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A template for a planar tetracoordinate heavier group 14 atom: Global study of $C_2Si_2X^q$ (X=C, Si, Ge, Sn, Pb; q=+1, 0, -1)

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Through the global isomeric study, we computationally identified the first structural template C_2Si_2X that could encompass a planar tetracoordinate X for all the heavier group 14 elements X either in the 0, +1 or -1 charge state. We thus significantly expanded the traditional 16/17/18ve rules to 19/20/21ve for ptX.

About 40 years ago, the possibility of making and stabilizing a carbon atom in a planar tetracoordinate pattern was proposed and tested.[1,2] Since then, such an "anti-traditional" and "non-natural" structural motif has been extensively explored and successfully expanded to compounds with one or more planar tetracoordinate carbon and non-carbon centers,[3-11] hypercoordinate centers,[12-18] and even nano-like systems with attractive applications.[19-23] Up to now, it has been generally accepted that 1) to achieve a planar tetra/hyper-coordinate structure, there need good "electronic" and "mechanical" matching between the planar center and the ligands, and 2) to retain a planar tetra/hyper-coordinate structure for laboratory detection, the energetic competition from other structural forms should be little, i.e., the target system should better be a global minimum so as to facilitate its laboratory detection. Due to these critical limitations, design of a stable planar tetra/hypercoordinate structure is very challengeable. Any finding of such exotic structures not only adds to new examples, but more importantly would testify or put forward new chemical rules.

To favourably stabilize a planar tetracoordinate structure in electronics, chemists have proposed important concepts, rules and strategies.[5,24-30] Firstly, many molecules with a ptX center according to the 16[2,7], 17[2,5,8,26,29,30] and 18[5,24,25,27-29] valence electrons have been shown to possess unique stability. Amongst, the 18ve counting rule is the most famous. Species with other electron-counting rules have

been little studied.[9-11] Secondly, for the most ptX systems (e.g., CAl_4^{2-}), the bonding between the planar center and the ligands is mainly "delocalized" with the ligand elements usually possessing small electronegativity (e.g., Al, Si). Recently, it has been shown that some elements with high electronegativity can be incorporated to form multiple bonding with the planar center.[27] Finally, in a model study of $AB_4^{2-/-}$ (A=C,Si,Ge; B=Al,Ga,In), it has been shown that aromaticity and covalency have opposite effects in determining a cluster's structure, and by suitably balancing both factors, the planar tetracoordinate structure can be obtained (e.g., $SiIn_4^{2-/-}$).[5]

Understandably, due to the larger atomic radius and weaker π-conjugation ability, the heavier main-group elements seem to be much more difficult to have a low-lying ptX than the first-row main-group elements. To the best of our literature survey, we are aware of no template that can allow all the heavier main-group elements in the same column to be stably positioned in a planar tetracoordinate fashion. For example, for the 17ve XAl_4^-, ptX is not the global minimum for X=Pb, whereas for the 18ve XAl_4^{2-} and 16ve XAl_4, the ptX is the global minimum only for X=Si and Ge (see Scheme S1).[2,5,7,8] Luckily, we will show in this work that a curved SiCCSi moiety can render all the heavier group 14 elements (M=Si, Ge, Sn, Pb) to have a global minimum ptX in various charged states (i.e., q=0, +1, -1) at the CCSD(T)/def2-TZVPP//B3LYP/def2-TZVPP level. There exists appreciable delocalized π-bonding within the SiCCSi ligand, which sharply contrasts the ptXs based on the well-known Al_4-skeleton with delocalized σ-bonding. Our work represents the first template for stabilizing all the heavier main-group elements in the same column.

A global "grid-based isomeric search"[31] was performed for 15 systems $C_2Si_2X^q$ (X=C, Si, Ge, Sn, Pb; q=0, ±1). Around 400 and 120 initial input structures were generated for each $C_2Si_2X^q$ (X=Ge, Sn, Pb; q=0, ±1) and each $C_2Si_2X^q$ (X=C, Si; q=0, ±1), respectively. In total, 4372 structural calculations were carried out at the B3LYP[32] level with the def2-SVP[33] basis set. Then for the low-lying structures

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within 30 kcal/mol, we employed B3LYP with larger basis set def2-TZVPP[34] for better geometrical and frequency prediction. The single-point energies with the zero-point vibrational energy (ZPVE) correction were performed on the low-lying isomers at the CCSD(T)[35]/def2-TZVPP//B3LYP/def2-TZVPP level. All calculations were carried out with Gaussian09[36] program package.

The key structural parameters of the $C_2Si_2X^q$ ground state structures are given in Figure 1 (X=C; q=0, ±1) and Figure 2 (X=Si, Ge, Sn, Pb; q=0, ±1). Of the total 15 $C_2Si_2X^q$ systems, the low-lying structures of seven have been previously studied, i.e., (X, q)=(C, 0/±1), (Si, 0/±1), (Ge, 0).[9,10] Inspiringly, the neutral C_2Si_3[9e] and charged $C_2Si_3^+$[9h] have been produced and characterized via the FTIR and mass spectroscopy techniques, respectively. The bonding properties of all the systems were discussed by comparing with the covalent radii studied by Pyykkö[37] and Mayer bond index.

We computed the T1 diagnostics for $C_2Si_2X^q$ (X=C, Si, Ge, Sn, Pb; q=0, ±1), which is an approximate measure of multi-reference character in the wave function. It has been established that a T1 value in excess of 0.02 indicates a significant multi-reference character for closed-shell systems.[38] For open-shell systems, it has been shown that T1 diagnostic values up to 0.045 may be acceptable.[39] Table S3 lists the T1 diagnostic values of the global structures. In our systems, except for C_3Si_2 (0.022) and $C_3Si_2^-$ (0.052) whose T1 values are a little high, while the others are well below the threshold and expected to bear little multi-reference character. For the higher energy isomers (30 kcal/mol), the T1 diagnostic values for both the open and closed-shell species are lower than the threshold. The detailed data are supplied in Supporting Information.

When X is C, the three systems are carbon-rich clusters $C_3Si_2^q$ (q=0, ±1). Their global nature is quite different from the other clusters with heavier X. The linear structure of $C_3Si_2^q$ (q=0, ±1) was a global minimum. As shown in Figure 1, the two C-C distances and one C-Si distance of $C_3Si_2^+$, C_3Si_2. $C_3Si_2^-$ are a little shorter than the conventional double bond,[34] while their Mayer bond index values are more than 1 (see Table S4). Thus, both C-C and C-Si bear the double bonding feature, indicative of the noticeable cumulenic characteristics. Note that the ptC structure is truly the local minimum for $C_3Si_2^+$. C_3Si_2. $C_3Si_2^-$, yet it is very high in energy with the relative energy being 18.6, 29.7 and 35.4 kcal/mol, respectively (see Table S9).

For $C_2Si_2X^q$ with heavier group 14 (X=Si, Ge, Sn, Pb; q=0, ±1), the global structure shows quite different feature from $C_3Si_2^q$ (X=C, q=0, ±1). Comparing with the covalent radii,[34] all the distances (see Figure 2) between central X-atom and ligands are of single bonding. The Mayer bond index values of X-Si$_1$/X-Si$_4$ lie in between 0.386/0.374 (X=Pb, q=+1/X=Pb, q=0) and 0.869/0.869 (X=Si, q=-1), and the Mayer bond index values of X-C$_2$/X-C$_3$ range from 0.314/0.314 (X=Sn, q=-1) to 0.778/0.778 (X=Si, q=0), both indicative of the single bonding (see Table S5). So $C_2Si_2X^q$ (X=Si,

minimum $C_3Si_2^q$ (q=0, ±1) at the level of CCSD(T)/def2-TZVPP//B3LYP/def2-TZVPP.

Ge, Sn, Pb; q=0, ±1) each have a planar tetracoordinate global minimum structure.

By analyzing the ground state structures of $C_2Si_2X^q$ (X=Si, Ge, Sn, Pb; q=0, ±1), we can find that although they differ either in the valence electrons or in the central X-atom, they each have a curved ligand skeleton SiCCSi. The bonding feature of this ligand skeleton can be discussed in terms of the bond distance, bond index and orbital aspects. Firstly, the C-C and C-Si bond lengths lie within the range of the conventional double bonds.[34] Secondly, the Mayer bond index values of Si$_1$-C$_2$/Si$_4$-C$_3$ range from 1.162/1.162 (X=Si, q=+1) to 1.648/1.648 (X=Pb, q=-1), and the Mayer bond index of C$_2$-C$_3$ lie in between 1.242 (X=Si, q=0) and 1.698 (X=Pb, q=-1). Thus, the bond index characteristics support the presence of the C=Si and C=C double bonds within SiCCSi. As a result, the SiCCSi ligand possesses the cumulenic property. The cumulenic SiCCSi is also supported by the natural bond orbital (NBO) analysis in Figure S1. As all molecules have similar orbitals, we choose C_2Si_2Ge as an example (see Figure 3). The π orbital (HOMO) is mainly positioned within the ligand-ligand bonding and the HOMO-5 is a delocalized π orbital, which is crucial for the molecule's stability. The two π orbitals not only demonstrate that the ligand skeleton is a cumulenic structure, but also help to stabilize the planar geometry to be the ground structure. It should be pointed out that as in most nonstoichiometric molecules, any one simple valence structure may not be sufficient to describe the unique bonding situation of the above ptX. Instead, it could have contribution from several resonant valence structures (see Scheme S2).

In addition, the natural population analysis (NPA) of the global structures are summarized in Table S6. The more electronegative
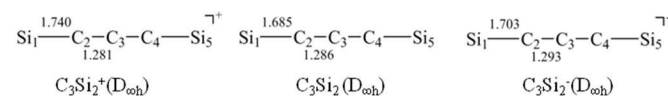

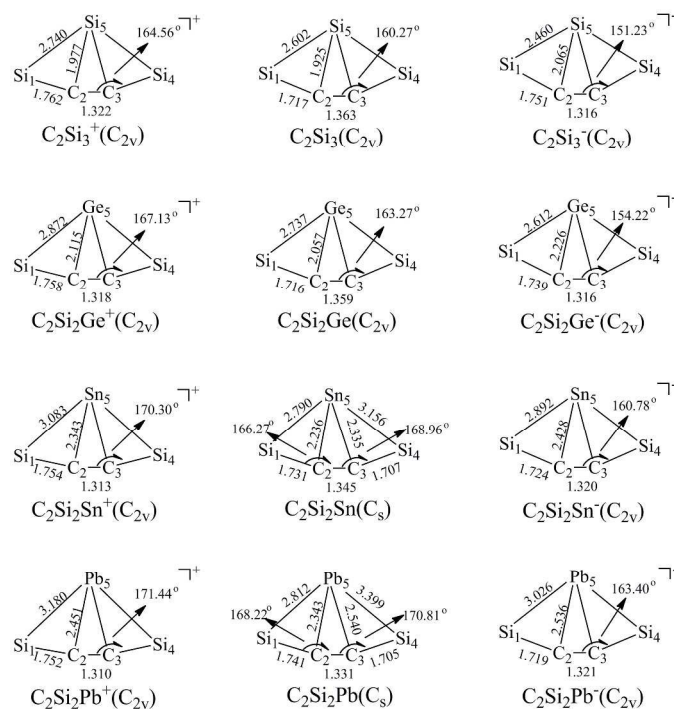Figure 1. The key geometrical parameters of the global

Figure 2. The key geometrical parameters of the global minimum $C_2Si_2X^q$ (X=Si, Ge, Sn, Pb; q=0, ±1) at the level of CCSD(T)/def2-TZVPP//B3LYP/def2-TZVPP.

carbon atoms carry negative charges, while the other atoms all possess the positive values. By comparing C_2Si_2X and $C_2Si_2X^+$, we can find that it is the two silicon atoms of the ligand skeleton SiCCSi that mainly lose electrons. However, from C_2Si_2X to $C_2Si_2X^-$, besides the two silicon atoms of SiCCSi, the central X-atom also attracts the additional negative charges. Clearly, with the increase of the valence electrons in the order $C_2Si_2X^+$ (19ve)<C_2Si_2X (20ve)<$C_2Si_2X^-$ (21ve), the Si-atom in SiCCSi becomes less positively charged. In Figure 2, we can find some interesting structural changes. From $C_2Si_2X^+$ to C_2Si_2X, the internal C_2-C_3 bond within the SiCCSi ligand is lengthened, while the other bonds (Si_1-C_2/Si_4-C_3, X-Si_1/X-Si_4 and X-C_2/X-C_3) become shortened. This is consistent with the corresponding SOMO ($C_2Si_2X^+$) and HOMO (C_2Si_2X) features, both of which are associated with the C_2-C_3 π anti-bonding and the π bonding within the X-Si_1-C_2/X-Si_4-C_3 rings. Similarly, from C_2Si_2X to $C_2Si_2X^-$, both the C_2-C_3 and X-Si_1/X-Si_4 bonds are shortened, which is caused by SOMO in $C_2Si_2X^-$. As a result of the above structural changes, the SiCCSi ligand skeleton becomes more curved with the increasingly smaller Si-C-C bond angles. In addition, for $C_2Si_2X^q$
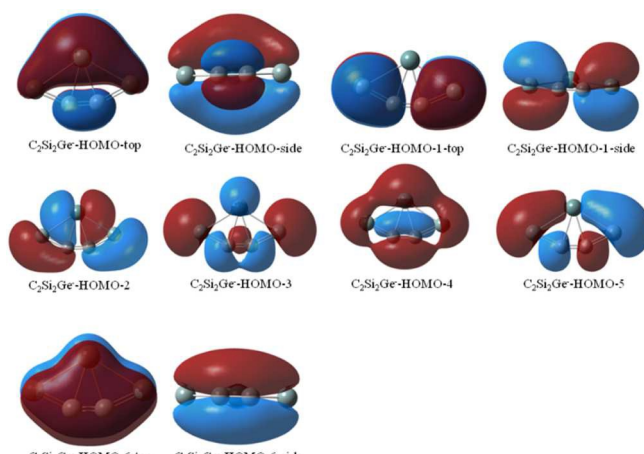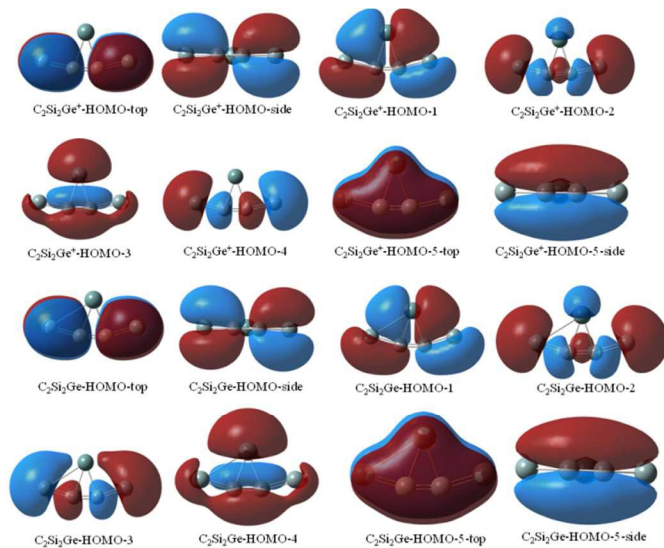

Figure 3 Molecular orbitals of the global minimum $C_2Si_2X^q$(X= Si, Ge, Sn, Pb; q=0, ±1) at the level of B3LYP/def2-TZVPP.

with the same valence electrons, the Si-C-C bond angles become wider on increasing the radius of central X-atom. The spin density of open-shell systems are summarized in Table S7. For q=+1, the spin density is mainly distributed over the ligand skeleton, especially on two silicon atoms. While for q=-1, the spin density is mostly localized on the central X-atom.

Based on our study of $C_2Si_2X^q$ (X=C, Si, Ge, Sn, Pb; q=0, ±1), the first template SiCCSi for stabilizing all the heavier group 14 elements in a ptX pattern was found. The SiCCSi ligand skeleton possesses the cumulenic characteristics, which should contribute to the stabilization of ptX. The good rigidity of the SiCCSi ligand and the appreciable interaction between the ligand the central X-atom cooperatively make the global ptX! As we know, most ptX species obey the 17ve and 18ve rules. Species with more than 18ve have been little studied. Notably, we are aware that most known ptX systems with 16/17/18ve bear the Al_4 ligand skeleton, which is associated with the σ-delocalization, Replacing Al_4 with the π-delocalized SiCCSi ligand can not only globalize ptX for all the heavier group 14 elements, but also expand the electron-counting rule to 19/20/21ve. So $C_2Si_2X^q$ (X=C, Si, Ge, Sn, Pb; q=0, ±1) should represent a new class of the ptX family. The present idea that stabilizing a ptX center by a π-delocalized ligand skeleton should open a new way towards designing novel ptX systems.

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Graphical abstract for

A template for a planar tetracoordinate heavier group 14 atom: Global study of

$C_2Si_2X^q$ (X=C, Si, Ge, Sn, Pb; q=+1, 0, -1)
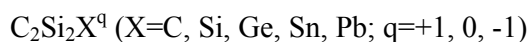
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We computationally identified the first universal structural template C_2Si_2X that could encompass a planar tetracoordinate X for all the heavier group 14 elements X either in the 0, +1 or -1 charge state.

$C_2Si_2X^q$

$\left(\begin{array}{c} X=Si,Ge,Sn,Pb \\ q=+1,0,-1 \end{array} \right)$