D3h [A-CE3-A]− (E = Al and Ga, A = Si, Ge, Sn, and Pb): A new class of hexatomic mono-anionic species with trigonal bipyramidal carbon

Yan-Bo Wu,1,a) Yan-Qin Li,1 Hui Bai,1 Hai-Gang Lu,1 Si-Dian Li,1 Hua-Jin Zhai,1 and Zhi-Xiang Wang,2,a)  
1 Institute of Molecular Science, Key Laboratory of Chemical Biology and Molecular Engineering of Education Ministry, Shansi University, Wucheng Road 92#, Taiyuan 030006, People’s Republic of China  
2 College of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, Yuquan Road 19#, Beijing 100049, People’s Republic of China  

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The non-classical trigonal bipyramidal carbon (TBPC) arrangement generally exists as transition states (TSs) in nucleophilic bimolecular substitution (Sn2) reactions. Nevertheless, chemists have been curious about whether such a carbon bonding could be stable in equilibrium structures for decades. As the TBPC arrangement was normally realized as cationic species theoretically and experimentally, only one anionic example ([At-C(CN)3-At]−) was computationally devised. Herein, we report the design of a new class of anionic TBPC species by using the strategy similar to that for stabilizing the non-classical planar hypercoordinate carbon. When electron deficient Al and Ga were used as the equatorial ligands, eight D3h [A-CE3-A]− (E = Al and Ga, A = Si, Ge, Sn, and Pb) TBPC structures were found to be the energy minima rather than TSs at both the B3LYP and MP2 levels. Remarkably, the energetic results at the CCSD(T) optimization level further identify [Ge-CAl3-Ge]− and [Sn-CGa3-Sn]− even to be the global minima and [Si-CAl3-Si]− and [Ge-CGa3-Ge]− to be the local minima, only slightly higher than their global minima. The electronic structure analyses reveal that the substantial ionic C−E bonding, the peripheral E−A covalent bonding, and the axial mc-2e (multi center-two electrons) bonding play roles in stabilizing these TBPC structures. The structural simplicity and the high thermodynamic stability suggest that some of these species may be generated and captured in the gas phase. Furthermore, as mono-anionic species, their first vertical detachment energies are differentiable from those of their nearest isomers, which would facilitate their characterization via experiments such as the negative ion photoelectron spectroscopy. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4867364]

I. INTRODUCTION

Carbon predominately adopts the classical linear sp, planar trigonal sp2, and tetrahedral sp3 hybridization bonding to bond to its neighbors. Besides, compounds featuring the non-classical carbon bonding pattern have also been well characterized. Sparked by the curiosity whether a transition state (TS) structure with a planar tetracoordinate carbon (ptC) can be stabilized, strategies to achieve the stable planar hypercoordinate carbon (phC) arrangement have been developed.1–8 Remarkably, the trigonal bipyramidal carbon (TBPC) arrangement has also attracted attention for more than three decades. As the TBPC arrangement was normally realized as cationic species theoretically and experimentally, only one anionic example ([At-C(CN)3-At]−) was computationally devised. Herein, we report the design of a new class of anionic TBPC species by using the strategy similar to that for stabilizing the non-classical planar hypercoordinate carbon. When electron deficient Al and Ga were used as the equatorial ligands, eight D3h [A-CE3-A]− (E = Al and Ga, A = Si, Ge, Sn, and Pb) TBPC structures were found to be the energy minima rather than TSs at both the B3LYP and MP2 levels. Remarkably, the energetic results at the CCSD(T) optimization level further identify [Ge-CAl3-Ge]− and [Sn-CGa3-Sn]− even to be the global minima and [Si-CAl3-Si]− and [Ge-CGa3-Ge]− to be the local minima, only slightly higher than their global minima. The electronic structure analyses reveal that the substantial ionic C−E bonding, the peripheral E−A covalent bonding, and the axial mc-2e (multi center-two electrons) bonding play roles in stabilizing these TBPC structures. The structural simplicity and the high thermodynamic stability suggest that some of these species may be generated and captured in the gas phase. Furthermore, as mono-anionic species, their first vertical detachment energies are differentiable from those of their nearest isomers, which would facilitate their characterization via experiments such as the negative ion photoelectron spectroscopy. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4867364]

However, the TBPC arrangement has been found in the equilibrium structures of several cationic species. Examples include D3h CH3A2+ (A = Li, Na, BeH, and MgH), D3h CLi5+ (Scheme 1-II), Si2(CH3)7+ (Scheme 1-III), and CH3(XH2)3+ (X = group 1, 2, 13, and 14 elements),12–16 among which CH3Li5+, CLi5+, and Si2(CH3)7+ were confirmed experimentally.13,14,16 As these cationic TBPC species were scaffold-free, TBPC could also be harnessed by molecular scaffolds such as anthracene10,11 and 2,6-bis (p-substituted phenyloxymethyl) benzene.17 It should be pointed out that the X-ray structure of these “scaffold-confined” TBPC species have the interatomic distances between the central carbon and the axial atoms (A) significantly longer than the normal C−A bond lengths.

In 2005, using anthracene as a scaffold was attempted to achieve anionic TBPC species, but was not successful, as revealed by its X-ray structure which indicated a classical sp3 carbon with a short axial C−O distance (1.470 Å) and a very long axial C−O distance (2.991 Å).18 In 2008, Bickelhaupt group proposed the “ball in a box” model to rationalize why the [Cl-CH3(Cl]− TBPC structure (Scheme 1-IV) is a TS, while the [Cl-SiH3(Cl]− analog (Scheme 1-V) is a minimum.19 After that, in 2009 they further suggested to use more rigid planar CR3, as the equatorial moiety to stabilize
the TBPC arrangement, and found that the $\sigma$-donating and $\pi$-accepting CN group significantly enhance the planarity of C(CN)$_3$- unit. Among their reported species, the anionic $D_{3h}$ \( [X-C(CN)\text{$_3$}-X^-] \) (\( X = \text{F, Cl, and Br} \)) are not minima, the $D_{3h}$ \( [I-C(CN)\text{$_3$}-I^-] \) may be a minimum, depending on the basis set used, but the $D_{3h}$ \( [\text{At}-C(CN)\text{$_3$}-\text{At}^-] \) (Scheme 1–VI) is a minimum regardless of used basis sets.\(^{20}\) To our knowledge, this is the first example of anionic TBPC species, but whether this species is a global minimum was not investigated. Herein, we report a strategy to obtain a class of TBPC structures, \([\text{Al}-\text{CE$_3$-A}^-]\) (\( E = \text{Al and Ga, A = Si, Ge, Sn, and Pb} \)), as well as their electronic structures. These hexatomic clusters are all energy minima. Of particular interest, \([\text{Sn-CGa$_3$-Sn}^-]\) and \([\text{I-CGa$_3$-I}^-]\) are global minima, which indicates that these two species could be formed easily by the laser vaporization in the gas phase and characterized by experiments such as the size-selected negative ion photoelectron spectroscopy.

II. COMPUTATIONAL DETAILS

For the heavy elements, Ga, Ge, Sn, and Pb, the relativistic effect was considered by using the correlation-consistent-like basis set aug-cc-pVDZ-PP\(^{21,22}\) and aug-cc-pVTZ-PP\(^{21,22}\) with accurate small-core relativistic pseudopotentials. The potential energy surfaces (PESs) were probed using stochastic search algorithms.\(^{23,24}\) Random structures were initially generated by GXYZ program\(^ {25,26}\) and then subjected to geometry optimizations at the B3LYP/BSI level, where BSI denotes 6-31+G(d) for C, Al, and Si, and aug-cc-pVDZ-PP for Ga, Ge, Sn, and Pb. To ascertain the convergence of the PES explorations, we run three sets of searches on the singlet PESs and two sets on the triplet PESs for each of total eight \( \text{A-CE$_3$-A}^- \) (\( E = \text{Al and Ga and A = Si, Ge, Sn, and Pb} \)) stoichiometries. The 20 lowest isomers of each stoichiometry were reoptimized and characterized to be energy minima at the B3LYP/BSII level (BSII denotes aug-cc-pVTZ for C, Al and Ga, A = Si, Ge, Sn, and Pb) to softness the rigidity of tetrahedral \( sp^3 \) carbon bonding, because the electron donation of the electropositive ligands can weaken the directionality of \( sp^3 \) hybridization.\(^ {34–44} \) Similarly, we hypothesized that such an electronic effect can be applied to achieve the non-classical TBPC species. In fact, this can be applied to understand the previously reported TBPC structures. For example, Frenking group found computationally that, when replacing the \( \text{SiH}_3 \) group in III with other electropositive groups (\( \text{XH}_3, X = \text{Ge-Pb}, \text{or XH}_2, X = \text{B-In} \)), all analogs of III are the TBPC minima.\(^ {15} \) As for the series of \( [X-C(CN)\text{$_3$}-X^-] \) (\( X = \text{F, Cl, Br, I, At} \)) mono-anions, when \( X \) goes from \( F \) to \( At \), the covalent bonding character of \( C-X \) bond decreases, thus the TBPC structure becomes more and more feasible.\(^ {20} \)

III. RESULTS AND DISCUSSION

A. The strategy

To achieve the non-classical phC structures, one strategy among others is to use electropositive atoms/ligands (e.g., Be, B, and Al or groups containing them) to soften the rigidity of tetrahedral \( sp^3 \) carbon bonding, because the electron donation of the electropositive ligands can weaken the directionality of \( sp^3 \) hybridization.\(^ {34–44} \) Similarly, we hypothesized that such an electronic effect can be applied to achieve the non-classical TBPC species. In fact, this can be applied to understand the previously reported TBPC structures. For example, Frenking group found computationally that, when replacing the \( \text{SiH}_3 \) groups in III with other electropositive groups (\( \text{XH}_3, X = \text{Ge-Pb}, \text{or XH}_2, X = \text{B-In} \)), all analogs of III are the TBPC minima.\(^ {15} \) As for the series of \( [X-C(CN)\text{$_3$}-X^-] \) (\( X = \text{F, Cl, Br, I, At} \)) mono-anions, when \( X \) goes from \( F \) to \( At \), the covalent bonding character of \( C-X \) bond decreases, thus the TBPC structure becomes more and more feasible.\(^ {20} \)
ordination, the bonding of the central carbon atoms in the TBPC species. At first, despite the hypercoordination of these TBPC species, all the WBI\textsubscript{E–A}, WBI\textsubscript{C–E}, and WBI\textsubscript{C–A} values in Table I. In terms of the “ball-in-box” model, the formation of efficient E–A, C–A, and C–C covalent bonding diminishes the space of the E\textsubscript{1}E\textsubscript{2} “box,” so the central carbon atom can be lifted from the bottom to the center of the box.

The degenerate LUMOs and occupied valence molecular orbitals (MO) of 1a are depicted in Fig. 2 and the similar MOs of 2a–8a are given in the supplementary material.\textsuperscript{51} As shown in Fig. 2, in the degenerate HOMO, the p\textsubscript{x} or p\textsubscript{y} atomic orbitals of Si bridge the p\textsubscript{x} atomic orbitals of Al atoms, forming a peripheral bonding around TBPC. These two bonding orbitals contribute to WBI\textsubscript{E–A}. Similar peripheral bonding orbitals exist in p\textsubscript{t}C species/molecules such as CAl\textsubscript{4}–39 C\textsubscript{2}Al\textsubscript{4},\textsuperscript{52} boraplanes,\textsuperscript{52} and neutral species with C(C)\textsubscript{4} unit\textsuperscript{53} and were considered to be the key factor for the stabilization of the p\textsubscript{t}C arrangement. The axial parts of HOMO–3 and degenerated HOMO–1 clearly show the linear Si–C–Si 3-center bonding characters, which are majorly responsible for the large WBI\textsubscript{E–Si}, value (0.79) but with the significantly long interatomic Si–Si distance (3.616 Å at the B3LYP/BSII level). HOMO–2 and HOMO–6 correspond to the axial C–Si bonding. The degenerate HOMO–5 contributes to C–Al bonding.

B. Design and characterization of TBPC species

Al atom has been used to realize various p\textsubscript{t}C species.\textsuperscript{24,34–36,39–50} Because Al is metallic with appreciable non-metallic character, the C–Al bond is mainly ionic, which helps to soften the rigidity of tetrahedral carbon, and on the other hand, it bears the weak covalent bonding character, which helps to maintain the hypercoordination skeleton. Thus to make a start, we tried to take CAl\textsubscript{3} as the middle fragment of the TBPC structure and searched for proper axial atoms by scanning the first three rows of the p-block elements. Delightfully, among 15 candidates, the D\textsubscript{3h} [A–CAL\textsubscript{4}–A] (A = Si (1a) and Ge (2a)) were found to be the energy minima with stable wavefunctions at the B3LYP/BSII level. On the basis of 1a and 2a, more TBPC species were found by using Al or Ga as the equatorial atoms (E) and Si, Ge, Sn, and Pb as the axial atoms (A). The resulted eight D\textsubscript{3h} structures, including 1a and 2a, are all energy minima at both the B3LYP/BSII and MP2/BSII levels. Their CCSD(T)/BSII optimized geometries are shown in Fig. 1. The equatorial C–Al distances (R\textsubscript{C–Al}) in 1a–4a range from 2.021 to 2.074 Å and C–Ga distances (R\textsubscript{C–Ga}) in 5a–8a are 2.128 to 2.181 Å. The interatomic distances of the “ball-in-box” model, the formation of efficient E–A, C–A, and C–E covalent bonding diminishes the space of the E\textsubscript{1}E\textsubscript{2} “box,” so the central carbon atom can be lifted from the bottom to the center of the box.

The degenerate LUMOs and occupied valence molecular orbitals (MO) of 1a are depicted in Fig. 2 and the similar MOs of 2a–8a are given in the supplementary material.\textsuperscript{51} As shown in Fig. 2, in the degenerate HOMO, the p\textsubscript{x} or p\textsubscript{y} atomic orbitals of Si bridge the p\textsubscript{x} atomic orbitals of Al atoms, forming a peripheral bonding around TBPC. These two bonding orbitals contribute to WBI\textsubscript{E–A}. Similar peripheral bonding orbitals exist in p\textsubscript{t}C species/molecules such as CAl\textsubscript{4}–39 C\textsubscript{2}Al\textsubscript{4},\textsuperscript{52} boraplanes,\textsuperscript{52} and neutral species with C(C)\textsubscript{4} unit\textsuperscript{53} and were considered to be the key factor for the stabilization of the p\textsubscript{t}C arrangement. The axial parts of HOMO–3 and degenerated HOMO–1 clearly show the linear Si–C–Si 3-center bonding characters, which are majorly responsible for the large WBI\textsubscript{E–Si}, value (0.79) but with the significantly long interatomic Si–Si distance (3.616 Å at the B3LYP/BSII level). HOMO–2 and HOMO–6 correspond to the axial C–Si bonding. The degenerate HOMO–5 contributes to C–Al bonding.

![FIG. 2. Degenerate LUMOs and occupied valence molecular orbitals of \([\text{Si-CAl\textsubscript{4}}\text{Si}]\).](image-url)

### TABLE I. The lowest vibrational frequencies ($\nu_{\text{min}}$), the HOMO-LUMO energy gaps (Gap), and the NBO analysis results, including the natural charges of C, the equatorial E atoms, and the apical A atoms ($Q_C$, $Q_E$, and $Q_A$), the total Wiberg bond indices of these atoms (WBI\textsubscript{C–E}, WBI\textsubscript{C–A}, and WBI\textsubscript{A–A}), and the Wiberg bond orders including C–E, C–A, E–A, and A–A (WBI\textsubscript{C–E}, WBI\textsubscript{C–A}, WBI\textsubscript{E–A}, and WBI\textsubscript{A–A}) of 1a–8a at B3LYP/BSII level.

<table>
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<tr>
<th>$\nu_{\text{min}}$</th>
<th>Gap</th>
<th>$Q_C$</th>
<th>$Q_E$</th>
<th>$Q_A$</th>
<th>WBI\textsubscript{C–E}</th>
<th>WBI\textsubscript{C–A}</th>
<th>WBI\textsubscript{E–A}</th>
<th>WBI\textsubscript{A–A}</th>
</tr>
</thead>
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<tr>
<td>[Si-CAl\textsubscript{4}Si]$^-$ (1a)</td>
<td>104</td>
<td>2.85</td>
<td>–2.64</td>
<td>0.52</td>
<td>0.05</td>
<td>2.55</td>
<td>1.15</td>
<td>2.84</td>
</tr>
<tr>
<td>[Ge-CAl\textsubscript{4}Ge]$^-$ (2a)</td>
<td>96</td>
<td>2.78</td>
<td>–2.63</td>
<td>0.50</td>
<td>0.05</td>
<td>2.53</td>
<td>1.17</td>
<td>2.79</td>
</tr>
<tr>
<td>[Sn-CAl\textsubscript{4}Sn]$^-$ (3a)</td>
<td>76</td>
<td>2.50</td>
<td>–2.78</td>
<td>0.46</td>
<td>0.20</td>
<td>2.34</td>
<td>1.34</td>
<td>2.66</td>
</tr>
<tr>
<td>[Pb-CAl\textsubscript{4}Pb]$^-$ (4a)</td>
<td>59</td>
<td>2.29</td>
<td>–2.77</td>
<td>0.46</td>
<td>0.19</td>
<td>2.31</td>
<td>1.38</td>
<td>2.60</td>
</tr>
<tr>
<td>[Si-CGa\textsubscript{3}Si]$^-$ (5a)</td>
<td>66</td>
<td>2.54</td>
<td>–2.39</td>
<td>0.41</td>
<td>0.08</td>
<td>2.74</td>
<td>1.18</td>
<td>2.80</td>
</tr>
<tr>
<td>[Ge-CGa\textsubscript{3}Ge]$^-$ (6a)</td>
<td>63</td>
<td>2.51</td>
<td>–2.35</td>
<td>0.40</td>
<td>0.07</td>
<td>2.77</td>
<td>1.20</td>
<td>2.75</td>
</tr>
<tr>
<td>[Sn-CGa\textsubscript{3}Sn]$^-$ (7a)</td>
<td>57</td>
<td>2.36</td>
<td>–2.50</td>
<td>0.35</td>
<td>0.23</td>
<td>2.59</td>
<td>1.32</td>
<td>2.62</td>
</tr>
<tr>
<td>[Pb-CGa\textsubscript{3}Pb]$^-$ (8a)</td>
<td>48</td>
<td>2.19</td>
<td>–2.47</td>
<td>0.34</td>
<td>0.23</td>
<td>2.60</td>
<td>1.35</td>
<td>2.57</td>
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</table>
FIG. 3. AdNDP bonding pattern obtained for [Si-CAl3-Si]− with occupation numbers indicated.

The detailed AdNDP analyses have revealed the bonding patterns more clearly. As shown in Fig. 3, there are five types of the occupied electrons in 1a, namely, three one-center-two-electron (1c-2e) lone pairs with occupation number (ON) of 1.91 |e|, two two-center-two-electron (2c-2e) Si–C–Si σ-bonds (ON = 1.97 |e|), two three-center-two-electron (3c-2e) Si–C–Si σ-bonds (ON = 1.84 |e|), and one four-center-two-electron (4c-2e) Si–C–Si–Al σ-bonds (ON = 2.00 |e|). The multiple-center bonding contributes to the stabilization of TBPC structure. For example, both 3c-2e σ-bonds and π-bond contribute to the rigidity of Si–C–Si axis and the 4c-2e σ-bonds to the peripheral cage refinement. The AdNDP results for other TBPC species are given in the supplementary material.51 For TBPC species with axial Si or Ge atoms, corresponding species 2a, 6a, and 7a have very similar AdNDP partitioning pattern for the occupied electrons. For those with axial Sn atoms (3a and 7a), the two 3c-2e σ-bonds in 1a become lone pairs, but the 3c-2e π-bond remains unchanged. For those with axial Pb atoms (4a and 8a), the 3c-2e π-bond in 3a or 7a becomes a 6c-2e σ-bond, which distributes more on Pb–C–Pb axis. Nevertheless, both the 3c-2e σ-bond in TBPC species with axial Si, Ge, or Sn atoms and the 6c-2e σ-bond in those with axial Pb atoms play an important role in keeping the rigidity of A–C–A axis.

C. Thermodynamic and kinetic stabilities

The species 1a–8a are the simplest anions with TBPC arrangement, which benefit their generation in the experiments. An effective experimental approach to capture such species could be the photoelectron spectroscopy. Previously, the smallest ptC species such as CaAl−, NaCaAl−, CaAlSi−, and CaAlGe− have been identified by PES.39–42 In a PES experiment, a targeted species is generated in the gas phase thermodynamically, and thus the abundances of isomers are controlled by their relative free energies on the basis of the Boltzmann distribution. To capture a targeted species in a PES experiment, it is highly desired that the species is a low-lying isomer among many possible isomers. Indeed, the PES-observed ptC species were all computationally verified to be global minima. To assess the experimental viability of our predicted TBPC species, we further explored the potential energy surfaces of CE3A2− (E = Al/Ga and A = Si–Pb) using stochastic search algorithm. Fig. 4 shows the CCSD(T) geometric and energetic results of the four lowest isomers of 1a, 2a, 6a, and 7a, the results for 3a–5a and 8a are given in the supplementary material.49, 51 Remarkably, 2a and 7a were found to be the global minima at the CCSD(T)/BSII level, and the second lowest isomers (2b and 7b) are 0.75 and 0.77 kcal/mol higher than 2a and 7a, respectively. 1a is the second lowest isomer, but it is only 0.01 kcal/mol higher than the global minimum 1b. 6a is the second lowest isomer that is 0.82 kcal/mol higher than the global minimum 6b. Other isomers, 1c, 2c, 6c, and 7c, are substantially higher than the TBPC structures by 4.71, 1.09, 3.35, and 2.03 kcal/mol. However, 3a–5a and 8a are relatively high energy isomers; they are 2.26, 8.00, 2.60, and 3.28 kcal/mol higher than their corresponding global minima (3b, 4b, 5b, and 8b), respectively. We have omitted these species from further discussion in the following.

FIG. 4. The CCSD(T)/BSII optimized structures, the point groups (in parentheses) and the relative energies (in kcal/mol) of other four lowest isomers of 1a, 2a, 6a, and 7a. The energies of TBPC isomers were referred as zero.
FIG. 5. RMSDs vs. simulation time for 1a, 2a, 6a, and 7a at both 298 and 373 K.

The kinetic stabilities of 1a, 2a, 6a, and 7a are further evaluated by the Born-Oppenheimer molecular dynamics (BOMD) simulation and isomerization reaction studies at density functional theory level. Because no isomers composing of two or more fragments were found, the most possible decay pathway for the four thermodynamically favorable species should be isomerization rather than dissociation. Taking CaSi$_3$ as an example, the isomer 1b is very similar in structure to TBPC species 1a and the isomerization of 1a to 1b only needs to squeeze the carbon in 1a out of the molecular center. The energy barrier for the process was predicted to be 9.02 kcal/mol at B3LYP/aug-cc-pVTZ level. Similar isomers were found for 2a, 6a, and 7a. At B3LYP/aug-cc-pVTZ (aug-cc-pVTZ-PP for Ga, Ge, and Sn) level, the energy barriers for the isomerizations were calculated to be 9.98, 8.87, and 10.04 kcal/mol, respectively. BOMD simulations at B3LYP/6-31G(d) (cc-pVDZ-PP for Ga, Ge, and Sn) level also suggested 1a, 2a, 6a, and 7a possess the very high kinetic stability. As shown in Fig. 5, the root-mean-square deviation (RMSD) curves in all these simulations have no significant increase, suggesting that the TBPC structures can be well-maintained at both 298 and 373 K during the simulation. The fluctuation of RMSD values is very small: the minimum values range from 0.04 to 0.07 Å, the maximum values range from 0.23 to 0.35 Å, and the average values range from 0.14 to 0.16 Å, respectively. Throughout the dynamic simulation, we could not see any indication of destruction of the TBPC structures.

On the basis of the study of the thermodynamic and kinetic stabilities of these species, we predict that the monoanionic global minima (2a and 7a) are very promising for experimental realization and 1a and 6a, which are close to global minima, could also have chance to be observed using the laser-ablation/vaporization or arc discharge techniques followed by the characterization in the negative ion photoelectron spectroscopy.

D. Vertical detachment energies

To aid the experimental observation, we computed the vertical detachment energies of these species at the OVGF/BSII level. Because 1b, 2b, 6b, and 7b are energetically competitive, we also calculated their VDEs to see whether the PES peaks can be resolved. The VDEs of 1a, 2a, 6a, and 7a were turned out to be 3.00, 2.83, 2.41, and 2.32 eV, respectively, which are all larger than those of their close isomers, being 2.49 (1b), 2.66 (2b), 2.27 (6b), and 2.26 (7b) eV, respectively. Since the HOMOs of these TBPC species are all degenerate, the PES peaks should be very high and could be regarded as the spectroscopic fingerprints of these species.

IV. CONCLUSIONS

The electropositive ligands have stabilization effect on pHC arrangement, which stems from the electron donation of such ligands that soften the rigid tetrahedral arrangement of sp$^3$ carbon bonding through weakening the directionality of sp$^3$ hybridization. Using a similar strategy, we designed a new class of the hexatomic mono-anionic species with non-classical TBPC bonding, D$_{3h}$ [A-CE$_3$-A]$^-$ (E = Al and...
Ga, A = Si, Ge, Sn, and Pb). The explorations of their potential energy surfaces at the B3LYP level and the elaborated examinations at the MP2 and CCSD level show that the eight species (1a–8a) are all minima, among which [Ge-CAl3-Ge]− (2a) and [Sn-CGa3-Sn]− (7a) are the global minima and [Si-CAl3-Si]− (1a) and [Ge-CGa3-Ge]− (6a) are the energetically competitive lowest local minima. The BOMD simulations and isomerization barriers indicate that the four species are kinetically stable. The electronic structure analyses reveal that the substantial ionic C–E bonding, the peripheral E–A covalent bonding, and the linear axial A–C–A multi-center-two electrons (mc-2e) bonding play roles in stabilizing these TBPC structures. The structural simplicity and the high thermodynamic stabilities of these species (1a, 2a, 6a, and 7a) suggest that they may be generated and captured in the gas phase. Furthermore, as mono-anionic species, their first vertical detachment energies are differentiable from those of gas phase. Furthermore, as mono-anionic species, their first vertical detachment energies are differentiable from those of gas phase. Moreover, as mono-anionic species, their first vertical detachment energies are differentiable from those of gas phase.

ACKNOWLEDGMENTS

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43See supplementary material at http://dx.doi.org/10.1063/1.4867364 for the MO plots and the AdNDP analysis results of 2a–8a and the CSD(T)/B3SI optimized geometries (in Cartesian coordinates) and absolute energies (in Hartree) of five lowest isomers of [A-C-E]-A (E = Al and Ga, A = Si, Ge, Sn, and Pb).