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Achieving Stable Hypercarbon CB$_6^{2-}$-Based Cluster-Assembled Complexes: A General Strategy

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A general strategy for designing stable hypercarbon CB$_6^{2-}$-based cluster-assembled compounds CpM(CB$_6$)$^{q-}$ (M = Li, Na, K, Be, Mg, and Ca) is proposed. This approach takes advantage of (1) the extra stability of a rigid organic aromatic Cp$^-$ deck, (2) the electrostatic interactions, (3) charge transfer based on orbital interaction, and (4) the good electronic match between the CB$_6^{2-}$ and CpM fragments. The nature and origin of various sandwich-type interactions and the requirements and technologies of the sandwiching decks' assembly and stabilization are generally classified and comprehensively revealed. The quite crucial to perform fusion stability investigation is performed by comprehensive thermodynamic stability calculations. The electrostatic and orbital interactions and charge transfer in our designed hypercarbon complexes CpM(CB$_6$)$^{q-}$ are revealed by detailed NBO analysis, orbital characterization, and frontier molecular orbital theory. Detailed analysis and comparison of the intrinsic difference of cluster-assembled compounds between hypercarbon phC CB$_6^{2-}$ and pentaatomic ptC CAl$_4^{2-}$ are performed.

1. Introduction

Highly symmetrical and chemically (quasi)inert clusters have long been sought because they may serve as ideal building blocks for tailored nanomaterials.[1] Clusters with closed shells of electrons have good prospects. Aromaticity is another important factor for determining stability. A good match between electronic and structural requirements and interaction types is the third crucial factor in determining the stability of compounds. It would be ideal if the above three conditions can be simultaneously achieved to give a cluster-enhanced stability.

The hypercarbon[2,3] cluster CB$_6^{2-}$(D_{6h})[3a] featuring a planar hexacoordinate carbon (phC) center, disclosed by Schleyer and co-workers in the process of searching for new aromatic systems, has attracted great attention. Such a high-symmetry aromatic cluster could become a building block in molecular complexes. Minyaev and Gribanova[3b] proposed heteroatomic extensions of CB$_6^{2-}$ with eight-membered-ring perimeters. Schleyer et al.[3c–e] theoretically demonstrated that CB$_6$ units with planar hexacoordinate carbon (or boron) can be grafted onto olefins, arenes, or saturated carbon systems. We are aware that Li et al.[4] theoretically designed CB$_6^{2-}$-based transition-metal sandwich-type complexes (e.g., [Fe(CB$_6$)$_2$]$^{2-}$).[4a] However, many doubts still exist for CB$_6^{2-}$ as potential building blocks or ligands in molecular compounds: (1) Li et al. considered only one sandwich-type interaction form, i.e., the face−face (f−f) form. Many other interaction-type forms (face−side (f-s), face-corner (f−c), side−side (s−s), side−corner (s−c), and corner−corner (c−c)) have been completely ignored or omitted! (2) The sandwich-type species (e.g., [Fe(CB$_6$)$_2$]$^{2-}$), designed by Li et al., are only minima on the potential energy surface. The authors did not address the issue of catenation between two CB$_6^{2-}$

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groups, which is quite crucial to such nonstoichiometric systems. Many fusion isomers could be energetically lower than (f−f) $[Fe(CB_6)_2]^{2-}$. (3) The synthesis equation ($[(C_5H_5)_2Fe] + 2B_6C^{2-} \rightarrow [(B_6C)_2Fe]^{2-} + 2C_5H_5^-$), proposed by Li et al., might be questionable in the actual synthesis due to the agglomeration and the possible strong interaction between the two CB_6^{2-} groups, and the solvent molecules interact with CB_6^{2-} groups. From the combinatorial viewpoint, the possibility of the two CB_6^{2-} groups interacting with each other and fusion together is inevitable. More recently, another group, Li et al.,[4c] theoretically designed some main-group metallocene-like complexes. This group still does not consider any fusion stabilities of such electron-deficient decks! With this background, we put forward an ignored but key issue: "How does one incorporate and stabilize the hypercarbon CB_6^{2-} into the assembled molecular compounds?" and "How can CB_6^{2-} become a building block or inorganic ligand?"

In order to gain insight into the above question and evaluate the intrinsic stability of the hypercarbon CB_6^{2-}-based sandwich-like compounds, we made an attempt to incorporate and stabilize the CB_6^{2-} into cluster-assembled molecular compounds in the "*homo-decked sandwich*"[5] and the "*hetero-decked sandwich*"[5] schemes based on a series of density functional theory calculations on charged $[DM(CB_6)]^{q-}$, neutral $(M^+)_q[DM(CB_6)]^{q-}$ (D = CB_6^{2-}, Cp^-; M = Li, Na, K, Be, Mg, Ca), and extended $(CpLi)_m(CB_6^{2-})$ species. At the B3LYP/6-31+G(d) level, we showed that the hypercarbon cluster CB_6^{2-} cannot be stabilized in the "homo-decked sandwich" form like $[M(CB_6)_2]^{q-}$ due to thermodynamical instability. However, the "hetero-decked sandwich" scheme (e.g., $[CpM(CB_6)]^{q-}$) is very effective in assembly. The good structural and electronic integrity of the CB_6^{2-} unit within the designed assembled systems leads us to propose that the hypercarbon CB_6^{2-} might act as a new kind of building block or inorganic ligand in combinational chemistry.

2. Computational Methods

Initially, we fully optimized the geometries of $[DM(CB_6)]^{q-}$ (D = CB_6^{2-}, Cp^-; M = Li, Na, K, Be, Mg, Ca) employing analytical gradients with a polarized split-valence double-ξ augmented with diffuse function basis set (6-31+G(d)) using B3LYP,[6a–d] i.e., Becke's hybrid three-parameter exchange functional with the Lee, Yang, and Parr correlation functional within Kohn–Sham theory, which is implemented in the Gaussian 03 package. After geometrical optimization, 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 a high-order saddle point with many imaginary frequencies. The higher theoretical method B3LYP/6-311++G(d, p) was also used to test the reliability of the results obtained at B3LYP/6-31+G(d) for some selected species. All the calculations were performed with the Gaussian-03 program.[6e]

3. Results and Discussions

First, we theoretically reveal (1) the nature and origin of various sandwich-type interactions and (2) the requirements and technologies of the sandwiching decks' assembly and stabilization. Then, we discuss the assembly and stabilization of the hypercarbon CB_6^{2-} deck, for which the effects of the counterions and the orbital analysis have been considered. Finally, we propose that the hypercarbon CB_6^{2-} cluster could be used as a

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robust building block in cluster-assembled molecular compounds and provide the viable possibility of the embellishment and functionalization of hypercarbon clusters.

Generally, the sandwiching decks are anions or neutral, and the core atoms are cations in the metallocenes. On the basis of deep analysis and comparison of a great deal of facts, we theoretically classify the sandwiching decks into two classes, i.e., electron-rich and electron-deficient decks. During the past half-century after the discovery of ferrocenes ($FeCp_2$)[7a] and dibenzene chromium ($CrBz_2$),[7b] the electron-rich-deck-based metallocenes[7c] and benzene-metallocenes[7d,e] have made explosive progress. At the beginning of the new century, many exotic nonstoichiometric[7f] molecules (for example, see feature article of ref 7f) (all-metal aromatic molecules, e.g., Al_4^{2-}[8a–c] (experimentally observed with counterion Li^+, Na^+, Cu^+ in 2001) and Al_3^-[8d–i] (experimentally observed in 1998), pentaatomic planar tetracoordinate carbon, e.g., CAl_4^{2-} (first theoretically characterized in 1991,[8j] and experimentally observed with counterion Na^+ in 2000[8k]), hypercarbon clusters, e.g., CB_6^{2-} (first theoretically characterized in 2000[3a])), which could be used as novel building blocks, ligands, and decks, have been discovered. Such building blocks represent another class of sandwiching decks, i.e., electron-deficient decks. The designing, assembly, and stabilization of electron-deficient-deck-based metallocenes, sandwich-type complexes and other cluster-assembled compounds are very interesting and quite crucial to provide an important extension to the traditional concept of sandwich-like complexes, to discover new phenomena and reveal the nature and origin of the stabilization mechanism of such metallocens, and to present a viable possibility to synthesize them in future experiments. In the following sections, we mainly discuss the electron-deficient-deck-based metallocenes.

A. Requirements of the Electron-Deficient Decks' (e.g., CB_6^{2-}) Assembly and Stabilization I. Nature of CB_6^{2-} Deck and the Origin of Fusion. Intuitively, the dianionic hypercarbon deck CB_6^{2-} bears both fusion and ionic character. 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:

(1) Ionic interaction: $D_1^{m-} + M^{q+} + D_2^{n-} \rightarrow (D_1^{m-})M^{q+}(D_2^{n-})$.

(2) Fusion interaction: (a) $D_1^{m-} + D_2^{n-} + M^{q+} \rightarrow M^{q+}[D_1D_2]^{(m+n)-}$.

In process 1, each sandwich deck (D_1^{m-} and D_2^{n-}) undergoes an electrostatic interaction with M^{q+} to form a sandwich-like structure $(D_1^{m-})M^{q+}(D_2^{n-})$. The nature of such a process is similar to that of $[Fe(CB_6)_2]^{2-}$, as Li et al. designed. Process 2 is associated with the "clustering fusion". In principal, there is a trend for any two decks to form a more coagulated cluster containing more bonds so as to lower the system energy. Such a process is quite crucial to electron-deficient decks (e.g., CB_6^{2-}), but completely ignored by Li et al. The competition between processes 1 and 2 determines whether formation of a sandwich-like complex can lead to energetic stabilization or not.

(3) If the fusion interaction overwhelms the ionic interaction because of the favorable cluster coagulation in the "homo-/hetero-decked sandwich" schemes, they are apt to form fusion isomers by catenation between two decks to form additional bonds to stabilize the systems. This process usually is directed to the electron-deficient decks (e.g., Al_4^{2-}, CB_6^{2-}).

(4) If the ionic interaction overwhelms the fusion interaction during the "homo-/hetero-decked sandwich" processes, they are apt to form the sandwich-type forms by electrostatic interaction between the two decks and the metal atoms. This process is usually associated with organic aromatic decks (e.g., Cp^- ($C_5H_5^-$), Bz (C_6H_6)).

II. Assembly Technologies of the Electron-Deficit Decks (e.g., CB_6^{2-}). The rich and mature chemistry of metallocenes[7c] (Cp_2M) and benzene-metallocenes[7d,e] (Bz_2M) suggested that the "homo-decked sandwich" scheme is a useful assembly technology. Such forms are usually applied to organic aromatic electron-rich decks (e.g., Cp^- ($C_5H_5^-$), Bz (C_6H_6)).

However, the recently discovered exotic all-metal aromatic units (e.g., Al_4^{2-}, Al_3^-, Al_6^{2-}) and the planar coordinate nonmetal decks (e.g., CAl_4^{2-}, CB_6^{2-}) are usually electron-deficient, and the "homo-decked sandwich" scheme is usually not effective to assemble and stabilize them.

In order to see clearly and understand correctly, here we have added some additional interpretation and notations on the criteria selected for assigning ligands to electron-deficient and electron-abundant sorts. On the basis of our series of works[5a–d] on the sandwich-type compounds and metallocenes, we intuitively divide the ligands or decks into electron-deficient and electron-abundant. It should be pointed out that the isolated negatively charged anions, e.g., $C_5H_5^-$ and CB_6^{2-}, are electronically unstable due to the autodetachment of redundant electrons. These anions can only stably exist in the form of salts with counterions. Thus, the pure and simple discussion of the isolated negatively charged anions, e.g., $C_5H_5^-$ and CB_6^{2-}, is useless. In the present work, the criteria selected for assigning ligands to electron -deficient and electron-abundant are based on the behaviors of the ligands in the cluster-assembled compounds during cluster-assembly processes. If the ligands or decks can sandwich metal atoms in the "homo-decked" sandwich scheme, and the cluster-assembled "homo-decked" sandwich compounds are quite stable, for example $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$, they are ground-state structures. The fusion stability has been effectively depressed in these organic rigid ligand-based "homo-decked" sandwich species. We call such ligands, e.g., $C_5H_5^-$ and C_6H_6, "electron-abundant" decks. If the ligands tend to fuse together to form an agglomeration in the traditional "homo-decked" sandwich complexes, but are only assembled in our recently proposed "hetero-decked" sandwich scheme, such as, CB_6^{2-}, we called such ligands "electron-deficient" decks.

As a further extension of the above taxonomy, we found that the recently discovered series of nonstoichiometric species (e.g., CAl_4^-, CAl_4^{2-}, Al_3^-, Al_4^{2-}, B_3^-, B_4^{2-}) could also be used as novel ligands or decks, which has been demonstrated by a series of our previous works. We have surprisingly discovered that these exotic ligands or decks cannot be assembled in the traditional "homo-decked" sandwich scheme, but are only assembled in our recently proposed "hetero-decked" sandwich scheme. On the basis of the above facts and discussions, we have assigned these nonstoichiometric species (e.g., CAl_4^-, CAl_4^{2-}, Al_3^-, Al_4^{2-}, B_3^-, B_4^{2-}) to "electron-deficient" ligands or decks. Although, such classification is somewhat arbitrary, we have sufficient facts that this clarification is still reasonable and valid in the cluster-assembled compounds. We have confidence that such clarification would shed insight on and guide the design of novel cluster-assembled compounds, sandwich-type complexes, and metallocenes. It should be kept in mind that we do not judge the ligands as electron-deficient/abundant on the basis of the formal charges attached to the decks.

B. Procedures to Achieve Stable Hypercarbon CB_6^{2-}-Based Cluster-Assembled Complexes I. Can Metal Atoms Effectively Separate, Protect, Assemble, and Stabilize the Aromatic Hypercarbon CB_6^{2-} Clusters? DFT structural optimizations at the B3LYP/6-31+G(d) level were

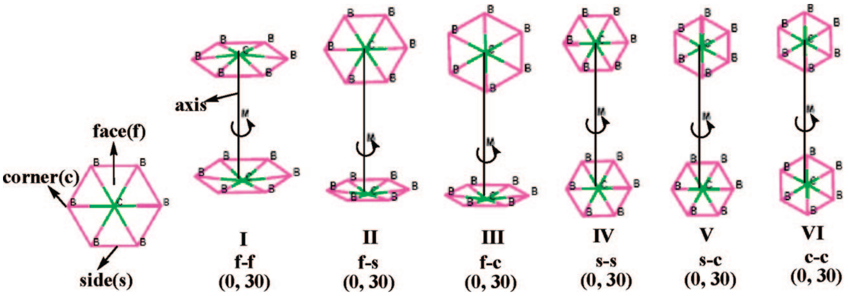

Figure 1. Six possible sandwich types of $[(CB_6)_2M]^{q-}$ (**I**−**VI**) for each M. In each type, one unit can rotate along the axis by 0°, 30°, and 90°.

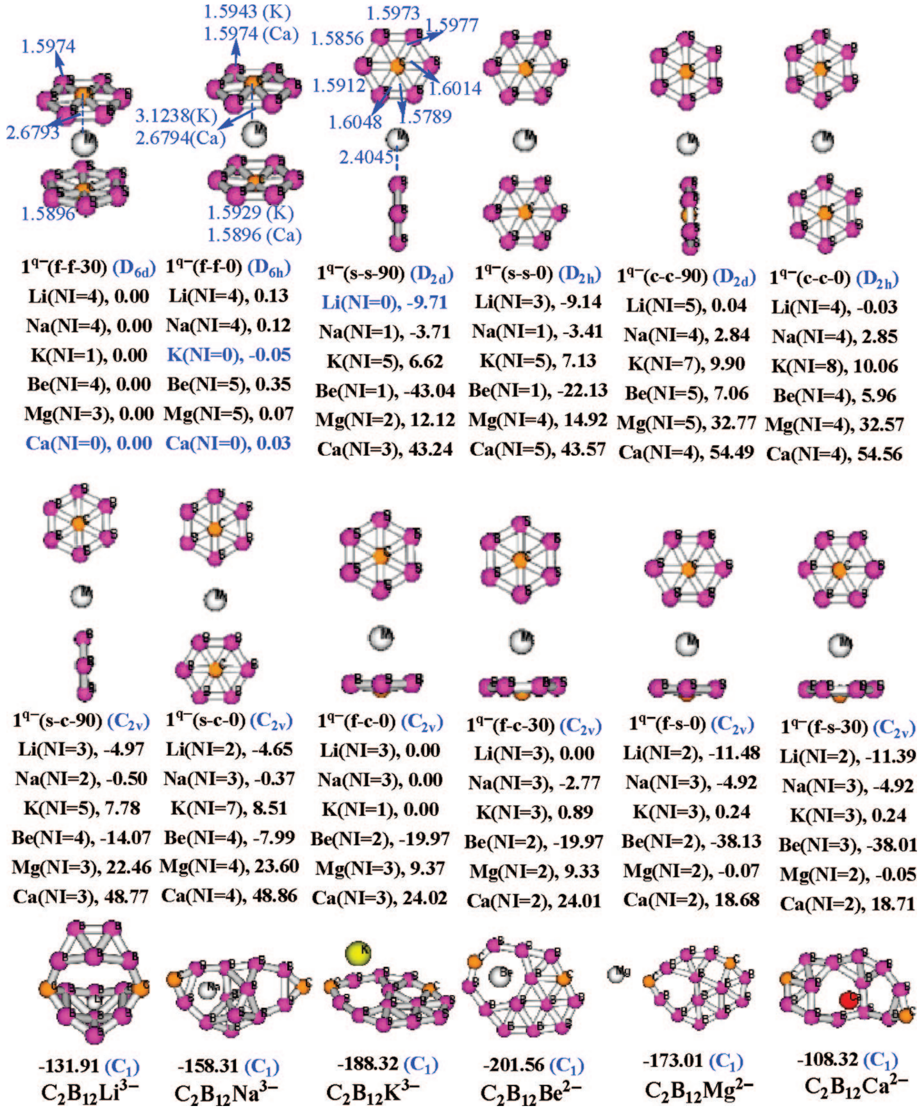

Figure 2. Most relevant $[C_2B_{12}M]^{q-}$ (M = Li, Na, K, $q = 3$; M = Be, Mg, Ca, $q = 2$) species at the B3LYP/6-31+G(d) level. The energy values are in kcal/mol. For simplicity, we generally use D_{6d} sandwich-like forms (f−f-30) as energy references. Some selected key geometry parameters are listed in the related minima structures. For the saddle points, we do not list the geometry parameters. The symmetry groups are presented in parentheses.

performed on the hypercarbon CB_6^{2-}-based sandwich complexes under investigation and imaginary frequencies in the traditional "homo-decked sandwich" forms $[(CB_6)_2M]^{q-}$ with M = Li, Na, K, $q = 1$; M = Be, Mg, Ca, $q = 0$. The possible sandwich types are systematically shown in Figure 1. The type **I** structure is similar to the well-known metallocene Cp_2M, in which two Cp^- adopt the face−face (f−f) type. After a detailed structural search at the B3LYP/6-31+G(d) level, the energy profiles of the most relevant $[C_2B_{12}M]^{q-}$ species, i.e., all sandwich forms and those with lowest-energy structures, are schematically shown in Figure 2. The other isomers can be found in the Supporting Information (SI). First, for all six main-group elements, the sandwich species **I**, **II**, an **III** have very close energies to each other and are all energetically lower than **IV**, **V**, and **VI**. Via the rotation of the CB_6 deck along different axes, **IV**−**VI** can be easily converted to the lower-energy **I**−**III**.

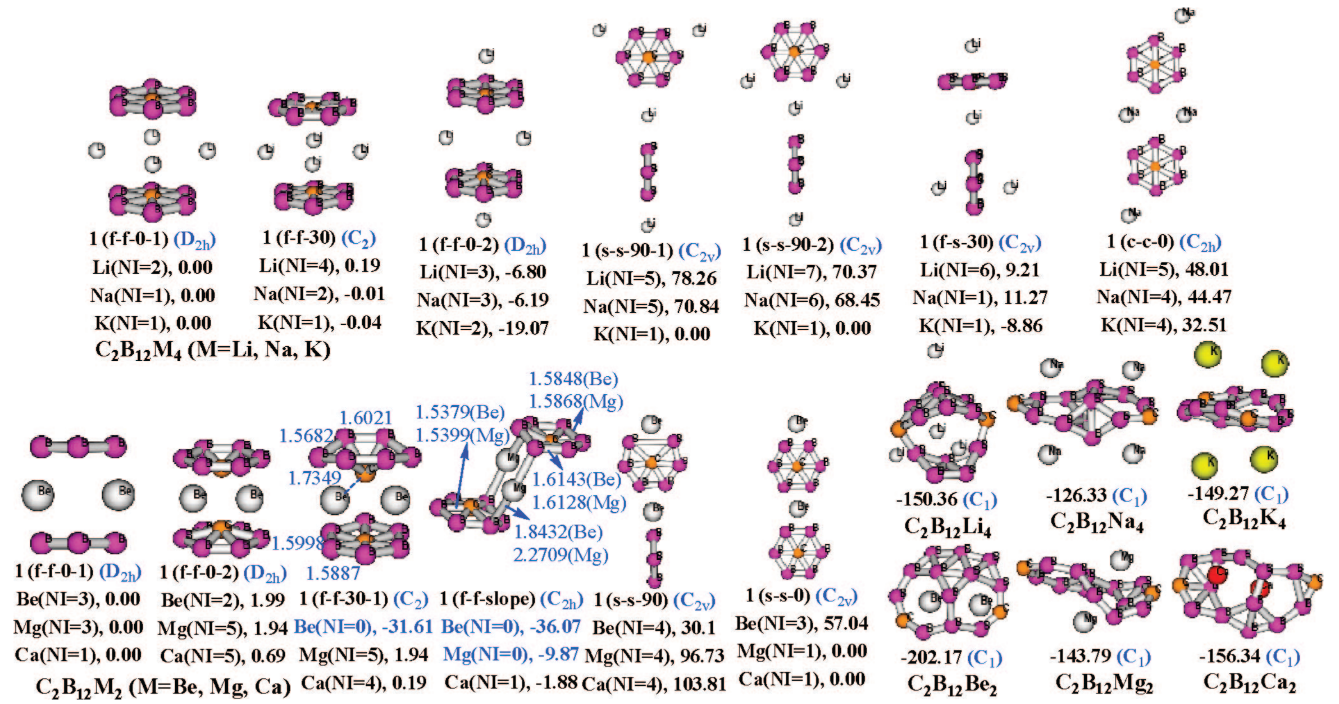

Figure 3. Most relevant $(M^+)_3[(CB_6)_2M]^{3-}$ (M = Li, Na, K) and $(M^{2+})[(CB_6)_2M]^{2-}$ (M = Be, Mg, Ca) at the B3LYP/6-31+G(d) level. Energy values are in kcal/mol. For simplicity, we generally use 1 (f−f-0–1) sandwich-like forms as energy references. Some selected key geometry parameters are listed in the related minima structures. For the saddle points, we do not list the geometry parameters. The symmetry groups are presented in parentheses.

The interconversion between **IV**−**VI** via simple rotation is also very easy, as indicated by the very small rotation frequency. Second, from Figure 2 we can see that the high-symmetry sandwich-type structures $[(CB_6)_2M]^{q-}$ only exist for Li (D_{2d}, s−s-90), Ca (D_{6h} (f−f-0), D_{6d} (f−f-30)), and K (D_{6h}, f−f-0). Many other high-symmetry sandwich-type structures are high-order saddle points with many imaginary frequencies. These high-symmetry optimum structures vanish or fuse together when symmetry constraints are removed. Moreover, there are many fusion isomers lower than the sandwich structures and are thus thermodynamically unstable. Third, for all six metals, the lowest-energy sandwich structure is not the global minimum. The low-lying isomers are fusion isomers lying 131.91, 158.31, 188.32, 201.56, 173.01, and 108.32 kcal/mol lower than the sandwich forms, respectively. “M” means the metal atom and superscript “*q*−” means the charge of the total system.

It should be pointed out that there are many studies[2c–t,3a,b,d,e,h,9] reporting the saddle points in the text to demonstrate their systematic and comprehensive consideration of various structures of the research systems, and the saddle points are used to compare with the corresponding minima in energies, geometries, and other electronic properties.

In this paper, we systematically and comprehensively consider various interaction forms and structures for six types of metals (M = Li, Na, K, Be, Mg, and Ca). For the same type of structure, among the six metal type complexes, some metal complexes are minima and other metal complexes are saddle points. To compare the results of different metal complexes, we listed the minima as well as the saddle points in the text. So, for the homo- and heterodecked (in section B.III) sandwich-type complexes, we listed all minima as well as the comparative saddle points in Figures 2, 3, and 4. We sincerely thought and suggested that such an arrangement is reasonable.

II. Effects of Counterions in the Homo-decked Assembled Compounds. We are aware that the most effective way to render the existence of multiply charged anions (MCAs) is to use a counterion. Many MCAs are ubiquitous in nature and are important constituents in solutions and solids.[10a–i] MCAs acquire their stability in the condensed phase through solvation

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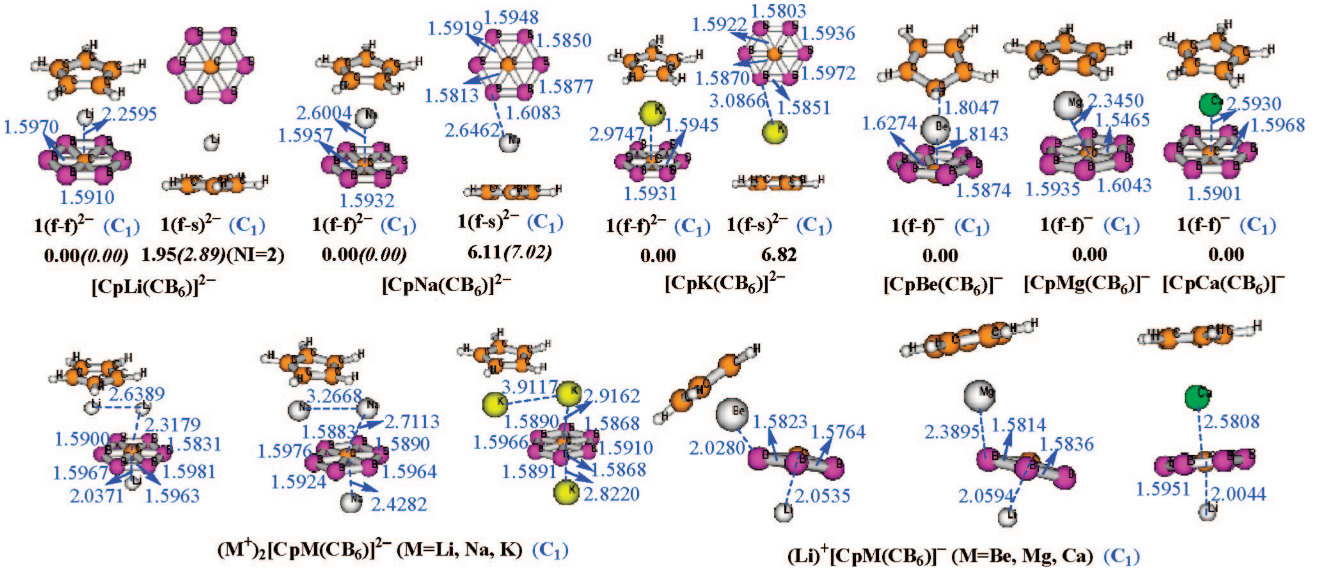


Figure 4. Sandwich forms of $[CpM(CB_6)]^{q-}$ (M = Li, Na, K, $q = 2$; M = Be, Mg, Ca, $q = 1$) and the lowest-energy saturated sandwich forms of $(M^+)_2[CpM(CB_6)]^{2-}$ (M = Li, Na, K) and $(Li^+)[CpM(CB_6)]^-$ (M = Be, Mg, Ca) obtained at the B3LYP/6-31+G(d) level. Energy values are in kcal/mol. Some selected key geometry parameters are listed in the related minima structures. For the saddle points, we do not list the geometry parameters. The symmetry groups are presented in parentheses.

and other electrostatic interactions. Of particular note, the hexaanions prototype square unit Hg_4^{6-} in Na_3Hg_2 crystals is known to have a rich and long history.[10j,k] It should be pointed that, as expected, multiply charged anions (MCAs) $[(CB_6)M(CB_6)]^{q-}$ are unstable toward electron dissociation. For simplicity, we use the high-symmetry sandwich-type structures $[(CB_6)_2Li]^{3-}$ (D_{2d}, s−s-90, NIMAG = 0) as an example to discuss such unstability; other MCAs should have the same results. For $[(CB_6)_2Li]^{3-}$ (D_{2d}, s−s-90), its top 10 occupied MOs have positive eigenvalues (0.04292, 0.04344, 0.05091, 0.05369, 0.06014, 0.06014, 0.15490, 0.15490, 0.15626, 0.15683 eV) when calculated by DFT. Similar situations are met in other di/trianions such as CB_6^{2-} and Al_4^{2-} and $[Al_4TiAl_4]^{2-}$, all of which have positive HOMO energies. However, these aromatic di/trianions can be effectively stabilized by introducing alkali-metal counterions into the systems while keeping the basic structures of the di/trianion unchanged, as shown in the cases of $[MAl_4]^-$ (M = Li, Na, Cu) and $[NaAl_4TiAl_4]^-$. According to Koopman's theorem, the negative values of the HOMO energies approximately represent the first-electron-detachment energies of the corresponding complexes. Figure 3 depicts all the sandwich forms of $(M^+)_q[(CB_6)_2M]^{q-}$ and those fusion isomers with lower energy than the sandwich forms. The other isomers can be found in the Supporting Information. For all six metals, many fused isomers have lower energies than the sandwich ones. The lowest-energy sandwich structure is not the global minimum point; the low-lying isomers are fusion isomers lying 150.36, 126.33, 149.27, 202.17, 143.79, and 156.34 kcal/mol lower than the sandwich forms for M = Li, Na, K, Be, Mg, and Ca, respectively. *This indicates that the salts of the CB_6^{2-}-based homo-decked sandwich complexes cannot exist for all six metals.*Here, the counterions introduce an electrostatic stabilization without altering the low-lying nature, which is the same as previous studies on metallocenes (including the traditional $CpMCp^{q-}$ [8c] and the novel $P_5MP_5^{q-}$,[11a–c] $N_4MN_4^{q-}$,[11f–i] and $Al_4MAl_4^{2-}$ [11d,e]).

III. Cooperation of Metal Atoms with the Organic Aromatic Deck $Cp^-(C_5H_5^-)$ Can Effectively Assemble and Stabilize the Aromatic Hypercarbon Cluster CB_6^{2-} in the Form of $[CpM(CB_6)]^{q-}$, $(M^+)_q[CpM(CB_6)]^{q-}$ (M = Li, Na, K), and $(Li^+)[CpM(CB_6)]^-$ (M = Be, Mg, Ca). As known from the preceding sections, the sandwich forms are not the low-lying structure for all 12 homo-decked systems: $[C_2B_{12}M]^{3-}$, $(M^+)_3[C_2B_{12}M]^{3-}$ (M = Li, Na, K) and $[C_2B_{12}M]^{2-}$, $(M^{2+})[C_2B_{12}M]^{2-}$ (M = Be, Mg, Ca). This indicates that the hypercarbon unit CB_6^{2-} cannot be used to sandwich the Li, Na, K, Be, Mg, and Ca atoms in the "homo-decked sandwich" scheme with and without counterions. Here, we apply the "hetero-decked sandwich" scheme, which have been demonstrated as a powerful and effective strategy to assemble and stabilize electron-deficient decks or building blocks into molecular compounds. A new class of sandwich compounds $[CpM(CB_6)]^{q-}$ can then be designed. Such compounds are intuitively of special interest because they contain both the classic organic aromatic unit Cp^- and the novel aromatic hypercarbon unit CB_6^{2-}.

Various isomeric forms for each of the six main-group elements (M = Li, Na, K, Be, Mg, and Ca) were searched. For simplicity, only the low-lying structures are shown in Figure 4. For each alkali metal M (Li, Na, K), there are two kinds of sandwich forms, $\mathbf{1^{q-}(f-f)}$ and $\mathbf{1^{q-}(f-s)}$, with the former associated with the "face (Cp^-)−face (CB_6^{2-})" (f−f) type and the latter with the "face (Cp^-) to side (CB_6^{2-})" (f−s) type. Except for M = Li, the $CpLi(CB_6)^{2-}$ (f−s) is a second-order saddle point; when the imaginary frequencies are removed, it converts to the f−f form. The two sandwich forms can easily convert to each other through the opening↔closing of the CB_6^{2-} deck. For each alkaline-earth metal M (Be, Mg, Ca), only one sandwich form, $\mathbf{1^{q-}(f-f)}$, exists, associated with the "face (Cp^-)−face (CB_6^{2-})" (f−f) type; their face−side $\mathbf{1^{q-}(f-s)}$ forms are finally convert to $\mathbf{1^{q-}(f-f)}$ during geometrical optimization. From Figure 4 we can see that the results obtained at the B3LYP/6-311++G(d, p) level agree quite well with that obtained at the B3LYP/6-31+G(d) level. Thus, we have confidence to conclude that our computational methods are reliable for such large systems due to the expensive CPU cost. Interestingly, among all the designed homo-decked and hetero-decked sandwich species, the hypercarbon unit CB_6^{2-} generally prefers to interact with the partner deck CB_6^{2-} or Cp^- at the face (CB_6 plane) site. The interaction forms are not disturbed

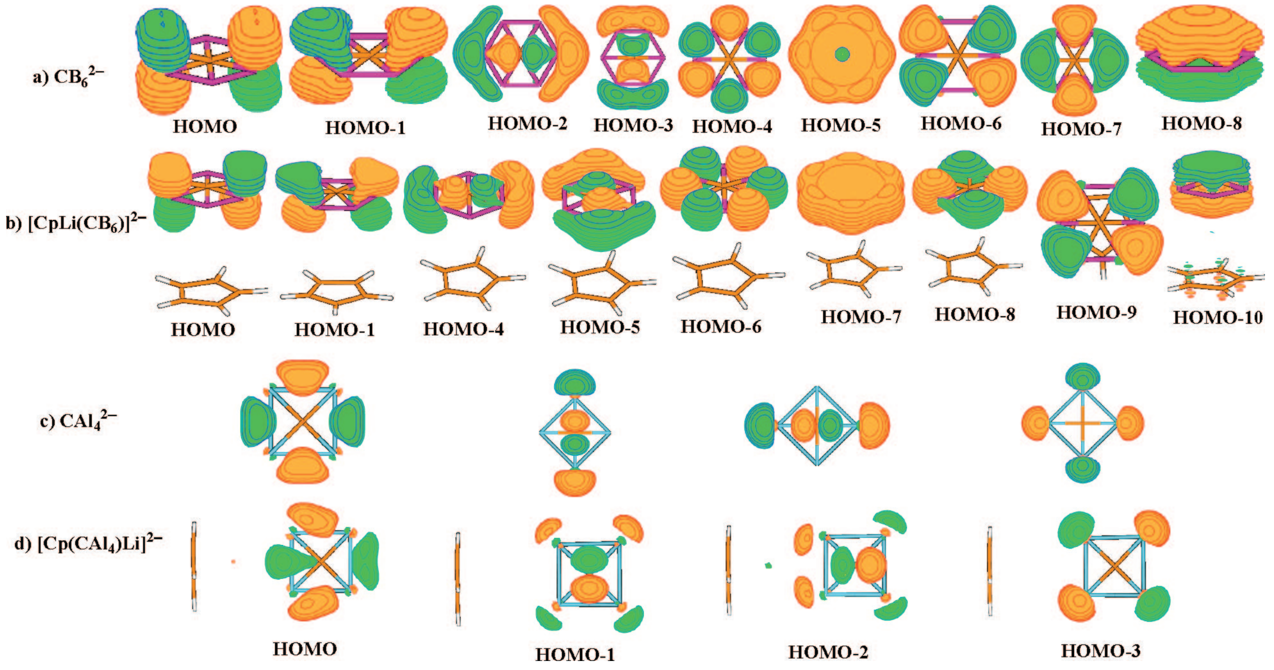


Figure 5. Characteristic orbitals[12a] of (a) CB_6^{2-}, (b) $[CpLi(CB_6)]^{2-}$, (c) CAl_4^{2-}, and (d) $[Cp(CAl_4)Li]^{2-}$ obtained at the B3LYP/6-31+G(d) level.

by the hypercoordinate center atoms. This is consistent with the already known decks such as the famous and versatile Cp^- and the carbon-free and exotic P_5^-, N_4^{2-}, and Al_4^{2-}, which prefer the traditional face−face interaction type. Among all the calculated $[CpM(CB_6)]^{q-}$ systems, the planar Cp^- structure is well maintained, indicative of the unique "rigidity" of this organic unit. The fusion tendency can be greatly suppressed with the introduction of the rigid sandwiching partner Cp^-. The large organic aromaticity allows Cp^- to keep its (near) D_{5h} structure. Any fusion with CB_6^{2-} will destroy the aromaticity of Cp^- to greatly raise the system energy. The rigid organic deck Cp^- can effectively assist the hypercarbon unit CB_6^- to sandwich metal atoms.

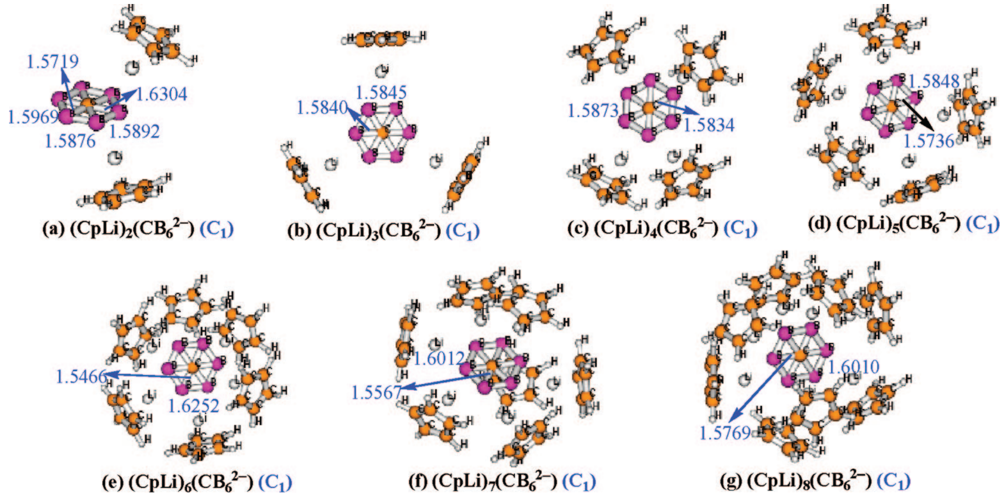
For the purpose of actual synthesis, we also designed neutral species $(M^+)_2[CpM(CB_6)]^{2-}$ (M = Li, Na, K) and $(Li^+)[CpM(CB_6)]^-$ (M = Be, Mg, Ca). Some low-lying saturated complexes are listed in Figure 4. As done in the present paper, our designed saturated model species $(M^+)_q[CpM(CB_6)]^{q-}$ (M = Li, Na, K) and $(Li^+)[CpM(CB_6)]^-$ (M = Be, Mg, Ca) in saturated sandwich-type forms should all be electronically stable. The recent preparation[11a] of the dianion sandwich species $[(P_5)_2Ti]^{2-}$ in solutions with the presence of two $[K(18\text{-crown-}6)]^+$ counterions should stimulate the realization of our designed novel sandwich species based on the hypercarbon unit CB_6^{2-}.

IV. Intrinsic Difference of Cluster-Assembled Compounds between Hypercarbon phC CB_6^{2-} and Penta-atomic ptC CAl_4^{2-}. In order to gain insight into the origin of planarity and exotic electronic structure of such novel sandwich-like compounds based on the hypercarbon unit CB_6^{2-}, we examined the molecular orbitals of the bare dianion CB_6^{2-} and model sandwich-like compound $[CpLi(CB_6)]^{2-}$. Figure 5 shows their nine highest orbitals: the HOMO, HOMO−1, and HOMO−8 are bonding π-orbitals, HOMO−2, HOMO−3, and HOMO−5 are bonding σ-orbitals, and HOMO−4, HOMO−6, and HOMO−7 are nonbonding ligand lone-pair orbitals. The structural planarity of these species is achieved through a strong six-center peripheral ligand−ligand bonding interaction in their HOMO−4. From Figure 5 we can see the shapes of orbitals in (a) bare CB_6^{2-} and (b) sandwich-like compound $[CpLi(CB_6)]^{2-}$, which are generally the same. Thus, the hypercarbon unit CB_6^{2-} can maintain its electronic and structural integrity in sandwich forms. Therefore, CB_6^{2-} could be used as a building block and inorganic ligand in designing planar hypercoordinate cluster-assembly molecular compounds.

Compared with the CAl_4^{2-}-based cluster-assembled molecular complexes, we found CAl_4^{2-} and CB_6^{2-} are quite different in their intrinsic stability; thus the low-lying structures of cluster-assembled compounds are different. For CAl_4^{2-}, the low-lying structures are face−side (f−s) forms due to the strong interactions between the metal atoms and the peripheral four-center σ-bonds, except for M = Be, where the face−face (f−f) is the low-lying structure. The Be−C covalent interaction is stronger than the ionic interaction between the Be atom and the peripheral σ-bond. For CB_6^{2-}, the situation is quite different. Usually, the σ-bonds are related to the backbone of the molecule, the π-bonds are related to the active electron cloud, and the σ-bonds (peripheral ligand−ligand bonds) are stronger than the π-bonds in metal−metal (Al−Al) bonds; thus σ-bonds are apt to interact with the CpM fragment to form face−side (f−s) sandwich-type low-lying structures. However, the situation is quite different from the nonmetal peripheral ligand−ligand bond (B−B). In such an inorganic cluster, the π-bonds are stronger than σ-bonds (peripheral ligand−ligand bonds) in B−B bonds; thus π-bonds are apt to interact with CpM fragment to form face−face (f−f) sandwich-type low-lying structures.

The NBO[12b–d] analysis demonstrates that our designed sandwich-type compounds can be viewed as ionic molecules comprising $(Cp^-)(Li^+)(CAl_4^{2-})$ (f−s) and $(Cp^-)(Li^+)(CB_6^{2-})$ (f−f). The NBO charges on each atom are Cp: −0.978, Li: +0.963, CAl_4: −1.945 and Cp: −0.969, Li: +0.965, CB_6: −1.967. Through electrostatic interactions, the fragments CpM and CAl_4^{2-}/CB_6^{2-} have been held together to form sandwich-like complexes.

From the viewpoint of frontier molecular orbital theory, we are aware that apart from electrostatic interactions, the overlap



(a) $(CpLi)_2(CB_6^{2-})$ (C_1) (b) $(CpLi)_3(CB_6^{2-})$ (C_1) (c) $(CpLi)_4(CB_6^{2-})$ (C_1) (d) $(CpLi)_5(CB_6^{2-})$ (C_1)

(e) $(CpLi)_6(CB_6^{2-})$ (C_1) (f) $(CpLi)_7(CB_6^{2-})$ (C_1) (g) $(CpLi)_8(CB_6^{2-})$ (C_1)

Figure 6. Structures and binding energies between the CB_6^{2-} unit and CpLi fragments of (a) bike-$(CpLi)_2(CB_6^{2-})$, (b) windmill-$(CpLi)_3(CB_6^{2-})$, and (c) rice-ball-$(CpLi)_4(CB_6^{2-})$ obtained at the B3LYP/6-31+G(d) level. $(CpLi)_m(CB_6^{2-})$ ($m = 5$–8) are obtained at the B3LYP/3-21G level. Limited computational resources do not allow us to calculate the larger species c−g at higher level. Selected key geometry parameters are listed in the related minima structures. For the saddle points, we do not list the geometry parameters. The symmetry groups are presented in parentheses.

between orbitals may favor the reaction between an electron donor and an electron acceptor. A high (in energy)-lying occupied orbital in the donor may overlap with a low-lying empty one in the acceptor, leading to a net stabilization.

The Li atom loses one p-electron to form Li^+; simultaneously, the Cp ring accepts one electron from the Li atom to form Cp^-, and electrostatic interactions hold Cp^- and Li^+ together to form a $(Cp^-)(Li^+)$ fragment. CpLi has an empty p-orbital on the Li atom, which can interact with the HOMOs (π-orbital for CB_6^{2-} and σ-orbital for CAl_4^{2-}) to form sandwich-like compounds $[CpLi(CAl_4)]^{2-}$/$[CpLi(CB_6)]^{2-}$. The negative charges (electrons) of (σ in CAl_4^{2-})/(π in CB_6^{2-}) are flowing into the LiCp fragments. This phenomenon can be vividly seen from the comparison of characteristic orbitals between bare CAl_4^{2-}/CB_6^{2-} and $[CpLi(CAl_4)]^{2-}$/$[CpLi(CB_6)]^{2-}$ in Figure 5. The electron clouds of the HOMO and HOMO−1 in $[CpLi(CB_6)]^{2-}$ are thinner than those of the degenerate HOMO and HOMO−1 in the free CB_6^{2-}. Also, the electron cloud of the HOMO in the free CAl_4^{2-} is fatter than that of the HOMO in $[CpLi(CAl_4)]^{2-}$.

From the above detailed discussion, we can conclud that the nature and origin of the stability of two different kinds of sandwich-type complexes should be ascribed to electrostatic interactions, charge transfer, and orbital interactions. For the pentaatomic ptC clusters (e.g., CAl_4^{2-}), their HOMOs (four-center, peripheral ligand−ligand σ-orbital) play a crucial role in stabilizing f−s sandwich-type complexes; thus the low-lying structures of such pptC-based compounds are face−side sandwich forms. For the hypercarbon phC clusters (e.g., CB_6^{2-}), their HOMOs (globally delocalized π-orbitals) determine their low-lying structures (face−face) of phC-based compounds.

V. Embellishment and Functionalization of Hypercarbon Clusters CB_6^{2-}. The above results call attention to the fundamental problem that isolation and protection is quite crucial in the hypercarbon cluster assembly and stabilization so as to avoid cluster fusion. From the prospective view of the applications, we discuss the isolation, protection, embellishment, and functionalization of hypercarbon clusters CB_6^{2-}. Their illustrative structures are shown in Figure 6. The capture and stabilization of hypercarbon clusters has attracted great interest toward molecular compounds. The "hetero-decked sandwich" scheme can effectively suppress the reactivity of hypercarbon cluster CB_6^{2-} by introducing neutral LiCp pairs (Figures 4 and 6). It is even possible that the reactivity of CB_6^{2-} can be completely suppressed by being fully "dressed" with eight LiCp pairs (Figure 6g) in eight directions. In this way, the hypercarbon CB_6^{2-} cluster is well-captured into a "rice-ball" structure (Figure 6c−e) and a "cage" structure (Figure 6f−g). We call such a hypercarbon-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 facilely "undressed" when we want to have CB_6^{2-} for further usage, and (3) thus, the manipulation of CB_6^{2-} assembly should be easy by simply capturing more hypercarbon CB_6^{2-} units dressed by LiCp pairs.

VI. Variability of Our Designed Hypercarbon CB_6^{2-}-Based Cluster-Assembled Compounds. We are aware that the planar hexacoordinate carbon (phC) CB_6^{2-} is not a global minimum. It is only a local minimum on the potential energy surface. The structure with the boron atom in the center of the molecular wheel is lower energetically than the phC CB_6^{2-} structure. Exchanging the central carbon atom with the peripheral boron atom will result in energetically low-lying isomers for the CB_6^{2-} system. We note that there are large structural differences between the two kinds of structures, i.e., a hypercarbon with the carbon atom in the center of the molecular wheel and a hyperboron with the boron atom in the center of the molecular wheel. The rearrangement and interconversion between the two structures are very difficult. More encouragingly, the viability of molecules with planar hexacoordinate carbon atoms is demonstrated by Schleyer et al. using density functional theory (DFT) calculations for CB_6^{2-} in Ref Science 2000, 290, 1937. Additionally, for the C_3B_4 system, although other C_3B_4 isomers are lower in energy, the activation barriers for the arrangements of the three planar carbon C_3B_4 minima into more stable isomers are appreciable, and experimental observation should be possible. In Ref Science 2001, 292, 2465, Schleyer et al. used DFT calculations to predict a series of hyperarenes with planar pentacoordinate carbon. The hyperarenes are low-lying local minima. As Schleyer et al. commented, borocarbon species, for which there is some mass spectrometric evidence, might be observed and identified, for example, in matrix isolation by vibrational spectroscopy. Thus, we have confidence to conclude that our designed hetero-decked sandwich-type compounds should be observed and identified with suitable experimental tools under proper environmental conditions.

4. Conclusions

In summary, we first reveal the nature and origin of various sandwich-type interactions and the requirements and technologies of the sandwiching decks' assembly and stabilization. Second, the present study described the systematic attempt to incorporate CB_6^{2-}, the first viable hypercarbon unit, into assembled molecular systems in various sandwich forms. The designed species await future experimental verification. A rich planar hypercarbon cluster-assembled molecular compound based on CB_6^{2-} can be foreseen. Such assembly procedures could also be applied to many other ionic metals (e.g., Sr^{2+}, Ba^{2+}, Rb^{+}, Cs^{+}, Al^{3+}, Ga^{3+}, In^{3+}, Cu^{+}, Ag^{+}, Au^{+}) and various planar hypercoordinate molecules such as NB_6^{-}, B_7^{-}, B_8^{2-}, and B_9^{-}. More importantly, the general strategy and the "hetero-decked" sandwich assembly and stabilization scheme have a general sense and significance and could be applied to many other ionic interaction-based metallocenes, sandwich-like complexes, or cluster-assembled compounds. Compared to the traditional metallocene with only Cp^{-} decks, our designed complexes represent a new class of metallocenes containing the aromatic phC unit CB_6^{2-}, among which CB_6^{2-} generally prefers to use its face (CB_6 planar) to interact with the partner deck. Thus, the designed sandwich species in this paper represent a new kind of metallocene. Moreover, during both the homo-decked and hetero-decked sandwiching processes, the structural planarity of CB_6^{2-} and the characteristic orbitals (Figure 5) are generally maintained. Thus, the phC unit CB_6^{2-} could indeed act as a new type of building block and inorganic ligand. Future studies on the building block/inorganic ligand chemistry of CB_6^{2-} are desired. Moreover, we analyzed in detail and compared the intrinsic difference of cluster-assembly compounds between hypercarbon phC CB_6^{2-} and pentaatomic ptC CAl_4^{2-} through NBO analysis, orbital characterization, and frontier molecular orbital theory. Finally, we proposed a viable scheme to embellish, functionalize, isolate, and protect hypercarbon clusters and possible boron carbide nanotubes.

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