Theor Chem Account (2008) 119:335–342
DOI 10.1007/s00214-007-0389-0

REGULAR ARTICLE

The Si-doped planar tetracoordinate carbon (ptC) unit CAl_3Si^- could be used as a building block or inorganic ligand during cluster-assembly

Li-Ming Yang · Yi-Hong Ding · Chia-Chung Sun

Received: 26 July 2007 / Accepted: 5 September 2007 / Published online: 9 October 2007

Abstract Currently, the molecular assembly and growth from a small building block to the bulk compounds have become a focus in various fields. Ever being chemical curiosities, the "anti-van't Hoff/Le Bel" realm that is associated with tetracoordinate or hypercoordiate planar centers has made vast progress. Being important in the fundamental research areas, the ptC species have potential applications in materials science. The existence of ptC in a divanadium complex and a large number of organometallic compounds have since been reported to possess ptC and these provide us with great hope that many more compounds with ptC building blocks may be synthesized in future. Herein, we report the assembly and stabilization of CAl_3Si^- in both the "*homo-decked sandwich*" and "*hetero-decked sandwich*" schemes at the B3LYP/6-311 + G(d) level. We show that while the Si-doped indeed introduces much complexity during assembly, the electronic and structural integrity feature of CAl_3Si^- is well conserved during cluster-assembly, characteristic of a "superatom". This study should be helpful in understanding the hetero-doped assembly mechanism of the ptC chemistry. Moreover, the present results are expected to enrich the flat carbon chemistry, superatom chemistry, metallocenes and combinational chemistry.

1 Introduction

The past three decades have witnessed considerable progress [1–71] in the "anti-van't Hoff/Le Bel" field of planar tetracoordinate carbon (ptC) [1–12] and related species, which demonstrate various uncommon properties (e.g., unusual geometry structures, exotic bonding features, unique coordinate environment, novel electronic structures, etc.) and continuously attract theoreticians and experimentalists to advance this realm [1–71]. Many kinds of ptC units have been experimentally known [13–25]. Surely, the further and ultimate goal is to design novel 1D, 2D and 3D cluster-assembled materials based on the concept "ptC". As Radom [20] commented, "…the design of such new types of solids will be a further, very exciting development…". Meanwhile, the miniaturization of semiconductor and microelectronic devices has greatly necessitated the investigations of clusters at molecular or nanoscale level [72–75].

Doped is a very important technique in materials science. We are aware that some hetero-doped ptC species (e.g., CSi_2X_2 ($X = Al$, Ga) [13,15], CGe_2Al_2 [15] and CAl_3X^{q-} ($X = Si$, Ge; $q = 0$, 1) [19,25], etc.) have been experimentally observed [13,15,19,25]. As a basic step towards understanding the doped effects of the assembly of the ptC units that might be utilized for future nano-devices and molecular materials, we made the first attempt to assemble a hetero-doped ptC unit. The Si-doped ptC unit CAl_3Si^- [19,25] is taken for our model design due to the wide interest on the binary Si_xAl_y [34,35] clusters and the border upon of Si and Al-elements in the period table. Investigations on the assembly of these exotic species might provide good examples to illustrate how a simple planar molecule is grown into larger (even up to nano-size) molecular materials. As a minimal model linkage of the two fields, we reported the first attempt to assemble the simplest experimentally observed

Electronic supplementary material The online version of this article (doi:10.1007/s00214-007-0389-0) contains supplementary material, which is available to authorized users.

L.-M. Yang · Y.-H. Ding (✉) · C.-C. Sun
State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, People's Republic of China
e-mail: yhdd@mail.jlu.edu.cn

L.-M. Yang
e-mail: ylmylmlmmlmm@yahoo.com

silicon-doped ptC unit CAl_3Si^- into molecular materials. Here we considered an important and widely applied strategy—"*sandwiching*", which is probably the most powerful one for assembly of a stable unit [e.g., $C_5H_5^-(Cp^-)$] into molecular materials and has gestated a rich chemistry of metallocene (Cp_2M) [76,77]. 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 mono-anionic CAl_3Si^- deck should also preferentially interact with metal atom via ionic interaction. In addition, the lower electronic negativity of alkali elements Li, Na, K and earth alkali 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 CAl_3Si^- deck in sandwich-like complexes. We found that for all the six metals: M = Li, Na, K, Be, Mg and Ca, the assembly of CAl_3Si^- cannot be realized in the traditional "*homo-decked sandwich*" form $[(CAl_3Si)_2M]^{q-}$. However, the "*hetero-decked sandwich*" [26–33,38–41][1] scheme has been successfully applied to exotic nonstoichiometry molecules: (1) all-metal aromatic systems (milestone prototype Al_4^{2-} [26] and high-strain three-membered ring Al_3^- [27]) and (2) ptC systems (high-symmetry dianion CAl_4^{2-} [28] and spin-embedded radical CAl_3Si [29]) (e.g., $[CpM(X)]^{q-}$, X = Al_4^{2-}, Al_3^-, CAl_4^{2-}, and CAl_3Si decks), thus indicates that "*hetero-decked sandwich*" scheme is a very powerful and effective assembly scheme in bridging the isolated clusters in molecular beams and the potential solid materials. We thus have confidence in assembly and stabilization of the hetero-doped ptC unit CAl_3Si^- in the "*hetero-decked sandwich*". Our results demonstrated that only the "*hetero-decked sandwich*" scheme can assemble and stabilize the hetero-doped ptC unit CAl_3Si^-. We can predict that the "*hetero-decked sandwich*" scheme is also very effective in assembly of other ptC molecules. The hetero-doped indeed introduces much complexity during cluster-assembly. Moreover, the electronic and structural integrity feature of CAl_3Si^- is well conserved during cluster-assembly, characteristic of a "superatom" [78,79] feature. Our results are expected to be helpful for understanding the hetero-doped mechanism of the ptC chemistry.

2 Computational methods

Initially, we fully optimized the geometries of $[D(CAl_3Si)M]^{q-}(D = CAl_3Si^-, Cp^-; M = Li, Na, K, q = 1; M = Be$, Mg, Ca, $q = 0$) employing analytical gradients with polarized split-valence basis set 6-311 + G(d) [80–82] using the hybrid method, which includes a mixture of Hartree–Fock exchange with density functional exchange correlation (B3LYP) [83–85]. 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. In order to get insight into the nature of our designed cluster-assembly species, we perform orbital analysis.[2] All the calculations were performed with the Gaussian-03 program.[3]

3 Theoretical results and discussion

Our research takes the following scheme: model sandwich species (singly or doubly 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. By 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 sandwich-like compounds $[(P_5)_2M]^{q-}$ [87–89], $[(Al_4)_2M]^{q-}$ [90,91], $[(N_4)_2M]^{q-}$ [92–95], and non-sandwich-like complexes $(C_5M_{2-n})^{n-}$ [96–98], X_4^{2-} (X = Al, Ga, In) [99,100], and Al_6^{2-} [101].

3.1 Homo-decked sandwich-type compounds: $[(CAl_3Si)_2M]^{q-}$

As model calculations, we first investigated the assembly of the ptC unit CAl_3Si^- in the traditional "*homo-decked sandwich*" form $[(CAl_3Si)_2M]^{q-}$ with M = Li, Na, K, $q = 1$; M = Be, Mg, Ca, $q = 0$ at the B3LYP/6-311 + G(d) level using the Gaussian 03 program. The possible sandwich types are shown in Fig. 1. The type **I** structure is similar to the well-known metallocene CpMCp, in which two Cp^- adopt the face–face (f–f) type. After a detailed structural search at the B3LYP/6-311+G(d) level, the energy profiles of the most relevant $[C_2Si_2Al_6M]^{q-}$ species, i.e., all sandwich forms and the lowest energy fusion form are schematically shown in Fig. 2. The other isomers can be found in supporting information (SI). The notation **1** (e.g., 1(s-s-90-1), 1(s-s-90-2), 1(s-c-90), etc. in Fig. 2) represents the sandwich-type structures and the notation **2** represents the low-lying fusion isomers. The structural differences between **1** and **2** in that the

---

[1] We are aware that another possibility is to apply "heteroleptic sandwich", see Ref: [34]. Also, we note that another possibility is to apply "mixed metallocenes $[M(\eta^5 - C_5Me_4R)(\eta^5 - P_5)]$", see Ref. [35] and "Heteroligands Ferrocene $FeCp(\eta^5 - E_5)$" see Ref: [36].

[2] MO pictures were made with MOLDEN3.4 program. Schaftenaar, G. MOLDEN3.4, CAOS/CAMM Center, The Netherlands, 1998.

[3] All calculations are performed using the Gaussian03 program package.

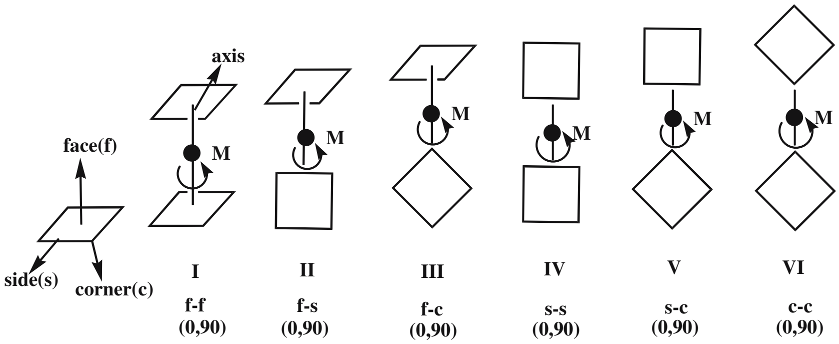


Fig. 1 Six possible sandwich types of $[(CAl_3Si)_2M]^{q-}$ (I–VI) for each M. In each type, one unit can rotate along the axis by 0° and 90°. Moreover, Si and Al atoms can be exchanged in each type. For simplicity and clarity, the central C atoms are omitted

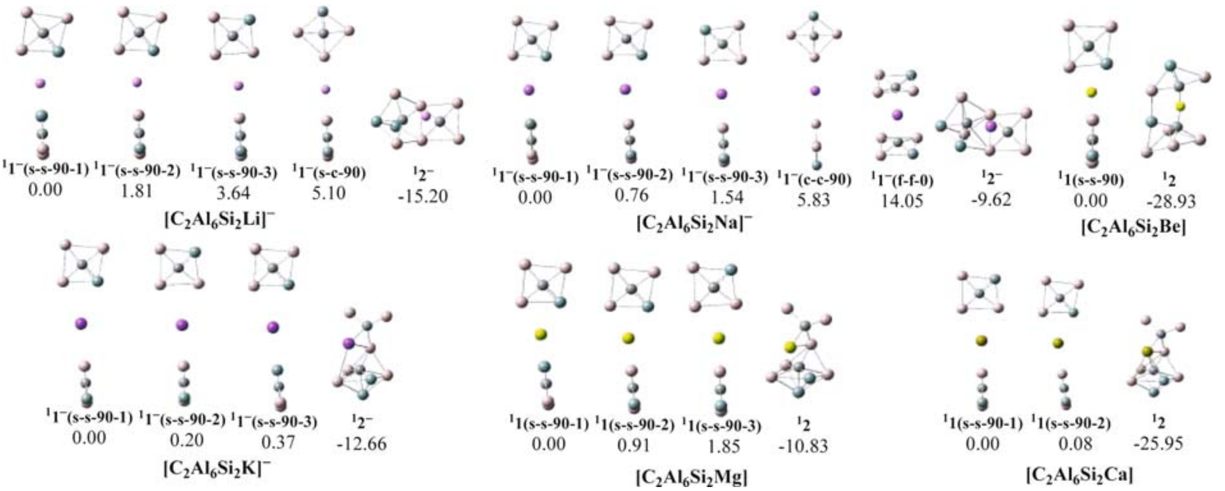


Fig. 2 Most relevant $[C_2Si_2Al_6M]^{q-}$ (M = Li, $q = 1$; M = Be, $q = 0$) species at the B3LYP/6-311 + G(d) level. The energy values are in kcal/mol. The *orange balls* represent Al atoms, the *black balls* represent C atoms, the gray *green balls* represent Si atoms. The *large*, *middle* and *small* purple balls represent K, Na and Li atoms, respectively. The *large*, *middle* and *small kelly balls* represent Ca, Mg and Be atoms, respectively

ptC CAl_3Si^- units are well retained in the sandwich-like species **1**, whereas the CAl_3Si^- units are fused together and destroyed in the fusion isomers **2**. Firstly, 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_3Si-deck along different axes, **I–III** can be easily converted to the lower energy **IV–VI**. The interconversion between **IV** and **VI** via simple rotation is also very easy, as can be indicated by the very small rotation frequency. Secondly, there are many fusion isomers lower than the lowest energy sandwich structure and is thus thermodynamically unstable. Herein, we only listed some key structures in the context, all the other structures can be found in SI.

3.2 Effect of counterions

Some of the above considered sandwich forms $[(CAl_3Si)_2M]^{q-}$ ($q = 1$, M = Li, Na, K) are singly negative charged. For actual synthesis, neutral species in salt forms are preferable. We thus investigate the properties of $(M)^+[(CAl_3Si)_2M]^-$ (M = Li, Na, K). For each M, various isomeric forms are considered at the B3LYP/6-311 + G(d) level. Figure 3 depicts all the sandwich forms of $(Li)^+$ $[(CAl_3Si)_2Li]^-$ and those with lower energy than the lowest energy sandwich form. The other isomers of $(Li)^+[(CAl_3Si)_2Li]^-$ and all the energy profiles of $(M)^+[(CAl_3Si)_2M]^-$ (M = Na, K) can be found in the supporting information. The notation **1** (e.g., 1(s-s-0-1), 1(s-s-0-2), 1(s-c-90-1), 1(s-c-90-2), etc. in Fig. 3) represents the sandwich-type structures, the notation **2** represents the low-lying fusion isomers. The structural differences between **1** and **2** in that the ptC CAl_3Si^- units are well retained in the sandwich-like species **1**, whereas the CAl_3Si^- units are fused together and destroyed in the fusion isomers **2**. For M = Li, Na and K, many fused isomers have lower energies than the sandwich one. This indicates that the salts of the CAl_3Si^--based homodecked sandwich complexes are less likely for M = Li, Na and K. Here, the counterions just introduce an electrostatic stabilization without altering the ground state nature, which is just the same as previous studies on metallocene (including

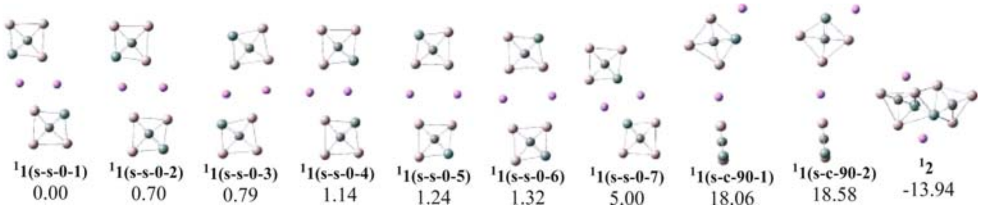


Fig. 3 Most relevant $(M)^+[(CAl_3Si)_2M]^-$ (M = Li) at the B3LYP/6-311 + G(d) level. Energy values are in kcal/mol. The *orange balls* represent Al atoms, the *black balls* represent C atoms, the *gray green* balls represent Si atoms. The *purple balls* represent Li atoms

the traditional $CpMCp^{q-}$ [76,77] and the novel $P_5MP_5^{q-}$ [87–89], $N_4MN_4^{q-}$ [93–95] and $Al_4MAl_4^{q-}$ [90–92]).

3.3 Hetero-decked sandwich-type compounds and counterion effects: $[CpM(CAl_3Si)]^{q-}$ and $(Li^+)_q[CpM(Cal_3Si)]^{q-}$

As known from the preceding sections, the *homo-decked sandwich* form is not the ground state structure for all nine homo-decked systems: $[C_2Si_2Al_6Li]^-$, $[C_2Si_2Al_6Li_2]$, $[C_2Si_2Al_6Na]^-$, $[C_2Si_2Al_6Na_2]$, $[C_2Si_2Al_6K]^-$, $[C_2Si_2Al_6K_2]$, $[C_2Si_2Al_6Be]$, $[C_2Si_2Al_6Mg]$ and $[C_2Si_2Al_6Ca]$. This indicates that the ptC unit CAl_3Si^- cannot be used to sandwich the atoms of Li, Na, K, Be, Mg and Ca-atoms in the traditional "*homo-decked sandwich*" scheme. Here, we propose that a rigid unit like the versatile c-$C_5H_5^-$ (Cp^-) might cooperate with the ptC unit CAl_3Si^- to sandwich the metal atoms M by avoidance of fusion. We call the new scheme "*hetero-decked sandwich*". A new class of sandwich compounds $[CpM(CAl_3Si)]^{q-}$ 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_3Si^-.

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 Fig. 4. Others can be found in supporting information. For each alkali metals M (Li, Na, K), there are three kinds of sandwich forms $\mathbf{1}^{q-}$ (f–s), $\mathbf{1}^{q-}$(f–c) and $\mathbf{1}^{q-}$ (f–f) exist, with the former associated with the "face (Cp^-)–face (CAl_3Si^-)" (f–f) type and the latter with the "face (Cp^-) to side (CAl_3Si^-)" (f–s) type. The three sandwich forms can easily convert to each other (the rotation frequency is very small). For each alkaline-earth metals M (Be, Mg, Ca), two kinds of sandwich forms $\mathbf{1}^{q-}$ (f–f), $\mathbf{1}^{q-}$ (f–s) exist, with the former associated with the "face (Cp^-)-face (CAl_3Si^-)" (f-f) type and the latter with the "face (Cp^-) to side (CAl_3Si^-)" (f-s) type. The two sandwich forms can easily convert to each other. Up to now, we have not been aware of any example that has two or three types of distinct sandwich forms. Interestingly, among all the designed homo-decked and hetero-decked sandwich species, the ptC unit CAl_3Si^- generally prefers to interact with the partner deck CAl_3Si^-or Cp^- at the side (Al–Al or Al–Si bonds) or corner (Al or Si atoms) site. This is in contrast 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-} that prefer the traditional face–face interaction type in the "*homo-decked sandwich*" scheme. Thus, the designed sandwich species in this paper represent a new kind of metallocene. Among all the calculated $[CpM(CAl_3Si)]^{q-}$ systems, the planar Cp^- structure is well maintained, indicative of the unique "rigidity" of this organic unit. Fusion of the Cp^- and CAl_3Si^- decks to form new C–Al, C–Si or C–M bonds is energetically unfavorable. The rigid organic deck Cp^- can effectively assist the ptC unit CAl_3Si^- to sandwich metal atoms.

For the purpose of actual synthesis, we also designed neutral species $(Li)^+[CpM(CAl_3Si)]^-$ (M = Li, Na, K, $q = 1$) (see Fig. 4) with counterions Li^+. For each M, the lowest lying sandwich isomer in charged $[CpM(CAl_3Si)]^{q-}$ is also the ground state structure in neutral $(Li)^+[CpM(CAl_3Si)]^-$. Surely, the counterions have little influence on the nature of the ground state structure. This is quite different from the situation of the homo-decked sandwich scheme. Thus, for simplicity, the structural and energetic details of the higher energy sandwich forms and other isomers are not given in the text, but can be found in SI.

The results of the above calculation demonstrate that the f–s, f–c and f–f interaction types are common phenomena in the extended systems. Such an interesting growth pattern might be applicable to the assembly of Si-containing ptC unit CAl_3Si^- into semiconductor nanoscale clusters or devices, and even bulk solids.

3.4 Nature and origin of fusion

The above results have demonstrated that the assembly of CAl_3Si^- can only be realized in the form of the "*hetero-decked sandwich*" scheme instead of the traditional "*homo-decked sandwich*" scheme. The "*homo-decked sandwich*" assembly would lead to fusion between two CAl_3Si^- decks. In order to get insight into the interactions of our designed sandwich-type complexes, let us analyze the origin of such fusion. Intuitively, the mono-anionic ptC deck CAl_3Si^- bears

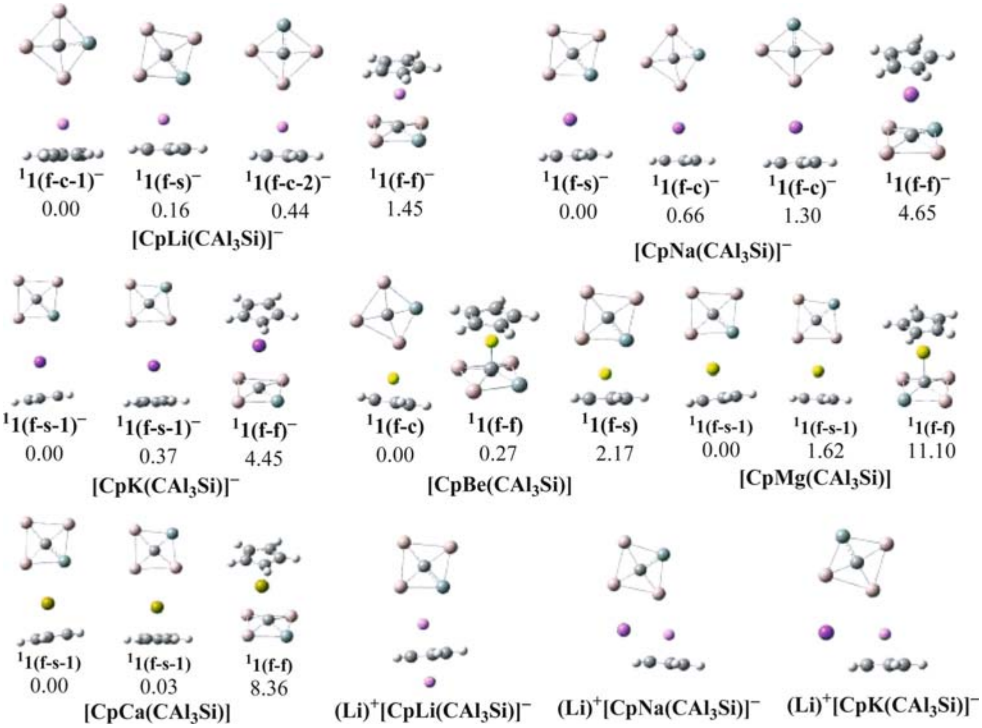


Fig. 4 The sandwich forms of $[\mathrm{CpM(CAl_3Si)}]^{q-}$ (M = Li, Na, K, q = 1; M = Be, Mg, Ca, q = 0) and the lowest energy saturated sandwich forms of $(\mathrm{Li}^+)[\mathrm{CpM(CAl_3Si)}]^-$ (M = Li, Na, K) obtained at the B3LYP/6-311 + G(d) level. Energy values are in kcal/mol. The *orange balls* represent Al atoms, the *black* and *white balls* represent C and H atoms, respectively. The *gray green balls* represent Si atoms. The *large*, *middle* and *small purple balls* represent K, Na and Li atoms, respectively. The *large*, *middle* and *small kelly balls* represent Ca, Mg and Be atoms, respectively

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

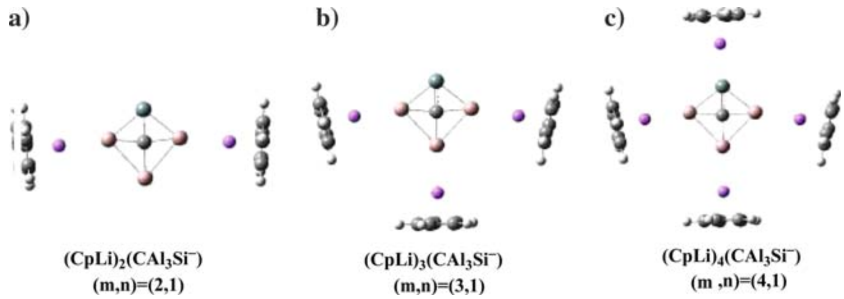
In process (1), each sandwich deck (D_1^{m-} and D_2^{n-}) undergoes the electrostatic interaction with M^{q+} to form a sandwich-like structure $(\mathrm{D}_1^{m-})\mathrm{M}^{q+}(\mathrm{D}_2^{n-})$. Process (2) is associated with the "clustering fusion". In principle, there is a trend for any two 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 ptC unit $\mathrm{CAl_3Si^-}$ is not strong enough to prevent from fusion. So, as shown in Sects. 2–4, the homo-decked sandwich structures are energetically much less stable than the fused isomers. Yet the situation is quite different in the novel "*hetero-decked sandwich*" form. The fusion tendency can be greatly suppressed due to the introduction of a rigid sandwiching partner $\mathrm{Cp^-}$. The large organic aromaticity allows $\mathrm{Cp^-}$ to perfectly keep its (near) D_{5h} structure. Any fusion with $\mathrm{CAl_3Si^-}$ will destroy the aromaticity of $\mathrm{Cp^-}$ to greatly raise the system energy. As a result, only in form of the novel "*hetero-decked sandwich*" scheme, can the ptC unit $\mathrm{CAl_3Si^-}$ be assembled into sandwich-like complexes.

3.5 Extended sandwich structures based on $\mathrm{CAl_3Si^-}$

It is known that some of metallocenes can form highly extended sandwich complexes ranging from nanoscales to polymers, and even to bulk solid materials [76,77]. We thus further designed the ptC-based extended systems containing more $\mathrm{Cp^-}$ and $\mathrm{CAl_3Si^-}$ units in the various *hetero-decked sandwich* forms at the B3LYP/6-311 + G(d) level. For systemic consideration, we considered various combinational forms according to different coordinated directions (face, side and corner) of the $\mathrm{CAl_3Si^-}$ unit. In Fig. 5, some selected low-lying species are shown. Many other designed extended sandwich structures can be found in SI.

Fig. 5 The low-lying extended sandwich complexes of $(\mathrm{CpLi})_m(\mathrm{CAl_3Si^-})_n$ obtained at the B3LYP/6-311 + G(d) level for $(m, n) = (2, 1)$, (3,1) and (4,1). The *orange balls* represent Al atoms, the *black* and *white balls* represent C and H atoms, respectively. The *gray green balls* represent Si atoms. The *purple balls* represent Li atoms

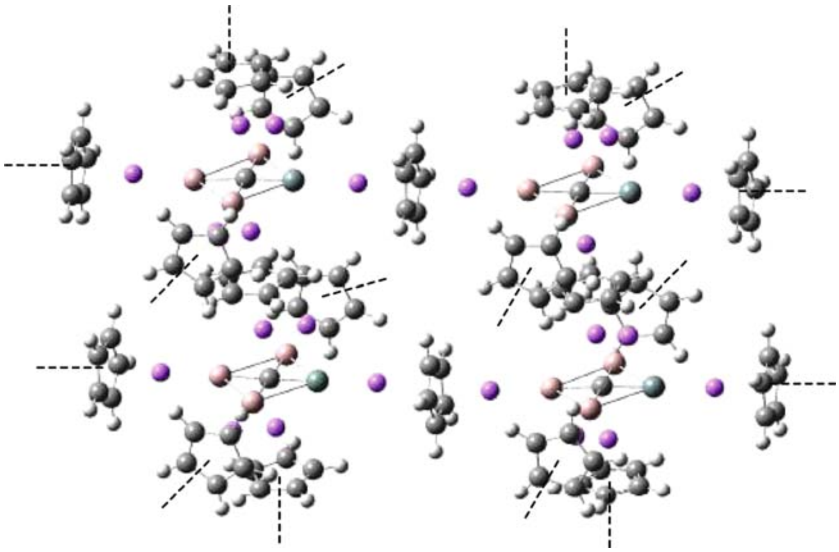


$(\mathrm{CpLi})_2(\mathrm{CAl_3Si^-})$ (m,n)=(2,1)

$(\mathrm{CpLi})_3(\mathrm{CAl_3Si^-})$ (m,n)=(3,1)

$(\mathrm{CpLi})_4(\mathrm{CAl_3Si^-})$ (m ,n)=(4,1)

Fig. 6 Hypothetical more highly extended 3D sandwich structure based on $\mathrm{CAl_3Si^-}$. The *dashed lines* show the cluster-growth direction in which more $\mathrm{CAl_3Si^-}$ or $\mathrm{Cp^-}$ decks can be added. The *orange balls* represent Al atoms, the *black* and *white balls* represent C and H atoms, respectively. The *gray green balls* represent Si atoms. The *purple balls* represent Li atoms



Surely, the growing mechanism from the simple extended sandwich structures (Fig. 5) to the much more highly extended 3D sandwich species with more $\mathrm{Cp^-}$ and $\mathrm{CAl_3Si^-}$ units is very viable. Such $\mathrm{CAl_3Si^-}$-based extended sandwich complexes might become candidates of a novel kind of potential microelectronic devices and semiconductor materials. For reasons of computational cost, we did not attempt to calculate these species. One illustrative example is given in Fig. 6.

4 Conclusions

In summary, our work described the first attempt to incorporate $\mathrm{CAl_3Si^-}$ into assembled molecular systems in various sandwich-like forms. The designed species await future experimental verifications. Our designed sandwich-like species can grow into a more highly extended sandwich species (in 1D, 2D and 3D molecular or nanoscale forms) based on $\mathrm{CAl_3Si^-}$, which might lead to the potential applications in the semiconductor materials or nanoscale devices. Such assembly procedures could also be applied to many other silicon (germanium)-containing ptC molecules such as $\mathrm{CAl_3Ge}$, $\mathrm{CAl_3Ge^-}$, $\mathrm{CSi_2X_2}$ (X = Al, Ga) and $\mathrm{CGe_2Al_2}$ etc. We hope that the present hetero-decked sandwich scheme might also be applicable to the assembly of the $\mathrm{CAl_3Si^-}$ deck in sandwiching transition metals (e.g. Fe, Co, Ni, etc.). Our study provides hints that a rich planar cluster-assembled molecular materials, nanoscale devices or even bulk solid chemistry based on ptC units containing the semiconductor element (Si, Ge, etc.) can be foreseen. Compared to the traditional metallocene with mere $\mathrm{Cp^-}$ decks, our designed complexes represent a new class of metallocene containing the ptC unit $\mathrm{CAl_3Si^-}$, among which $\mathrm{CAl_3Si^-}$ generally prefers to use its side (Al–Al or Al–Si bonds) or corner (Al or Si atoms) to interact with the partner deck rather than in form of the traditional face–face interaction type for the known decks $\mathrm{Cp^-}$, $\mathrm{P_5^-}$, $\mathrm{Al_4^{2-}}$, and $\mathrm{N_4^{2-}}$. 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 $\mathrm{CAl_3Si^-}$ and the characteristic orbitals (Fig. 7) are generally well kept. Thus, the silicon-doped ptC unit $\mathrm{CAl_3Si^-}$ could act as a new type of superatom, which might be the first theoretical evidence, to the best of our knowledge. Future studies on the "superatom" chemistry of $\mathrm{CAl_3Si^-}$ are desired. Finally, based on the above points, the "*hetero-decked sandwich*" scheme bridges and enriches the planar carbon chemistry,

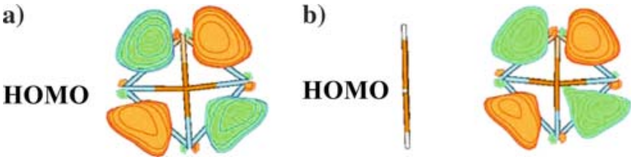


Fig. 7 The B3LYP/6-311 + G(d) orbital diagrams of (a) $[CAl_3Si]^-$ and (b) $[CpLi(CAl_3Si)]^-$

semiconductor materials, metallocene and superatom chemistry and is thus well suited to the combinational chemistry.

Acknowledgments 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).

References

1. Hoffmann R, Alder RW, Wilcox CF Jr (1970) J Am Chem Soc 92:4992
2. Hoffmann R (1971) Pure Appl Chem 28:181
3. Sorger K, Schleyer PvR (1995) J Mol Struct 338:317
4. Streitwieser A, Bachrach SM, Dorigo A, Schleyer PvR (1995) In: Sapse A-M, Schleyer PvR (eds) Lithium chemistry; Wiley, New York, p 1
5. Rottger D, Erker G (1997) Angew Chem Int Ed 36:812
6. Radom L, Rasmussen DR (1977) Pure Appl Chem 70:1977
7. Choukroun R, Cassoux P (1999) Acc Chem Res 32:494
8. Siebert W, Gunale A (1999) Chem Soc Rev 28:367
9. Boldyrev AI, Wang L-S (2001) J Phys Chem A 105:10759
10. Minkin VI, Minyaev RM, Hoffmann R (2002) Russ Chem Rev 71:869
11. Keese R (2006) Chem Rev 106:4787
12. Merino G, Méndez-Rojas MA, Vela A, Heine TJ (2007) Comput Chem 28:362
13. Schleyer PvR, Boldyrev AI (1991) J Chem Soc Chem Commun 1536
14. Boldyrev AI, Schleyer PvR (1991) J Am Chem Soc 113:9045
15. Boldyrev AI, Simons J (1998) J Am Chem Soc 120:7967
16. Ritter SK (2003) Chem Eng News 81(50):23
17. Li X, Wang L-S, Boldyrev AI, Simons J (1999) J Am Chem Soc 121:6033
18. Li X, Zhang HF, Wang LS, Geske GD, Boldyrev AI (2000) Angew Chem Int Ed 39:3630
19. Wang LS, Boldyrev AI, Li X, Simons J (2000) J Am Chem Soc 122:7681
20. Wilson E (2000) Chem Eng News 78(34):8
21. Geske GD, Boldyrev AI (2002) Inorg Chem 41:2795
22. Zakrzewski VG, Niessen von W, Boldyrev AI, Schleyer PvR (1993) Chem Phys Lett 174:167
23. Nayak SK, Rao BK, Jena P, Li X, Wang LS (1999) Chem Phys Lett 301:379
24. Boldyrev AI, Li X, Wang LS (2000) Angew Chem Int Ed 39:3307
25. Li X, Zhan HJ, Wang LS (2002) Chem Phys Lett 415:357
26. Yang LM, Ding YH, Sun CC (2007) Chem Eur J 13:2546–2555
27. Yang LM, Ding YH, Sun CC (2006) Chem Phys Chem 7:2478–2482
28. Yang LM, Ding YH, Sun CC (2007) J Am Chem Soc 129:658–665
29. Yang LM, Ding YH, Sun CC (2007) J Am Chem Soc 129:1900–1901
30. Yang LM, Wang J, Ding YH, Sun CC (2007) Organometallics 26:4449
31. Yang LM, Wang J, Ding YH, Sun CC (2007) J Phys Chem A ASAP article, jp074645y
32. Yang LM, Ding YH, Tian WQ, Sun CC (2007) Phys Chem Chem Phys ASAP article, b707898f
33. Yang LM, Ding YH, Sun CC (2007) J Phys Chem A (in press)
34. Wang XB, Wang LS (1997) J Chem Phys 107:7667 and references therein
35. Kumar V, Bhattacharjee S, Kawazoe Y (2000) Phys Rev B 61:8541 and references therein
36. Perez N, Heine T, Barthel R, Seifert G, Vela A, Mendez-Rojas MA, Merino G (2005) Org Lett 7:1509–1512
37. Sateesh B, Reddy AS, Sastry GN (2007) J Comp Chem 28:335–343
38. Merino G, Beltran H, Vela A (2006) Inorg Chem 45:1091–1095
39. Padma ME (2004) J Eur J Inorg Chem 2723–2732
40. Frunzke J, Lein M, Frenking G (2002) Organometallics 21:3351–3359
41. Scherer OJ, Bruck T (1987) Angew Chem 99:59
42. Scherer OJ, Bruck T (1987) Angew Chem Int Ed 26:59
43. Exner K, Schleyer PvR (2000) Science 290:1937
44. Wang Z-X, Schleyer PvR (2001) Science 292:2465
45. Wang Z-X, Schleyer PvR (2002) Angew Chem Int Ed 41:4082–4085
46. Zhai H-J, Kiran B, Li J, Wang L-S (2003) Nat Mater 2:827–833
47. Zhai HJ, Alexandrova AN, Birch KA, Boldyrev AI, Wang L-S (2003) Angew Chem 115:6186–6190
48. Zhai HJ, Alexandrova AN, Birch KA, Boldyrev AI, Wang L-S (2003) Angew Chem Int Ed 42:6004–6008
49. Rasmussen DR, Radom L (1999) Angew Chem Int Ed 38:2875
50. Wang ZX, Manojkumar TK, Wannere C, Schleyer PvR (2001) Org Lett 3:1249
51. Wang Z-X, Schleyer PvR (2001) J Am Chem Soc 123:994
52. Sahin Y, Hartmann M, Geiseler G, Schweikart D, Balzereit C, Frenking G, Massa W, Berndt A (2001) Angew Chem Int Ed 40:2662
53. Wang Z-X, Schleyer PvR (2002) J Am Chem Soc 124:11979
54. Merino G, Mendez-Rojas MA, Vela A (2003) J Am Chem Soc 125:6026–6027
55. Merino G, Mendez-Rojas MA, Beltran HI, Corminboeuf C, Heine T, Vela A (2004) J Am Chem Soc 126:16160
56. Priyakumar UD, Reddy AS, Sastry GN (2004) Tetrahedron Lett 45:2495
57. Priyakumar UD, Sastry GN (2004) Tetrahedron Lett 45:1515
58. Pancharatna PD, Mendez-Rojas MA, Merino G, Vela A, Hoffmann R (2004) J Am Chem Soc 126:15309–15315
59. Li SD, Ren GM, Miao CQ, Jin Z-H (2004) Angew Chem Int Ed 43:1371
60. Li S-D, Miao C-Q, Guo J-C, Ren G-M (2004) J Am Chem Soc 126:16227
61. Lein M, Frunzke J, Frenking G (2003) Angew Chem Int Ed 42:1303–1306
62. Li S-D, Ren G-M, Miao C-Q (2004) Inorg Chem 43:6331
63. Li SD, Miao CQ, Ren GM (2004) Eur J Inorg Chem 2232–2234
64. Drhardt S, Frenking G, Chen Z-F, Schleyer PvR (2005) Angew Chem Int Ed 44:1078
65. Li S-D, Guo J-C, Miao C-Q, Ren G-M (2005) Angew Chem Int Ed 44:2158
66. Minyaev RM, Gribanova TN (2000) Russ Chem Bull 109:783–796
67. Gribanova TN, Minyaev RM, Minkin VI (2001) Mendeleev Commun 169–170

68. Minyaev RM, Gribanova TN, Starikov AG, Minkin V (2001) I Mendeleev Commun 213–214
69. Minyaev RM, Gribanova TN, Starikov AG, Minkin V (2002) I Dokl Chem 382:41–45
70. Minkin VI, Minyaev RM (2004) Mendeleev Commun 43–46
71. Wang Y, Huang YH, Liu R (2006) Z Chem Eur J 12:3610–3616
72. Miller D (1996) A B Nature 384:307
73. Jarrold MF (1991) Science 252:1085
74. Honea EC, Ogura A, Murray CA, Raghavachari K, Sprenger WO, Jarrold MF, Brown WL (1993) Nature 366:42
75. Ho KH, Shvartsburg AA, Pan B, Lu ZY, Wang CZ, Wacker JG, Fye JL, Jarrold M (1998) F Nature 392:582
76. Peckham TJ, Gomez-Elipe P, Manners I (1998) In: Togni A, Halterman RL (eds) Metallocenes, vol. 2. Wiley-VCH, Weinheim, p 724
77. Togni A, Halternan RL (eds) (1998) Metallocenes: synthesis, reactivity, applications Wiley-VCH, Weinheim
78. Bergeron DE, Castleman AWJr , Morisato T, Khanna SN (2004) Science 304:84–87
79. Bergeron DE, Roach PJ, Castleman AW, Jones N, Khanna SN (2005) Science 307:231–235
80. McLean AD, Chandler GS (1980) J Chem Phys 72:5639–5648
81. Clark T, Chandrasekhar J, Spitznagel GW, Schleyer PvR (1983) J Comput Chem 4:294–299
82. Frisch MJ, Pople JA, Binkley JS (1984) J Chem Phys 80:3265–3269
83. Parr RG, Yang W (1989) Density-functional theory of atoms and molecules. Oxford University Press, Oxford
84. Becke AD (1992) J Chem Phys 96:2155–2160
85. Perdew JP, Chevary JA, Vosko SH, Jackson KA, Pederson MR, Singh DJ, Fiolhais C (1992) Phys Rev B 46:6671–6687
86. Frisch MJ et al (2003) Gaussian03 (RevisionA.1) Gaussian, Inc. Pittsburgh (Full citations see supporting information)
87. Urnezius E, Brennessel WW, Cramer CJ, Ellis JE, Schleyer PvR (2002) Science 295:832
88. Lein M, Frunzke J, Frenking G (2003) Inorg Chem 42:2504
89. Frunzke J, Lein M, Frenking G (2002) Organometallics. 21:3351
90. Mercero JM, Ugalde JM (2004) J Am Chem Soc 126:3380
91. Mercero JM, Formoso E, Matxain JM, Eriksson LA, Ugalde JM (2006) Chem Eur J 12:4495–4502
92. Mercero JM, Matxain JM, Ugalde JM (2004) Angew Chem Int Ed 43:5485
93. Cheng LP, Li QS (2003) J Phys Chem A 107:2882
94. Cheng LP, Li QSJ (2005) Phys Chem A 109:3182
95. Guan J, Li QS (2005) J Phys Chem A 109:9875
96. Merino G, Mendez-Rojas MA, Vela A (2003) J Am Chem Soc 125:6026–6027
97. Merino G, Mendez-Rojas MA, Beltran HI, Corminboeuf C, Heine T, Vela A (2004) J Am Chem Soc 126:16160
98. Pancharatna PD, Mendez-Rojas MA, Merino G, Vela A, Hoffmann R (2004) J Am Chem Soc 126:15309–15315
99. Li X, Kuznetsov AE, Zhang HF, Boldyrev AI, Wang LS (2001) Science 291:859
100. Kuznetsov AE, Boldyrev AI, Li X, Wang L-S (2001) J Am Chem Soc 123:8825–8831
101. Kuznetsov AE, Boldyrev AI, Zhai H-J, Li X, Wang L-S (2002) J Am Chem Soc 124:11791