ORIGINAL PAPER

CSi$_2$Ga$_2$: a neutral planar tetracoordinate carbon (ptC) building block

Li-ming Yang · Xiao-ping Li · Yi-hong Ding ·
Chia-chung Sun

Abstract Ever being a large curiosity, the "anti-van't Hoff/Le Bel" realm that is associated with tetracoordinate or hypercoordinate planar centers has made rapid progress. In particular, it has been disclosed that silicon and gallium can be embedded in various planar species. However, to our best knowledge, assembly of silicon— and gallium-embedded planar units has never been reported, though such assembled species might be used as potential nanoscale devices. Here we report the first attempt on how to design assembled molecular compounds featuring silicon— and gallium-embedded planar tetracoordinate carbon (ptC) units. Taking the special silicon- and gallium-embedded ptC unit CSi$_2$Ga$_2$ as an example, we performed density functional calculations on a series of model compounds [DM(CSi$_2$Ga$_2$)]$^{q+}$ as well as the saturated compounds (Cl$^-$)$_q$[CpM(CSi$_2$Ga$_2$)]$^{q+}$ (D = CSi$_2$Ga$_2$, Cp$^-$(C$_5$H$_5$$^-$); M = Li, Na, K, Be, Mg, Ca) and the more extended sandwich-like species. For the six metals, CSi$_2$Ga$_2$ can only be assembled in the "*hetero-decked sandwich*" scheme (e.g., [CpM(CSi$_2$Ga$_2$)]$^{q+}$) so as to avoid cluster fusion. Interestingly, among all the designed sandwich species, CSi$_2$Ga$_2$ generally prefers to interact with the partner deck at the corner (Ga atoms) or face (CSi$_2$Ga$_2$ planes) sites. Such interaction types serve as an interesting growth pattern that might be applicable to the assembly of Si- and Ga-embedded ptC unit CSi$_2$Ga$_2$ into highly extended sandwich-like complexes. Our results for the first time showed that the Si- and Ga-embedded ptC unit CSi$_2$Ga can act as a new type of building block. The present results are expected to enrich planar tetracoordinate carbon chemistry and metallocenes.

Introduction

Every since the first conceptual proposal of "planar tetracoordinate carbon (ptC)" by Hoffmann et al. in early 1970s,[1, 2] "planar" chemistry ("hypercoordinate flat carbon", "flat nonmetals", and "flat metals"), which demonstrate various uncommon properties (e.g., unusual geometry structures, exotic bonding features, unique coordinate environment, novel electronic structures, etc.), has attracted considerable attention[3–78]. However, due to the inherent high preference for keeping tetrahedral or other non-planar structures, design of planar-tetracoordinate-carbon-containing (ptC) systems is very difficult and has remained a continuous challenge in both theory and experiment. So, any discovery of such planar systems should be encouraging. Generally, there are two feasible approaches (electronic and strain forces method) to maintain the planar structure by carefully choosing both the central and surrounding atoms in all the known planar tetra- or hyper-coordinate species[13–35]. Among which, pentaatomic planar tetracoordinate species (pptC)[13–35] attracted special interest due to the fact that they maintain their planarity simply through electronic factors, i.e., the central atom-ligand and ligand-ligand interactions. Such small units are potentially applicable as building blocks in future designing of planar coordinate species. Meanwhile, the miniaturization race made the investigations of clusters at molecular level quite crucial and necessary.

L.-m. Yang · X.-p. Li · 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

Among the pentaatomic ptC units, the closed-shell CSi_2Ga_2 is a special case, as Merino[12] commented, "It is a five atomic molecule and in fact it is the simplest possible ptC molecule. In this case, planar geometries can be favored over tetrahedral when (1) Jahn-Teller instability (even if within the ligand-ligand interactions only) makes the latter locally unstable and (2) the number of valence electrons allows for maximum C-ligand and ligand-ligand bonding. The optimal case for planar structures occurs with 18 valence electrons, where three σ and one π bond occur as well as one ligand-ligand bond." Additionally, two semiconductor-elements Si and Ga are embedded in the CSi_2Ga_2, the information obtained from the studying of CSi_2Ga_2 should shed insight into the assembly and stabilization of other C, Si, and Ga-based mixed clusters. Thus, CSi_2Ga_2 can become an ideal candidate to come into the molecular compounds due to its unique properties addressed above.

Investigation 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 complexes. As a minimal model linkage of the two fields, we reported the first attempt to assemble the ptC unit CSi_2Ga_2 into molecular compounds. 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 complexes and has gestated a rich chemistry of metallocenes (Cp_2M)[79]. It is known that in traditional metallocenes (Cp_2M), the interaction between the metal atom and the sandwiching unit is mainly ionic. It is thus reasonable to expect that the CSi_2Ga_2 deck should also preferentially interact with the metal atom via ionic interaction. In addition, the lower electronegativity 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 CSi_2Ga_2 deck in sandwich-like complexes. Recently, we have shown that the "hetero-decked sandwich scheme" is especially powerful in assembly and stabilization of nonstoichiometric molecules, such as Al_3^-, [28] Al_4^{2-}, [29] CAl_4^{2-},[30] and CAl_3Si[31]. In the present paper, we found that for all six metals: M = Li, Na, K, Be, Mg and Ca, the assembly of CSi_2Ga_2 cannot be realized in the traditional "*homo-decked sandwich*" form [(CSi_2Ga_2)$_2$M]$^{q+}$. However, the "*hetero-decked sandwich*"[28–35] scheme can effectively assemble and stabilize the Si- and Ga-embedded ptC unit CSi_2Ga_2 into molecular compounds. Although, the Si- and Ge-hetero-doping indeed introduces much complexity during cluster-assembly, the electronic and structural integrity feature of CSi_2Ga_2 is well conserved during cluster-assembly, characteristic of a building block feature. Our results would shed insight into the hot research area of the binary or ternary clusters. Also, our results are expected to be helpful for understanding the trinary clusters' assembly and stabilization and the hetero-doping mechanism of the ptC chemistry.

Computational methods

Initially, we fully optimized the geometries of [D(CSi_2Ga_2) M]$^{q+}$ (D = CSi_2Ga_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)[89–92]. 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. All calculations were performed with the Gaussian-03 program.[93]
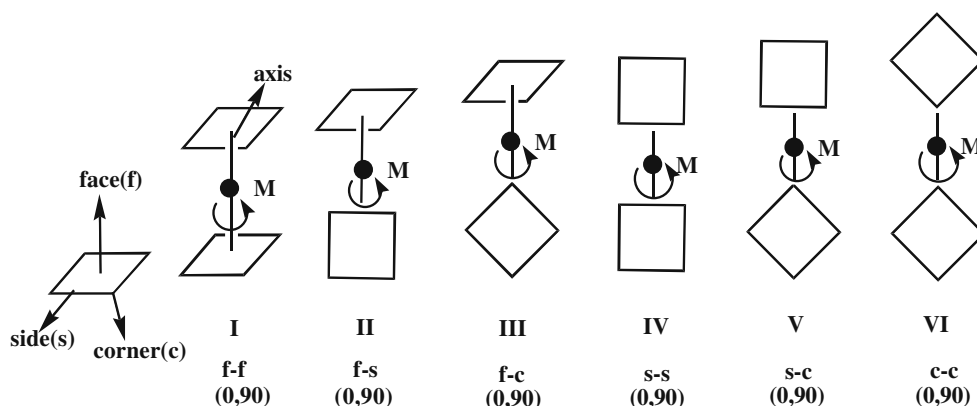
Results and discussions

In a number of cases, the B3LYP method has been proved to be cost effective, saver of disk space sounds and reliable in predicting structures and energies. 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. Thus, we have confidence that DFT method could get reliable information on the structures and energies, etc. in the present system.

[(CSi_2Ga_2)$_2$M]$^{q+}$

As model calculations, we first investigated the assembly of the CSi_2Ga_2 unit in the traditional "*homo-decked sandwich*" form [(CSi_2Ga_2)$_2$M]$^{q+}$ with M = Li, Na, K, q=1; M = Be, Mg, Ca, q=2 at the B3LYP/6–31+G(d) level. The possible sandwich types are shown in Fig. 1. The type **I** structure is similar to the well-known metallocenes 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, and for the sake of space, the energy profiles of the most relevant [$C_2Si_4Ga_4M$]$^{q+}$ species with real frequencies, i.e., all sandwich forms and those low-lying structures, are schematically shown in Fig. 2. Many other structures can be found in **SI**. 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 CSi_2Ga_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
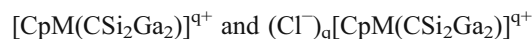
Fig. 1 Six possible sandwich types of $[(CSi_2Ga_2)_2M]^{q+}$ (I–VI) for each M. In each type, one unit can rotate along the axis by 0° and 90°. For clarity, the center C-atom is omitted

be indicated by the small rotational frequency. Secondly, there are many fusion isomers lower than the lowest-energy sandwich structure and is thus thermodynamically unstable.

Effect of counterions

The above considered sandwich forms $[(CSi_2Ga_2)_2M]^{q+}$ (q=1 and 2) are positively charged. For actual synthesis, neutral species in salt forms are preferable. We thus investigated $(Cl^-)_q[(CSi_2Ga_2)_2M]^{q+}$ (M = Li, Na, K, q=1; M = Be, Mg, Ca, q=2). For the sake of space, only sandwich-type structures and lowest-lying structures are listed in Fig. 3. Many other structures can be found in **SI**. For all the six type metals M = Li, Na, K, Be, Mg and Ca, many fused isomers have lower energies than the sandwich ones. This indicates that the salts of the CSi_2Ga_2-based homo-decked sandwich complexes can not exist for all six main-group metals (M = Li, Na, K, Be, Mg and Ca).

$[CpM(CSi_2Ga_2)]^{q+}$ and $(Cl^-)_q[CpM(CSi_2Ga_2)]^{q+}$

The preceding sections show that the sandwich form is not the ground state structure for $[C_2Si_4Ga_4Li]^+$, $[C_2Si_4Ga_4Na]^+$, $[C_2Si_4Ga_4K]^+$, $(Cl^-)[C_2Si_4Ga_4Li]^+$, (Cl^-) $[C_2Si_4Ga_4Na]^+$, $(Cl^-)[C_2Si_4Ga_4K]^+$, $[C_2Si_4Ga_4Be]^{2+}$, $[C_2Si_4Ga_4Mg]^{2+}$, $[C_2Si_4Ga_4Ca]^{2+}$, $(Cl^-)_2[C_2Si_4Ga_4Be]^{2+}$, $(Cl^-)_2[C_2Si_4Ga_4Mg]^{2+}$ and $(Cl^-)_2[C_2Si_4Ga_4Ca]^{2+}$ systems. This indicates that the ptC unit CSi_2Ga_2 can not be used to sandwich the atoms of Li, Na, K, Be, Mg, and Ca in the traditional "*homo-decked sandwich*" scheme. We applied the "*hetero-decked sandwich*"[28–35] scheme to sandwich the metal atoms M with the ptC unit CSi_2Ga_2 and the classic organic aromatic unit Cp^- by avoidance of fusion. A new class of sandwich compounds $[CpM(CSi_2Ga_2)]^{q+}$ 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 CSi_2Ga_2.

Fig. 2 Most relevant species $[C_2Si_4Ga_4M]^{q+}$ (M = Li, Na, K, q=1; M=Be, Mg, Ca, q=2) obtained at the B3LYP/6–31+G (d) level. The energy values are in kcal/mol

Fig. 3 Most relevant
$(Cl^-)_q[C_2Si_4Ga_4M]^{q+}$ (M = Li,
Na, K, q=1, M = Be, Mg,
Ca, q=2) obtained at the
B3LYP/6–31+G(d) level. Ener-
gy values are in kcal/mol. Note
that "NI" represents the number
of imaginary frequencies. The
saddle points (NI=1) of coun-
terion saturated sandwich-type
structures are only used as
energy references

1(s-c-0)   -40.48
0.00 (NI=1)
$(Cl^-)[Li(CSi_2Ga_2)_2]^+$

1(s-c-0)   -47.15
0.00 (NI=1)
$(Cl^-)[Na(CSi_2Ga_2)_2]^+$

1(s-c-0)   -50.96
0.00 (NI=1)
$(Cl^-)[K(CSi_2Ga_2)_2]^+$

1(s-s-0)   -50.66
0.00 (NI=1)
$(Cl^-)_2[Be(CSi_2Ga_2)_2]^{2+}$

1(s-s-0)   -54.38
0.00 (NI=1)
$(Cl^-)_2[Mg(CSi_2Ga_2)_2]^{2+}$

1(s-s-0)   -52.12
0.00 (NI=1)
$(Cl^-)_2[Ca(CSi_2Ga_2)_2]^{2+}$

Various isomeric forms for each of the six main-group
elements (M = Li, Na, K, Be, Mg and Ca) were researched.
For simplicity, only the low-lying structures are shown in
Fig. 4. 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**. For each M, there are two
kinds of sandwich forms 1^{q+}(f–f) and 1^{q+}(f–c) with the
former associated with the "face (Cp$^-$)-face (CSi$_2$Ga$_2$)" (f-f)
type and the latter with the "face (Cp$^-$)-corner (CSi$_2$Ga$_2$)"
(f-c) type. For M = Li, Na and K, the sandwich form 1^{q+}(f-f)

1(f-f)
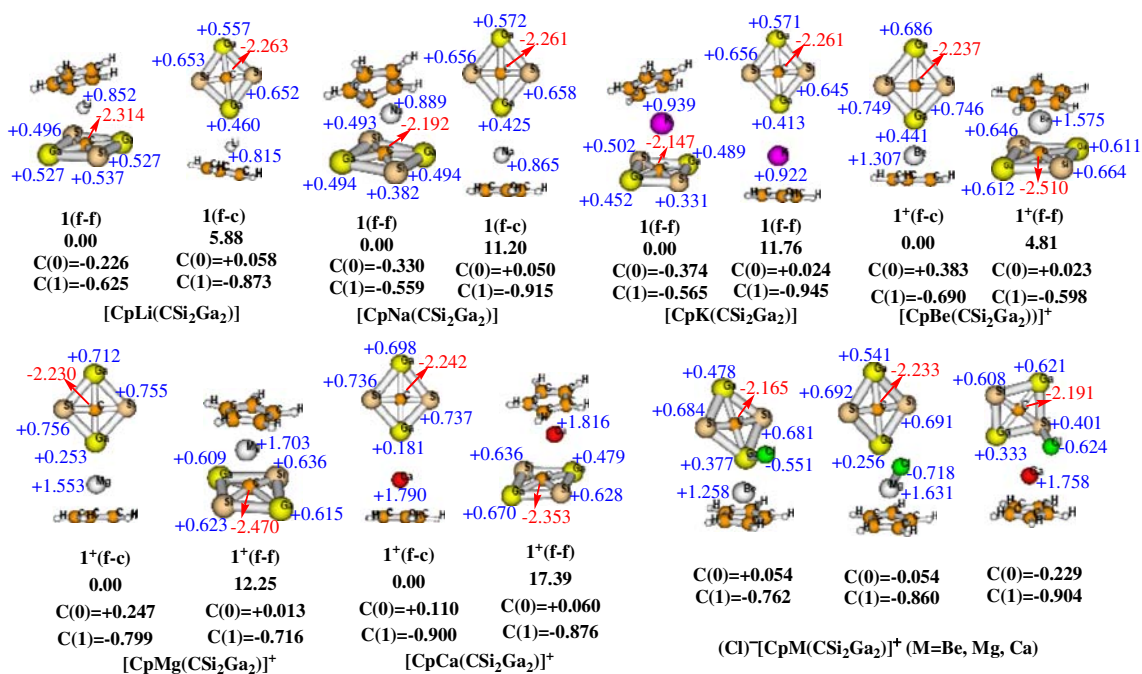**0.00**
C(0)=-0.226
C(1)=-0.625

1(f-c)
5.88
C(0)=+0.058
C(1)=-0.873

[CpLi(CSi$_2$Ga$_2$)]

1(f-f)
0.00
C(0)=-0.330
C(1)=-0.559

1(f-c)
11.20
C(0)=+0.050
C(1)=-0.915

[CpNa(CSi$_2$Ga$_2$)]

1(f-f)
0.00
C(0)=-0.374
C(1)=-0.565

1(f-f)
C(0)=+0.024
C(1)=-0.945

[CpK(CSi$_2$Ga$_2$)]

1$^+$(f-c)
0.00
C(0)=+0.383
C(1)=-0.690

1$^+$(f-f)
4.81
C(0)=+0.023
C(1)=-0.598

[CpBe(CSi$_2$Ga$_2$))]$^+$

1$^+$(f-c)
0.00
C(0)=+0.247
C(1)=-0.799

1$^+$(f-f)
12.25
C(0)=+0.013
C(1)=-0.716

[CpMg(CSi$_2$Ga$_2$)]$^+$

1$^+$(f-c)
0.00
C(0)=+0.110
C(1)=-0.900

1$^+$(f-f)
17.39
C(0)=+0.060
C(1)=-0.876

[CpCa(CSi$_2$Ga$_2$)]$^+$

C(0)=+0.054
C(1)=-0.762

C(0)=-0.054
C(1)=-0.860

C(0)=-0.229
C(1)=-0.904

(Cl$^-$)[CpM(CSi$_2$Ga$_2$)]$^+$ (M=Be, Mg, Ca)

Fig. 4 The sandwich forms of [CpM(CSi$_2$Ga$_2$)]$^{q+}$ and the lowest-energy
sandwich forms of (Cl$^-$)[CpM(CSi$_2$Ga$_2$)]$^+$ (M = Be, Mg, Ca, q=1)
obtained at the B3LYP/6–31+G(d) level. Energy values are in kcal/mol.
"C(0)" and "C(1)" denotes the natural charge distributions on the

fragments CSi$_2$Ga$_2$ and Cp, respectively. The NBO charges of C, Si and
Ga-atoms in CSi$_2$Ga$_2$ units and Cl, M-atoms are listed in the hetero-
decked sandwiching structures

is the ground state structure, whereas for M = Be, Mg and Ca, the sandwich form 1^{q+}(f-c) is the ground state structure. The two sandwich forms can easily convert to each other via simple rotation as revealed by the very small rotation frequency associated with the internal rotation of CSi_2Ga_2-deck. Interestingly, among all the designed homo-decked and hetero-decked sandwich species, the ptC unit CSi_2Ga_2 generally prefers to use its corner (Ga atoms) or face (CSi_2Ga_2 planes) to interact with the partner deck (CSi_2Ga_2 or Cp^-). Thus, the designed sandwich species in this paper represent a new kind of metallocenes. Among all the calculated $[CpM(CSi_2Ga_2)]^{q+}$ systems, the planar Cp^- structure is well maintained, indicative of the unique "rigidity" of this organic unit. More interestingly and importantly, the planarity of the ptC unit CSi_2Ga_2 is well-conserved during cluster-assembly. Fusion of the Cp^- and CSi_2Ga_2 decks to form new C-Ga, C-Si or C-M bonds is energetically unfavorable. The rigid organic deck Cp^- can effectively assist the ptC unit CSi_2Ga_2 to sandwich metal atoms.

For purpose of future synthesis, we also designed neutral species $(Cl^-)[CpM(CSi_2Ga_2)]^+$ (M = Be, Mg, Ca, q=1) (see Fig. 4) with counterions Cl^-. Note that the chemistry and properties of fluorin (F) and related species are usual different from that of other halogens (Cl, Br, I), in order to achieve the general viewpoints and conclusions, we chose Cl^- as counterion rather than F^-. Moreover, the computational demanding of Cl^- is less than that of Br^- and I^-. For each M, the lowest-lying sandwich isomer for charged $[CpM(CSi_2Ga_2)]^{q+}$ is also the ground sate structure for neutral $(Cl^-)_q[CpM(CSi_2Ga_2)]^{q+}$. The counterions saturated species for the hetero-decked sandwich-like complexes are electronically stable and energetic ground state, which made us have sufficient confidence in the future synthesis.

The results of the above calculation demonstrate that the f-f, f-c, and f-s interaction types are common phenomena in the extended systems. Such an interesting growth pattern might be applicable to the assembly of Si- and Ga-embedded ptC unit CSi_2Ga_2 into more highly extended 1D, 2D, and 3D sandwich-type molecular compounds.

In order to get insight into the origin of planarity and exotic electronic structure of such novel sandwich-like compounds based on the ptC unit CSi_2Ga_2, we examined the molecular orbitals of bare CSi_2Ga_2, and sandwich-like compound $CpLi(CSi_2Ga_2)$. Figure 5 shows their highest occupied molecular orbitals (HOMOs): the ligand-ligand bonding HOMO. 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 Fig. 5 we can see the shapes of orbitals in a) bare CSi_2Ga_2, b) sandwich-like compound $CpLi(CSi_2Ga_2)$ are generally the same. Thus, the ptC unit CSi_2Ga_2 can maintain its electronic and structural integrity in sandwich form. Therefore, CSi_2Ga_2 could be used as a building block in designing planar tetracoordinate carbon complexes, even planar bulk solid materials. The originality of planarity of other simple pentatomic species has been previously revealed in several nice papers[13–15, 17–19, 22–24, 47–52].

In order to get insight into the interactions of our designed hetero-decked sandwich-type complexes $CpM(CSi_2Ga_2)^{q+}$, we perform detailed NBO[32] analysis. The NPA charges on the CSi_2Ga_2-unit in the face-corner (f-c) sandwich form are +0.058|e|, +0.050|e|, +0.024|e|, +0.383|e|, +0.247|e| and +0.110|e|, for M = Li, Na, K, Be, Mg and Ca, respectively (Although, for M = Li, the face-corner (f-c) is a saddle point, we still perform the NBO analyses on the saddle point $CpLi(CSi_2Ga_2)$ (f-c) in order to make a qualitatively comparison with (f-f) form). The NPA charges on the center-C-atoms of CSi_2Ga_2-unit (see Fig. 4) in the hetero-decked sandwich-type form (f-c) are -2.263|e|, −2.261|e|, −2.261|e|, −2.237|e|, −2.230|e| and −2.242|e|, for M = Li, Na, K, Be, Mg and Ca, respectively. The NPA charges on the CSi_2Ga_2-unit in the face-face (f-f) sandwich form are -0.226|e|, −0.330|e|, −0.374|e|, +0.023|e|, +0.013|e| and +0.060|e|, for M = Li, Na, K, Be, Mg and Ca, respectively. The NPA charges on the center-C-atoms of CSi_2Ga_2-unit (see Fig. 4) in the hetero-decked sandwich-type form (f-f) are −2.314|e|, −2.192|e|, −2.147|e|, −2.510|e|, −2.470|e| and −2.353|e| for M = Li, Na, K, Be, Mg and Ca, respectively. Generally speaking, the NBO results indicate that the NPA charges are presented as interesting

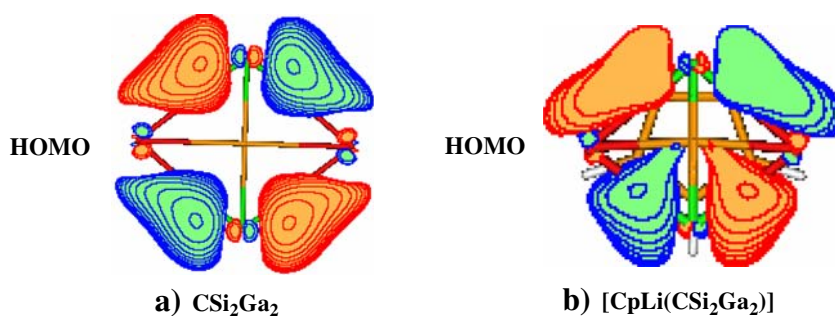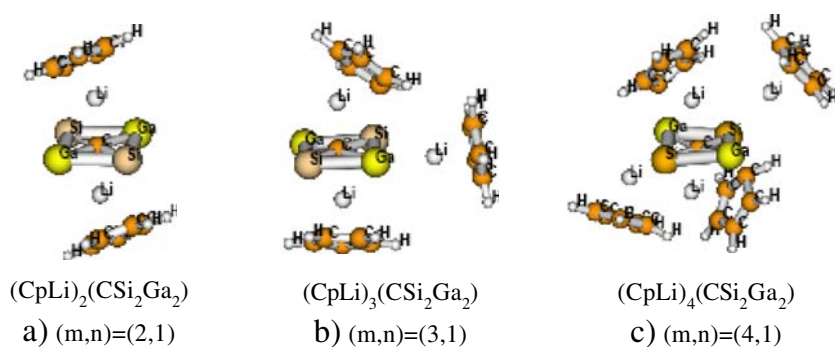**Fig. 5** The B3LYP/6–31+G(d) characteristic orbitals[94] of a) CSi_2Ga_2, b) $[CpLi(CSi_2Ga_2)]$

HOMO

a) CSi_2Ga_2

HOMO

b) $[CpLi(CSi_2Ga_2)]$

$(CpLi)_2(CSi_2Ga_2)$ $(CpLi)_3(CSi_2Ga_2)$ $(CpLi)_4(CSi_2Ga_2)$
a) (m,n)=(2,1)   **b)** (m,n)=(3,1)   **c)** (m,n)=(4,1)

"sandwich" distributions in the CSi_2Ga_2-units in the hetero-decked sandwich-type compounds, i.e., in the CSi_2Ga_2-incorporated hetero-decked sandwich-like complexes the planar tetracoordinate carbon atoms serve as the negatively charged nonmetal centers, the Ga and Si atoms at the periphery form positively charged rings. In summary, the above NPA charges on the CSi_2Ga_2-units are slightly a departure from the neutral charge state, but that are qualitatively consistent with the zero charges. Such phenomena are mainly ascribed to the small charge transfer between the metal atoms and the CSi_2Ga_2-units in the hetero-decked sandwich species.

On the other hand, the NPA charges on the metal atoms range from +0.815|e| to +0.852|e|, from +0.865|e| to +0.889|e|, from +0.922|e| to +0.939|e|, from +1.307|e| to +1.575|e|, from +1.553|e| to +1.703|e|, from +1.790|e| to +1.816|e|, for M = Li, Na, K, Be, Mg, Ca, respectively. We can see that the NPA charges on alkali-atoms (Li, Na, and K) are slightly a departure to formally positive charge +1. For alkali-earth atoms (Be, Mg and Ca), the NPA charges are slightly departure to formally positive charge +2, whereas for Be, the departure is slightly larger due to its large covalent property. Moreover, the NPA charges on the Cp-fragments range from −0.559|e| to −0.945|e| in the hetero-decked sandwich-like species.

Extended sandwich structures based on CSi_2Ga_2

It is known that some metallocenes can form highly extended sandwich complexes ranging from nanoscales to polymers, even to bulk solid materials[79]. We thus further designed the ptC-based extended systems containing more Cp^- and CSi_2Ga_2 units in various "*hetero-decked sandwich*" forms at the B3LYP/6–31+G(d) level. For systemic consideration, we considered various combinational forms according to different coordinated directions (face, side, and corner) of the CSi_2Ga_2 unit. In Fig. 6, some selected low-lying energy species are shown.

Conclusions

In summary, the present study described the first attempt to incorporate neutral ptC unit CSi_2Ga_2 into assembled molecular systems in sandwich forms. The designed species await future experimental verification. Such assembly procedures could also be applied to many other ptC molecules such as CAl_3Ge, CAl_3X^- (X = Si, Ge), CSi_2Al_2, CGe_2Al_2, etc. Compared to the traditional metallocenes, our designed complexes represent a new class of metallocenes containing the exotic ptC unit CSi_2Ga_2, among which CSi_2Ga_2 generally prefers to use its corner (Ga atoms) and face (CSi_2Ga_2 planes) to interact with the partner deck. Thus, the designed sandwich species in this paper represent a new kind of metallocenes. More importantly, the organic aromatic rigid Cp^- ligand plays a crucial role in stabilizing the new hetero-decked sandwich-type compounds. Moreover, during both the homo-decked and hetero-decked sandwiching processes, the electronic and structural integrity of CSi_2Ga_2 and the characteristic orbitals (Fig. 5) are generally well kept. Thus, the ptC unit CSi_2Ga_2 could act as a new type of building block, which might be the first theoretical evidence, to the best of our knowledge. Future studies on the building block or inorganic ligand chemistry of CSi_2Ga_2 are desired. Finally, based on the above points, the new scheme "*hetero-decked sandwich*" bridges the ptC chemistry, metallocenes and is thus well suited to the combinational chemistry.

References

1. Hoffmann R, Alder RW, Wilcox CF Jr. (1970) J Am Chem Soc 92:4992 doi:10.1021/ja00719a044
2. Hoffmann R (1971) Pure Appl Chem 28:181
3. For review articles, see (a) Sorger K, Schleyer PvR (1995) J Mol Struct 338:317
4. Streitwieser A, Bachrach SM, Dorigo A, Schleyer PvR (1995) Lithium Chemistry. In: Sapse A-M, Schleyer PvR (Eds) New York, Wiley, p. 1
5. Rottger D, Erker G (1997) Angew Chem Int Ed 36:812 doi:10.1002/anie.199708121
6. Radom L, Rasmussen DR (1998) Pure Appl Chem 70:1977 doi:10.1351/pac199870101977
7. Choukroun R, Cassoux P (1999) Acc Chem Res 32:494 doi:10.1021/ar970304z
8. Siebert W, Gunale A (1999) Chem Soc Rev 28:367 doi:10.1039/a801225c
9. Boldyrev AI, Wang L-S (2001) J Phys Chem A 105:10759 doi:10.1021/jp0122629
10. Minkin RM, Minyaev RH (2002) Russ Chem Rev 71:869 doi:10.1070/RC2002v071n11ABEH000729
11. Keese R (2006) Chem Rev 106:4787 doi:10.1021/cr050545h
12. Merino G, Méndez-Rojas MA, Vela A, Heine T (2007) J Comput Chem 28:362 doi:10.1002/jcc.20515
13. Schleyer PvR, Boldyrev AI (1991) J Chem Soc Chem Commun 1536 doi:10.1039/c39910001536
14. Boldyrev AI, Schleyer PvR (1991) J Am Chem Soc 113:9045 doi:10.1021/ja00024a003
15. Boldyrev AI, Simons J (1998) J Am Chem Soc 120:7967 doi:10.1021/ja981236u
16. Ritter SK (2003) Chem Eng News 81(50):23
17. Li X, Wang L-S, Boldyrev AI, Simons JJ (1999) Am Chem Soc 121(25):6033 doi:10.1021/ja9906204
18. Li X, Zhang HF, Wang LS, Geske GD, Boldyrev AI (2000) Angew Chem Int Ed 39:3630 doi:10.1002/1521-3773(20001016)39:20<3630::AID-ANIE3630>3.0.CO;2-R
19. Wang LS, Boldyrev AI, Li X, Simons J (2000) J Am Chem Soc 122:7681 doi:10.1021/ja993081b
20. Wilson E (2000) Chem Eng News 78(34):8
21. Geske GD, Boldyrev AI (2002) Inorg Chem 41:2795 doi:10.1021/ic0112241
22. Zakrzewski VG, Niessen von W, Boldyrev AI, Schleyer PvR (1993) Chem Phys Lett 174:167
23. Boldyrev AI, Li X, Wang LS (2000) Angew Chem Int Ed 39:3307 doi:10.1002/1521-3773(20000915)39:18<3307::AID-ANIE3307>3.0.CO;2-#
24. Li X, Zhan HJ, Wang LS (2002) Chem Phys Lett 357:415 doi:10.1016/S0009-2614(02)00488-8
25. Havenith RWA, Fowler PW, Steiner E (2002) Chem Eur J 8:1068 doi:10.1002/1521-3765(20020301)8:5<1068::AID-CHEM1068>3.0.CO;2-Z
26. Wang Y, Huang YH, Liu RZ (2006) Chem Eur J 12:3610 doi:10.1002/chem.200501320
27. Li S-D, Miao C-Q, Ren G-M, Guo J-C (2006) Eur J Inorg Chem 2567–2571 doi:10.1002/ejic.200600118
28. Yang LM, Ding YH, Sun CC (2006) Chem Phys Chem 7:2478–2482 doi:10.1002/cphc.200600564
29. Yang LM, Ding YH, Sun CC (2007) Chem Eur J 13:2546–2555 doi:10.1002/chem.200601223
30. Yang LM, Ding YH, Sun CC (2007) J Am Chem Soc 129:658–665 doi:10.1021/ja066217w
31. Yang LM, Ding YH, Sun CC (2007) J Am Chem Soc 129:1900–1901 doi:10.1021/ja068334x
32. We are aware that another possibility is to apply "heteroleptic sandwich", see Ref: Merino G, Beltran H, Vela A (2006) Inorg Chem 45:1091–1095 doi:10.1021/ic051391r
33. Also, we note that another possibility is to apply "mixed metallocenes $[M(\eta^5-C_5Me_4R)(\eta^5-P_5)]$", see Ref: Padma EJ, Malar (2004) Eur J Inorg Chem 2723–2732 doi:10.1002/ejic.200400058
34. And "Heteroligands Ferrocene FeCp(η^5-E_5)" see Ref: Frunzke J, Lein M, Frenking G (2002) Organometallics 21:3351–3359 doi:10.1021/om020397a
35. Scherer OJ, Bruck T (1987) Angew Chem 99:59; Angew Chem Int Ed 26:59
36. Collins JB, Dill JD, Jemmis ED, Apeloig Y, Schleyer PvR, Seeger R, Pople JA (1976) J Am Chem Soc 98:5419 doi:10.1021/ja00434a001
37. Cotton FA, Millar M (1977) J Am Chem Soc 99:7886 doi:10.1021/ja00466a021
38. Erker G, Wicher J, Engel K, Resenfeldt F, Dietrich W, Kruger C (1980) J Am Chem Soc 102:6344 doi:10.1021/ja00540a032
39. Keese R (1982) Nachr Chem Tech Lab 30:844
40. Stahl D, Maquin F, Gaumann T, Schwarz H, Carrupt P-A, Vogel P (1985) J Am Chem Soc 107:5049 doi:10.1021/ja00304a005
41. McGrath MP, Radom L (1992) J Am Chem Soc 114:8531 doi:10.1021/ja00028a048
42. Luef W, Keese R (1993) Adv Strain Org Chem 3:229
43. Rottger D, Erker G, Frohlich R, Grehl M, Silverio SJ, Hyla-Kryspin I, Gleiter R (1995) J Am Chem Soc 117:10503 doi:10.1021/ja00147a011
44. Sorger K, Schleyer PvR, Fleischer R, Stalke DJ (1996) Am Chem Soc 118(29):6924–6933 doi:10.1021/ja9603362
45. Sorger K, Schleyer PvR, Stalke D (1996) J Am Chem Soc 118:1086 doi:10.1021/ja9521280
46. Hyla-Kryspin I, Gleiter R, Romer M-M, Deveny J, Gunale A, Pritzkow H, Siebert W (1997) Chemistry 2:294
47. Rasmussen DR, Radom L (1999) Angew Chem Int Ed 38:2875 doi:10.1002/(SICI)1521-3773(19991004)38:19<2875::AID-ANIE2875>3.0.CO;2-D
48. Wang ZX, Manojkumar TK, Wannere C, Schleyer PvR (2001) Org. Lett. 3:1249 doi:10.1021/ol015573a
49. Wang Z-X, Schleyer PvR (2001) J Am Chem Soc 123:994 doi:10.1021/ja0038272
50. Sahin Y, Hartmann M, Geiseler G, Schweikart D, Balzereit C, Frenking G, Massa W, Berndt A (2001) Angew Chem Int Ed 40:2662 doi:10.1002/1521-3773(20010716)40:14<2662::AID-ANIE2662>3.0.CO;2-V
51. Wang Z-X, Schleyer PvR (2002) J Am Chem Soc 124:11979 doi:10.1021/ja0265310, and references therein
52. Merino G, Mendez-Rojas MA, Vela A (2003) J Am Chem Soc 125(20):6026–6027 doi:10.1021/ja034307k
53. Merino G, Mendez-Rojas MA, Beltran HI, Corminboeuf C, Heine T, Vela A (2004) J Am Chem Soc 126:16160 doi:10.1021/ja047848y
54. Priyakumar UD, Reddy AS, Sastry GN (2004) Tetrahedron Lett 45:2495 doi:10.1016/j.tetlet.2004.02.017
55. Priyakumar UD, Sastry GN (2004) Tetrahedron Lett 45:1515 doi:10.1016/j.tetlet.2003.12.019
56. Pancharatna PD, Mendez-Rojas MA, Merino G, Vela A, Hoffmann R (2004) J Am Chem Soc 126(46):15309–15315 doi:10.1021/ja046405r
57. Li SD, Ren GM, Miao CQ, Jin Z-H (2004) Angew Chem Int Ed 43:1371 doi:10.1002/anie.200353068
58. Li SD, Ren GM, Miao CQ (2005) J Phys Chem A 109:259 doi:10.1021/jp040259u
59. Esteves PM, Ferreira NBP, Corroa RJ (2005) J Am Chem Soc 127:8680 doi:10.1021/ja042971a
60. Perez N, Heine T, Barthel R, Seifert G, Vela A, Mendez-Rojas MA, Merino G (2005) Org Lett 7:1509–1512 doi:10.1021/ol050170m

61. Sateesh B, Reddy AS, Sastry GN (2007) J Comp Chem 28:335–343 doi:10.1002/jcc.20552

62. Exner K, Schleyer PvR (2000) Science 290:1937 doi:10.1126/science.290.5498.1937

63. Wang Z-X, Schleyer PvR (2001) Science 292:2465 doi:10.1126/science.1060000

64. Wang Z-X, Schleyer PvR (2002) Angew Chem 114:4256–4259, Angew Chem Int Ed 41:4082–4085 doi:10.1002/1521-3773(20021104)41:21<4082::AID-ANIE4082>3.0.CO;2-Q

65. Zhai H-J, Kiran B, Li J, Wang L-S (2003) Nat Mater 2:827–833 doi:10.1038/nmat1012

66. Zhai HJ, Alexandrova AN, Birch KA, Boldyrev AI, Wang L-S (2003) Angew Chem 115:6186–6190; *Angew. Chem. Int. Ed.* **2003**, *42*, 6004–6008 doi:10.1002/anie.200351874

67. Li S-D, Miao C-Q, Guo J-C, Ren G-M (2004) J Am Chem Soc 126(49):16227 doi:10.1021/ja045303y

68. Lein M, Frunzke J, Frenking G (2003) Angew Chem 115:1341–1345. Angew Chem Int Ed 2003, 42, 1303–1306 doi:10.1002/anie.200390336

69. Li S-D, Ren G-M, Miao C-Q (2004) Inorg Chem 43:6331 doi:10.1021/ic049623u

70. Li SD, Miao CQ, Ren GM (2004) Eur J Inorg Chem 2232–2234 doi:10.1002/ejic.200400223

71. Drhardt S, Frenking G, Chen Z-F, Schleyer PvR (2005) Angew Chem Int Ed 44:1078 doi:10.1002/anie.200461970

72. Li S-D, Guo J-C, Miao C-Q, Ren G-M (2005) Angew Chem Int Ed 44:2158 doi:10.1002/anie.200462476

73. Minyaev RM, Gribanova TN (2000) Russ Chem Bull 109:783–796 doi:10.1007/BF02494697

74. Gribanova TN, Minyaev RM, Minkin VI (2001) Mendeleev Commun 169–170 doi:10.1070/MC2001v011n05ABEH001461

75. Minyaev RM, Gribanova TN, Starikov AG, Minkin VI (2001) Mendeleev Commun 213–214 doi:10.1070/MC2001v011n06ABEH001496

76. Minyaev RM, Gribanova TN, Starikov AG, Minkin VI (2002) Dokl Chem 382:41–45 doi:10.1023/A:1014429323457

77. Minkin VI, Minyaev RM (2004) Mendeleev Commun 43–46 doi:10.1070/MC2004v014n02ABEH001911

78. Nayak SK, Rao BK, Jena P, Li X, Wang LS (1999) Chem Phys Lett 301:379 doi:10.1016/S0009-2614(99)00024-X

79. Jutzi P, Burdord N (1998) Main Group Metallocenes. In: Togni A, Halterman RL (eds) Metallocenes, Vol. 1. Wiley-VCH, Weinheim, p. 3

80. Urnezius E, Brennessel WW, Cramer CJ, Ellis JE, Schleyer PvR (2002) Science 295:832 doi:10.1126/science.1067325

81. Lein M, Frunzke J, Frenking G (2003) Inorg Chem 42:2504 doi:10.1021/ic020592h

82. Frunzke J, Lein M, Frenking G (2002) Organometallics 21:3351 doi:10.1021/om020397a

83. Mercero JM, Ugalde JM (2004) J Am Chem Soc 126:3380 doi:10.1021/ja039074b

84. Mercero JM, Formoso E, Matxain JM, Eriksson LA, Ugalde JM (2006) Chem Eur J 12:4495 doi:10.1002/chem.200600106

85. Mercero JM, Matxain JM, Ugalde JM (2004) Angew Chem Int Ed 43:5485 doi:10.1002/anie.200460498

86. Cheng LP, Li QS (2003) J Phys Chem A 107:2882 doi:10.1021/jp027350n

87. Cheng LP, Li QS (2005) J Phys Chem A 109:3182 doi:10.1021/jp045348l

88. Guan J, Li QS (2005) J Phys Chem A 109:9875 doi:10.1021/jp0525944

89. Becke AD (1993) J Chem Phys 98:5648 doi:10.1063/1.464913

90. Lee C, Yang W, Parr RG (1988) Phys Rev B 37:785 doi:10.1103/PhysRevB.37.785

91. Clark T, Chandrasekhar J, Spitznagel GW, Schleyer PvR (1983) J Comput Chem 4:294 doi:10.1002/jcc.540040303

92. Frisch MJ, Pople JA, Binkley JS (1984) J Chem Phys 80:3265 doi:10.1063/1.447079

93. Gaussian03 (RevisionA.1) (2003) Frisch, M. J. et.al. Gaussian, Inc., Pittsburgh, PA. (Full citations see Supporting Information)

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