

Investigation of the Typical Triangular Structure B_3 in Boron Chemistry: Insight into Bare All-Boron Clusters Used as Ligands or Building Blocks

Li-ming Yang, Jian Wang, Yi-hong Ding,* and Chia-chung Sun

State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, People's Republic of China

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Even though boron clusters are quite significant, bare boron clusters as ligands in chemical compounds are still unknown. Triangular B_3 is a key constituent of all-boron clusters and widely applied in the boron compounds. As a basic step toward understanding the assembly and stabilization of bare all-boron clusters and the possibility of their fusion during the cluster-assembly process, we made the first attempt to assemble the smallest bare all-boron unit B_3^- . Both the “homo-decked sandwich” and “hetero-decked sandwich” schemes were applied to the assembly of B_3^- at the B3LYP/6-311++G(d, p) level. For all the considered alkali- and alkaline earth metals, B_3^- can only be assembled in “hetero-decked sandwich” scheme (e.g., $CpMB_3^{q-}$) so as to avoid cluster fusion, whereas it cannot be assembled in the traditional “homo-decked sandwich” scheme ($B_3MB_3^{q-}$) because of thermodynamic and kinetic instability. Various assembled species in extended frameworks are designed. In particular, the dimerization of the hetero-decked sandwich-like $CpMB_3^{q-}$ could lead to a new type of antiaromatic triple-decker sandwich-like complexes $CpMB_6MCP^{2q-}$ that contain the all-boron antiaromatic unit B_6^{2-} . Our work supports the experimental identification of the B_6^{2-} anion (with M^+ counterions) in a photoelectron spectroscopy study. Additionally, the electronic and structural properties of B_3^- are well conserved during cluster-assembly, characteristic of a “superatom” feature. Our results are expected to be helpful for understanding the assembly and stabilization of bare all-boron cluster chemistry. Also, our work should give insight toward designing and understanding bare boron clusters as potential new ligands for coordination chemistry and as new building blocks for materials science. Interestingly, our results should provide hints to embellish, functionalize, isolate, and protect bare all-boron clusters.

1. Introduction

Nowadays, the molecular assembly and growth from a small building unit to the bulk compound have become a focus in various fields.¹ Boron compounds have attracted intense interest because of their wide applications² and their essential roles in advancing chemical bonding models.³ The recently discovered small bare all-boron clusters that feature planar or quasi-planar shapes⁴ surprised the scientific community, as the chemistry of boron has been diversely featured by three-dimensional structures. In addition to the fundamental interest in developing chemical bonding theory, bare all-boron species might have potential applications as potential new ligands for coordination chemistry and as new building blocks for materials science. Hopefully, the already existent high-temperature superconducting MgB_2 solid^{5a-c} containing a planar B_6 -fragment and the recent successful synthesis of the triple-decker $(Cp^*ReH_2)B_5Cl_5$ and $(Cp^*)_2B_6H_4Cl_2$ compounds^{5d-e} containing B_5Cl_5 and $B_6H_4Cl_2$ structural fragments provide hope that many more compounds with bare all-boron building blocks may be synthesized in the future. Up to now, some theoretical efforts have been reported toward designing potential sandwich-like complexes based on the bare all-boron units B_6^{2-} ,^{6a,b} B_7^- ,^{6c} B_8^{2-} ,^{6d,e} and B_{8-14} .^{6f} However, such designed half-sandwich or sandwich-like compounds all ignored a key issue: the possibility of fusion between two or more boron cluster units during cluster-assembly. Also, to our surprise, B_3^- ,^{7a-d} a key constituent of

all-boron clusters and the simplest aromatic all-boron unit, has not received as much attention as other larger all-boron clusters. To the best of our knowledge, no B_3^- -based assembled molecular compounds have been reported.

Triangular structure dominates a very important position in boron chemistry. The triangular bare all-boron clusters $B_3^{0,\pm 1}$ have even been experimentally isolated.^{7a-e-g} As a basic step toward understanding the fusion effects of the assembly and stabilization of the bare all-boron units, we made the first attempt to assemble the smallest bare all-boron aromatic unit B_3^- .^{7a-d} Attempts were made to apply both “homo-decked sandwich” and “hetero-decked sandwich” schemes to the assembly of B_3^- at the B3LYP/6-311++G(d, p)⁸ level. We show that the electronic and structural properties of B_3^- are well conserved during cluster-assembly, characteristic of a “superatom”⁹ feature.

We believe that study of the B_3^- -based assembled molecular species should represent another important task and challenge for the following reasons. (1) Ring strain. The strain energies of the three-membered ring (TMR) decks are usually much larger than that of the four-, five-, and higher-membered rings decks. When used for sandwiching, the TMR deck may be structurally destroyed to take other forms so as to release the strain energy. This might be one reason that the reported sandwich-like complexes with the TMR decks are usually very rare compared with those with the four- and five-membered ring decks. So, how to maintain the highly strained B_3^- unit in the assembled molecular compounds is a great challenge. (2) Fusion. Whether B_6M^{-10a} actually results from the fusion of two

* Author to whom correspondence should be addressed. E-mail: yhdd@mail.jlu.edu.cn.

B_3^- units with presence of M^+ or from other mechanisms is still uncertain. It is of great interest to explore the fusion stability of $B_3MB_3^{q-}$ comprising the bare all-boron aromatic unit B_3^- . (3) Aromaticity and antiaromaticity. In particular, such a study might provide a picture for the interconversion between aromatic B_3^- and antiaromatic B_6^{2-} ,¹⁰ both of which have been experimentally characterized. (4) Isomerism. To our knowledge, previous theoretical studies have been restricted to the determination of the structural and energetic properties of various $[B_nM]^{q\pm}$ isomers. But we feel that the detailed isomerism knowledge between various structural forms is more related to the laser vaporization processes of these species. It is known that in traditional metallocenes (Cp_2M), the interaction between metal atom and the sandwiching unit is mainly ionic. It is thus reasonable to expect that the monoanionic B_3^- deck should also preferentially interact with the metal atom via ionic interaction. In addition, the lower electronegativity of alkali elements Li, Na, and K and alkali earth Be, Mg, and Ca make them apt to form ionic interactions, which makes alkali and earth alkali metals good candidates to test the ionic interaction of B_3^- deck in sandwich-like complexes.

Here, we report the first attempt on design of the assembled molecular species based on the B_3^- unit. By investigating the structures and stability of a series of compounds $[DM(B_3)]^{q-}$ ($D = B_3^-, Cp^-$; $M = Li, Na, K, Be, Mg, Ca$) at the B3LYP/6-311++G(d, p)⁸ level, we showed that the B_3^- unit cannot be stabilized in the “homo-decked sandwich” form like that of $B_3MB_3^{q-}$ because of its thermodynamical instability and kinetic lability. Instead, we applied the “hetero-decked sandwich” scheme to assemble B_3^- in the form of $CpMB_3^{q-}$ as well as the extended species $-CpMB_3M\cdots Cp^-$. The isomerism presented here gave a good support to the photoelectron spectroscopy study by Alexandrova et al.^{10a,f} Moreover, we for the first time showed that when assisted by a rigid partner like Cp^- , the B_3^- unit possesses the “superatom” feature. Realization of the B_3^- -incorporated sandwich compound is very promising.

2. Computational Methods

Initially, we fully optimized the geometries of $[DM(B_3)]^{q-}$ ($D = B_3^-, Cp^-$; $M = Li, Na, K, Be, Mg, Ca$) by employing the 6-311++G(d, p) basis set and the hybrid density functional theory method B3LYP,⁸ i.e., Becke’s hybrid three-parameter exchange functional with the LYP correlation functional. After geometrical optimization, normal mode vibrational analysis was performed to check whether the obtained structure is a true minimum point with all real frequencies, a first-order transition state with only one imaginary frequency, or high-order saddle points with many imaginary frequencies. To confirm whether the obtained transition states connect with the right isomers, intrinsic reaction coordinate (IRC)¹¹ calculations were performed at the B3LYP/6-311++G(d, p) level. The higher theoretical method B3LYP/6-311++G(2d, 2p) was also used to test the reliability of the results obtained at B3LYP/6-311++G(d, p) for some selected species. In order to get insight into the nature of our designed homo- and hetero-decked sandwich-type complexes, we performed detailed natural bond orbital (NBO)¹² (NPA charge distributions) and orbital¹³ (characterized orbitals) analyses on the designed sandwich-like species at the B3LYP/6-311++G(d, p) level. Despite its widespread use, aromaticity is more a concept rather than a directly measurable quantity. Consequently, measurements of aromaticity rely on many diverse criteria.¹⁴ Among them, the nucleus-independent chemical shift (NICS), based on the “absolute magnetic shielding” taken at the center of a ring compound, is widely used and has

been proven to be accurate for ordinary cyclic carbon compounds.¹⁵ Recently this method has also been successfully used for inorganic cyclic aromatic compounds,¹⁶ including the characterization of the so-called d-orbital aromaticity.¹⁷ Thus, the NICS values were also calculated at the B3LYP/6-311++G(d, p) level. A positive value of the NICS indicates that the molecule is antiaromatic, and a negative value indicates the aromaticity of the molecule. The NICS calculated at the center of the ring plane (NICS(0)) describes the σ aromaticity, and the NICS above 1 Å out of the ring plane (NICS(1)) describes the π aromaticity of the molecule. All the calculations were performed with the Gaussian-03 program.¹⁸

3. Results and Discussions

3.1. $B_3MB_3^{q-}$. We considered various isomers of $[B_6M]^{q-}$ ($M = Li, Na, K, Be, Mg, Ca$) at the B3LYP/6-311++G(d, p) level. A selected set of the low-energy structures identified in the search are presented in Figure 1, from which we can see that the high-lying sandwich-like isomer $B_3MB_3^{q-}$ ($Ho-M1^{q-}$) is only a minimum point, and can easily be converted to the lower-energy isomer MB_6^{q-} $Ho-M2^{q-}$ with the barriers being 9.4(9.6), 13.4, 14.0, 7.8, 17.2, and 11.1 kcal/mol for $M = Li, Na, K, Mg, Ca$, respectively, at the B3LYP/6-311++G(d, p) and B3LYP/6-311++G(2d, 2p) (in italics within parentheses) levels. During the long thermodynamic equilibrium, the sandwich-like isomer $Ho-M1^{q-}$ finally invert into the ground state antiaromatic isomer $Ho-M6^{q-}$. Thus, the sandwich form $Ho-M1^{q-}$ is thermodynamically quite unstable and kinetically labile. For some relevant species, the energies obtained at the two levels are close and the nature of the stationary points is the same, i.e., the minimum is still minimum, the first-saddle point is still first-saddle point at the two theoretical levels. From Figure 1 we can see that the results obtained at the B3LYP/6-311++G(2d, 2p) level agree quite well with that obtained at the B3LYP/6-311++G(d, p) level. Note that the notation $Ho-M1^{q-}$ stands for the homo (Ho)-decked sandwich isomer (the deck is B_3^- unit). “ M ” means the metal atom and superscript “ $q-$ ” means the charge of the total system.

The isomerization information of $[B_6M]^{q-}$ might have further implications. In the gas-phase photoelectron spectroscopy study by Alexandrova et al.,^{10f} the laser vaporization of appropriate boron-mixed targets leads to the generation of the $[B_6M]^-$ anion. In principle, during the laser vaporization process, many B_6M^- isomers (not merely the high-energy sandwich isomer $Ho-M1^-$) may be formed. As shown in Figure 1, various isomers may eventually convert to the ground state isomer $Ho-M1^{q-}$ in the long duration under thermal conditions.

Although boron has a rich and diverse chemistry, it differs substantially from that of aluminum. The bare free B_6^{2-} and the B_6^{2-} unit in ground state structure of MB_6^{q-} are planar, in contrast to the 3D octahedral structure found for the isoelectronic Al_6^{2-} and MA_6^{q-} . The former is aromatic, while the latter is antiaromatic. The structure and chemical bonding of a series of MA_6^- have been elucidated. It was shown that Al_6^{2-} can be considered as the fusion of two Al_3^- units. The three-dimensional π - and σ -aromaticity of Al_6^{2-} have been evaluated by Kuznetsov et al.^{10g} The chemical bonding in antiaromatic MB_6^- can be interpreted in terms of combinations of two aromatic B_3^- fragments. The antiaromatic nature of B_6^{2-} is established by orbital analysis of ring current effects at the D_{2h} equilibrium geometry of the dianion by Alexandrova et al.^{10f}

The above results seem to contrast the common belief that “aromaticity” is usually associated with the high stability, and that antiaromaticity is usually associated with the low stability.

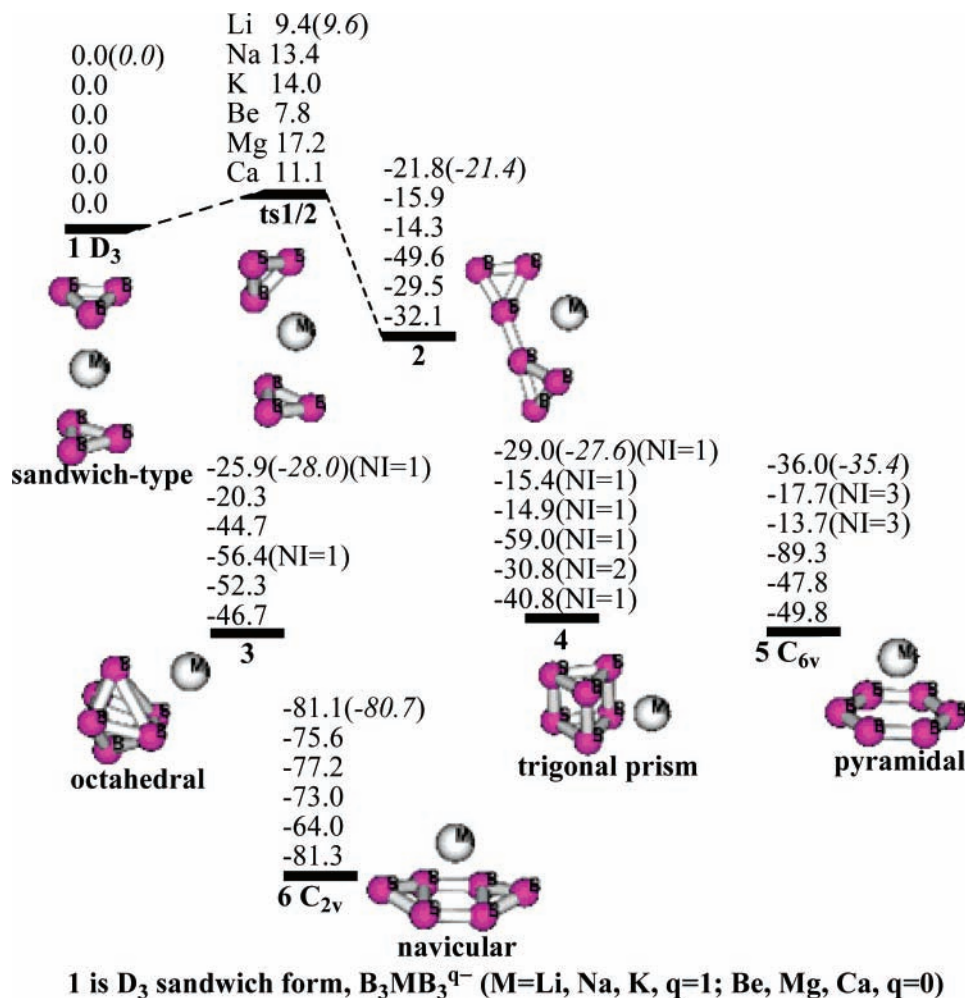


Figure 1. Schematic energy profile for $[B_6M]^{q-}$ (M = Li, Na, K, $q = 1$; M = Be, Mg, Ca, $q = 0$) calculated at the B3LYP/6-311++G(d, p) and B3LYP/6-311++G(2d, 2p) (in italics within parentheses) levels. Energy values are in kcal/mol. For simplicity, the notations “Ho–M” and “q⁻” for isomers are omitted. The “NI=n” means the number of imaginary frequencies of the stationary point. The pink colored balls represent boron atoms.

The homo-decked sandwich forms Ho-M1^{q-} are just local minima on hyper-energy surface. They are thermodynamically unstable and kinetically labile toward fusion to B₆-clusters. The sandwiched alkali- and alkaline earth main-group metals M cannot effectively hinder the fusion of two B₃⁻ decks. The present results clearly demonstrate that the importance of performing kinetic and fusion studies for a novel compound with exotic structures. Thus, the B₃⁻ unit cannot be stabilized in the homo-decked sandwich form B₃MB₃^{q-}.

3.2. CpMB₃^{q-}. The above “discouraging” results drive us to ask the question again: “How to incorporate the bare all-boron aromatic unit B₃⁻ into the assembled molecular materials?” We are aware that the organic aromatic species c-C₅H₅⁻ (Cp⁻) has been well-known to be a versatile unit in sandwiching metal-atoms and has gestated a rich chemistry of mononuclear metallocenes (CpMCp).^{19a} Very recently, the Cp⁻-pairs were even found to sandwich the direct Zn–Zn bond to form the first stable Zn–Zn bonded species CpZn₂Cp (also as the first dinuclear metallocene).^{19b,c} This indicates that Cp⁻ is a powerful sandwich deck. We were thus led to wonder whether the B₃⁻ unit can cooperate with the organic aromatic deck Cp⁻ to sandwich metal atoms. Luckily, it is indeed the case!

We applied the “hetero-decked sandwich”^{19d–h} scheme for assembly of the bare all-boron units into molecular materials, i.e., metal (M) atoms are sandwiched by different decks in the form of DMD* (D, D* = sandwich decks). By taking advantage

of the high stability of Cp⁻, a new class of sandwich compounds CpMB₃^{q-} can be designed. Such compounds are intuitively of special interest because they contain both the classic organic aromatic unit Cp⁻ and the novel bare all-boron aromatic unit B₃⁻. Different from the homo-decked sandwich scheme, the ground state structure is the sandwich isomer Het-M1 that has three types of sandwich forms, i.e., face–face (f-f), face-side (f-s), and face-corner (f-c). The first “face” means the plane of Cp⁻, while for the second “face”, “side” and “corner” mean the plane, side (B–B bond) and one B-atom of B₃⁻, respectively. “Het” stands for the “hetero Cp⁻ and B₃⁻ decks”. At the B3LYP/6-311++G(d, p) level, the (f-f) form is more stable except for M = Be for which the (f-c) form is more stable than the (f-f) form because of the large covalent interaction between Be and B atoms. The Het-M1(f-f) ↔ Het-M1(f-s) ↔ Het-M1(f-c) process can vividly be viewed as the opening ↔ closure of the B₃⁻ deck above the “ground” deck Cp⁻ and the rotation of the B₃⁻ deck along the threefold axis of B₃⁻. The rearrangement of the sandwich form Het-M1 to other high-energy isomers is generally difficult with considerable barriers. Thus, the ground state sandwich isomer Het-M1 can be viewed as both thermodynamically and kinetically stable. Some selected low-lying configurations for CpMB₃^{q-} are listed in Figure 2. In order to evaluate the stabilities of our designed hetero-decked sandwich-type complexes, we calculated the binding energies of the designed sandwich species. From Figure 2, we can see that the

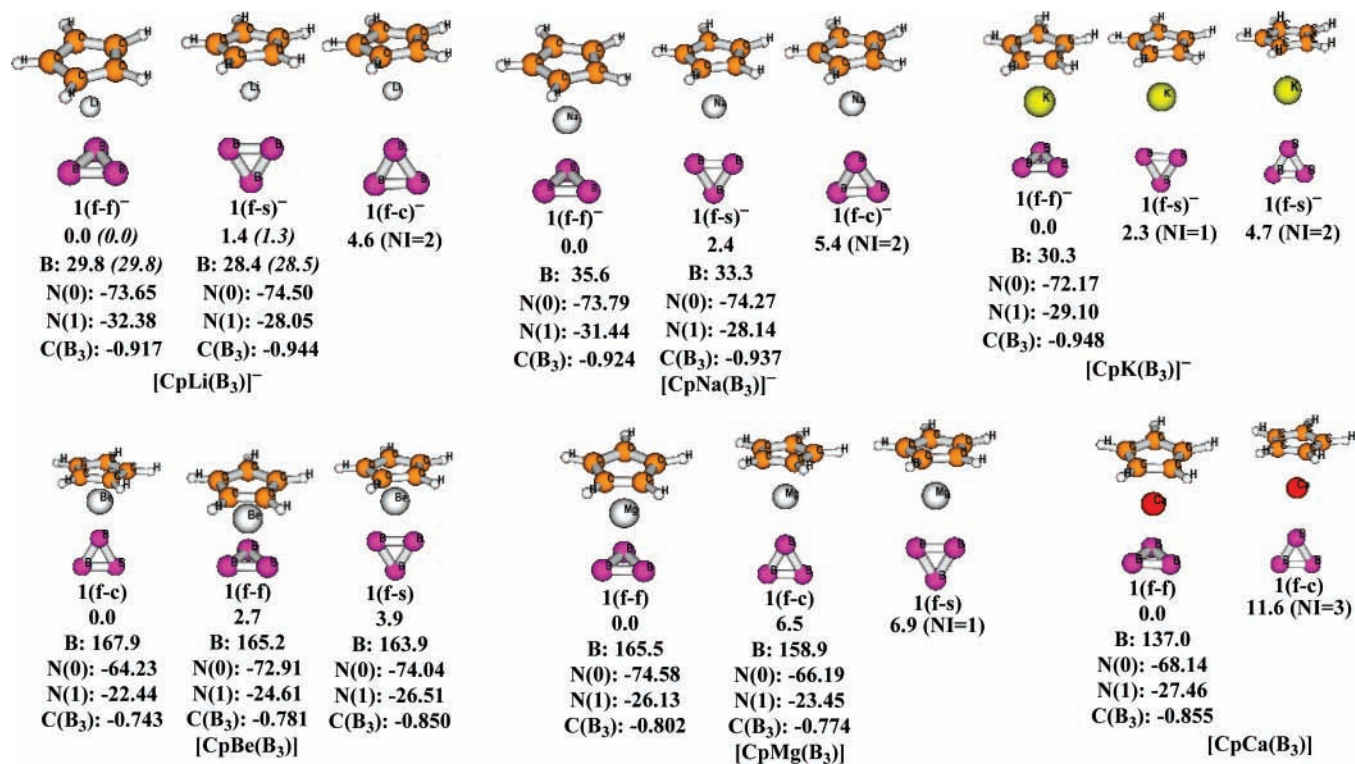


Figure 2. Low-lying structures for CpMB_3^{q-} ($M = \text{Li, Na, K, } q = 1$; $M = \text{Be, Mg, Ca, } q = 0$) obtained at the B3LYP/6-311++G(d, p) and B3LYP/6-311++G(2d, 2p) (in italics within parentheses) levels. Energy values are in kcal/mol. “B” denotes the binding energies between B_3^- and CpM^{q+} ($M = \text{Li, Na, K, } q = 0$; $M = \text{Be, Mg, Ca, } q = 1$). “N(0) and N(1)” denotes the nucleus-independent chemical shift (NICS) at the ring center and 1 Å above the ring of B_3^- , respectively. “C” denotes the natural charge distributions on the fragment B_3 units. “NI=n” means the number of imaginary frequencies of the stationary point. For the saddle points, we only list the relative energies and do not perform property analysis. Note that for $M = \text{Ca}$, the (f-s) form is not in existence during optimization. The pink colored balls represent boron atoms.

binding energies between the fragments B_3^- and CpM^{q+} of our designed species are ranging from 30 to 168 kcal/mol. Such large binding energies are responsible for the existence of our designed hetero-decked sandwich-type compounds CpMB_3^{q-} ($M = \text{Li, Na, K, } q = 1$; $M = \text{Be, Mg, Ca, } q = 0$).

For some relevant species, e.g., CpLiB_3^- , we used the higher method B3LYP/6-311++G(2d, 2p) to testify to the reliability of the results obtained at the B3LYP/6-311++G(d, p) level. From Figure 2, we can see that the (f-f) form of CpLiB_3^- is the ground state with the relative energies 0.0(0.0) kcal/mol at two levels. The (f-s) form of CpLiB_3^- is slightly energetically higher than the (f-f) form, about 1.4(1.3) kcal/mol at the two theoretical levels. The binding energies between the fragments B_3^- and CpM^{q+} of CpLiB_3^- are 29.8(29.8) and 28.4(28.5) kcal/mol for the (f-f) and (f-s) sandwich-type forms, respectively. That indicates the results agree well with each other at the two levels.

Among all the considered $[\text{CpMB}_3]^{q-}$ systems, the planar Cp^- structure is well maintained, indicative of the unique “rigidity” of this organic unit. Fusion of the Cp^- and B_3^- decks to form new C–B or C–M bonds is energetically unfavorable, in sharp contrast to the situation for the $[\text{B}_6\text{M}]^{q-}$ systems. This results in the high stability of the hetero-decked sandwich complexes $[\text{CpMB}_3]^{q-}$. Thus, the rigid organic deck Cp^- can effectively assist the all-boron aromatic deck B_3^- to sandwich metal atoms. The “hetero-decked sandwich” scheme can both thermodynamically and kinetically stabilize the B_3^- unit by avoiding fusion. In contrast to the traditional homo-decked sandwich scheme, the present “hetero-decked sandwich” scheme can effectively incorporate the B_3^- unit into the assembled molecular compounds—a new type of metallocene.

In order to get the insight into the interactions of our designed hetero-decked sandwich-type complexes, we perform detailed

NBO¹² analysis. The NPA charges on alkali-atoms (Li, Na, and K) range from 0.836 to 0.852 |e|, from 0.872 to 0.882 |e|, and 0.906 |e| in $[\text{CpM}(\text{B}_3)]^-$ for $M = \text{Li, Na, and K}$, respectively. For the alkaline earth atoms, the NPA charges are range from 1.514 to 1.537 |e|, from 1.640 to 1.661 |e|, and 1.712 |e| in the $[\text{CpM}(\text{B}_3)]$ for $M = \text{Be, Mg, and Ca}$, respectively. We can see that the NPA charges on alkali-atoms (Li, Na, and K) are in slight departure to ionic limit +1. For alkaline earth atoms (Be, Mg, and Ca), the NPA charges are slight departure to ionic limit +2, whereas for Be, the departure is slight larger because of its large covalent property. For the B_3 units, the NPA charges are range from -0.917 to -0.944 |e|, from -0.924 to -0.937 |e|, and -0.948 |e| in $[\text{CpM}(\text{B}_3)]^-$ for $M = \text{Li, Na, and K}$, respectively. Thus, the NPA charges distributed on B_3 units in the alkali-metal hetero-decked sandwich complexes are nearly equal to the charge on the bare free B_3^- . For the alkaline earth metal, the NPA charges on the B_3 units are range from -0.743 to -0.850 |e|, from -0.774 to -0.802 |e|, and -0.855 |e| in $[\text{CpM}(\text{B}_3)]$ for $M = \text{Be, Mg, and Ca}$, respectively. In summary, the NBO analysis demonstrated that the positive and negative charges are primarily localized at the M-atoms and B_3 units, respectively, indicative of the major molecular formula $(\text{Cp}^-)\text{M}^{q+}(\text{B}_3^-)$ ($q = 1$ for $M = \text{Li, Na, K}$ and $q = 2$ for $M = \text{Be, Mg, Ca}$). It should be noted that the departure from the formula $(\text{Cp}^-)\text{M}^{q+}(\text{B}_3^-)$ is slight larger for $M = \text{Be}$, because of its large covalent property compared with other metals.

Aromaticity is another interesting property in the sandwich-type complexes. We thus investigate the aromaticity of our designed hetero-decked sandwich-like complexes through NICS(0) and NICS(1) probes. The results are listed in Figure 2, from which we can see that the aromaticity (“N(0) and N(1)” values in Figure 2) of the B_3^- units within the assembled compounds

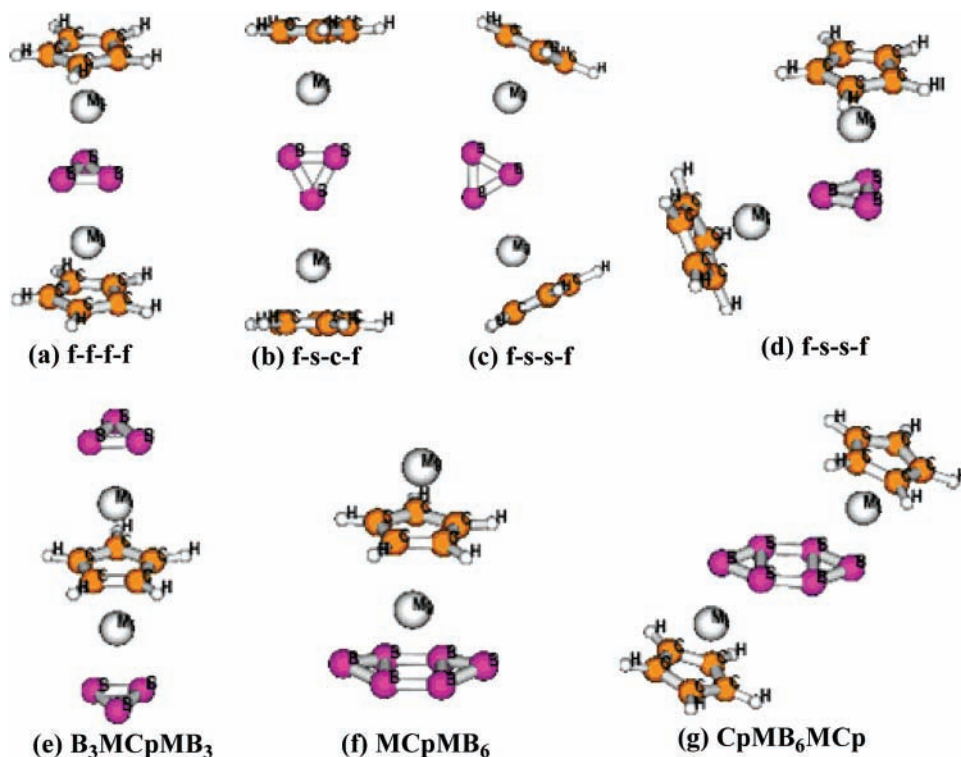


Figure 3. Illustrative structures of $[\text{Cp}_2\text{B}_3\text{M}_2]^q$, $\text{B}_3\text{MCpMB}_3^q$, and MCpMB_6^q ($M = \text{Li, Na, K, } q = -1$; $M = \text{Be, Mg, Ca, } q = +1$) calculated at the B3LYP/6-311++G(d, p) level.

nearly amounts to -73.60 (N(0)) and -28.19 (N(1)) ppm as that in the free B_3^- , suggestive of the good aromaticity-conservation in the cluster-assembly.

Thus, from the above detailed analyses of the electronic, structural, and aromatic properties of our designed hetero-decked sandwich-type complexes, we have confidence to conclude that B_3^- could indeed act as a new type of building block or inorganic ligand in the cluster-assembled molecular compounds.

Generally, our designed B_3^- -based hetero-decked sandwich species are similar to the heavier homologues CpMAI_3^{q-} in both sandwich-type interaction forms and the order of relative energies. The (f-f) forms constitute the ground state for $M = \text{Li, Na, K, Mg, and Ca}$. For $M = \text{Be}$, the (f-c) form is slight more stable than (f-f) form in both systems. However, some differences are still existent in the two systems. The (f-s) sandwich forms are not existent in the CpMAI_3^{q-} system, whereas the (f-s) sandwich forms are minima for $M = \text{Li, Na, and Be}$. For $M = \text{K and Mg}$, the (f-s) sandwich forms are saddle-points. For $M = \text{Ca}$, we do not search the stationary point of the (f-s) sandwich form in the potential energy surface, because the (f-s) form converts to (f-f) during the geometrical optimization.

3.3. Nature and Origin of Fusion. Why can the assembly of B_3^- only be realized in form of the “hetero-decked sandwich” scheme instead of the traditional “homo-decked sandwich” scheme? Why would the “homo-decked sandwich” assembly lead to fusion between two B_3^- decks? To answer these questions, we analyze the origin of such fusion. Intuitively, the monoanionic inorganic aromatic bare all-boron cluster B_3^- bears both the fusion and ionic characters. From a combinational viewpoint, when the decks D_1^{m-} and D_2^{n-} and one M^{q+} ion are brought together, two types of reaction processes might take place, i.e.,

- (1) ionic interaction: $\text{D}_1^{m-} + \text{M}^{q+} + \text{D}_2^{n-} \rightarrow (\text{D}_1^{m-})\text{M}^{q+}(\text{D}_2^{n-})$
- (2) fusion interaction: (a) $\text{D}_1^{m-} + \text{D}_2^{n-} + \text{M}^{q+} \rightarrow \text{M}^{q+}[\text{D}_1\text{D}_2]^{(m+n)-}$.

In process 1, each sandwich deck (D_1^{m-} and D_2^{n-}) undergoes the electrostatic interaction with M^{q+} to form a sandwich-like structure $(\text{D}_1^{m-})\text{M}^{q+}(\text{D}_2^{n-})$. Process 2 is associated with the “clustering fusion”. In principle, there is a trend for any two decks to form a more coagulated cluster containing more bonds so as to lower the system energy.

The competition between the processes 1 and 2 determines whether formation of a sandwich-like complex can lead to energetic stabilization or not. In the traditional “homo-decked sandwich” form, the fusion interaction overwhelms the ionic interaction because of the favorable cluster coagulation. The bonding within the inorganic aromatic B_3^- is not strong enough to prevent from fusion. So, as shown in section 3.1, the homo-decked sandwich structures are energetically much less stable than the fused isomers. Yet situation is quite different in the novel “hetero-decked sandwich” form. The fusion tendency can be greatly suppressed because of the introduction of a rigid sandwiching partner Cp^- . The large organic aromaticity allows Cp^- to perfectly keep its (near) D_{5h} structure. Any fusion with B_3^- will destroy the aromaticity of Cp^- to greatly raise the system energy. As a result, only in form of the novel “hetero-decked sandwich” scheme can the inorganic aromatic bare all-boron cluster B_3^- be assembled into sandwich-like complexes.

3.4. $-\text{CpMB}_3\text{M}...\text{Cp}-$. We also investigated the possibility of extended molecular compounds that contain three decks, i.e., two Cp^- and one B_3^- or one Cp^- and two B_3^- at the B3LYP/6-311++G(d, p) level. For each M , we considered the assembly possibilities in that B_3^- could use its face, side, or corner to interact with Cp^- in the extended structures. Some selected low-lying structures are showed in Figure 3. For compounds (Figure 3e and 3f) with one Cp^- and two B_3^- , the fused structures MCpMB_6^q ($M = \text{Li, Na, K, } q = -1$; $M = \text{Be, Mg, Ca, } q = +1$) are energetically more stable than $\text{B}_3\text{MCpMB}_3^q$ by 56.9, 54.2, 59.9, 44.4, 49.7, and 59.6 for $M = \text{Li, Na, K, Be, Mg, and Ca}$, respectively.

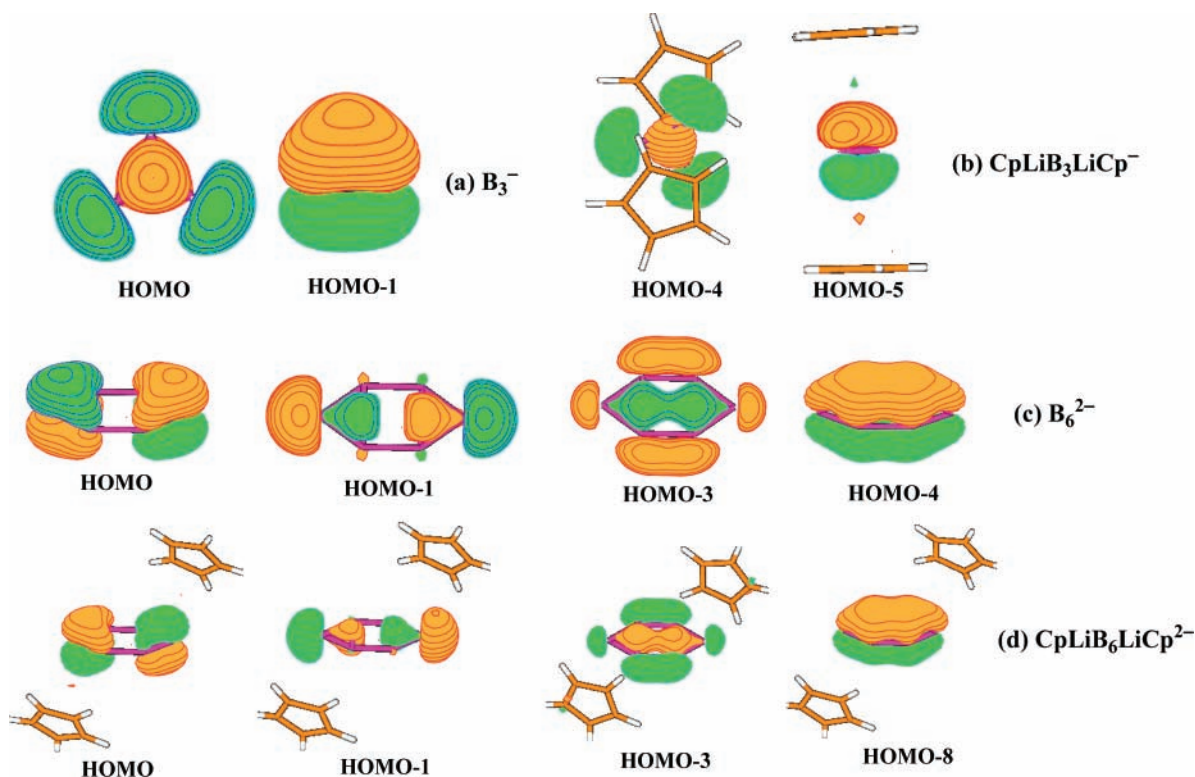


Figure 4. Characteristic orbitals of (a) B_3^- , (b) $CpLiB_3LiCp^-$, (c) B_6^{2-} , (d) $CpLiB_6LiCp^{2-}$ are obtained at B3LYP/6-311++G(d, p) level.

Second, in view of the strong fusion tendency of two B_3^- units to form B_6^{2-} , we explore the direct dimerization of two hetero-decked sandwich complexes $CpMB_3^{q-}$. The association of each B_3^- unit results in a triple-decker sandwich-like complex $CpMB_6MCp^{2q-}$ with $M = Li, Na, K; q = 1$ and $M = Be, Mg, Ca; q = 0$. The released heat is as large as $-56.8, -62.1, -64.7, -149.3, -130.2$, and -124.3 kcal/mol for $M = Li, Na, K, Be, Mg$, and Ca , respectively. The species (Figure 3g) should represent the first sandwich-like complexes based on the all-boron antiaromatic unit B_6^{2-} . The “hetero-decked sandwich” scheme can effectively incorporate the bare all-boron aromatic unit B_3^- and antiaromatic unit B_6^{2-} into various sandwich-like complexes. These interesting sandwich-like complexes are very promising and await future experimental synthesis.

Generally, the structural and orbital features of the bare all-boron cluster B_3^- are well conserved during the hetero-decked sandwich forms $CpMB_3^{q-}$ (f-f) and $CpMB_3MCp^{q-}$ (f-f-f). Figures 4a and 4b illustrate the characteristic orbitals¹³ of $CpLiB_3LiCp^-$ as well as the comparative B_3^- . We can see that the two characteristic orbitals in the free B_3^- , i.e., one delocalized σ (HOMO) and one delocalized π (HOMO-1) that contribute to the so-called “double-fold aromaticity”, can be found in multi-hetero-decked sandwich compound $CpLiB_3LiCp^-$. A significant difference is that the HOMO and HOMO-1 orbitals in the free B_3^- are moved to HOMO-4 and HOMO-5 in $CpLiB_3LiCp^-$, respectively. Thus, the delocalized σ and π orbitals are greatly stabilized upon hetero-decked sandwiching. For the free B_6^{2-} , its HOMO-1 and HOMO-3 are two globally delocalized σ -MOs, which makes it σ -antiaromatic, and HOMO and HOMO-4 are two globally delocalized π -MOs, which makes it π -antiaromatic. Thus, B_6^{2-} is double (σ and π) antiaromatic. From Figures 4c and 4d, we can see that the double antiaromatic properties of B_6^{2-} are well conserved in the extended sandwich-like species $CpLiB_6LiCp^{2-}$ during the cluster-assembly process. Interestingly, the globally delocalized HOMO-4 (π -MO) is

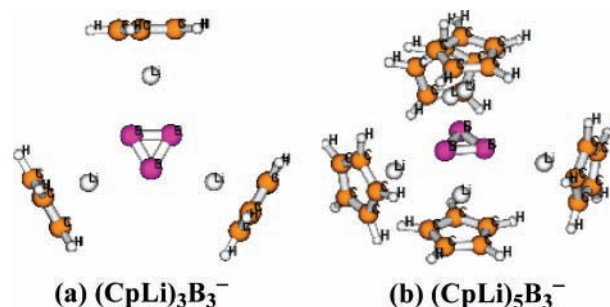


Figure 5. The highly extended sandwich-type structures of (a) rice-ball- $(CpLi)_3B_3^-$ and (b) cage- $(CpLi)_5B_3^-$ are obtained at B3LYP/6-31+G(d) level.

moved to HOMO-8 and greatly stabilized upon forming the hetero-decked sandwich complex.

3.5. Embellish and Functionalize Bare All-Boron Clusters. The above results call attention to the fundamental problem that isolation and protection are quite crucial in bare all-boron cluster assembly and stabilization so as to avoid the cluster fusion. From the prospective view, we discuss the isolation (i.e., to separate the boron clusters from each other, to preclude fusion), protection, embellishment, and functionalization of the bare all-boron clusters in the cluster-assembly molecular compounds. Their illustrative structures are listed in Figure 5. The capture and stabilization of bare all-boron clusters has become a great challenge toward molecular materials and solids. The “hetero-decked sandwich” scheme can effectively suppress the reactivity of bare all-boron cluster B_3^- by introducing neutral LiCp pairs (Figures 2, 3a–d, and 5a,b). It is even possible that the reactivity of B_3^- can be completely suppressed by being fully “dressed” with five LiCp pairs (Figure 5b) in five directions. In this way, the bare all-boron B_3^- cluster is well captured into a “rice-ball” structure (Figure 5a) and a “cage” structure (Figure 5b). We call such a bare-all-boron-cluster-stabilization method “sandwich-

stabilization". The advantages of the new method are that (1) the steric effect can easily be introduced by choosing suitable "dressers" (e.g., change LiCp to LiCp* with all H-atoms substituted by methyl groups), (2) the neutral LiCp pairs can be facily "undressed" when we want to have B₃⁻ for further usage, and (3) thus, the manipulation of B₃⁻-assembly should be easy by simply capturing more all-boron B₃⁻ units dressed by LiCp pairs.

We are aware that gas-phase anions B₁₂^{-20a} B₂₀^{-20b,c} and their neutral species have been experimentally observed and theoretically characterized. Moreover, pure boron nanotubes have been successfully synthesized,^{20d} and their functionalization has attracted intense interest. Our "sandwich-stabilization" method might provide a viable scheme to functionalize, isolate, and protect bare all-boron cluster and BNT.

4. Conclusions

In conclusion, we performed detailed DFT studies on six systems [DM(B₃)]^{q-} (D = B₃⁻, Cp⁻; M = Li, Na, K, Be, Mg, and Ca). We found the all-boron aromatic unit B₃⁻ can only be assembled in the hetero-decked sandwich forms CpMB₃^{q-} rather than the homo-decked sandwich forms B₃MB₃^{q-} because of its thermodynamical instability and kinetical lability toward conversion to the lower-lying B₆-clusters. Moreover, various extended compounds were designed. The isomerism provided a framework to well support the photoelectron spectroscopy study by Alexandrova et al. Compared with the traditional metallocenes with all Cp⁻ decks with organic aromaticity, our designed CpMB₃^{q-} and CpMB₆MCp^{2q-} represent two new classes of metallocenes containing the all-boron aromatic B₃⁻ and antiaromatic B₆²⁻ units, respectively. They (CpMB₃^{q-} and CpMB₆MCp^{2q-}) represent the first type of synthesizable all-boron-based sandwich complexes and await future experimental verification. Additionally, our results could be applicable to higher alkali (Rb, Cs) and alkaline earth (Sr, Ba) metals and other bare all-boron clusters B_n. We hope that the present hetero-decked sandwich scheme might also be applicable to the assembly of the B₃⁻ deck in sandwiching transition metals (e.g., Fe, Co, Ni, etc.). Further investigation on the B₃⁻-based transition metal sandwich-type complexes is currently in progress. Moreover, during the hetero-decked sandwiching process, the electronic and structural properties of bare all-boron B₃⁻ and B₆²⁻ units are well conserved. This indicates that when assisted by a rigid partner like Cp⁻, the B₃⁻ and B₆²⁻ units possess the "superatom" feature. To the best of our knowledge, this is the first theoretical indication that the all-boron clusters B₃⁻ and B₆²⁻ might be two new examples of "superatom". Future studies on the "superatom" chemistry of B₃⁻ and B₆²⁻ are greatly desired. Finally, we propose a viable scheme to embellish, functionalize, isolate, and protect bare all-boron clusters.

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