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The Boron-Boron Triple Bond? A thermodynamic and force field based interpretation of the N-Heterocyclic Carbene (NHC) Stabilization Procedure

R. Köppe, and H. Schnöckel *

Recently, the NHC→B≡B←NHC molecule **1** has been published in *Science* where it is described as a stabilized B_2 molecule in its $^1\Sigma$ excited state (B_2^*). The bonding of **1** based on sophisticated calculations and the BB distances of the solid compound was discussed as the first example of a B_2 triple bond in a stable molecule. Now we present an only experimentally based interpretation of **1** via detailed thermodynamic considerations, including its fragmentation to B_2 molecules. Furthermore, from the vibrational spectrum force constants (f_{BB} for the BB bond and and f_{BC} for the BC bond) were extracted, which are classical examples to indicate single, double and triple CC bonds in organic chemistry. The consequence of both properties of **1** (ΔE and f) generates a new interpretation which is in contrast to the triple bond donor-acceptor description visualized by arrows and which casts a critical light on the interpretation of any NHC "stabilized" molecule.

Introduction

During the last two decades an unprecedented renaissance of main group chemistry has been developed.[1] High-lighted areas are e.g.: nanoscaled species like metalloid clusters as intermediates between normal valence compounds and bulk metals on one hand,[2-6] and, on the other hand, reactive molecules containing multiple bonding stabilized either via bulky ligands [7,8] or via N-heterocyclic carbenes (NHCs).[9,10] As an outstanding example in the latter field we will concentrate here on a compound containing an unusual B-B bond.[11-13]
Though there have already been presented some nice molecules before, which contain electron precise boron-boron bonds [14,15] as well as BB bonds containing additional π-bonding,[16-18] two years ago the outstanding impressive molecule NHC→B≡B←NHC (**1**) (Figure 1) was published in *Science* under the title "Ambient-Temperature Isolation of a Compound with a Boron-Boron Triple Bond".

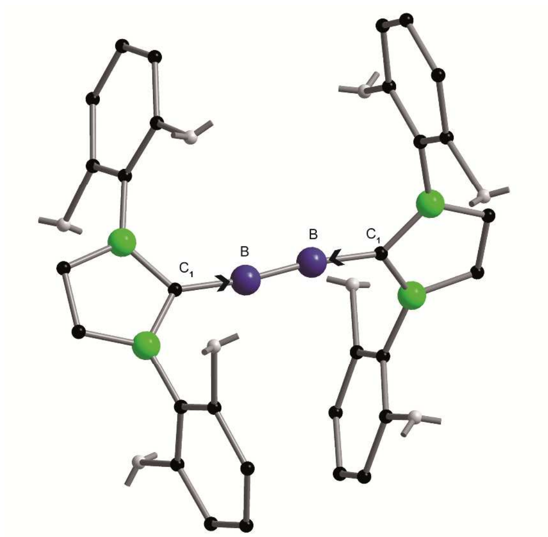

Fig. 1. The structure of **1** in the crystalline state and its interpretation as a donor-acceptor molecule symbolized via two arrows along the C_1B bond. The two methyl groups of each of the 8 grey C-atoms are omitted for clarity. The following distances (Å) are essential for the discussion: d(BB) = 1.45; d(BC) = 1.49; d(C_1N) = 1.39.

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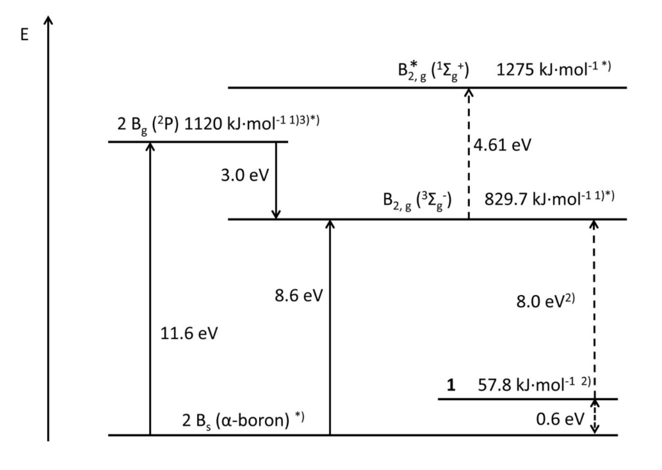
† Electronic Supplementary Information (ESI) available: Details of the theoretical calculations (thermodynamic data and force constants). See DOI: 10.1039/b000000x/

1 has been characterized via its X-ray solid state structure exhibiting a short B-B distance which is however longer than expected [19], via different NMR spectroscopic investigations, via three intensive IR bands, and an elemental analysis.[11,12] Furthermore, detailed quantum chemical investigations including the calculated UV/VIS spectrum have been presented. These calculations and the visualization of the orbitals involved in the multiple bonding were the basis for the interpretation summarized in the above-mentioned title[11] and for a highlight article in the same issue of *Science.*[12] Since this triple bond interpretation has also been predicted theoretically[20] and was also included in recent reviews,[21,10] we feel that it is time to make a cut and to give a different, only experimentally based interpretation for this nice compound **1** in order to increase our understanding of its unusual bonding and in order to prevent already beginning confusion, especially in the textbooks.[22] Furthermore we will show that any mainly "orbital based" interpretation in which an NHC stabilization is involved should make us cautious. Compound **1** was chosen for this discussion as an impressive example for the NHC stabilization, since many other molecules containing B-B bonding exhibit suitable reference data because the variation of the B-B vibration indicates the degree of "stabilization". Thus, we want to discuss **1** with respect to its thermodynamic property (Section 1) and its molecular vibrations (Section 2) for which the bond strengths (force constants) are an essential basis; i.e. we want to discuss two properties which are basic for every bonding discussion in the entire field of chemistry.[23-25]

Thermodynamic view

Today the thermodynamic stability of every species, even of reactive ones, is available via quantum chemical calculations.



*) "+2 NHC" omitted for clarity;
1) [26]; 2) calculated for **1a**: 35.7 kJ·mol^{-1} and 8.23 eV; 3)[27]

Fig. 2. Energy diagram for solid boron, B-atoms, B_2 molecules (B_2, B_2^*) and the decomposition of **1** to B_2 and 2 NHCs. Calculated (dashed lines) and experimentally obtained values [26]. For **2** see Supplementary Information.

Sometimes, additional experimental data make this discussion more confident. Unfortunately, this discussion is missing for **1** [28,20] and its interpretation as a donor acceptor stabilized molecule visualized by two arrows (Figure 1). In Figure 2 the calculated and the experimentally obtained thermodynamic data of molecule **1** and of solid boron together with the hot gaseous molecules / atoms B_1 [ground state ^2P],[27,30] B_2 [ground state $^3\Sigma_g^-$][26] and B_2^*[excited state $^1\Sigma_g^+$] are summarized.

Therefore, fundamental thermodynamic considerations could be the starting point for every bonding discussion before any other investigation will go into detail. The most remarkable conclusion from Figure 2 is that, with respect to the gaseous species B atoms, B_2 ($^3\Sigma$) and B_2^* ($^1\Sigma$), solid boron and the gaseous compound **1** are nearly on the same thermodynamic level: e.g. 2 boron atoms are 11.6 eV (1120 kJ·mol^{-1}) above solid boron and 11.0 eV above **1**.[29,30] However, since the boiling point of boron at 3900°C exhibits its robustness based on strong covalent B-B bonds, it is hard to believe that the gaseous B_1, B_2, B_2^* species can be obtained from **1** via heating, i.e. energy transfer from outside.[31] Nevertheless, at least theoretically in a Gedankenexperiment the dissociation of **1** to B_n-species and 2 NHCs can be allowed. However, the observation of a similar energy transfer starting from boron and from **1** to get gaseous B_1, B_2 and B^*_2 should be alarming!
Now we will discuss the reverse Gedankenexperiment, i.e. we look at the gaseous species B_1, B_2 and $B_2^*$and allow B_2^* a) to condense to solid boron or b) to react with 2 NHC molecules to **1** in the gas phase.
At about 2000 K the following gaseous boron species are in equilibrium with solid boron: i.e. the relative concentration of B_1, B_2 and B_2^* is 10^{18}:10^{12}:1 (see Supplementary Information). Now we concentrate on the excited B_2^* molecule[32] though its relative concentration in the gas phase is extremely low. Nevertheless this B_2^* molecule was the basis for the theoretical discussion of **1** and its triple bond character.
a) When B_2^* is condensed to form solid boron, 13.2 eV (1275 kJ·mol^{-1}) are gained, because the multiple bond of B_2^* is changed to solid boron containing only single bonds like in a polymerization process. Thus, there is a dramatic exothermic rearrangement of atoms and electrons, and one of the strong covalent bonded allotropes of boron with their high thermal robustness is formed. The large energy gain which is connected with this process will cause a strong heating of boron, which is no problem for this material, and which finally heats the environment. The conclusion of this Gedankenexperiment is, that solid boron and its structure has nothing to do with the bonding and structure of B_2^*. Therefore, nobody would conclude that B_2^* is stabilized in solid boron!
b) Now we look at the reaction of B_2^* with 2 NHC molecules in the gas phase: This formation of **1** is strongly exothermic with 12.6 eV (1221 kJ·mol^{-1}) because the electrons are rearranged, new bonds are formed, and the original bonds are changed. The large energy gain of this gas phase reaction should result in the heating of **1** and its fragmentation; i.e. this fragmentation process would start by breaking the weakest bonds: However,

in principle, this fragmentation can be avoided [33-38] – at least theoretically – if the heat can be transferred fast enough to the environment, e.g. via radiation. Anyway, if **1** really would survive in this exothermic reaction starting from B_2^* and 2 NHC, one has to conclude: The final state of this reaction (i.e. **1**) is energetically far below the starting point (B_2^* + 2 NHC) (12.6 eV), i.e. electron distribution and bonding of the educts and products must be extremely different. In one word, the final state **1** has nearly nothing to do with the educts (B_2^* and 2 NHC molecules), like in the case of solid boron! Consequently, the bonding situation in **1** can hardly be symbolized as a slight modification of the educts via arrows (Figure 1), which suggest only a weak donor (NHC) – acceptor (B_2^*) interaction in which the bonding of the educts is still visible.

However, to look more carefully to the energetic situation of the final electron distribution within the "C-B-B-C" core, especially with respect to the BC bonding, one has to start with the ground state of B_2 (8 eV (772 kJ·mol^{-1}) above **1**); with its BB single bond and without BC contacts to 2 NHCs. If the BB bond is not changed during the reaction with 2 NHCs, the formation of two BC single bonds will consume 772 kJ·mol^{-1}, i.e. each BC bond consumes 386 kJ·mol^{-1}, nearly the expected value of the BC single bond energy 372 kJ·mol^{-1} [39]. However, this intermediate electronic situation of **1** with one BB and two BC single bonds has to drop into a more stable energetic valley, if the energy of the B_2 molecule is increased after its formation from B_2* as starting point. Subsequently, this intermediate possessing only single bonds has to consume 445 kJ·mol^{-1} (4.61 eV), which is nearly quantitatively possible by the formation of two BC double bonds, which are each estimated to be at 230 kJ·mol^{-1} , i.e. slightly more stable than the BC single bond [40]. Thus the following situation for the central C=B-B=C core results which is in line with the most prominent neutral resonance structure presented in Scheme 1. Finally, after distribution of the π electrons from the BC bonds to the whole CBBC core, this thermodynamic Gedankenexperiment results in a 4-electron-4- center π bond (Scheme 2).

In order to confirm the conclusion of a rearrangement of electrons in **1** which is completely different from that of the educts, we look at the forces between the atoms of **1** which are visible by its vibrational spectrum i.e. by its IR and Raman spectrum and compare this situation with that of the B_2^* molecule.

Determination and discussion of the force constants of 1

For the bonding discussion of **1**, the most convincing structured property concerning the BB bond was its short distance.[11,19,41-43] Much more reliable and sensitive for the experimental characterization of a bond and especially of multiple bonds are the force constants which reflect directly the situation of the bonding electrons between two nuclei. More accurately, the force constant f (spring constant: Force = f·Δr) represents the restoring force which resists to a small elongation (Δr) of the atoms from the equilibrium distance.[44] The relevance of force constants for the discussion of bond properties has recently been shown for the Zn-Zn bond in $Zn_2Cp_2^*$,[45] has been highlighted for the discussion of S-S multiple bonds[46] and, as a classical example, is convincingly demonstrated in fundamental organic chemistry, where the relation of the force constants of a CC single bond to a double and a triple bond is about 1:2:3.[47,48] Therefore, a discussion of force constants of bonds between carbon and its direct neighbor element boron should also be a convincing measure to discuss BB and BC bonds especially whether or not multiple bonding is involved.

Table 1. Some vibrational frequencies of the model compound **1a**, their assignment via the potential energy distribution (PED), and their isotopic shifts.

	ν/cm^{-1}	Δν(^{10}B/^{11}B)	Δν(^{12}C/^{13}C)	Δν(^{14}N/^{15}N)	PED
a_1	1156.94	2.53	9.88	20.27	22 % $\nu_S(CN_2)$ + 60 % $\nu_S(NC_H)$
b_2	1298.74	11.8 5	13.55	20.29	40 % $\nu_{as}(BC)$ + 30 % $\nu'_S(NC_H)$[a)]
a_1	1450.95	6.93	8.29	26.56	20 % $\nu_S(CN_2)$ + 22 % $\nu_S(NC_H)$
b_2	1505.32	5.3	22.52	35.34	23 % $\nu_{as}(BC)$ + 23 % $\nu'_S(CN_2)$
a_1	1582.80	0.85	0.04	2.55	61 % ν_S(C=C) (in phase)
b_2	1585.54	0.35	1.35	3.85	58 % ν'_S(C=C)
a_1	1769.50	64.72	10.79	11.09	47 % ν(BB) + 43 % ν_S(BC)

[a)]ν_S‘ means ν (symmetric) but out of phase motion.

Table 2. BB and BC force constants (mdyn·Å^{-1}) and distances (Å) experimentally determined and calculated in brackets from a weak BC bond of H_3B–CO via a 2e2c single bond of H_2B-CH_3 to a double bond in HB=CH_2

Molecule	f_{BB}/f_{BC}	r_{BB}/r_{BC}
B_2 ($^3\Sigma_g^-$)	3.6[a] (3.3)	1.59[a] (1.64)
B_2^* ($^1\Sigma_g^+$)	(7.7)	(1.40)
B_2Cl_4	3.4 [b] (2.83)	1.73 (1.70)
H_3B–CO	2.8 [c] (3.7)	(1.52)
H-B=CH_2	(7.8)	(1.39)
H_2B-CH_3	(4.0)	(1.56)
1a	(6.0/5.2)	(1.49/1.49)

(..) calculated values (c.f. Supplementary Information) a)[49] b)[50] c)[51]

Unfortunately, force constants cannot directly be obtained from the vibrational spectra, because the observed spectra are the result of interactions of the hypothetical isolated motions within every bond or special entities of a molecule. However, the so-called normal-coordinate analysis[52] allows extracting the force constants for every bond, if the molecule and the number of vibrations are not too large. Therefore, instead of the determination of the force constant of **1** (there are 390 vibrations) we have chosen the model compound **1a** in which the NHC of **1** is substituted by the most simple NHC containing only H ligands: $C(NH)_2(CH)_2$, and only 54 vibrations are obtained. Since the vibrations and the vibrational coupling within the CBBC moieties of **1** and **1a** are similar[53] and since the relevant structural data of the N_2CBBCN_2 unit of **1a** and **1** are nearly identical (c.f. below), this simplification is allowed. The normal coordinate analysis of the vibrations of the N_2CBBCN_2 core of **1a** is collected in Table 1.
The potential energy distribution (PED) [52] exhibits the strong coupling of the BB, BC and CN vibrations, which is a first hint for a strong BC bonding! Furthermore, the resulting force constants (mdyn·Å^{-1}) f_{BB}, f_{BC} and $f_{BB/BC}$ give a convincing picture of the bonding in the core of **1a** and also of **1.**[54]

$$f_{BB} = 6.0\ (1.49\ Å) \qquad f_{BC} = 5.2\ (1.49\ Å) \qquad f_{BB/BC} = 0.16$$

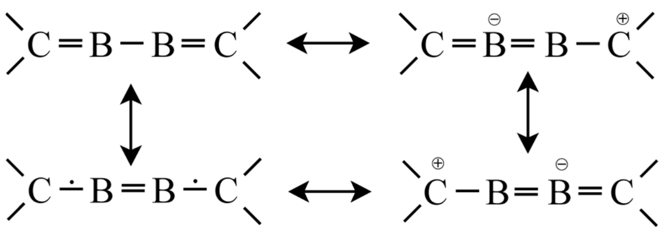
In order to get a feeling for these values and to discuss them, we will compare them with force constants of some species summarized in Table 2.
In order to decide about the possible multiple bond strength of the BB bond in **1** we must obtain reliable reference data for a BB single bond. As far as we know, only a single experimental value with 3.4 mdyn·Å^{-1} has been published for B_2Cl_4.[50] Perhaps this value represents a weak BB single bond, because the BB distance in B_2Cl_4 with 1.73 Å is relatively large. The value for f_{BB} of the B_2 triplet molecule ($^3\Sigma$) in its ground state with 3.6 mdyn·Å^{-1} is a little bit larger; however, the distance of the BB bond is significantly shorter (1.59 Å). Both parameters of this B_2 molecule are difficult to access because of the triplet character of B_2 and two "binding" electrons in orthogonal π-bonds.[55,50] In order to have a BB bond situation similar to that of **1** with a linear X-B-B-X moiety [56] , we have finally calculated the force constants [mdyn·Å^{-1}] within the O=B-B=O [57] species (O  CH_2) for which already the vibrational spectrum of the matrix isolated species was obtained two decades ago:[58]

$$f_{BB} = 3.5\ (r_{BB} = 165\ pm)$$
$$f_{BO} = 13.9\ (r_{BO} = 121.3\ pm)$$
$$f_{BB/BO} = 0.05$$

The force constant f_{BB} of 3.5 mdyn·Å^{-1} corresponds to a BB single bond though the BB distance is shorter than in B_2Cl_4 and longer than in B_2 ($^3\Sigma$) (Table 1). However, the Lewis formula O=B-B=O is in accordance with the values of the BB and BC force constants. The value of the interaction force constant $f_{BB/BO}$ is, like that of **1a**, unexpectedly low (mostly about 10% of the stretching force constants), which demonstrates that the changes within the BB bond have only a small influence on BC bonds (**1a**) or BO bonds in B_2O_2. However, these interactions are, as expected, significantly larger for **1a** than for B_2O_2, i.e. for a more ionic compound.
The only example for a BB multiple bond within the molecules of Table 1 is observed in the excited B_2^* molecule: The large value of f_{BB} of 7.7 mdyn·Å^{-1} is in line with a small BB distance of 1.4 Å, i.e. a strong double bond is present in this molecule.
From all these data we are now able to interpret the f_{BB}= 6.0 mdyn·Å^{-1}and f_{BC}=5.2 mdyn·Å^{-1} force constant of **1a**:
The BB bond should be addressed as a strong 1.5 BB bond and the BC bond as a weak 1.5 BC one.
These results are in line with the thermodynamic discussion, from which the BB bond in B_2^* has lost its strong double bond character and, even more important, the value of the BC force constant forbids to address it as a donor-acceptor bond. This BC bond is even significantly stronger than a 2e2c bond! Therefore, mainly the two strong BC bonds of **1** are responsible for the large energy gain of 12.6 eV discussed in the thermodynamic part. [60,59,24,25]
The results of the thermodynamic data and of force constant determinations of **1** both accessible by observables show that a reassessment is pending concerning the bond description of **1**. For a conclusive interpretation we have to decide whether to rely, besides the measured bond distance, on the predominant occupation of selected calculated MOs,[61] or – and this is the bonding description of multiple bonds we favor – to prefer an interpretation based on observed thermodynamic relationships and the force constants based on the observed vibrational spectra. These force constants reflect the slope of the potential energy curve near the equilibrium distance and are thus a confident measure of the bond strength. This argument has already been impressively demonstrated in the evaluation of CC multiple bonds in the past[48] so that we had applied it also for assessing the GaGa multiple bonds that were under discussion about 20 years ago.[62-65] Even at that time, we were able to show that the bond described as a GaGa triple bond was just a slightly stronger single bond.[66-69]

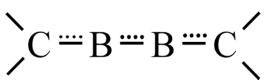
Conclusions

Thus, from the thermodynamic and the force constant discussion a new description of bonding results for **1** [70]. To sum up, **1** does not contain a BB triple bond and the description as a stabilization of an excited B_2^* molecule via "arrows" of 2 NHC molecules is strongly misleading.[72] Therefore a bonding situation results which can be described by the following resonance structures containing 4 π electrons for the BB and two BC bonds; i.e. the situation for these three bonds is just between single and double ones:



Scheme 1

Therefore, we prefer a simpler description for this 4-electron 4-center π-bond via the following formula:



Scheme 2

To sum up, the bonding within **1** is determined by an overall electron transfer from the "triple" bond of B_2^* to the BC bonds. This partial electron transfer is completed in the isolated normal valent B_2O_2 molecule, and consequently a BB single bond results:

$$\overline{O}=B-B=\overline{O}$$

Furthermore, from the discussion of **1** presented here a fundamental conclusion for the reaction of any NHC (cyclic (diamino) carbenes as well as for cyclic (alkyl)(amino) carbenes) like in **2** during the "stabilization" of a reactive species X has to be drawn, in order to avoid serious problems for the description of bonding in many fields of inorganic chemistry: are the bonds between the **X** species and the NHC molecule - concluded from thermodynamics and from force constants as significant indicators of bond strength - weak donor-acceptor bonds symbolized by arrows, or are there strong covalent bonds which are possibly increased to have partial multiple bond character.[72] The analysis of the variation of the BB vibration of **1** provides an easy indicator for the degree of its stabilization. Therefore, the bonding description of **1** presented here may also show exemplarily that the bonding discussion of any other NHC stabilized reactive species has to been seen critically. Anyway, the description of such bonding by arrows is at least strongly misleading, [73] as a more general controversy has already shown.[74-76] However, our critical description does not lower the excellent work of H. Braunschweig and G. Robinson, but it increases the understanding of the bonding of their unprecedented compounds.

Acknowledgements

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Given that the covalent radii of C and B are ca. 0.76 and 0.84 Å [80] and that a CC triple bond is ca. 1.18 Å in acetylene, an only slightly longer BB triple bond of ca. 1.30 Å (1.18 x 0.84 ÷ 0.76), which is roughly proportionate to the different covalent radii of B and C, might have been expected (1.45 Å) for B≡B (Figure 1). On the other hand, the B-C bond length (1.49 Å) is shorter than might be expected for a B-C single bond, and it lies (just) within the range known for B-

C double bonds in methylene boranes (1.351 - 1.488 Å [40]) suggesting that the B-C bond has multiple character.

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[23] Even two years after the publication of **1** (ref. 11-13) a further nice BB containing compound **2** has been published (ref. 24), just when we had finished this manuscript. However, even for **2**, which does not contain the cyclic di(amino)carbene of **1** but a cyclic (alkyl)(amino)carbene (CAAC) (ref. 25), a thermodynamic as well as a force constant discussion based on the vibrational spectra is missing.

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[41] However, there are well-known examples that the distance between two atoms can be a misleading property for the characterization of a bond (e.g. the BB distances in B_2H_6 with 1.77 Å without a direct bond is similar to the 2e2c BB bond in B_2Cl_4 (1.72 Å); furthermore, the following NaNa distances (Å) show that there is no correlation between bonding and distance: in solid NaCl (3.44), Na_{metal}: 3.72, Na_2-molecule: 3.0, $(NaCl)_2$-molecule: 2.81 (see ref. 42,43).

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[44] Larger elongation to infinity distance between the vibrating entities means the dissociation energy ΔE_{diss} mostly is not a representative measure of a bond, as the educt and the (fragmentation) products have different electronic and structural properties. Therefore, the force constant represents a more reliable characterization of a bond!

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[47] f_{CC} [] /[$mdyn\cdot Å^{-1}$]: C_2H_6 (4.4); C_2H_4 (9.1); C_2H_2 (15.6) (ref. 48).

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[53] This is convincingly and exemplarily shown for the BB vibration and its $^{10}B/^{11}B$ and $^{12}C/^{13}C$ (in brackets) shifts (all in cm^{-1}) 1: 1702 (63.4; 9.5); 1a: 1770 (64.7; 10.8). Even for **2** a very similar bonding can be expected: 1686 cm^{-1} (60.3; 11.8 cm^{-1}).

[54] f_{XY} means the stretching force constant between the atoms X and Y. The interaction force constant $f_{XY/WZ}$ means the interaction between two bonds, i.e. whether or not and to which extent there is a restoring force within the XY bond if the WZ bond is elongated.

[55] The BB bond in B_{12} units of α-boron is, as expected, much smaller (about f_{BB} 1.3 $mdyn\cdot Å^{-1}$), since there is an electron deficient situation of only 13 doubly occupied orbitals and 30 equivalent BB bonds [50].

[56] There are already published calculated [78] and experimentally obtained [79] examples with a central X-BB-X moiety, for which a BB triple bond has been calculated. However, our normal coordinate analysis for the most prominent example $[O{\equiv}B\text{-}B{\equiv}B\text{-}B{\equiv}O]^{2-}$ [78] a different formula $[O\text{-}B\text{-}B{=}B\text{-}B\text{-}O]^{2-}$ has to be concluded due to the following calculated force constants:f_{BO} = 10.26, f_{BB}= 3.70, f_{BB}(central) = 5.51 $mdyn\cdot Å^{-1}$, i.e. the situation of $B_4O_2^{2-}$ is comparable to the discussion of **1** presented here, and also contradicts the BB triple bond interpretation.

[57] The following results are obtained for N≡C-C≡N isoelectronic to OBBO: r(CN) = 1,1755, r(CC) = 1.3836 Å, f_{CN} = 17.81, f_{CC} = 7.29 $mdyn\cdot Å^{-1}$, i.e. there is a strengthened CC single bond.

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[60] The BB compound **2** containing two cyclic (alkyl)(amino)carbenes (c.f. ref. 24) which has been published recently, may be just between the bonding of **1** and O=B─B=O. Thus, the latter one represents an extreme situation with a BB single bond. In analogy the BB single bond may also be present if two electron drawing carbenes like CCl_2 are the ligands: Cl_2C=B─B=CCl_2. In this case, like for the (alkyl)(amino) carbenes of **2**, the HOMO is increased and the LUMO is decreased in comparison to **1**; i.e. these carbenes, e.g. in **2**, are better donors and acceptors (c.f. ref 25).

[61] The occupation of single MOs in principle is not directly correlated with a bond, because these separated occupation numbers are no observables. Only the sum of all MOs, their occupation numbers and energies result in observables like the distance and the force constant.

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[66] For formal GaGa single / double / triple bonds the following GaGa force constants (mdyn·$Å^{-1}$) and distances (Å; in brackets) are obtained: $Ga_2H_6^{2-}$: 0.75 (2.58); $Ga_2H_4^{2-}$: 0.98 (2.46); $Ga_2H_2^{2-}$: 1.01 (2.41). In order to show that no heavy atom effects are responsible for this drastic difference to the situation in the first period (e.g. for organic chemistry), we have studied the situation within the following AsAs-bonded molecules, though arsenic is the element next to the neighbor of Ga in the periodic table; i.e. As and Ga differ by two electrons: As_2H_4: 1.38 (2.49); As_2H_2: 2.61 (2.27); As_2: 4.22 (2.12) (ref. 67).

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[70] Furthermore, the here presented critical description is also in line with the convincing comments on the BB and BC distances. [19]

[71] The same is valid for **2** (c.f. ref. 24) which has nothing to do with B_2^* and the discussed threefold bonding of **1** (c.f. ref. 11); i.e. all argumentation presented here for **1** and its misleading bonding discussion shall be applied to **2**. However, for **2** there are slightly stronger BC bonds, which correspond to the higher stability of **2** in comparison to **1**. This property is in line with the exothermic behavior of solid boron carbides (ref. 30) and their covalent BC bonds, c.f. Supporting Information.

[72] Even the CN_2 vibrations of the NHC moiety of **1** show that they are strongly involved in the bonding and vibration to the "reactive" molecule B_2^* (c.f. Table 1), i.e. a new covalent bonded molecule is formed with hardly any relation to the "educts" B_2/B_2^* and 2 NHCs.

[73] Furthermore, a description of this kind generates serious confusion for teaching inorganic chemists. [77]

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Graphical and textual Abstract for the

Table of Contents:

In contrast to a recently highlighted B_2 triple bond description of the NHC → B2 ← NHC molecule an only experimentally based (thermodynamic and vibrational force constants) interpretation casts a critical light on any NHC "stabilized" molecule.