

Hunting dimers

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Abstract HBCBH and HAICAIH are related electron-deficient molecules, predicted as local minima on their respective potential energy surfaces. Different views of their electronic structure—as allenes, carbenes, or carbones—prompted two research groups to a friendly competition exploring the predilection of these small molecules to dimerize. Many such dimers emerged from the calculations, some with large enthalpies favoring dimerization. Most interesting among these is an octahedral didehydro-carborane (or alane). The menagerie of $(\text{HECEH})_2$, $E = \text{B}, \text{Al}$ structures obtained shows great variety in its bonding patterns. That variety is instructive, for it points to the necessity of examining dimerization for any theoretically postulated metastable molecule. We also learn of the continuing utility of simple Lewis structures, the acid–base reactivity of carbones and carbenes, and the dominant role of electron deficiency in borane and alane chemistry.

Keywords Borylene · Alane · Bonding analysis · Dimerization · Quantum chemical calculations

Dedicated to Professor Eluvathingal Jemmis and published as part of the special collection of articles celebrating his 60th birthday.

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1 Introduction

This is a story of friends disagreeing, of doing the right thing for, perhaps, the wrong reason. A story also of conflicting views of chemical bonding and molecular properties, demonstrating that dispute and contention are healthy ingredients of science. And in the end, a story of science working as it should and being fun too.

Not too long ago, one of us (RH) wrote with some friends an exhortatory, if not self-righteous, article chiding fellow theoreticians for claiming stability for molecules in fact lacking kinetic persistence under ambient conditions [1]. The authors advised that prior to making such a claim people minimally examine the barrier for and enthalpy of dimerization and perhaps reaction with normal components of laboratory atmospheres. Another one of us (GF) wrote the only negative review of that paper [2], pointing out that what the authors said was just obvious.

The conflicting positions of RH and GF—which also play a major role in the present work—can partly be traced back to their scientific upbringing. While the scientific career of RH took shape in the surrounding of classical synthetic organic and inorganic chemistry, where molecules are considered stable (using here the colloquial sense of the word) only if they are “bottleable”,¹ the attitude of GF was strongly influenced by his early work in gas-phase ion chemistry, where the recording of an associated spectroscopic signal is sufficient to prove the existence of a molecule. The former viewpoint is dominant in chemistry, which has historically had a particularly strong connection to industry, where compounds, of course, have to be around long enough to be handled in bulk.

¹ A neologism, but one with an obvious meaning.

However, a molecule is a molecule, no matter how long it stays around. Its lifetime is, of course, dependent on the height of the barriers surrounding the minimum on the potential energy surface in which it lies. Shallow as that minimum might be, as a detectable species a molecule becomes a proper object of study of chemical science in its acquisition of knowledge of the material world on a molecular scale. Molecules that are “stable” in the latter sense may not be of practical use, may never be available in macroscopic bulk, yet can still be objects of fascinating and scientifically illuminating research in gas-phase chemistry or low-temperature matrix-isolation studies.

Some time later, GF published a paper on the carbones $\text{Cp}^*\text{ECECp}^*$, $E = \text{B, Al, Ga, In, Tl}$ [3]. He could not keep himself from hypothesizing stability in the solid state for these. RH, inclined to view the carbones of GF [4–8] as nucleophilic carbenes, thought they would likely dimerize, a quintessential, highly exothermic reaction of carbenes. RH asked AYuR to examine some potential barrier-free dimerizations. Indeed, a couple of these were quickly found.

Rather than telling GF of this directly, or, for that matter, publishing a paper, RH wrote to GF, gently asking if GF had explored dimerization of his carbones. In suggesting to GF such potential reactivity, when he knew that in fact they would dimerize, at least computationally, RH was perhaps being coy. But he also was acting on a principle that he long ago learned in teaching introductory chemistry: the best way for someone to learn anything, truly learn it, is to do it him- or herself.

The dimerization of $\text{C}(\text{ECp}^*)_2$ [3] had indeed not been considered by GF in his work on group-13 diyl-substituted carbones CL_2 , which exhibit donor–acceptor bonds $\text{L} \rightarrow \text{C} \leftarrow \text{L}$ between strong σ -donors L such as PR_3 or NHC (N-heterocyclic carbene) and a divalent C(0) atom that possess two electron lone pairs at carbon rather than only one σ lone pair in carbenes CR_2 [4–8].

Complexes with group-13 diyl substituents ER ($E = \text{B} - \text{Tl}$), which are unsupported by additional donor groups, were long considered to be “unbottleable” compounds until R.A. Fischer and coworkers isolated in 1997 $(\text{CO})_4\text{FeAlCp}^*$, which was the first mononuclear complex with an unsupported ER ligand [9]. Given the stability of the latter compound and the carbodicarbones $\text{C}(\text{NHC})_2$, which had first theoretically been predicted by GF and coworkers [4] before they were isolated by Bertrand [10] and by Fürstner [11], it seemed plausible to suggest that $\text{C}(\text{ECp}^*)_2$ are accessible targets for synthetic efforts. A fact that was not considered by GF is the existence of a very strong donor moiety (the divalent C(0) atom as double donor) and the acceptor center E in the same molecule. This could induce strong intermolecular donor–acceptor interactions between two $\text{C}(\text{ECp}^*)_2$ molecules, which

could prevent isolation of the monomeric species under “normal” laboratory conditions.

In responding to RH, GF told him of another, simpler carbene system, HECEH , $E = \text{B, Al, Tl}$ [12]. The boron compound $\text{C}(\text{BH})_2$ had already been synthesized in a low-temperature matrix by Andrews et al. [13] RH thought these would dimerize readily as well.

Sure enough, GF and his able coworkers (the coauthors of this paper) found first one dimer, formed with no activation energy from the monomer. Then, a second one. Soon both groups were at it, finding daily new minima with unusual geometries, ones that pose a challenge for explaining the bonding in the molecules. The outcome of this competition that evolved into collaboration is this paper. It focuses on $(\text{HECEH})_2$, $E = \text{B, Al}$. The Cp analogues, with their own special features, will be described in a separate publication.

We have found 12 minima $(\text{HECEH})_2$ for $E = \text{B}$, 5 for $E = \text{Al}$, each more stable than two monomers (HECEH) . And not by small energies, either—by as much as 98 kcal/mol per dimer. Rather than give a table with the dimers found, we find it more instructive to first describe the electronic structure of the monomers, then indicate the reasoning that led us to explore certain dimer geometries, followed by our population of the dimer zoo.

2 Methods

The geometries of the molecules have been optimized without symmetry constraints at the gradient-corrected density functional theory (DFT) level of theory using Becke’s exchange functional [14] in conjunction with Perdew’s correlation functional [15]. The calculations were carried out with split-valence basis sets of doubly polarized triple- ζ -quality developed by Weigend and Ahlrichs [16]. This level of theory is denoted as BP86/def2-TZVPP. Improved single-point energies were computed at the CCSD(T)[17–19]/def2-TZVPP level of theory using BP86/def2-TZVPP-optimized geometries. The nature of the stationary points on the potential energy surface was characterized by calculating the Hessian matrices. The calculations were carried out with the Gaussian09 program package [20]. The NBO [21] charges were obtained using the NBO 3.1 program implemented in the Gaussian program package. The AIM [22] analysis was carried out using a modified version of AIMPAC [23] using a BP86/def2-TZVPP wavefunction.

3 Boron monomers HBCBH

The Marburg group found two minima for this molecule with $E = \text{B}$, with geometries given in **1B** and **2B** (Fig. 1).

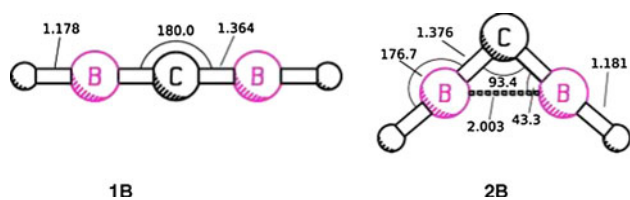
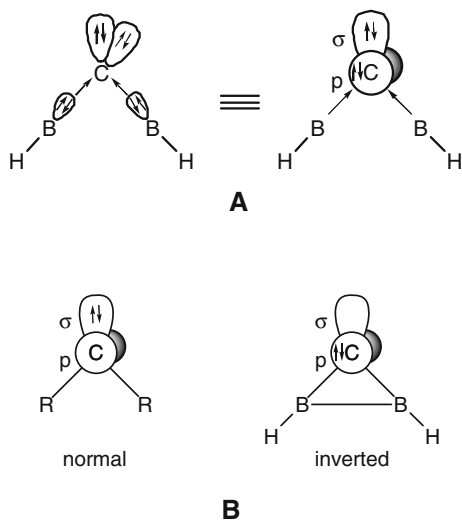


Fig. 1 Optimized geometries of **1B** and **2B** at CCSD(T)/cc-pVQZ. Distances are given in Å, angles in degrees



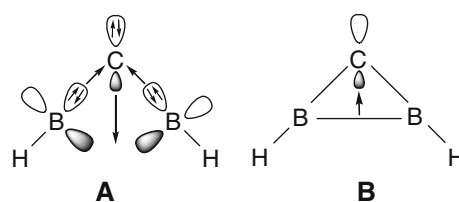
Scheme 1 Schematic view of the bonding situation in **2B** as a carbene (**A**) and as diboracyclopropenylidene (**B**)

With the best calculations, they (in cooperation with the Wesley Allen group [12]) could apply to the problem (FPA at FC-CCSD(T)/cc-pVQZ + ZPVE correction + Core-correlation correction + Relativistic correction + DBOC), these geometries are nearly equal in energy ($\Delta E < 0.1$ kcal/mol) and separated by a barrier of ~ 2 kcal/mol.

The electronic structure of the linear isomer **1B** is clear. It is a boraallene, with two perpendicular two electron π systems that are polarized toward the carbon atom, which carries a negative partial charge of $-0.81 e$ [12]. No doubt **1B** is very electron deficient, but still C–B multiply bonded, as the distances indicate.

The bent isomer is seen by GF and RH through different spectacles (Scheme 1). GF sees it as a carbene, described by valence structure **A**. There are two lone pairs on carbon, two donor bonds from B to C, and no B–B bond. Supporting this carbene perspective are two strong proton affinities [12].

RH, who has been looking at carbenes for over 40 years [24], sees in the bent structure of HBCBH, a boron analogue of cyclopropenylidene (isoelectronic with its dication). Normal carbenes (valence structure **B** left) have a σ lone pair below a $p(\pi)$ orbital. But (as RH saw it) bent



Scheme 2 Different perspectives of GF (**A**) and RH (**B**) of the B–B interactions in **2B**. The occupied $p(\pi)$ orbital at C is not shown

HBCBH would have an “inverted” orbital ordering (**B** right), the carbene $p(\pi)$ orbital pushed below σ (in the process becoming occupied, instead of σ), by interaction with the empty $2p(\pi)$ orbitals of the borons.

The essential difference between the two viewpoints is that in **A** there is no B–B bond, but a filled σ lone pair, while in **B** there is a B–B bond and an empty σ orbital. Does the calculated BB bond length of 2.00 Å help us decide between the two pictures? A normal B–B single bond length unsupported by hyperconjugation is around 1.75 Å (e.g., in planar H_2B-BH_2 [25]). To GF, the weak B–B interaction in bent HBCBH (if any; he sees no bond critical point there) is due to a mixing in of a symmetric boron in-plane orbital combination into the carbene center σ lone pair. To RH, 2.00 Å in **B** looks like a B–B bond that is weakened by donation from the B–B bonding orbital into the unfilled carbon σ orbital (Scheme 2).

What do the orbitals of the molecules tell us? The LUMO + 1, LUMO, HOMO and HOMO – 1 of HBCBH (**2B**) are shown in Fig. 2. The HOMO is the carbene $p(\pi)$ orbital, which extends to the $p(\pi)$ orbitals of boron in a bonding fashion, while the LUMO + 1 is the nonbonding

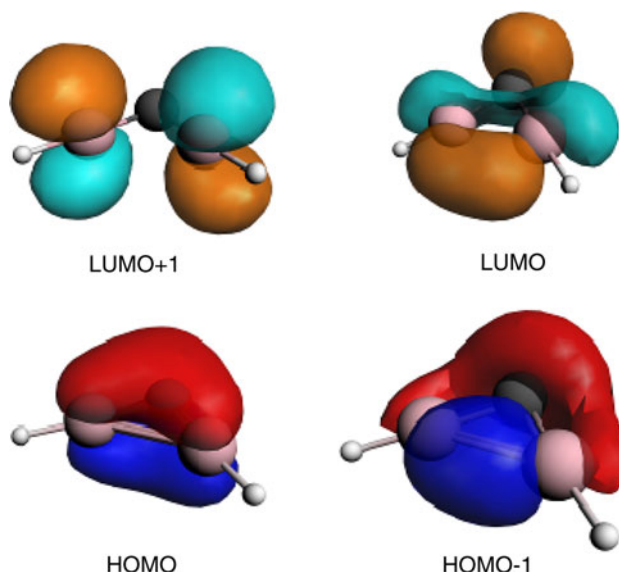


Fig. 2 The shape of the LUMO + 1, LUMO, HOMO, and HOMO – 1 of **2B**

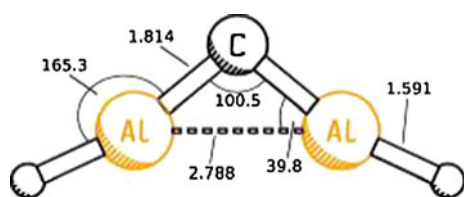


Fig. 3 Optimized geometries of **2Al** at CCSD(T)/cc-pVQZ. Distances are given in Å, angles in degree

π orbital. Both orbitals are similar to the lowest lying π orbitals of the allyl system. There is substantial B–B and C lone pair character in both the HOMO – 1 and the LUMO σ orbitals. So both GF and RH are right. Or both wrong. To put it another way, the bonding situation is sufficiently flexible to allow both viewpoints.

4 Aluminum monomers HAICAIH

Optimization of the structure of the aluminum homologue HAICAIH gave only the bent structure **2Al** as an energy minimum (Fig. 3). The linear form **1Al** is a second-order saddle point, which is 7.3 kcal/mol (CCSD(T)/TZVPP) higher in energy than **2Al**.

The frontier orbitals of **2Al** (Fig. 4) show the same energy ordering, and they look similar to those of **2B**. The backside lobe of the carbon σ orbital in the HOMO – 1 of **2Al** appears to be larger than in **2B**, which could mean that the Al–Al bonding contribution in the former species is larger than B–B bonding in **2B**. Note that the C–Al–H angle in **2Al** is smaller (165°) than the C–B–H angle in **2B** (177°); the hydrogens at Al are thus “bent” in the direction one would expect if there were an Al–Al bond in this molecule. The Al–Al distance of 2.79 Å

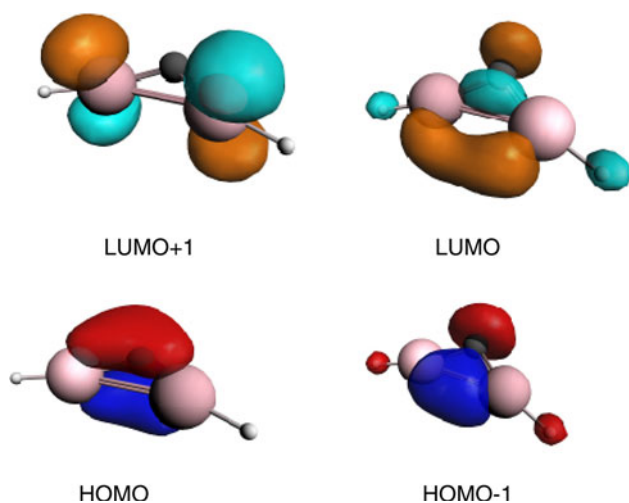


Fig. 4 The shape of the LUMO + 1, LUMO, HOMO, and HOMO – 1 of **2Al**

is long, but closer to an unsupported Al–Al single bond of ~ 2.60 Å (as in planar $\text{H}_2\text{Al}-\text{AlH}_2$ [25]) than what one sees in the boron case.

What becomes productive at this point is not further argument about the bonding situation, but getting at what chemistry the two viewpoints suggest.

5 Possible reactions of the two isomers of HECEH

Whatever bonding viewpoint one chooses for these molecules, there is no question that (a) they will be overall electron deficient, and yet (b) in them are centers of basicity and acidity. (a) would lead one to expect for the boron dimers some diborane-like structures, but, more interestingly, nonclassical structures of the type that Armin Berndt has so beautifully given us [26]. (b) would point to acid–base reaction–initiated dimerizations.

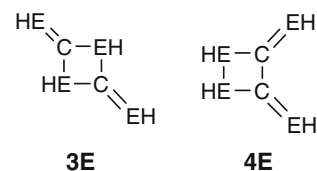
The allene and acid–base (carbene or carbene) perspectives on the linear isomer would lead us naturally to look at 2 + 2 cycloadditions of type **3E** or **4E** (not worrying about orbital symmetry constraints for the moment) (Scheme 3).

A carbene (not carbene) perspective leads one to consider ethylene-type dimers **5E** and **6E** and to spirocyclic compound **7E**, a product of a typical carbene cyclopropanation (Scheme 4).

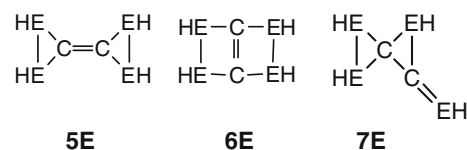
We will find molecules like these, with some real surprises in their geometries. But none of the Lewis-structure-based considerations in fact point to what emerged in calculations as the global minima on the $(\text{HECEH})_2$ surfaces.

6 Computational approach

We calculated all structures with methodology detailed in the Appendix; the energies given below the isomers are



Scheme 3 Dimers **3E** and **4E** that come from a formal 2 + 2 cycloaddition of **2E**



Scheme 4 Ethylene-type dimers **5E** and **6E** and spirocyclic dimer **7E**

CCSD(T) energies relative to two separated monomers. Table S1 of the Supplementary Information (SI) shows the energies at CCSD(T) and at PBE0 and BP86, which generally concur.

All five structures **3B–7B** that were anticipated above as the results of 2 + 2 cycloaddition and carbene dimerization were indeed found as energy minima, albeit with significant structural modifications indicative of the electronic unsaturation remaining in these structures.

One thing we should say at the outset is that while the impetus to the dimer chase was dimerization, the actual process of finding the optimum dimer geometries took on a life of its own. Both groups began by optimizations of two dimers brought close to each other. But both ended up by optimizing likely Lewis structures. The important difference in these approaches is that while success in the former guarantees no activation energy for dimerization (to a more stable dimer; an entropy “barrier” might still exist and govern ΔG), the latter tells us precious little about whether dimerization encounters a barrier.

And this matters; for the lesson of organic chemistry is that as far as kinetic persistence goes, large activation energies can trump exothermicities, even large ones. Witness, for example, the stability of your body in the presence of molecular oxygen. Or our ability to isolate the isomers of benzene—prismane, benzvalene, Dewar benzene.

7 A family of dimers with four-membered BCBC rings

The 2 + 2 cycloaddition with head-to-tail coordination of the $C(BH)_2$ monomers leads to structures **3B(Anti)** and **3B(Syn)**, which are 56 kcal/mol and 55 kcal/mol lower in energy than two monomers (Fig. 5). The exocyclic BH moieties are significantly tilted (relative to the **3E** Lewis structure) either to two different boron atoms of the ring (**3B(Anti)**) or to the same boron atom (**3B(Syn)**) with the former isomer being slightly lower in energy. One way to think about this tilting is that the exocyclic borons in these structures formally carry an empty orbital in the ring plane. That low-lying orbital “would like” to find some electron density; it locates it at the ring boron and the atoms it is bonded to.

We want to point out that the four-membered C_2B_2 ring in both isomers is not planar but slightly puckered and that there are two significantly different C–B bond lengths in the ring. The very short exocyclic C–B bonds, which have essentially the same distances as in monomeric $C(BH)_2$, suggest double-bond character, while π conjugation in the formally 2π -aromatic ring appears negligible.

The puckered ring in **3B(Anti)** and **3B(Syn)** suggests that there might be isomers, which have transannular B–B or C–C bonds. While we did not find an energy minimum structure which has a transannular C–C bond, we found

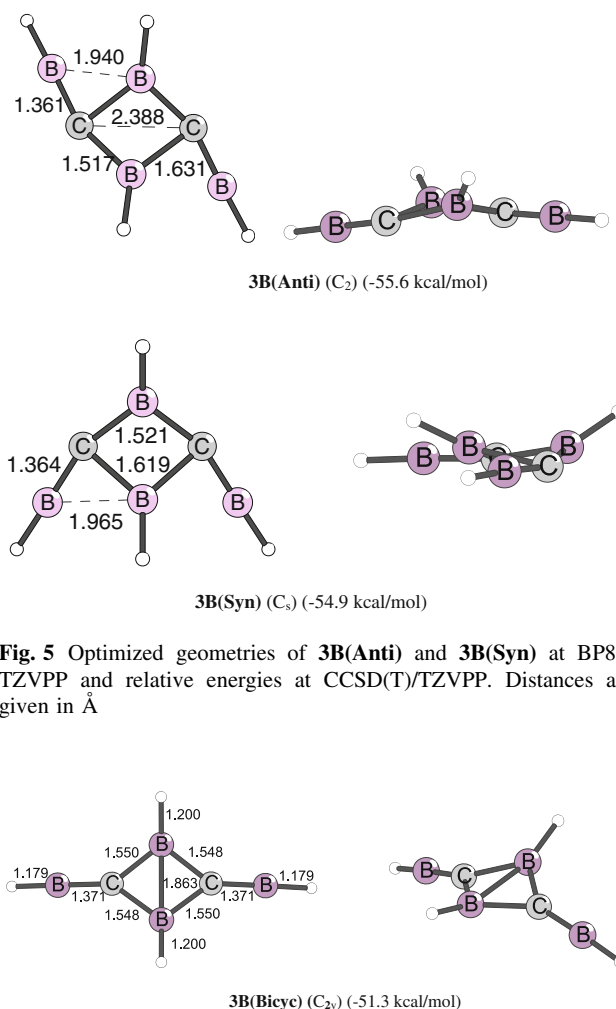


Fig. 5 Optimized geometries of **3B(Anti)** and **3B(Syn)** at BP86/TZVPP and relative energies at CCSD(T)/TZVPP. Distances are given in Å

Fig. 6 Optimized geometry of **3B(Bicyc)** at BP86/TZVPP and relative energy at CCSD(T)/TZVPP. Distances are given in Å

structure **3B(Bicyc)**, which has a puckered four-membered ring with a long (1.86 Å) transannular B–B bond. One is hard-pressed to write a Lewis structure for this electron-deficient molecule. The isomer **3B(Bicyc)** is 51 kcal/mol lower in energy than two monomers **1B**, which means that it is slightly (4 kcal/mol) less stable than **3B(Anti)** (Fig. 6).

As we look at the **3B(Anti)**, **3B(Syn)**, and **3B(Bicyc)** structures, we see pretty similar energies, and like distances as well in the “outer” CBH regions. It occurred to us that we might have here a family of structures with small barriers between them. **3B(Anti)** and **3B(Syn)** could interconvert through a D_{2h} geometry resembling **3E** and that in turn might have a puckering escape route to **3B(Bicyc)**. To probe this, we formed an “average” D_{2h} structure, with a square inner ring, and linear $C-B_{exo}-H$. The energy of such a structure is -50 kcal/mole, not much above the 3 minima. This is a really flexible group of structures.

8 Ethylene-like structures, their collapse products, and a surprise

For the ethylene-type dimer that comes from a formal head-on dimerization of $C(BH)_2$, **5E**, we found structure **5B** as an energy minimum. But a surprise here—the equilibrium geometry has D_{2d} symmetry, where the three-membered rings are orthogonal to each other. Not what we would expect of an ethylene!

The planar D_{2h} form **5B(TS)** is a transition state for rotation about the C–C bond. The equilibrium geometry of **5B** thus belongs to the class of compounds, which possess “anti-van’t-Hoff” geometries, with no electronic prodding (donor/acceptor substitution) or steric push. It has been shown in earlier studies that carbon compounds that have electropositive substituents such as boron prefer anti-van’t-Hoff equilibrium geometries [27–30] (Fig. 7).

The peculiar equilibrium structure and bonding situation of **5B** merits further discussion. Taking the Lewis structure **5E** at face value, would lead one to think of a planar molecule, which has a C=C double bond. But the C–C distance in **5B(TS)** is even a bit longer than a C–C standard single bond (1.54 Å)!

Figure S1 of the Supplementary Information shows the occupied valence orbitals of planar **5B(TS)**. In contrast to the simple valence structure of an ethylene, not one but two out-of-plane π MOs are occupied. One of these is C–C bonding (HOMO – 5), and the other C–C antibonding (HOMO – 2); both are shown in Fig. 8. One way to think of this situation is that the π^* MO of the ethylene is so stabilized by interaction with four empty B 2p orbitals as to be occupied. Another way to think of the two occupied π

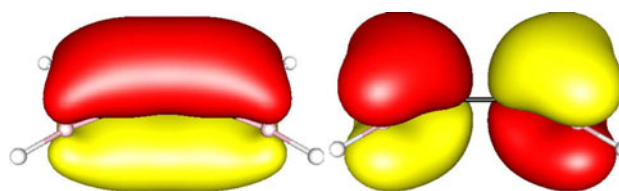


Fig. 8 Two occupied MOs of **5B(TS)**

MO's is as the bonding and antibonding combinations of two cyclopropenium-type lowest π orbitals. Either way, one can see why the C–C bond is so long in planar **5B(TS)**. The appearance of two occupied π MOs underlines the strong driving force of the boron atoms to have eight valence electrons. There are now four electrons available for filling four $p(\pi)$ AOs of boron. The MOs of the twisted energy minimum structure **5B**, which are shown in Figure S2 of Supplementary Information, exhibit striking similarities with those of **5B(TS)**.

Because there are two occupied out-of-plane π MOs in **5B(TS)**, there are only ten occupied valence MOs left for the eleven σ bonds. Rotation of the three-membered rings by 90° to equilibrium structure **5B** actually improves the bonding situation a little—the out-of-plane and in-plane MOs of **5B(TS)** can mix, which enhances the C–C and the C–B bonding via hyperconjugation. Figure S2 of the SI shows the occupied valence orbitals of perpendicular **5B**. There are now two degenerate pairs of C–C π bonding (HOMO – 3 and HOMO – 3') and C–C π antibonding orbitals (HOMO – 1 and HOMO – 1'). The C–C hyperconjugation that we attribute to this structure is displayed by the shape of the degenerate orbitals HOMO – 5 and HOMO – 5', which also enhance C–B bonding. Thus, the C–C and the C–B bonds in **5B** are both a bit shorter than in **5B(TS)**. The C–C bond formation reaction $2 \mathbf{1B} \rightarrow \mathbf{5B}$ is exothermic by only 13 kcal/mol, which indicates that the C–C bond in **5B** is weak.

We also calculated the triplet state **5B(Triplet)**, which was found to be 8.9 kcal/mol higher in energy than the singlet state **5B**. Both molecules have D_{2d} symmetry, where the three-membered rings are orthogonal to each other. The triplet species **5B(Triplet)** has a C–C bond length characteristic more of a double bond (1.44 Å); the components of the double bond are a σ bond and two singly occupied π -type hyperconjugative interactions. There are now fewer electrons available for π -donation into the $p(\pi)$ orbital of boron, which leads to slightly longer C–B bonds (1.44 Å) in **5B(Triplet)** compared to the C–B bonds in **5B** (1.42 Å). Although the C–C bond in **5B(Triplet)** is significantly shorter and the C–B bond only slightly longer than in **5B**, which also possesses longer B–B bonds than in the triplet species, singlet **5B** is lower in energy than **5B(Triplet)**.

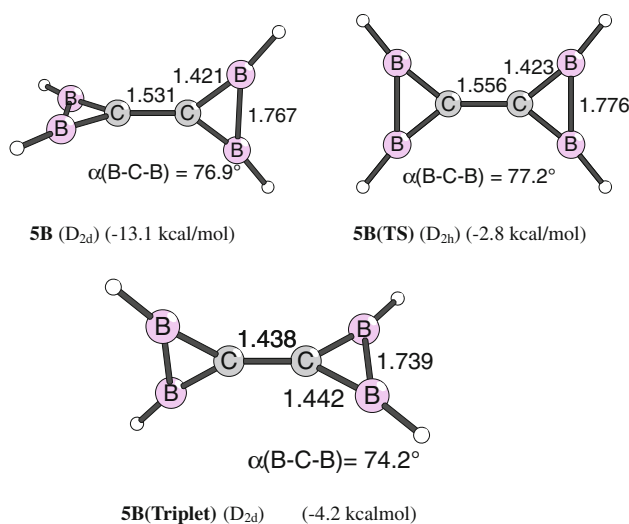


Fig. 7 Optimized geometries of **5B**, **5B(TS)**, and **5B(Triplet)** at BP86/TZVPP and relative energies at CCSD(T)/TZVPP. Distances are given in Å, angles in degrees

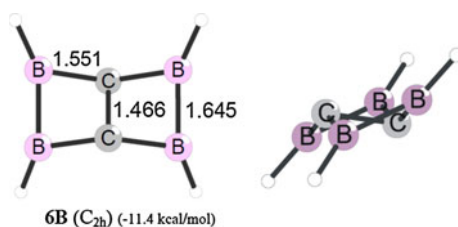


Fig. 9 Optimized geometry of **6B** at BP86/TZVPP and relative energy at CCSD(T)/TZVPP. Distances are given in Å

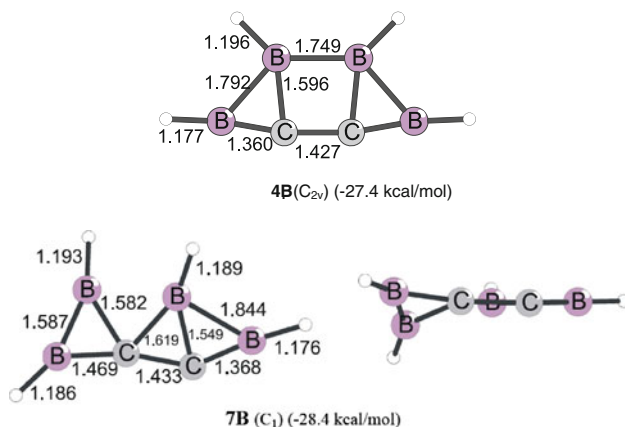


Fig. 10 Optimized geometries of **4B** and **7B** at BP86/TZVPP and relative energies at CCSD(T)/TZVPP. Distances are given in Å

There is another way to form an ethylene, the **6E** structure; this is minimum **6B**. Unlike **4B**, the equilibrium geometry of **6B** is not planar. In fact, it is quite contorted, with trigonal pyramidal carbon atoms and two puckered four-membered rings. The C–C distance in **6B** (1.47 Å) is significantly shorter than in **5B** (1.53 Å), while the C–B distances in the former compound (1.55 Å) are clearly longer than in the latter (1.42 Å). Isomers **5B** and **6B** are close in energy, with the latter 2 kcal/mol less stable than the former (Fig. 9).

6B looks strained at its carbons; later on, when we look at the Al analogue, we will find a much less strained (and more stable) molecule. The dimerization of **1B** yielding **6B** is exoenergetic by only 11 kcal/mol.

Returning to the relatively unstable ethylene-like **5B(TS)** structure, two distortions from it, involving B–B and B–C bond formation, take us to two further minima we have found, the substantially more stable **4B** and **7B** (Fig. 10).

The somewhat nonplanar compound **7B** may be considered as a bond-swap isomer of **4B**, where the B–B ring in the four-membered ring of the latter molecule is broken and a new C–B bond is formed. The same reaction may take place to the left-hand and to the right-hand side of the four-membered ring, which means that there are two energetically degenerate pathways for breaking the B–B

bond of **4B**. Since **7B** is only 1.0 kcal/mol lower in energy than **4B**, one might imagine a degenerate rearrangement between the two forms of **7B** via **4B** as intermediate.

4B may also be seen as a Lewis structure **4E** that exercises its electron deficiency. And highly unsymmetrical **7B** can be thought of in another way, as a realization of hypothetical Lewis structure **7E**, followed by tilting of the exocyclic B in that structure toward a ring, to satiate its electron deficiency.

The stabilizing deformations we see, whether of **7E** to **7B**, of **5B(TS)** to **4B** and **7B**, support an underlying idea that helps us understand these structures: the B atoms in these molecules, even if one has a Lewis structure, are fundamentally electron deficient. If electron density be available in the molecule, the B centers will make use of it, by further bonding.

We have now exhausted the simple dimer structures that bear some relationship to Lewis structures suggested by double bond or carbene reactivity. Yet there remain four minima that were located theoretically, and remarkably, three of these are close to the lowest in energy among the structures we have found. This shows clearly the limits of a Lewis-structure-based intuition, as remarkably useful as this simple heuristic device is.

9 Polyhedral $C_2B_4H_4$

The most stable dimer of **1B**, which we found in our extensive calculations, is the octahedral-looking isomer 1,6-dicarbaborane(4) **8B**, the global minimum (so far) on this surface, at some 65 kcal/mol below two monomers (Fig. 11).

First, how could this dimer form? Pretty simply, compound **8B** can be considered as the result of a cycloaddition of the carbones (or inverted carbene) **1B** where the carbon lone pair π donor orbital on one monomer donates electronic charge into the electron-deficient boron atoms of the other monomer (Fig. 4). This could be achieved through HOMO–LUMO interactions between two monomers, the most obvious driving force for the dimerization (Fig. 12).

The octahedral dimer was a shock to both groups. But perhaps we should not have been surprised, for the geometry is connected to several structures that form a part

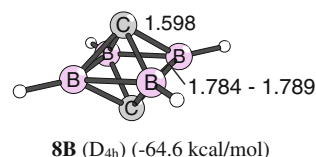


Fig. 11 Optimized geometry of **8B** at BP86/TZVPP and relative energy at CCSD(T)/TZVPP. Distances are given in Å

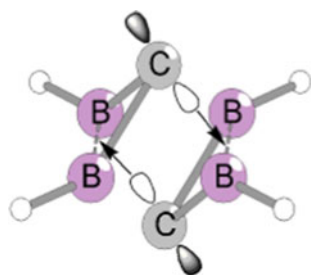


Fig. 12 Interactions between two $C(BH)_2$ molecules, leading to the octahedral dimer **8B**

of RH's scientific history, and have a Marburg connection as well. And one to our friend Jemmis too.

If you add two axial H's to **8B**, you get the octahedral 1,3-carborane, $C_2B_4H_6$, a known molecule that is related to the stable deltahedral $[B_6H_6]^{2-}$ boron hydride [31–33]. While the corresponding didehydro system—the molecule we calculate—is not known, two molecules that are related are.

First of all, the octahedral neutral $B_6(NR_2)_6$, $R = Me, Et$, highly stabilized neutral B_6H_6 derivatives, are known [34–36]. If one replaces (mentally) two BR by C, one gets the **8B** molecule. Second, Halet, Saillard and coworkers have calculated some M_4N_2 clusters with a *hypercloso*, 6 skeletal-electron-pair count, looking for cross-ring bonding [37, 38]. One series of molecules they examined was $[N_2(M(CO)_3)_4]^{2+}$, $M = Fe, Ru, Os$. The isoelectronic substitution of N^+ by C, and the isolobal replacement of $M(CO)_3$, $M = Fe, Ru, Os$ by BH takes their molecule back to **8B** (Fig. 13).

Halet, Saillard and their coworkers found some cross-polyhedron $N \cdots N$ bonding, and so do we find $C \cdots C$ bonding in **8B**. A close look at the geometry of **8B** shows that the carbons are pulled toward each other. The CC separation is a long 1.94 Å, but the CBC angle is 72° , less than the 90° for BBB. Analysis of the electronic structure supports the assignment of C–C bonding in **8B**. The AIM analysis shows that there is a C–C bond path in the molecule

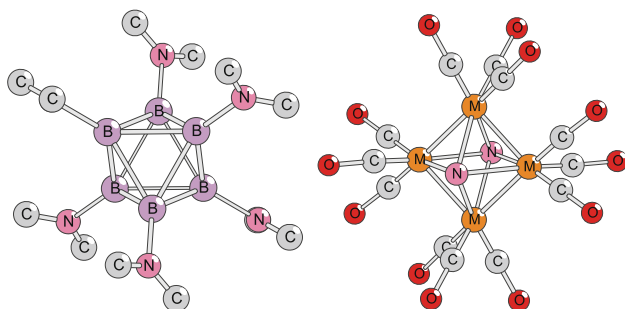


Fig. 13 Experimentally known octahedral complexes $B_6(NR_2)_6$, and $[N_2(M(CO)_3)_4]^{2+}$, $M = Fe, Ru, Os$

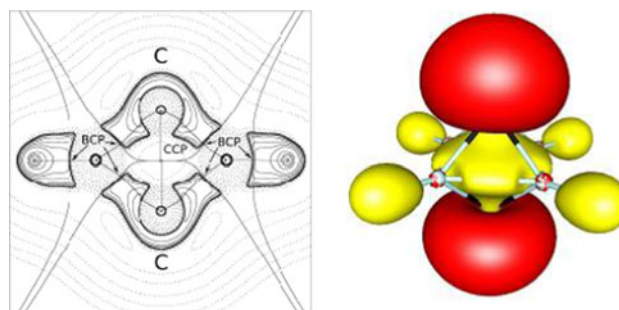
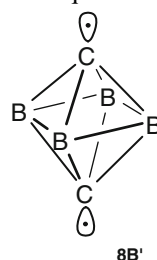


Fig. 14 (left) Laplacian of **8B**. (right) HOMO – 1 of **8B**

(Fig. 14, left). The shape of the HOMO – 1 (Fig. 14, right) reveals substantial bonding overlap of the lone pair or radical type MO.

Viewing **8B** as a didehydrocarborane, [39] **8B'**, raises several questions



1. A didehydroaromatic (the $[B_nH_n]^{2-}$ systems can be profitably seen as 3D aromatic) calls up the p-benzyne story [40]. In that C_6H_4 molecule, the antisymmetric radical lobe combination is filled, a consequence of through-bond coupling. Which combination is filled in **8B'**? It turns out to be the symmetric one.

2. **8B/8B'** is formally a diradical. How could there be a $C \cdots C$ bonding interaction in it? Well, the situation is akin to that in the [1.1.1] propellane. There is substantial through-bond and some through-space coupling of the radical lobes, bringing the symmetric combination lower in energy.

3. If we take the diradical perspective seriously, where then is its triplet state? We compute it as 54 kcal/mol above the ground state. A broken symmetry calculation of the singlet lowers its energy only minimally; the ground state is a good closed shell singlet.

4. If **8B/8B'** is a diradical, might it itself dimerize? The spin-coupling situation here is hardly simple—there are singlet, triplet, and quintet states to consider. And broken symmetry solutions, zwitterionic structures, as well. It turns out that **8B'** should dimerize—the energy of the dimer of dimers (**8B**)₂ shown in Fig. 15 is –25 kcal/mol relative to two **8B** molecules, with no activation energy for the process.

5. So dimerization of the $C(BH)_2$ dimer is exothermic in turn and requires in our calculations no activation energy. This small subuniverse of chemistry will not halt at dimerization. We foresee polymerization.

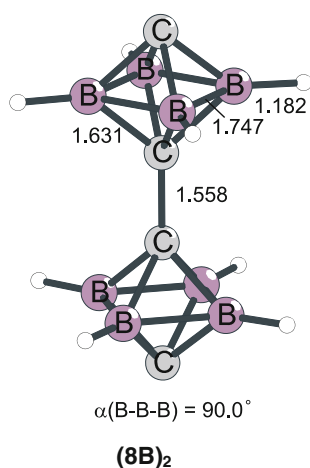


Fig. 15 Optimized geometry of **(8B)₂** at BP86/TZVPP. Distances are given in Å

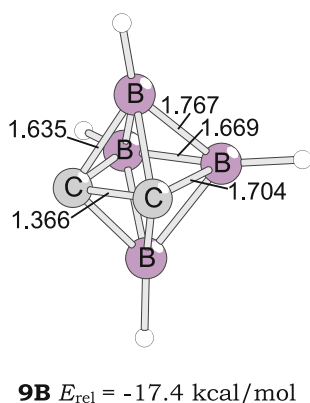


Fig. 16 Optimized geometry (C_{2v}) of **9B** at BP86/TZVPP and relative energy at CCSD(T)/TZVPP. Distances are given in Å

A second carborane-like minimum we find is **9B**. This is a didehydro-*cis*-carborane, which has near C_{2v} symmetry² (Fig. 16). This cage is not that stable relative to the trans-isomer, **8B** (Fig. 16).

The extended Wade–Mingos rules would point one to a bicapped tetrahedron for a system with 12 skeletal electrons [41]. In fact that is the geometry of the third polyhedral minimum we find. This is structure **10B**, which has a bicyclic B_4H_4 fragment that is bridged by a C_2 fragment, or a bicapped tetrahedron, the tetrahedron composed of $C_2(\text{BH})_2$. The unusual C_{2v} isomer is 53 kcal/mol lower in energy than two monomers **1B**. The very short C–C distances in **9B** and **10B** are remarkable (Fig. 17).

Note the close relationship between **9B** and the much more stable **10B**. All it takes to convert one into the other is

² The optimized geometry which is shown in Supporting Information deviates slightly from C_{2v} symmetry. Figure 16 gives the average values for the bond lengths.

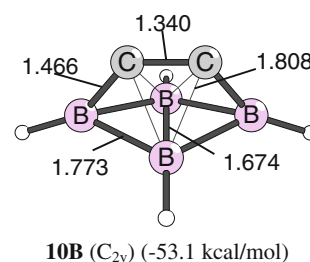


Fig. 17 Optimized geometry of **10B** at BP86/TZVPP and relative energy at CCSD(T)/TZVPP. Distances are given in Å

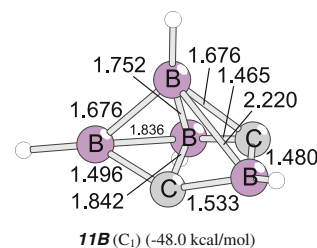


Fig. 18 Optimized geometry of **11B** at BP86/TZVPP and relative energy at CCSD(T)/TZVPP. Distances are given in Å

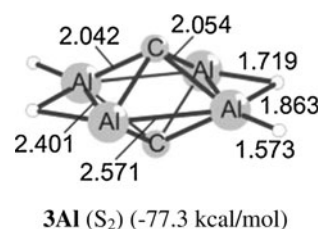


Fig. 19 Optimized geometry of **3Al** at BP86/TZVPP and relative energy at CCSD(T)/TZVPP. Distances are given in Å

a simple 90° rotation of the CC rod relative to the $(\text{BH})_4$ part. The barrier for this process is small but real.

The last minimum we found is **11B**, a highly unsymmetrical yet low energy geometry, which may be related to, but departs significantly from a bicapped tetrahedron (Fig. 18).

We have searched for other isomers based on ringing the changes on the bicapped tetrahedron; none were found.

10 The aluminum dimers $C_2\text{Al}_4\text{H}_4$

The computational search for energy minima of $\text{C}(\text{AlH})_2$ dimers gave structures that are similar to but also distinctively different from the $\text{C}(\text{BH})_2$ dimers. Only five energetically low-lying structures, **1Al**–**5Al**, were found for the aluminum dimers. All of these are significantly more stable relative to the monomer than in the boron case. The relative

Fig. 20 Optimized geometries of **1Al** and **2Al** at BP86/TZVPP and relative energy at CCSD(T)/TZVPP. Distances are given in Å

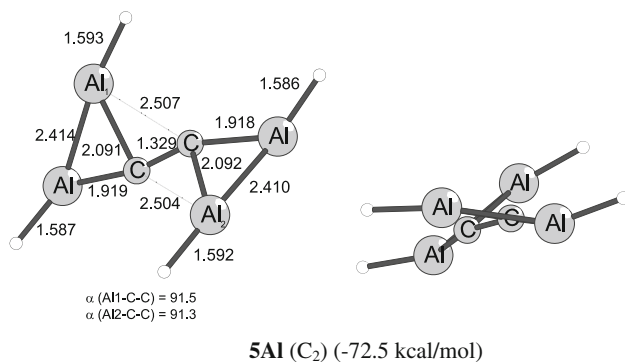
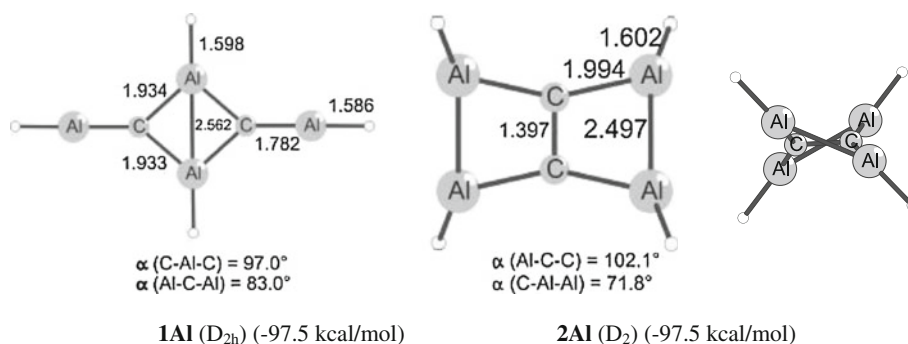


Fig. 21 Optimized geometry of **5Al** at BP86/TZVPP and relative energy at CCSD(T)/TZVPP. Distances are given in Å

energies of the compounds at the different levels of theory are given in Table S2 in Supplementary Information.

The polyhedral analogue of the *trans*-carborane, **3Al**, is among the five. It is not as stable as some of the other structures. Note the two bridging hydrogens in the structure. Much less is known of the chemistry of simple and polyhedral alanes than of boranes [42]. But easy motion of hydrogens in and out of bridging positions is typical of electron-deficient boranes (Fig. 19).

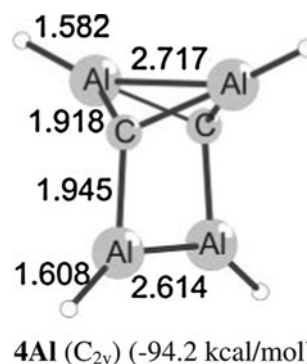
Competing to be the most stable Al dimers are the structures **1Al** and **2Al**. Both have analogues in the B dimers. **2Al**, while still nonplanar, is stabilized in the Al series, because the naturally longer Al–Al distances (compared to B–B) impose less stress on the molecule—this is visible in the more normal angles at C, and the shorter C=C distance.

Note also that **1Al** is planar, whereas the B analogue **3B** was puckered. The external C–Al distances are very short, indicative of a double bond. The stabilizations of these dimers are remarkable (Fig. 20).

Dimer **5Al** looks like a highly distorted version of Lewis structure **5E**. While the C–C distance is a typical double bond one, the rest of the structure is most peculiar (Fig. 21).

The final structure, **4Al**, is quite stable. And this geometry we have not encountered in the boron case (we

Fig. 22 Optimized geometry of **4Al** at BP86/TZVPP and relative energy at CCSD(T)/TZVPP. Distances are given in Å



searched for it, of course), nor is it one for which one could draw a simple Lewis structure. One can imagine reaching it from **1Al** by folding the central ring, bringing the external aluminiums together. The distances in the structure are quite normal for single bonds (Fig. 22).

These are all the $C(AlH)_2$ structures we found.

11 Concluding Remarks

What fun to find such a rich family of dimers, 12 (and counting) for $(HBCBH)_2$, 5 for $(HAICAlH)_2$, each with fascinating bonding peculiarities! The main lessons to be drawn from this study are pretty obvious:

1. Look for dimerization whenever you predict a stable structure for a molecule.
2. Lewis structures constitute a wonderful heuristic scheme, and a good guide to possible structures. As are potential frontier orbital interactions, acid–base reactivity foremost among them.
3. However, when one has molecules whose Lewis structures are very electron deficient (or put alternatively, have low-lying empty orbitals), then one had better watch out for additional bonding. As Armin Berndt's molecules and the ones we calculate show, one then gets some pretty weird structures.

Finally, it is clear that all of chemistry is wonderfully intertwined. Who would have thought that carborane chemistry might be connected to $C(BH)_2$?

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