35–37] level. Details of the theoretical methods are given in the SI.

The five lowest isomers of B$_2$Al$_3^-$ are presented in Figure 2 (Iso I-V). The global minimum (GM) structure (Iso I) has a direct B-B contact of 1.553 Å. One of the Al atoms bridges the two B atoms, and the other two Al atoms coordinate the two B atoms radially, resulting in a C_{2v} symmetry. Noteworthy, the B—B bond length (1.553 Å) is longer than that in the reported NHC→B≡B←NHC molecule (1.449 Å).[14] Instead of being a disproof, the longer B—B bond in B$_2$Al$_3^-$ is an indicator of significant electron donation from Al. As a result, the negative charges on B repulse atoms away from each other. Table 1 summarizes the experimental and calculated VDE values of Iso I and Iso II at three different levels of theory. Excellent agreement is
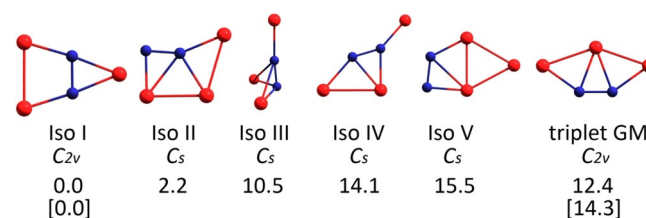

Figure 2. Five lowest energy singlet spin state isomers and one triplet spin state isomer of B$_2$Al$_3^-$, their point group symmetries, and zero-point energy corrected relative energies (in kcal mol^{-1}) at the CCSD(T)/aug-cc-pwCVTZ and CAS(8,8) NEVPT2/aug-cc-pwCVTZ levels of theory [in square brackets]. The solid rods between atoms facilitate visualization, and do not necessarily represent bonds here and elsewhere. B is blue, Al is red.

Chemistry–A European Journal

Communication
doi.org/10.1002/chem.202001159

Chemistry Europe
European Chemical
Societies Publishing

Table 1. Calculated and experimental VDEs (eV) of $B_2Al_3^-$.

Neutral configuration	Iso I			
	EXPT.	OVGF[a]	VDE CCSD(T)[b]	TD-DFT[c]
$1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2 4a_1^2$ $2b_2^2 5a_1^1$	2.59	2.57	2.56	2.42
$1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2 4a_1^2$ $2b_2^1 5a_1^2$	3.26	3.25	3.31	3.15
Iso II				
$1a'^2 2a'^2 3a'^2 4a'^2 5a'^2$ $1a''^2 6a'^2 7a'^1$	2.59	2.83	2.76	2.56
$1a'^2 2a'^2 3a'^2 4a'^2 5a'^2$ $1a''^2 6a'^2 7a'^1$	3.26	3.23	3.42[d]	3.02

[a] TD-M11/aug-cc-pwCVTZ.[38] [b] OVGF/aug-cc-pwCVTZ.[39,40] [c] CCSD(T)/aug-cc-pwCVTZ. [d] EOM-CCSD/aug-cc-pwCVTZ.

Figure 3. Chemical bonds of Iso I of $B_2Al_3^-$ (A) and N_2 (B) recovered by the AdNDP analysis. The compositions of the triple bonds are high-lighted by a box.

observed between the experiment and theory within three different theoretical methods for Iso I. The calculated VDEs of Iso I are plotted as red sticks in Figure 1. This unambiguous agreement confirms that Iso I is indeed the main contributor to the ion beam and the measured photoelectron spectrum. The small relative energy difference of Iso II (2.2 kcal mol^{-1} at CCSD(T) level) makes it a possible candidate to be observed in the PES as well.

Since its calculated first VDE at CCSD(T) level of theory (blue stick in Figure 1) is also within the tail of the first EBE band of the spectrum, we do not rule out the possibility of the existence of Iso II in the ion beam. The most stable triplet spin state isomer is higher in energy than the singlet spin state GM (Iso I) by 12.4 kcal mol^{-1} at CCSD(T), hence, its population is expected to be negligible.

To understand the nature of the B–B interaction and test the presence of the triple bond in the GM structure, we turn to an in-depth analysis of its bonding using Adaptive Natural Density Partitioning (AdNDP) method[41] which was designed to produce illustrative Lewis-like bonding patterns in molecules,[42,43] clusters[31,44–48] and solids.[49,50] It was previously found that AdNDP is basis-set and method independent.[51–53] It revealed three s-type lone pairs on Al atoms with occupation numbers (ONs) of 1.96–1.67 $|e|$, two s-type lone pairs on two B atoms with ON = 1.46 $|e|$, one 2c-2e B-B σ bond with ON = 1.89 $|e|$, and two 5c–2e π bonds involving all B and Al atoms with ON = 2.00 $|e|$. The last two fully delocalized 5c–2e bonds could also be viewed as two direct B–B 2c–2e π bonds with somewhat lower ON values, that is, 1.67–1.61 $|e|$. This indicates that the contribution to these 5c–2e π bonds from B–B 2c–2e π bonds is major, that is, approximately 80%. Overall, the three Al atoms provide about 0.4 $|e|$ to each π bond, and this is an example of highly polar covalent bonding. Hence, the communication between the B atoms can be qualitatively considered as a combination of one σ bond and two π bonds, making it a classical textbook triple bond analogous to that of N_2 shown in Figure 3 B. All bonds recovered by the AdNDP analysis are in full agreement with canonical molecular orbitals (Figure S1). Indeed, electron donation from Al to B is the key for generating the triple bond, and is also consistent with the
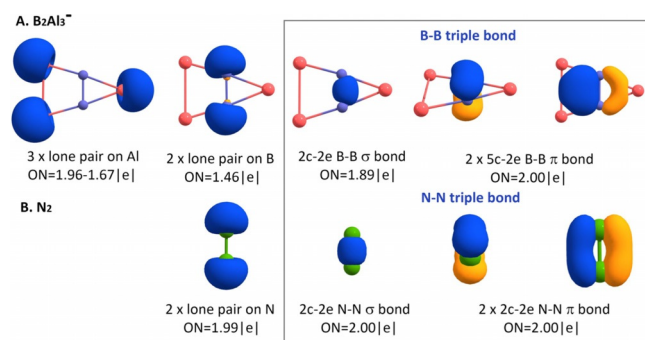
relatively longer B≡B bond length due to Coulomb repulsion, which is also supported from the charge distribution point of view (Figure S2). The sum of negative charges on B-B moiety is found to be −2.474 $|e|$ and −2.676 $|e|$, according to the NBO[54–57] and QTAIM[58–63] analyses, respectively (Figure S2). The NBO-based bond order is found to be 2.42, while AdNDP predicts it to be 2.59 (see the Supporting Information for more details). Although B atoms could not accept all four electrons to become ideal $B^{2-} \equiv B^{2-}$ kernel, the B triple bond is formed due to the delocalized interactions, as shown by the electronic structure calculations. The bonding analysis of ideal $B^{2-} \equiv B^{2-}$ fragment is presented in Figure S3. Apparently, $B^{2-} \equiv B^{2-}$ is unstable toward the spontaneous ejection of electrons, though it is still a good model, which is fully isoelectronic to N_2 molecule.

The assessment of B–B bond character based on relaxed force constants (FCs),[64–67] unfortunately, is not straightforward. FC of B≡B stretching mode is found to be 3.8 (hereinafter, in mdyn Å^{-1}), which is close to the previously reported value for B=B.[67,68] However, it is reasonable to expect B≡B in $B_2Al_3^-$ to be somewhat weaker and longer than in classical covalent compounds. For instance, relaxed FCs of $Na_3Al_2^-$ (0.95) and Na_4Al_2 (1.08), both having Al≡Al triple bonds, are lower than the relaxed FC responsible for stretching mode (1.43) in RR'Al=AlRR' molecule.[7] Obviously, the atomic environment of the bond affects FC tremendously, and, for instance, bulky ligands (as in RR'Al=AlRR') can significantly strengthen the bond. On the contrary, the B≡B skeleton in $B_2Al_3^-$ acquires extra electrons, thus increasing the Coulomb repulsion. As a consequence, we should expect elongation of the bond and decrease of the FC. For the detailed discussion regarding the relaxed FCs, refer to a recent article by Zhang et all[7] and Supporting Information where this discussion is deepened alongside with some notes about the bond dissociation energy.

The AdNDP analysis of Iso II is displayed in Figure S4. It is interesting to find that it also has the triple B≡B bond. The two s-type lone pairs, one σ bond and two π bonds are all similar to their counterparts of the GM Iso 1, thus confirming that the B≡B kernel in $B_2Al_3^-$ is indeed an isoelectronic analogue of N_2.

To conclude, we have computationally designed and experimentally observed a $B_2Al_3^-$ cluster the GM of which has a B≡B

Chemistry–A European Journal

Communication
doi.org/10.1002/chem.202001159

Chemistry Europe
European Chemical
Societies Publishing

triple bond. PES spectrum exhibits two electronic transitions up to ≈ 3.5 eV, both of which agree perfectly with the calculated values of the GM structure, suggesting that the computationally predicted structure corresponds to the one observed in the experiment. The AdNDP analysis indicates that the B≡B triple bond consists of one σ and two genuine π bonds. However, due to the significant Coulomb repulsion, this bond is predictably weaker than in other, especially, neutral B species. We have shown that it is possible to design a classical B≡B triple bond, similar to that of N_2, without any stabilizing bulky ligands. We anticipate that this work will not only promote a further search for other electronically enriched species but will also facilitate the design of solid-state compounds featuring B^{2-}≡B^{2-} building blocks, which could be stabilized by the metal ions.

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

Keywords: ab initio calculations · B≡B triple bond · boron clusters · photoelectron spectroscopy

[1] R. C. Fischer, P. P. Power, *Chem. Rev.* **2010**, *110*, 3877.
[2] K. P. Huber, G. Herzberg, *Molecular Spectra and Molecular Structure, IV. Constants of Diatomic molecules*, Van Nostrand, New York, **1984**.
[3] a) R. Dagani, *Chem. Eng. News* **1997**, *75*, 9; b) R. Dagani, *Chem. Eng. News* **1998**, *76*, 31.
[4] J. Su, X.-W. Li, R. C. Crittendon, G. H. Robinson, *J. Am. Chem. Soc.* **1997**, *119*, 5471.
[5] a) Y. Xie, R. S. Grev, J. Gu, H. F. S. Schaefer, P. v. R. Schleyer, J. Su, X.-W. Li, G. H. Robinson, *J. Am. Chem. Soc.* **1998**, *120*, 3773; b) K. W. Klinkhammer, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2320; *Angew. Chem.* **1997**, *109*, 2414; c) F. A. Cotton, A. Cowley, H. X. Feng, *J. Am. Chem. Soc.* **1998**, *120*, 1795; d) T. L. Allen, W. H. Fink, P. P. Power, *J. Chem. Soc. Dalton Trans.* **2000**, 407; e) R. Ponec, G. Yuzhakov, X. Gironés, G. Frenking, *Organometallics* **2004**, *23*, 1790.
[6] R. J. Wright, M. Brynda, P. P. Power, *Angew. Chem. Int. Ed.* **2006**, *45*, 5953; *Angew. Chem.* **2006**, *118*, 6099.
[7] X. Zhang, I. A. Popov, K. A. Lundell, H. Wang, C. Mu, W. Wang, H. Schnöckel, A. I. Boldyrev, K. H. Bowen, *Angew. Chem. Int. Ed.* **2018**, *130*, 14256.

[8] M. F. Zhou, N. Tsumori, Z. H. Li, K. N. Fan, L. Andrews, Q. A. Xu, *J. Am. Chem. Soc.* **2002**, *124*, 12936.
[9] A. Papakondylis, E. Miliordos, A. Mavridis, *J. Phys. Chem. A* **2004**, *108*, 4335.
[10] L. C. Ducati, N. Takagi, G. Frenking, *J. Phys. Chem. A* **2009**, *113*, 11693.
[11] M. P. Mitoraj, A. Michalak, *Inorg. Chem.* **2011**, *50*, 2168.
[12] N. Holzmann, A. Stasch, C. Jones, G. Frenking, *Chem. Eur. J.* **2011**, *17*, 13517.
[13] S.-D. Li, H.-J. Zhai, L.-S. Wang, *J. Am. Chem. Soc.* **2008**, *130*, 2573.
[14] N. Fey, A. G. Orpen, J. N. Harvey, *Coord. Chem. Rev.* **2009**, *253*, 704.
[15] H. Braunschweig, R. D. Dewhurst, K. Hammond, J. Mies, K. Radacki, A. Vargas, *Science* **2012**, *336*, 1420.
[16] P. Pyykkö, S. Riedel, M. Patzschke, *Chem. Eur. J.* **2005**, *11*, 3511.
[17] R. Köppe, H. Schnöckel, *Chem. Sci.* **2015**, *6*, 1199.
[18] N. Holzmann, M. Hermann, G. Frenking, *Chem. Sci.* **2015**, *6*, 4089.
[19] J. Böhnke, H. Braunschweig, P. Constantinidis, T. Dellermann, W. C. Ewing, I. Fischer, K. Hammond, F. Hupp, J. Mies, H.-C. Schmitt, A. Vargas, *J. Am. Chem. Soc.* **2015**, *137*, 1766.
[20] J. Böhnke, H. Braunschweig, W. C. Ewing, C. Hörl, T. Kramer, I. Krummenacher, J. Mies, A. Vargas, *Angew. Chem. Int. Ed.* **2014**, *53*, 9082; *Angew. Chem.* **2014**, *126*, 9228.
[21] J. Böhnke, H. Braunschweig, T. Dellermann, W. C. Ewing, K. Hammond, J. O. C. Jimenez-Halla, T. Kramer, J. Mies, *Angew. Chem. Int. Ed.* **2015**, *54*, 13801; *Angew. Chem.* **2015**, *127*, 14006.
[22] S. Ghorai, E. D. Jemmis, *Chem. Eur. J.* **2017**, *23*, 9746.
[23] F. Fantuzzi, M. A. C. Nascimento, *Chem. Eur. J.* **2015**, *21*, 7814.
[24] F. Fantuzzi, C. B. Coutinho, R. R. Oliveira, M. A. C. Nascimento, *Inorg. Chem.* **2018**, *57*, 3931.
[25] R. Saha, S. Pan, P. K. Chattaraj, *ACS Omega* **2018**, *3*, 13720.
[26] a) X. Zhang, K. A. Lundell, J. K. Olson, K. H. Bowen, A. I. Boldyrev, *Chem. Eur. J.* **2018**, *24*, 9200; b) K. A. Lundell, X. Zhang, A. I. Boldyrev, K. H. Bowen, *Angew. Chem. Int. Ed.* **2017**, *56*, 16593; *Angew. Chem.* **2017**, *129*, 16820; c) I. A. Popov, X. Zhang, B. W. Eichhorn, A. Boldyrev, K. H. Bowen, *Phys. Chem. Chem. Phys.* **2015**, *17*, 26079; d) J. T. Gish, I. A. Popov, A. I. Boldyrev, *Chem. Eur. J.* **2015**, *21*, 5307.
[27] a) M. Tacke, H. Schnöckel, *Inorg. Chem.* **1989**, *28*, 2895; b) M. Mocker, C. Rob, H. Schnöckel, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1754; *Angew. Chem.* **1994**, *106*, 1860; c) A. Ecker, H. Schnöckel, *Z. Anorg. Allg. Chem.* **1996**, *622*, 149.
[28] W. Li, L. Kong, C. Chen, J. Gou, S. Sheng, W. Zhang, H. Li, L. Chen, P. Cheng, K. Wu, *Sci. Bull.* **2018**, *63*, 282.
[29] M. Kulichenko, N. Fedik, K. V. Bozhenko, A. I. Boldyrev, *J. Phys. Chem. B* **2019**, *123*, 4065.
[30] G. Liu, N. Fedik, C. Martinez-Martinez, S. M. Ciborowski, X. Zhang, A. I. Boldyrev, K. H. Bowen, *Angew. Chem. Int. Ed.* **2019**, *58*, 13789; *Angew. Chem.* **2019**, *131*, 13927.
[31] M. Kulichenko, N. Fedik, K. V. Bozhenko, A. I. Boldyrev, *Chem. Eur. J.* **2019**, *25*, 5311.
[32] A. P. Sergeeva, B. B. Averkiev, H.-J. Zhai, A. I. Boldyrev, L.-S. Wang, *J. Chem. Phys.* **2011**, *134*, 224304.
[33] C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158.
[34] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650.
[35] G. D. Purvis, R. J. Bartlett, *J. Chem. Phys.* **1982**, *76*, 1910.
[36] K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, *157*, 479.
[37] K. A. Peterson, T. H. Dunning, *J. Chem. Phys.* **2002**, *117*, 10548.
[38] L. S. Cederbaum, *J. Phys. B* **1975**, *8*, 290.
[39] J. V. Ortiz, *Int. J. Quantum Chem. Symp.* **2009**, *36*, 321.
[40] J. S. Lin, J. V. Ortiz, *Chem. Phys. Lett.* **1990**, *171*, 197.
[41] D. Y. Zubarev, A. I. Boldyrev, *Phys. Chem. Chem. Phys.* **2008**, *10*, 5207.
[42] N. Fedik, A. I. Boldyrev, *J. Phys. Chem. A* **2018**, *122*, 8585.
[43] D. Y. Zubarev, A. I. Boldyrev, *J. Org. Chem.* **2008**, *73*, 9251.
[44] N. Fedik, M. Kulichenko, D. Steglenko, A. I. Boldyrev, *Chem. Commun.* **2020**, *56*, 2711.
[45] O. A. Gapurenko, R. M. Minyaev, N. Fedik, V. V. Koval, A. I. Boldyrev, V. I. Minkin, *Struct. Chem.* **2018**, *29*, 805.
[46] N. Fedik, M. Kulichenko, A. I. Boldyrev, *Chem. Phys.* **2019**, *522*, 134.
[47] N. Fedik, A. I. Boldyrev, A. Muñoz-Castro, *Phys. Chem. Chem. Phys.* **2019**, *21*, 25215.

[48] C. Liu, N. V. Tkachenko, I. A. Popov, N. Fedik, X. Min, C.-Q. Xu, J. Li, J. E. McGrady, A. I. Boldyrev, Z.-M. Sun, *Angew. Chem. Int. Ed.* **2019**, *58*, 8367; *Angew. Chem.* **2019**, *131*, 8455.

[49] N. V. Tkachenko, D. Steglenko, N. Fedik, N. M. Boldyreva, R. M. Minyaev, V. I. Minkin, A. I. Boldyrev, *Phys. Chem. Chem. Phys.* **2019**, *21*, 19764–19771.

[50] M. Kulichenko, N. Fedik, D. Steglenko, R. M. Minyaev, V. Minkin, A. I. Boldyrev, *Chem. Phys.* **2020**, *532*, 110680.

[51] A. P. Sergeeva, A. I. Boldyrev, *Comments Inorg. Chem.* **2010**, *31*, 2.

[52] M. P. Kelley, I. A. Popov, E. R. Batista, P. Yang, *Nat. Commun.* **2020**, *11*, 1558.

[53] M. Kulichenko, N. Fedik, A. I. Boldyrev, A. Muñoz-Castro, *Chem. Eur. J.* **2020**, *26*, 2263.

[54] NBO 7.0. E. D. Glendening, J, K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, P. Karafiloglou, C. R. Landis, and F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison **2018**.

[55] L. Suidan, J. K. Badenhoop, E. D. Glendening, F. Weinhold, *J. Chem. Educ.* **1995**, *72*, 583.

[56] F. Weinhold, C. R. Landis, E. D. Glendening, *Int. Rev. Phys. Chem.* **2016**, *35*, 399.

[57] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735–746.

[58] AIMAll (Version 19.10.12), Todd A. Keith, TK Gristmill Software, Overland Park KS, USA, **2019** (aim.tkgristmill.com).

[59] R. Bader, *Atoms in Molecules: A Quantum Theory,* Oxford University Press, USA, **1994**.

[60] P. L. A. Popelier in *The Chemical Bond* (Eds.: G. Frenking, S. Shaik), Wiley-VCH, Weinheim, **2014**, pp. 271–303.

[61] C. Lepetit, P. Fau, K. Fajerwerg, M. L. Kahn, B. Silvi, *Coord. Chem. Rev.* **2017**, *345*, 150–181.

[62] R. F. W. Bader, *Acc. Chem. Res.* **1985**, *18*, 9.

[63] F. Cortes-Guzman, R. F. W. Bader, *Coord. Chem. Rev.* **2005**, *633*, 249.

[64] http://www.oc.tu-bs.de/Grunenberg/compliance.html (accessed on Feb. 21, **2020**).

[65] K. Brandhorst, J. Grunenberg, *J. Chem. Phys.* **2010**, *132*, 184101.

[66] K. Brandhorst, J. Grunenberg, *Chem. Soc. Rev.* **2008**, *37*, 1558.

[67] J. Grunenberg, *Chem. Sci.* **2015**, *6*, 4086.

[68] M. Maekawa, C. G. Daniliuc, P. G. Jones, J. Hohenberger, J. Sutter, K. Meyer, M. D. Walter, *Eur. J. Inorg. Chem.* **2013**, 4097.