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Design of Sandwichlike Complexes Based on the Planar Tetracoordinate Carbon Unit CAl_4^{2-}

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Abstract: Ever being a large curiosity, a series of simple "planar tetracoordinate carbon (ptC)" molecules have been recently characterized by experiments. Incorporation of such exotic ptC units into the assembled molecular materials, which will bridge the isolated clusters in molecular beams and the potential solid materials, is very challenging. In this paper, we described the first attempt on how to assemble the fewest-number ptC unit CAl_4^{2-} into molecular materials in sandwich forms on the basis of the density functional theory calculations on a series of model compounds $[D(CAl_4)M]^{q-}$ as well as the saturated compounds $[D(CAl_4)M_n]$ (($D = CAl_4^{2-}$, $Cp^-(C_5H_5^-)$; M = Li, Na, K, Be, Mg, Ca). For M = Li, Be, Mg, and Ca, the ptC unit CAl_4^{2-} can only be assembled in our newly proposed "heterodecked sandwich" scheme (e.g., $[Cp(CAl_4)M]^{q-}$ (M = Li, Na, K, $q = 2$; M = Be, Mg, Ca, $q = 1$)) so as to avoid cluster fusion. For M = Na and K, the ptC unit CAl_4^{2-} can be assembled in both the traditional "homodecked sandwich" $[(CAl_4)_2M]^{q-}$ (M = Li, Na, K, $q = 3$; M = Be, Mg, Ca, $q = 2$) and the novel heterodecked sandwich schemes. Moreover, the counterions were found to have an important role in determining the type of the ground structures for the homodecked sandwich. Various assembled species in extended frameworks were designed. Notably, among all the designed sandwich species, the ptC unit CAl_4^{2-} generally prefers to interact with the partner deck at the side (Al−Al bond) or corner (Al atom) site. This has not been reported in the sandwich complexes on the basis of the known decks such as Cp^-, P_5^-, N_4^{2-}, and Al_4^{2-}, for which only the traditional face−face interaction type was considered. Our results for the first time showed that the ptC unit CAl_4^{2-} can act as a new type of "superatom". The present results are expected to enrich the flat carbon chemistry, superatom chemistry, metallocenes, and combinational chemistry.

Introduction

In early 1970s, Hoffmann et al.[1] first considered the possible existence of "planar tetracoordinate carbon (ptC)". Since then, ptC molecules have been the focus of numerous computational studies as well as attempted syntheses.[2−4] Stimulated by the ptC studies, a rich chemistry of the "hypercoordinate flat carbon", "flat nonmetals", and "flat metals" has been foreseen.[5] As Wilson said, "...But most of the proposed and synthesized structures have contained large networks of atoms surrounding the carbon to stabilize the planar structures."[3h] In 1991, Schleyer and Boldyrev[3a,b] computationally succeeded in the first design of a series of simple molecules with central planar tetracoordinate atoms, that is, OAl_4, NAl_4^-, NAl_3Si, BAl_3Si, and CAl_2Si_2. These molecules maintain their planarity simply through electronic factors, that is, the central atom−ligand and ligand−ligand interaction. They thus outlined an "18-electron rule". This rule was later substantiated by Boldyrev and Simons[3c] in 1998 on the basis of the computational studies on CAl_2Si_2, CAl_2Ge_2, and CGa_2Si_2. These interesting molecules each contain only five atoms. "However, no one expected that these compounds could be synthesized", as Ritter said.[3d]

In 1999, Li et al.[3e] unexpectedly observed the first fewest-number ptC molecule CAl_4^- by means of the combined photoelectron spectroscopy and computational studies. In a similar way, Li et al. and Wang et al. characterized the planar species CAl_4^{2-} (with one counterion Na^+),[3f] CAl_3X, and CAl_3X^- (X = Si, Ge)[3g] in 2000. These works not only

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10.1021/ja066217w CCC: $37.00

confirmed the 18-electron rule but also extended it to the "17-electron rule". CAl_4^{2-} is the first experimentally characterized smallest closed-shell ptC molecule. In particular, it was shown[3f] that $Na^+[CAl_4^{2-}]$ is the first experimentally realized salt-stabilized ptC molecule, and the ptC species CAl_4^{2-} can maintain its structural integrity in the presence of one or two counteractions. Thus, as stated in Li et al.'s paper,[3f] "These findings represent the first step toward the realization of bulk materials based on crystal structural units containing the ptC dianion $[CAl_4^{2-}]$ as a novel building block". In 2003 and 2004, Merino and co-workers[4q,4r] theoretically proposed a new kind of pentaatomic ptC molecule C_5^{2-}, which is stabilized by alkaline metals and contains a central planar tetracoordinate carbon linked to two three-membered rings. In 2004, Pancharatna et al.[4u] theoretically predicted the potential existence of C_5^{2-} in extended structures.

Now that many ptC units have been experimentally known, the further and ultimate goal is surely to design novel one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) cluster-assembled materials on the basis of the concept "ptC". As Wilson reported in ref 3h, Radom commented, "...the design of such new types of solids will be a further, very exciting development...". Among the pentaatomic ptC units, the closed-shell CAl_4^{2-} can become an ideal candidate to come into the molecular materials and bulky solids because of its experimental availability and unique properties, that is, aromaticity, planarity, and simplicity. In 2002, by means of ab initio calculations, Geske and Boldyrev[3i] showed that two CAl_4^{2-} groups remain separated in a dimeric structure $((Na^+)_2[CAl_4^{2-}])_2$ and proposed the possible existence of the solid ionic salt with the $(Na^+)_2[CAl_4^{2-}]$ stoichiometry. Here, we considered an important strategy, "sandwiching", which is probably the most powerful one for assembly of a stable unit (e.g., cyclopentadienyl anion: $C_5H_5^-$ (Cp^-)) into molecular materials and has resulted in a rich chemistry of metallocenes (Cp_2M^{q-}).[6] Up to now, the homodecked sandwich complexes based on the non-Cp^- aromatic units such as P_5^-,[7a−c] Al_4^{2-},[7d−e] and N_4^{2-} [7f−i] have been synthesized or computationally designed. The homodecked sandwich scheme has even been applied to the hypothetical planar hexacoordinate carbon unit CB_6^{2-}[5a] by Li et al.[3o, 5k] Their work represents the first attempt to design sandwichlike compounds on the basis of planar units. However, to our great surprise, whether or not the ptC unit CAl_4^{2-} (which is also experimentally known in the salt form) can be used in sandwiching has never been tested. In this paper, we made the first attempt to design the assembled systems in sandwich forms on the basis of the ptC unit CAl_4^{2-}. We found that for M = Li, Be, Mg, and Ca, the assembly of CAl_4^{2-} cannot be realized in the traditional homodecked sandwich form $[(CAl_4)_2M]^{q-}$. However, our newly proposed heterodecked sandwich scheme (e.g., $[Cp(CAl_4)M]^{q-}$) is very effective in assembly. For M = Na and K, both the traditional homodecked sandwich and the novel heterodecked sandwich schemes are applicable. Moreover, we disclosed that the charge counterions play a significant role in determining the ground structures of ptC for the homodecked sandwich scheme. This point has not been revealed in any previous studies on metallocenes. The good structural integrity of the CAl_4^{2-} unit within the designed assembled systems leads

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us to propose that the ptC unit CAl_4^{2-} might act as a new kind of "superatom"[8] in combinational chemistry.

Computational Methods

Initially, we fully optimized the geometries of $[D(CAl_4)M]^{q-}$ (D = CAl_4^{2-}, Cp^-; M = Li, Na, K, Be, Mg, Ca) employing analytical gradients with polarized split-valence double-ξ augmented with diffuse function basis set (6-31+G(d)) using the hybrid method, which includes a mixture of Hartree−Fock exchange with density functional exchange correlation (B3LYP).[9a−d] After geometrical optimization, vibrational analysis was performed to check whether the obtained structure is a true minimum point with all real frequencies or a first-order transition state with only one imaginary frequency. The more sophisticated MP2/6-31+G(d)[e] and B3LYP/6-311+G(2df,p) methods are also used to test the reliability of the B3LYP/6-31+G(d) results for geometries and energies for selected species. All calculations were performed with the Gaussian-03 program.[9f]

Results and Discussions

Our research takes the following scheme: model sandwich species (singly or multiply charged anions), saturated sandwich species (with counterions), and extended sandwich species. It is known that model calculations will shed insight into the neutral saturated species for the actual synthesis. Through comparing the various properties of model species and saturated species, we could know the effects of counterions in various aspects. Such a scheme has been applied to many other doubly charged or multiply charged anions model systems such as sandwichlike compounds $[(P_5)_2M]^{q-}$,[7a−c] $[(N_4)_2M]^{q-}$,[7f−i] and $[(Al_4)_2M]^{q-}$ [7d−e] and non-sandwichlike complexes $(C_5M_{2-n})^{n-}$,[4q,4r,4u] X_4^{2-} (X = Al, Ga, In),[7j−k] Al_6^{2-},[7l] Si_5^{2-},[7m] Si_6^{2-},[7n] B_6^{2-},[7o−p] B_8^{2-},[7q] and $[Pt@Pb_{12}]^{2-}$.[7r] Moreover, besides the interest of model calculations, a few doubly charged anions have been experimentally observed in gas phase.[7s−w] Notably, multiply charged anions have even been observed in the gas phase very recently.[7x−z] In several cases,[7a−r] the B3LYP method has been proved to be cost-effective and reliable in predicting structures and energetics. The successful applications of the B3LYP method by our own and other groups motivate us to perform the B3LYP/6-31+G(d) calculations for the present system in a systematic way. However, since some systems we study contain the singly, doubly, and even multiply charged anions, we also applied the more sophisticated and cost-expensive MP2/6-31+G(d) method for relevant species.

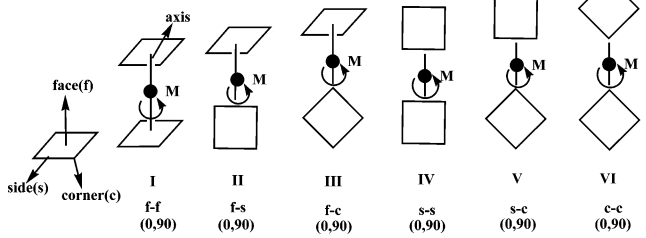

Figure 1. Six possible sandwich types of $[(CAl_4)_2M]^{q-}$ (**I**−**VI**) for each M. In each type, one unit can rotate along the axis by 0° and 90°.

$[(CAl_4)_2M]^{q-}$. As model calculations, we first investigated the assembly of the CAl_4^{2-} unit in the traditional homodecked sandwich form $[(CAl_4)_2M]^{q-}$ with M = Li, Na, K, $q = 3$; M = Be, Mg, Ca, $q = 2$ at the B3LYP/6-31+G(d) level. The possible sandwich types are 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 $[C_2Al_8M]^{q-}$ species, that is, all sandwich forms and those with lower energy than the lowest-energy sandwich form, are schematically shown in Figure 2. The other isomers can be found in the Supporting Information (SI). First, for all the six main-group elements, the sandwich species **IV**, **V**, and **VI** have very close energies to each other and are all energetically lower than **I**, **II**, an **III**. Via the rotation of the CAl_4^{2-}-deck along different axes, **I**−**III** can be easily converted to the lower-energy **IV**−**VI**. The interconversion between **IV**−**VI** via simple rotation is also very easy, as can be indicated by the small rotational frequency. Second, we searched various isomers, among which the lowest-energy structure of sandwich species is generally also the global minimum point on the potential energy surface of the whole system $[(CAl_4)_2M]^{q-}$. It is thus thermodynamically stable. Herein, we only listed some key structures in the context. All the other structures can be found in the SI. For the only one exception M = Be, the ground-state isomer is a fused form lying 12.63 kcal/mol lower than the sandwich form (s−s(90)).

Effect of Counterions. The above considered sandwich forms $[(CAl_4)_2M]^{q-}$ ($q = 2$ and 3) are negatively charged. For actual synthesis, neutral species in salt forms are preferable. We thus investigated $(nM)^{q+}[(CAl_4)_2M]^{q-}$ (M = Li, Na, K, $q = 3$, $n = 3$; M = Be, Mg, Ca, $q = 2$, $n = 1$). Figure 3 depicts all the neutral sandwich forms and the lowest-energy non-sandwich isomer that has lower energy than the lowest-energy sandwich form. The other non-sandwich isomers are shown in the SI. Only for M = Na and K, the sandwich structure is the ground state, whereas for M = Li, Be, Mg, and Ca, the fused isomers have lower energies. This indicates that the salts of the CAl_4^{2-}-based homodecked sandwich complexes can exist for M = Na and K, whereas those for M = Li, Be, Mg, and Ca cannot. We are aware that the sandwich structure for M = Li, Mg, and Ca without counterions is the ground state. Interestingly, without counterions, the lowest-energy sandwich structure takes the s(c)−s(c) form, whereas with counterions, it takes the f−f form (except for M = Be that still takes the s−s form). Clearly, the charge counterions play a significant role on the type of ground-state structures for all the considered M (except M = Be) for homodecked sandwich scheme. This should bring special caution in design of the synthesizable sandwich complexes. One cannot deduce the salt structure of the CAl_4^{2-}-based homodecked sandwich complex simply from the charged model.

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(10) Note that for the known decks such as the famous and versatile Cp^- and the carbon-free and exotic P_5^-, N_4^{2-}, and Al_4^{2-}, only the face−face (f−f) sandwich-type has been reported in sandwichlike compounds.[7a−i] Herein, to our best knowledge, we for the first time systematically considered and classified various kinds of sandwich-type forms: face−face (f−f), face−side (f−s), face−corner (f−c), side−side (s−s), side−corner (s−c), and corner−corner (c−c), thus extending the sandwich-type interactions forms beyond the traditional metallocenes' face−face (f−f) forms. Moreover, we also considered the fusion stability and fusion isomers of various sandwich-type forms.

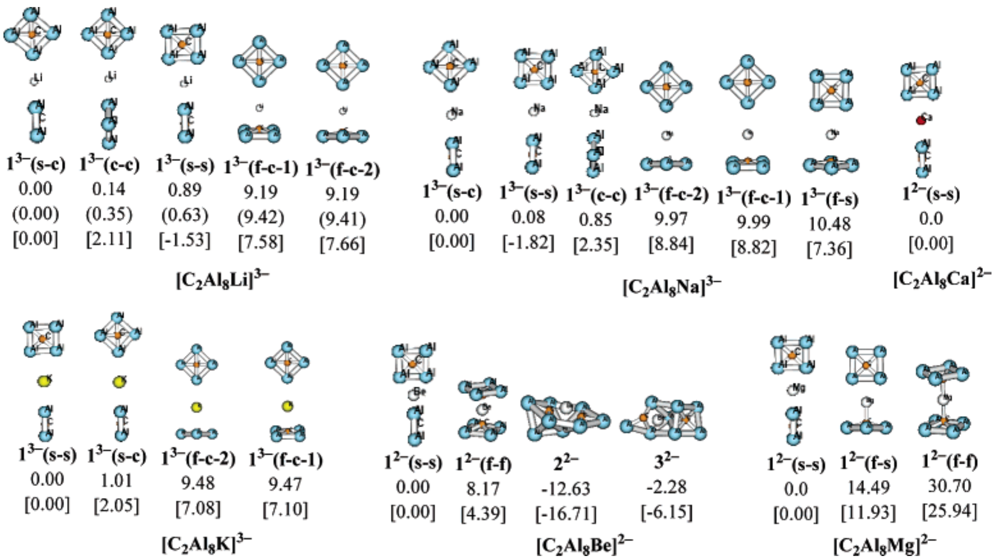

Figure 2. Most relevant $[C_2Al_8M]^{q-}$ species at the B3LYP/6-31+G(d), MP2/6-31+G(d) (in []), and B3LYP/6-311+G(2df,p) (in ()) levels. The energy values are in kcal/mol.

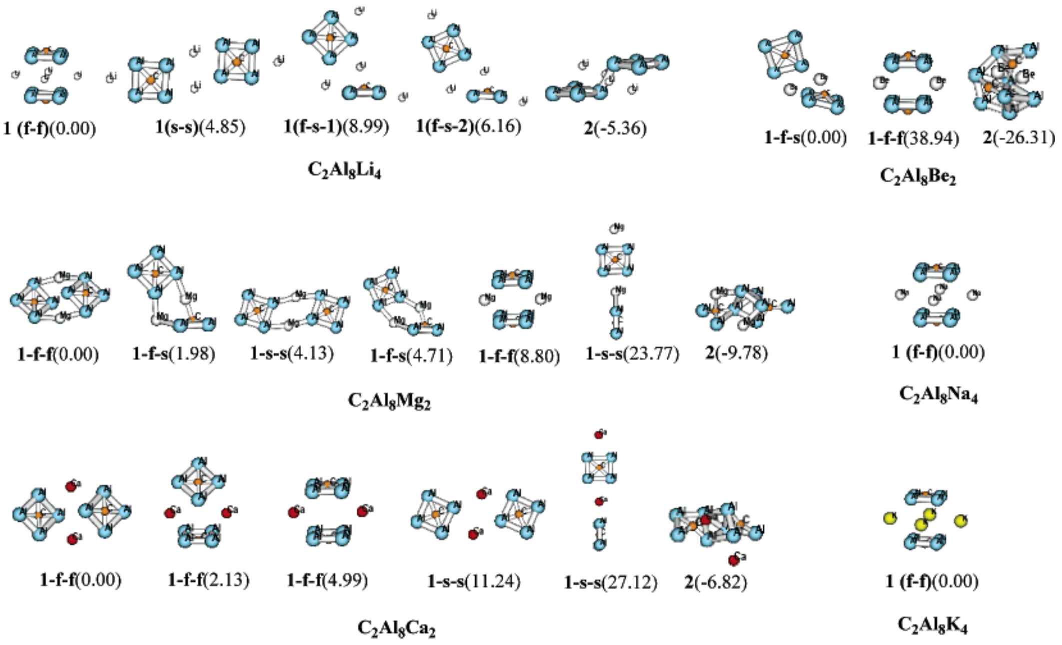

Figure 3. Most relevant $C_2Al_8M_q$ at the B3LYP/6-31+G(d) level. Energy values are in kcal/mol.

Consideration of the charge-compensated species is indispensable for the stabilization! However, such a feature has not been revealed in any previous studies on metallocenes (including the traditional Cp_2M^{q-} [6] and the novel $[(P_5)_2M]^{q-}$,[7a−c] $[(N_4)_2M]^{q-}$,[7f−i] $[(XB_6)_2M]^{q-}$,[3o,5k] and $[(Al_4)_2M]^{q-}$ [7d−e]).[10]

$[Cp(CAl_4)M]^{q-}$ and $(Li^+)_q[Cp(CAl_4)M]^{q-}$. The preceding sections show that the sandwich form is not the ground-state structure for $[C_2Al_8Be]^{2-}$, $[C_2Al_8Be_2]$, $[C_2Al_8Mg_2]$, $[C_2Al_8Ca_2]$, and $[C_2Al_8Li_4]$ systems. This indicates that the ptC unit CAl_4^{2-} cannot be used to sandwich the atoms of Li, Be, Mg, and Ca in the traditional homodecked sandwich scheme. We proposed that a rigid unit like the versatile c-$C_5H_5^-$ (Cp^-) might cooperate with the ptC unit CAl_4^{2-} to sandwich the metal atoms M by avoidance of fusion. We called the new scheme heterodecked sandwich.[11] A new class of sandwich compounds $[Cp(CAl_4)M]^{q-}$ can then be designed. Such compounds are intuitively of special interest because they contain both the classic organic aromatic unit Cp^- and the novel ptC unit CAl_4^{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 lower-lying structures are shown in Figure 4. For each M, there are two kinds of sandwich forms 1^{q-}(f−s) and 1^{q-}(f−f) with the former associated with the "face (Cp^-)−side (CAl_4^{2-})" (f−s) type and the latter with the "face (Cp^-)−face (CAl_4^{2-})" (f−f) type. Generally, the sandwich form 1^{q-}(f−s) is the ground-state structure with the conversion barrier of

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[11] We are aware that another possibility is to apply "heteroleptic sandwich", see Merino, G.; Beltran, H.; Vela, A. *Inorg. Chem.* **2006**, *45*, 1091−1095.

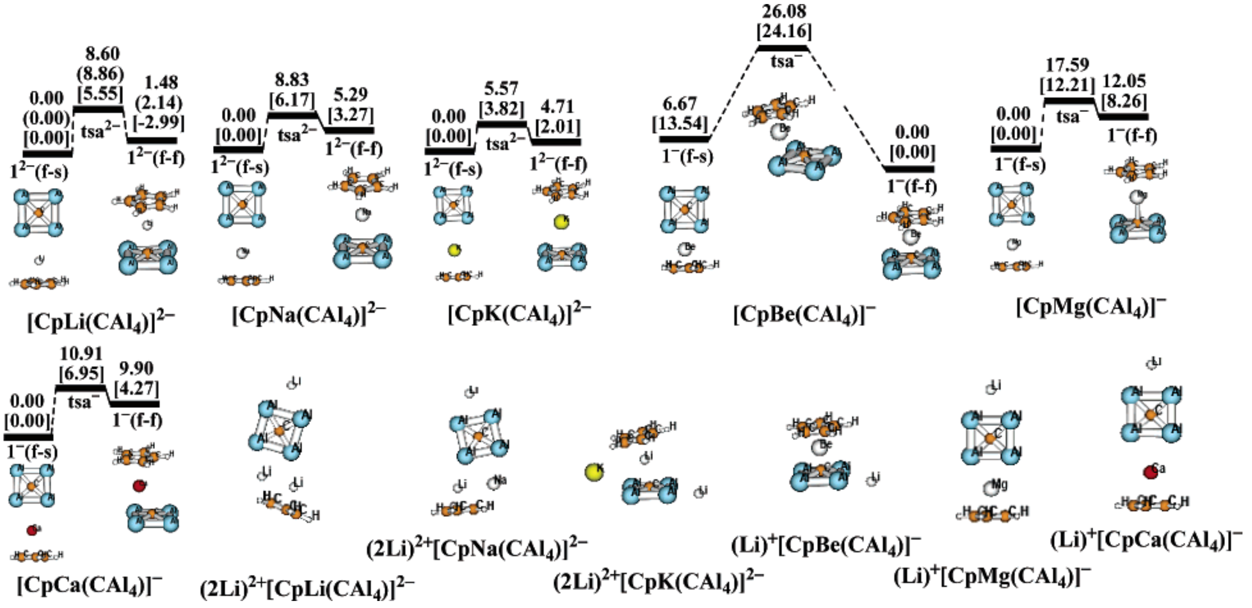

Figure 4. The sandwich forms of [Cp(CAl$_4$)M]$^{q-}$ and the lowest-energy sandwich forms of (Li$^+$)$_q$[Cp(CAl$_4$)M]$^{q-}$ obtained at the B3LYP/6-31+G(d), MP2/6-31+G(d) (in []), and B3LYP/6-311+G(2df,p) (in ()) levels. Energy values are in kcal/mol.

less than 7.5 kcal/mol to 1^{q-}(f−f). The only exception is M = Be, for which the sandwich isomer 1^-(f−f) is the ground-state structure and lower in energy than 2^-(f−s) by 6.67 kcal/mol. Moreover, both 1^{q-}(f−f) and 1^{q-}(f−s) are separated by a high-energy transition state at 26.08 kcal/mol. Thus, both sandwich forms can be experimentally observable for M = Be. This should raise particular interest. Up to now, we have not been aware of any example that has two types of distinct sandwich forms. Interestingly, among all the designed homodecked and heterodecked sandwich species, the ptC unit CAl$_4^{2-}$ generally prefers to use its side (Al−Al bond) or corner (Al atom) to interact with the partner deck (CAl$_4^{2-}$ or Cp$^-$). For the known decks such as the famous and versatile Cp$^-$ and the carbon-free and exotic P$_5^-$, N$_4^{2-}$, and Al$_4^{2-}$, only the face−face (f−f) sandwich type has been reported in sandwichlike compounds.[7a−i] Herein, to our best knowledge, we for the first time systematically considered and classified various kinds of sandwich-type forms: face−face (f−f), face−side (f−s), face−corner (f−c), side−side (s−s), side−corner (s−c), and corner−corner (c−c), thus extending the sandwich-type interactions forms beyond the traditional metallocenes' face−face (f−f) forms. Thus, the designed sandwich species in this paper represents a new kind of metallocenes. Among all the calculated [Cp(CAl$_4$)M]$^{q-}$ systems, the planar Cp$^-$ structure is well maintained, indicative of the unique "rigidity" of this organic unit. Fusion of the Cp$^-$ and CAl$_4^{2-}$ decks to form new C−Al or C−M bonds is energetically unfavorable. The rigid organic deck Cp$^-$ can effectively assist the ptC unit CAl$_4^{2-}$ to sandwich metal atoms.

For the purpose of future synthesis, we also designed neutral species (Li$^+$)$_q$[Cp(CAl$_4$)M]$^{q-}$ (M = Li, Na, K, q = 2; M = Be, Mg, Ca, q = 1) (see Figure 4) with counterions Li$^+$. For each M, the lowest-lying sandwich isomer for charged [Cp(CAl$_4$)M]$^{q-}$ is also the ground-state structure for neutral (Li$^+$)$_q$[Cp(CAl$_4$)M]$^{q-}$. Surely, the counterions have little influence on the nature of the ground-state structure. This is quite different from the situation of the homodecked sandwich scheme. The higher-energy sandwich forms and other isomers are shown in the SI.

The higher-level B3LYP/6-311+G(2df,p) method is used to test the reliability of the B3LYP/6-31+G(d) results for geometries and energies for seven [C$_2$Al$_8$Li]$^{3-}$ species in Figure 2 and five [Cp(CAl$_4$)Li]$^{2-}$ species in Figure 4. We can see that the B3LYP results using 6-31+G(d) and 6-311+G(2df,p) basis sets are in excellent agreement with each other. As one referee pointed out, the B3LYP method is not good at describing the long-rang interaction. Herein, we alternatively applied the more sophisticated MP2 method to some of the singly, doubly, and multiply charged anions. From Figures 2 and 4, we can see that the relative energies at MP2/6-31+G(d) level are generally lower than those at B3LYP/6-31+G(d) level. At MP2/6-31+G(d) level, the main structures, that is, side−side (s−s) and side−corner (s−c) for homodecked sandwich species and face−side (f−s) and face−face (f−f) forms for heterodecked sandwich species, are also energy minima and constitute the lower-lying isomers. Generally speaking, at the MP2 level, the relative energies of the forms in which the CAl$_4^{2-}$ deck takes the face interaction become lowered relative to the corresponding values at the B3LYP level. So, the MP2 method energetically favors the face interaction. Such preference at the MP2 level will slightly change the relative energy of some species. In more detail, for M = Li, Na for the homodecked sandwich species, the relative energy order between side−corner (s−c) and side−side (s−s) forms is slightly reversed. For the heterodecked sandwich species, only for M = Li, the relative energy order between face−face (f−f) and face−side (f−s) forms is slightly reversed. We can generally say that at both B3LYP and MP2 levels, the two low-lying forms for both homodecked and heterodecked sandwich species are close in energy and can easily be transformed into each other by one CAl$_4$-deck rotation.

The completely saturated homodecked sandwich complexes (nM)$^{q+}$[(CAl$_4$)$_2$M]$^{q-}$ can "formally" be considered as the respective (M$^{(4-q)+}$)$_{n+1}$[CAl$_4^{2-}$])$_2$ dimers. The ((Na$^+$)$_2$[CAl$_4^{2-}$])$_2$ dimer has been computationally studied by Geske and Boldyrev.[3i] For the four isomers reported in their work, our B3LYP/6-31+G(d) relative energies are in good agreement with their

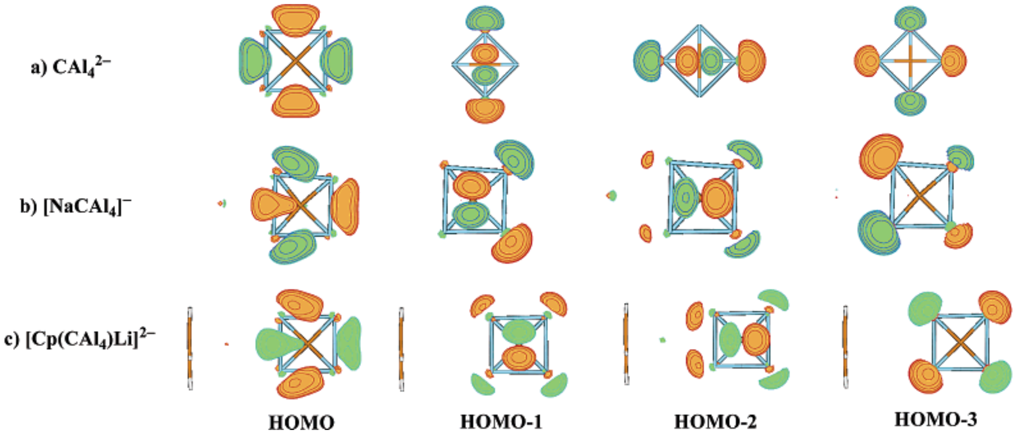

Figure 5. The B3LYP/6-31+G(d) orbital diagrams[9g] of (a) CAl_4^{2-}, (b) $[Na(CAl_4)]^-$, and (c) $[Cp(CAl_4)Li]^{2-}$.

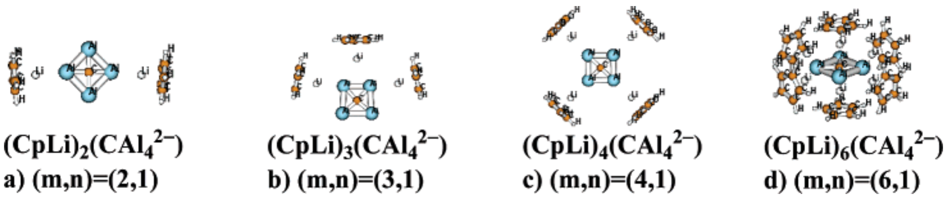

Figure 6. Selected extended sandwich complexes obtained at the B3LYP/6-31+G(d) level for a−c.

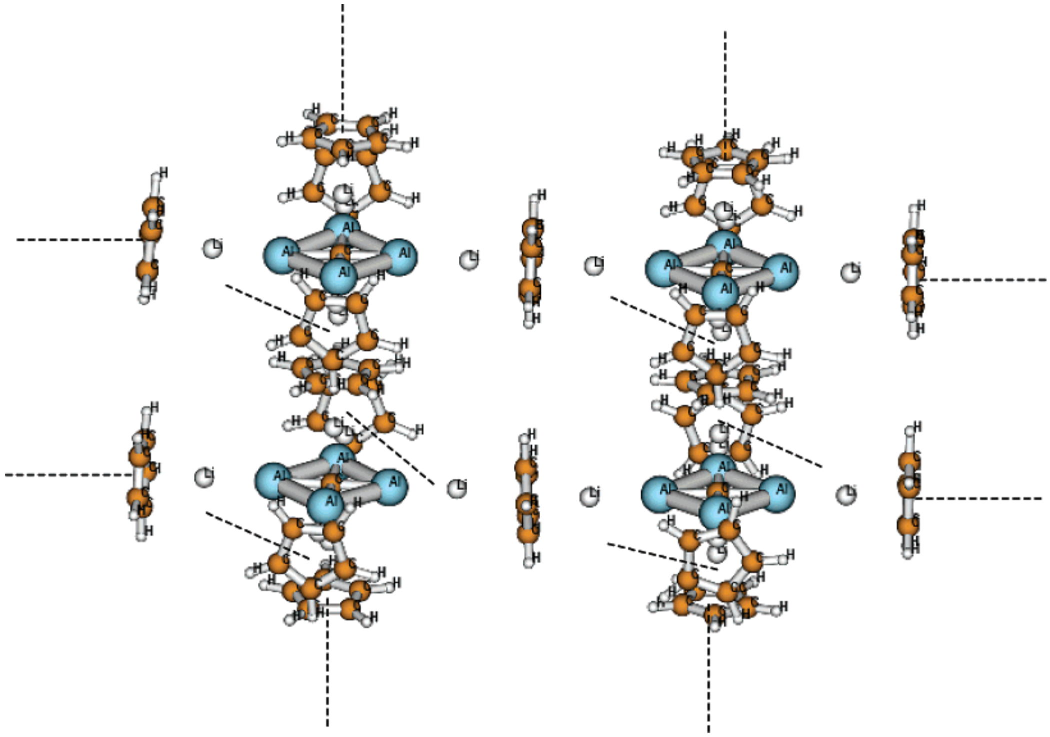

Figure 7. Illustrative more highly extended 3D sandwich structure on the basis of CAl_4^{2-}. The dashed lines show the cluster-growth direction in which more CAl_4^{2-} or Cp^- decks can be added.

B3LYP/6-311+G(d) values (see SI). From the viewpoint of “dimerization”, we predicted that a new dimer $((K^+)_2[CAl_4^{2-}])_2$ could also exist. However, our results also showed that the four dimers $((Li^+)_2[CAl_4^{2-}])_2$ and $(M^{2+}[CAl_4^{2-}])_2$ (M = Be, Mg, Ca) cannot exist because they can fuse to more stable isomers with no planar ptC unit CAl_4^{2-}.

The above discussions deal with the thermodynamic or kinetic stability of the designed CAl_4^{2-}-based metallocenes toward isomerization. For the multiply charged anions (MCAs), it is very desirable to inspect their electronic stability since generally, the MCAs can lose an electron because of the intramolecular Coulombic repulsion and then dissociate. Thus, we calculated the relative stability between the MCAs and the corresponding monoanions at the B3LYP/6-31+G(d) level. As expected, the three trianions $[(CAl_4)_2M]^{3-}$ (M = Li, Na, and K) (s−s) have higher energies than the corresponding $[(CAl_4)_2M]^-$ by 51.78, 48.57, and 46.21 kcal/mol. The six dianions $[CpM(CAl_4)]^{2-}$ also have higher energies than the corresponding monoanions by 25.22 (f−s) and 28.73 (f−f) for M = Li, 20.09 (f−s) and 23.20 (f−f) for M = Na, and 19.92 (f−s) and 21.16 (f−f) for M = K. It seems that the above nine MCAs are electronically unstable with respect to electron detachment. However, it has been shown[12a−i] that the repulsive Coulomb barrier (RCB) plays the most important role in determining the physical and chemical properties of multiply charged anions (MCAs). The superposition of the short-range binding of the electron and the long-range Coulomb repulsion gives rise to a potential barrier (RCB) for the outgoing electron. The RCB can render substantial lifetimes to the MCAs. In fact, a few free MCAs in gas phase have been experimentally observed recently.[12a−i] Therefore, the RCB could hopefully increase the electronic stability of $[(CAl_4)_2M]^{3-}$ (M = Li, Na, and K) (s−s) and $[CpM(CAl_4)]^{2-}$ to some extent. Accurate evaluation of the RCB has to be accomplished using tunable laser photodetachment,[12i] which is beyond the scope of the present paper. Interestingly, the dianions $[(CAl_4)_2M]^{2-}$ (M = Be, Mg, Ca) (s−s) are energetically lower than $[(CAl_4)_2M]^{-}$ by 3.76, 6.86, and 6.54 kcal/mol, respectively. Thus, the three dianions are already electronically stable with respect to the electron detachment. Inclusion of the RCB may even render $[(CAl_4)_2M]^{2-}$ (M = Mg, Ca) (s−s) to exist in gas phase. Note that $[(CAl_4)_2Be]^{2-}$ (s−s) is unstable with respect to conversion to other low-lying fused isomers.

The most effective way to render the existence of MCAs is to use counterions. Many multiply charged anions (MCAs) are ubiquitous in nature and are important constituents in solutions and solids.[12a−i] MCAs acquire their stability in the condensed phase through solvation 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.[12j−k] As done in the present paper, our designed saturated model species $(nM)^{q+}[(CAl_4)_2M]^{q-}$ and $(Li^+)_q[Cp(CAl_4)M]^{q-}$ in saturated sandwich-type forms should all be electronically stable. The recent preparation[7a] of the dianion sandwich species $[(P_5)_2Ti]^{2-}$ in solutions with the presence of two [K(18-crown-6)]$^+$ counterions should stimulate the realization of our designed novel sandwich species on the basis of the ptC unit CAl_4^{2-}.

To get insight into the origin of planarity and exotic electronic structure of such novel sandwichlike compounds on the basis of ptC unit CAl_4^{2-}, we examined the molecular orbitals of bare dianion CAl_4^{2-}, experimentally characterized anion $Na^+[CAl_4^{2-}]$,[3f] and model sandwichlike compound $[Cp(CAl_4)Li]^{2-}$. Figure 5 shows their four highest orbitals: the ligand−ligand bonding HOMO and three nonbonding ligand lone-pair orbitals HOMO-1, HOMO-2, and HOMO-3. The structural planarity of these species is achieved through a strong four-center peripheral ligand−ligand bonding interaction in their highest occupied molecular orbital (HOMO). From Figure 5, we can see that the shapes of orbitals in (a) bare CAl_4^{2-}, (b) anion $Na^+[CAl_4^{2-}]$, and (c) sandwichlike compound $[Cp(CAl_4)Li]^{2-}$ are generally the same. Thus, the ptC unit CAl_4^{2-} can maintain its electronic and structural integrity in both salt and sandwich forms. Therefore, CAl_4^{2-} could be used as a building block and superatom in designing planar bulk solid materials. The originality of planarity of other simple pentatomic species has been previously revealed in several nice papers.[3a−c,3e−g,3j−l]

Extended Sandwich Structures Based on CAl_4^{2-}. It is known that some metallocenes can form highly extended sandwich complexes ranging from nanoscales to polymers, even to bulk solid materials.[6] We thus further designed the ptC-based extended systems containing more Cp^- and CAl_4^{2-} units in various heterodecked sandwich forms at the B3LYP/6-31+G(d) level to show the structural and electronic integrity of CAl_4^{2-} as a superatom during assembly. For systemic consideration, we considered various combinational forms according to different coordinated directions (face, side, and corner) of the CAl_4^{2-} unit. In Figure 6, some selected species with the possible lowest-energy are shown. Many other designed extended sandwich structures can be found in SI.

Surely, the growing mechanism from the simple extended sandwich structures (Figure 6) to the much more highly extended 3D sandwich species with more Cp^- and CAl_4^{2-} units is very viable. Such CAl_4^{2-}-based extended sandwich complexes might become candidates of a novel kind of potential microelectronic devices and semiconductor materials. For reason of computational cost, we did not attempt to calculate these species. One illustrative example is given in Figure 7.

Conclusions

In summary, the present study described the first attempt to incorporate CAl_4^{2-}, one of the fewest-number ptC units, into assembled molecular systems in sandwich forms. The designed species await future experimental verification. They could exist in the three-dimensional solid ionic salt as predicted for $((Na^+)_2[CAl_4^{2-}])_2$ dimer by Geske and Boldyrev.[3i] A rich planar world based on CAl_4^{2-} can be foreseen. Such assembly procedures could also be applied to many other ptC molecules such as CAl_3X (X = Si, Ge), CAl_3X^- (X = Si, Ge), CSi_2X_2 (X = Al, Ga), and CGe_2Al_2. Compared to the traditional metallocenes with mere Cp^- decks, our designed complexes represent a new class of metallocenes containing the ptC unit CAl_4^{2-}, among which CAl_4^{2-} generally prefers to use its side (Al−Al bond) or corner (Al atom) to interact with the partner deck rather than in the form of the traditional face−face interaction type for the known decks Cp^-, P_5^-, Al_4^{2-}, and N_4^{2-}. Thus, the designed sandwich species in this paper represent a new kind of metallocenes. Moreover, during both the homodecked and heterodecked sandwiching processes, the structural planarity of CAl_4^{2-} and the characteristic orbitals (Figure 6) are generally well kept. Thus, the fewest-number ptC unit CAl_4^{2-} could act as a new type of superatoms,[8] which might be the first theoretical evidence, to the best of our knowledge. Future studies on the superatom chemistry of CAl_4^{2-} are desired. Finally, on the basis of the above points, the new scheme heterodecked sandwich bridges the ptC, metallocenes, and superatom chemistry and is thus well suited to the combinational chemistry.

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To the best of our knowledge, our work represents the first systematic study on planar species covering various sandwich interaction types, counterion effects, and fusion stability. Li et al.'s theoretical work on designing sandwich complexes on the basis of CB_6^{2-} has only considered traditional face−face (f−f) sandwich interaction type and has not studied the fusion stability. However, for such exotic structures, it is very desirable to inspect their fusion stability to design synthesizable molecular materials. In fact, for another exotic unit Al_4^{2-} (highly electron-deficient, large resonance stabilization energies, and threefold all-metal aromaticity), Seo and Corbett[9h] have pointed out that "the challenge would be to have the M_4^{2-} units completely separated from each other because an incomplete separation may lead to fusion of the M_4^{2-} building blocks to form larger clusters". Our work should be useful for future study of cluster-assembled molecular materials.

Acknowledgment. This work is supported by the National Natural Science Foundation of China (No. 20103003, 20573046), Excellent Young Teacher Foundation of Ministry of Education of China, Excellent Young People Foundation of Jilin Province, and Program for New Century Excellent Talents in University (NCET).

Supporting Information Available: Full citations for ref 9f, additional references on ptC before year 1995, the detailed calculated properties of a series of model compounds $[D(CAl_4)M]^{q-}$ as well as the saturated compounds $[D(CAl_4)M_n]$ ((D = CAl_4^{2-}, Cp^-; M = Li, Na, K, Be, Mg, Ca) {$^1[(CAl_4)_2M]^{3-}$ (M = Li, Na, K),$^1[(CAl_4)_2M]^{2-}$ (M = Be, Mg, Ca), $^1C_2Al_8M_4$ (M = Li, Na, K), $^1C_2Al_8M_2$ (M = Be, Mg, Ca),$^1[Cp(CAl_4)_2M]^{2-}$ (M = Li, Na, K),$^1[Cp(CAl_4)M]^-$ (M = Be, Mg, Ca),$^1(Li_2)^{2+}[Cp(CAl_4)M]^{2-}$ (M = Li, Na, K), and $^1(Li)^+[Cp(CAl_4)M]^-$ (M = Be, Mg, Ca)}. The calculated properties and the structural data of various extend systems. This material is available free of charge via the Internet at http://pubs.acs.org.

JA066217W