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Planar Hypercoordinate Motifs in Two-Dimensional Materials

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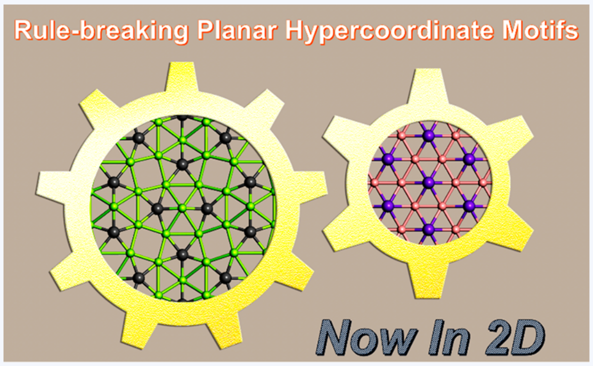

CONSPECTUS: As one of the most important and versatile elements, carbon renders itself as one of the most fundamental and cutting-edge topics in chemistry, physics, and materials science. Many carbon-based chemical rules were established accordingly. While the tetrahedral predilection of tetracoordinate carbon has been a cornerstone of organic chemistry since 1874, almost a century later tetracoordinate carbon was found to be able to adopt planar structures known as planar tetracoordinate carbon (ptC), which are stabilized electronically by good π-acceptor (delocalization of a lone electron pair of ptC) or σ-donor (promoting electron transfer to electron-deficient bonding) substituents or mechanically by appropriate steric enforcement. The experimental and theoretical achievements for the rule-breaking ptC species totally refreshed our understanding of chemical bonding and triggered exploration of peculiar molecules featuring planar pentacoordinate carbon (ppC) and planar hexacoordinate carbon (phC) as well as other outlandish species such as planar hypercoordinate silicon.

While the planar hypercoordinate carbon chemistry has been gradually established for molecules in the past five decades, there is growing interest in pursuing their extension systems, especially in two-dimensional (2D) space as a result of the recent extensive studies of graphene and its analogues. Though the natural 2D layered crystals do not contain any planar hypercoordinate carbon or silicon, several 2D nanosheets featuring planar or quasi-planar hypercoordinate ones have been theoretically suggested. Encouragingly, these unique planar configurations possess decent stabilities, and some of them are even the global minimum structure, exhibiting great potential for experimental realization. As the nature of a material is mainly determined by its structural characteristics (e.g., dimensionality, crystallography, and bonding), the combination of planar hypercoordinate chemistry and 2D nanoscience not only endows these rule-breaking systems with the merits of 2D materials but also may offer various promising properties and applications. For example, an unusual negative Poisson's ratio can be found in ppC-containing Be_5C_2 and planar pentacoordinate silicon (ppSi)-containing CaSi monolayers, of which the former has an anisotropic Dirac cone and the latter is a semiconductor with a desirable band gap for the semiconductor industry. Specially, shortly after the theoretical prediction, a planar hexacoordinate silicon (phSi)-containing Cu_2Si monolayer was experimentally synthesized and characterized with the 2D Dirac nodal line fermion, which offers a platform to achieve high-speed, low-dissipation nanodevices.

In this Account, we review the recent progress, mostly by density functional theory (DFT) computations, in designing 2D materials with planar hypercoordinate motifs. We describe the key achievements in this field, paying special attention to the "bottom-up" and "isoelectronic substitution" design strategies. In addition, the fundamental stabilization mechanisms of planar hypercoordinate motifs in an infinite layer are discussed. We hope that this Account will inspire more experimental and theoretical efforts to explore nanomaterials with such unconventional chemical bonding.

INTRODUCTION

The main-group elements typically obey the well-precedented bonding rules. One prominent case is carbon, which generally has a maximum coordination number of 4 in known molecules. Its conventional bonding rule outlines the tetrahedral tetracoordination, planar tricoordination, and linear dicoordination configurations. Among them, the tetrahedral predilection of tetracoordinate carbon is one of cornerstones in organic chemistry and biochemistry. However, tetracoordinate carbon need not always implement the tetrahedral arrangement. In 1968, Monkhorst described a unique planar tetracoodinate carbon (ptC) in a transition state (i.e., planar methane) for the interconversion of tetrahedral carbon-centric enantiomers.[1] Two years later, by analyzing the molecular orbitals of the hypothetic planar methane, Hoffmann, Alder,

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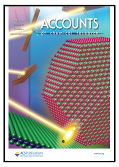

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and Wilcox[2] proposed that the key to stabilizing the ptC moiety is to delocalize/incorporate the electron density from its $2p_z$ orbital by using good π acceptors/σ donors. Alternatively, the ptC moiety can be enforced to have the strained geometry by steric constraints.[2,3] In 1991, Schleyer and Boldyrev[4] further codified the bonding rules for the ptC moiety based on joint electronic and geometrical considerations. Since then, ptC chemistry has been a novel subject of extensive studies, and many ptC molecules have been achieved in both simulations and experiments.[5−7]

The rule-breaking ptC has stimulated studies on constructing other types of planar carbon having coordination numbers larger than 4, such as planar pentacoordinate carbon (ppC)[8,9] and planar hexacoordinate carbon (phC).[10] The central planar hypercoordinate carbon element can be further replaced with silicon (Si), germanium (Ge), boron (B), or even transition metal elements.[5,11,12] During the past five decades, the family of planar hypercoordinate species has been greatly enriched. These unique bonding patterns not only are of fundamental significance for enriching our knowledge on chemical bonding but also lead to entirely new types of molecules.

Reduced dimensionality and outlandish topology, which may bring unexpected properties and applications, are always desirable for materials innovation. It is not a surprise that the past several years have witnessed increasing interest in extending planar hypercoordinate bonding into macroscopic nanomaterials. In particular, driven by the rapid research progress on two-dimensional (2D) materials,[13] substantial attempts have been made to design 2D materials with such rule-breaking chemical bonding. This Account focuses on the recent efforts in the arena of 2D materials featuring planar hypercoordinate carbon or silicon. We describe the key achievements in this field together with our initial motivations and construction strategies and discuss the fundamental stabilizing mechanisms of planar hypercoordinate species in an infinite layer. In addition, we give a glimpse of planar hypercoordinate elements beyond carbon and silicon in 2D nanosheets.

THEORETICAL PROCEDURE FOR DESIGNING A NEW 2D MATERIAL

In silico structure prediction based on modern quantum mechanics (dominated by DFT) and structural evolution methods has been vital for the rational design and innovation of 2D materials. In this section, we briefly outline the theoretical framework for designing a 2D material, restricting our discussion to a typical two-step computational protocol,[14,15] which addresses the most fundamental issues for a newly predicted 2D material: (1) whether the material is stable (thermodynamically, dynamically, thermally, and mechanically) and (2) whether the material is a global minimum on the potential energy surface (PES). The former is a necessity, and the latter is a plus.

The stability is of the largest concern for any predicted 2D material. Typically, the thermodynamic, dynamic, thermal, and mechanical stabilities are evaluated. Thermodynamic stability can be implicitly indicated by the calculated cohesive energy, which is the energy difference of the atoms in the neutral free states and the crystalline bonding state. A more positive cohesive energy represents a stronger connected network and a higher thermodynamic stability. The thermal stability can be implicitly indicated by first-principles molecular dynamics (FPMD) simulations in the *NVT* ensemble. It is expected that the candidate has a high (at least 300 K) critical temperature, which is the temperature at which the structural integrity is maintained throughout the full simulation process. Specially, to give a reasonable assessment of the thermal stability, the duration of simulation should be long enough to ensure the convergence of the 2D system with respect to total energy and atomic positions; in this regard, typically a total time of 10 ps is a satisfactory choice.[14,15] The dynamic stability is even more critical: a predicted nanosheet should have no (or insignificant) imaginary phonon modes in its phonon spectrum. To meet the mechanical stability criteria, the calculated elastic constants C_{ij} of a 2D material should satisfy $C_{11}C_{22} - C_{12}{}^2 > 0$ and $C_{66} > 0$.

Addressing the aforementioned stability issues can guarantee that the predicted 2D material is a stable local minimum. Since a global minimum holds greater potential for experimental realization, it is also important to carry out a global minimum search in the 2D space. Currently, various structure prediction methods and computer software are available. Interfacing with the DFT code VASP, the particle swarm optimization implemented in the CALYPSO code[16] is the most widely used approach to search for a global minimum in the 2D space at a given chemical composition.

DESIGN STRATEGIES TO ACHIEVE 2D MATERIALS WITH PLANAR HYPERCOORDINATE MOTIFS

The unusual planar hypercoordinate bonding arrangements in molecules are essentially stabilized by electronic effects and also by mechanical effects (e.g., steric enforcement from small rings and cages). Similar stabilization mechanisms are expected to hold true for 2D materials and have been utilized to design the 2D analogues, especially the concept of electronic stabilization. It should be noted that the mechanical stabilization for the 2D systems is implicitly reflected by the electronic stabilization because the planar hypercoordinate moieties are confined in a 2D plane and stabilized with the help of electronic-stabilization-induced steric forces. To understand the stabilization mechanisms of a 2D structure, we generally study its charge distribution, examine its deformation charge density, and analyze its chemical bonding patterns by the SSAdNDP method.[17]

Typically, the rule-breaking 2D materials are designed by three strategies, namely, bottom-up, isoelectronic substitution, and direct global minimum search. The bottom-up strategy contains two steps: finding a promising building block candidate and then assembling the candidate in a 2D plane. The key of the isoelectronic substitution strategy is to find a planar hypercoordinate nanosheet, followed by substituting the atoms of interest but retaining the number of valence electrons. The direct global minimum search strategy is a convenient way to design a rule-breaking 2D nanosheet, during which an electron-deficient ligand might be adopted, such as B, Al, or Be. Most 2D materials containing planar hypercoordinate motifs that we have designed in past decade are based on the bottom-up and isoelectronic substitution concepts since they are very effective and helpful in the construction of new candidates, and the global minimum search strategy is widely used to examine whether a newly predicted material is of the lowest energy in the 2D space.

■ PLANAR TETRACOORDINATE CARBON IN 2D MATERIALS

Though many ptC molecules have been predicted and some of them have been observed experimentally,[5−7] achieving a ptC-containing 2D nanosheet is still considerably challenging because it is very difficult to electronically and mechanically fit the unfavorable ptC moiety into the infinite 2D space. Encouragingly, in a landmark study in 2004, Hoffmann and co-workers[18] predicted the first 2D system containing ptC, namely, a C_5Pt 2D network (Figure 1). This network can be regarded as the assembly of Pt^{2+} and the ptC C_5^{2-} moiety, the smallest carbon cluster containing ptC predicted by Merino and co-workers.[19,20] Although the stability of the C_5Pt network was not fully explored, it does provide a feasible route for designing a ptC 2D material: a ptC-containing molecule can serve as a building block to realize a ptC-containing 2D nanosheet. This strategy is similar to the bottom-up synthesis strategy in experiment.

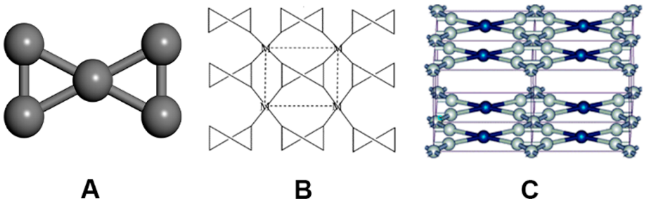


Figure 1. (A) Geometric structure of the C_5^{2-} moiety. (B) Schematic diagram of a 2D framework containing C_5 building blocks bridged by metal ions. (C) Geometric structure of the C_5Pt 2D network. Reproduced from ref 18. Copyright 2004 American Chemical Society.

In light of the ptC bonding in the CB_4 molecule (Figure 2A),[21] in 2009 Wu et al.[22] designed a B_2C monolayer (Figure 2B,C) in which each C atom binds to four B atoms nearly in the same plane to form a quasi-ptC moiety with a buckling of 0.08 Å. The B_2C monolayer exhibits good thermal, mechanical, and dynamical stabilities and has been suggested as a superconductor with a theoretical transition temperature of ~19.2 K.[23] However, a subsequent comprehensive global minimum search on 2D boron−carbon compounds executed by Luo et al.[24] revealed that this B_2C monolayer is not the lowest-energy configuration on the PES. In the global minimum structure, half of the C atoms are ptC (Figure 2D), which is similar to the T11 ptC CB_4 motif previously reported by Pei and Zeng.[21] They also demonstrated that the same ptC moiety can be found in the "most stable" B_3C and B_5C monolayer structures. However, both the B_3C and B_5C monolayers are unstable, as they have large imaginary frequencies in their phonon spectra. Very recently, Chang et al.[25] theoretically designed a quasi-ptC-containing B_4C_3 monolayer based on a B_4C_3 neutral cluster (Figure 2E).[10] The B_4C_3 monolayer exhibits strong visible-light adsorption and holds good potential for photocatalytic CO_2 reduction.

While several ptC-containing 2D materials have been proposed, it is still difficult to place ideal ptC motifs in a global minimum 2D structure. In 2014, we found that the bottom-up strategy can be used to conquer this challenge.[26] In this case, a D_{2h} $C_2Al_6^{2-}$ building block featuring ptC was designed first (Figure 2F), followed by the construction of an Al_2C monolayer (Figure 2G) in which all of the C atoms are ideal ptC. The Al_2C monolayer has good thermal and dynamical stabilities and was confirmed as the global minimum in the 2D space. This nanosheet is a semiconductor with an indirect band gap of 1.02 eV and anisotropic carrier mobility. Besides, a quasi-ptC was found in the second-lowest-energy Al_2C nanosheet, which possesses a pentagon configuration similar to that in the PdS_2 monolayer.[27] It should be noted that in parallel to our work, Zeng and co-workers[28] also reported this Al_2C nanosheet, which was identified by using a direct global search. They found that such an Al_2C nanosheet could serve as a promising donor material in solar cells. For instance, the theoretical power conversion efficiency of the Al_2C/WSe_2 van der Waals heterojunction can reach ~18.4%. Moreover,

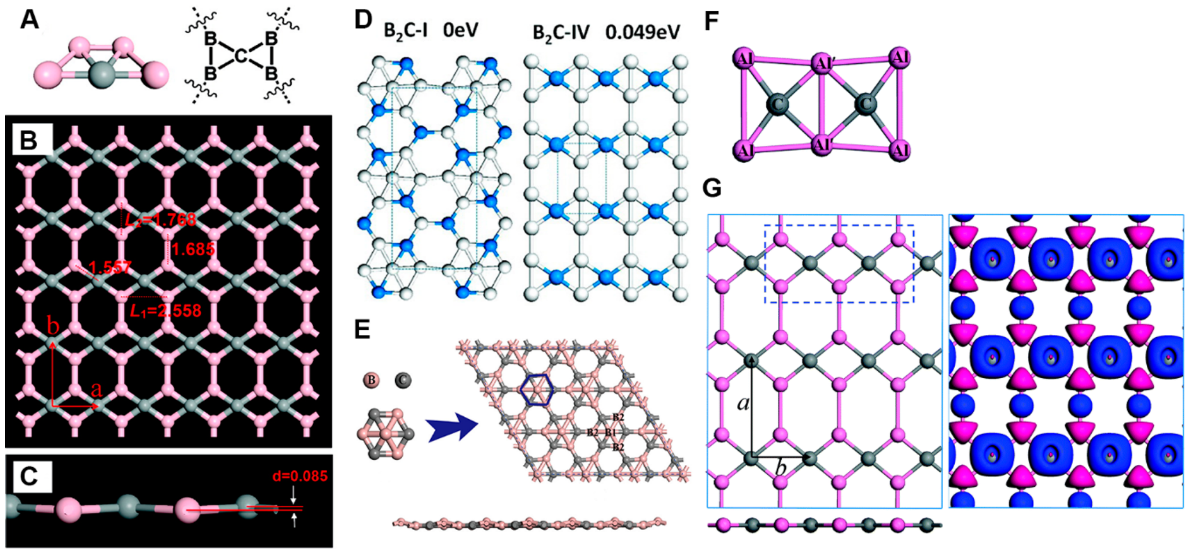


Figure 2. (A) Views of the CB_4 molecule (left) and building block (right). (B) Top and (C) side views of the B_2C monolayer. (D) Two low-energy B_2C structures from the global minimum search. (E) Geometric structures of the B_4C_3 molecule and B_4C_3 monolayer. (F) View of $C_2Al_6^{2-}$. (G) Structure (left) and deformation charge density (right) of the Al_2C monolayer. Blue and red refer to electron-rich and -deficient areas, respectively. Reproduced from (A−C) ref 22, (D) ref 24, and (E) ref 25 and with permission from (F, G) ref 26. Copyright 2009, 2011, and 2019 American Chemical Society and 2014 Royal Society of Chemistry, respectively.

their global search outlined two other ptC-containing nanosheets, namely, AlC and Al_3C monolayers.

The exploration of the basic building blocks is very helpful for us to understand the extended 2D system. The fundamental stabilization mechanism of ptC in the Al_2C monolayer can be deduced from its $C_2Al_6^{2-}$ building block. In the $C_2Al_6^{2-}$ molecule, the natural charges are $-2.53e$ for the ptC and $+0.42e$ (or $+0.70e$) for the Al ligands, indicating the good ability of Al as a σ donor to maintain the basic ptC unit. Moreover, in $C_2Al_6^{2-}$ the electrons in the p_z orbitals of the ptC centers are well delocalized, thus stabilizing the unique ptC molecule. In the Al_2C monolayer, which is very similar to the $C_2Al_6^{2-}$ molecule, considerable electron transfer ($0.8e$) from the electropositive Al ligands to the ptC atoms occurs, and the electrons are well delocalized over Al−C bonds (Figure 2G). This electron-stabilizing mechanism has also been found in many 2D systems containing planar hypercoordinate motifs.[14,15,22,25] Thus, the electronic stabilization mechanism established in ptC molecules[2] also plays an essential role in the extended 2D materials.

A recent theoretical study by Liu et al.[29] reported a BeC monolayer identified by a global minimum search that is a global minimum featuring ideal ptC. The BeC monolayer is a semiconductor with an indirect band gap of 1.01 eV and ultrahigh room-temperature carrier mobilities.

The ptC and quasi-ptC motifs can also be stabilized by using transition metal atoms. In 2012, by means of an intensive structural search, Zhang and co-workers[30] obtained a 2D tetragonal TiC sheet that is a natural narrow-band-gap semiconductor (0.21 eV) involving quasi-ptC atoms (0.88 Å buckling). The TiC monolayer exhibits substantial ferromagnetism when tailored into nanoribbons and hence is promising for applications in electronics and spintronics. Recently, Zhou et al.[31] predicted a new class of quasi-ptC TaCX monolayers (X = Cl, Br, I). Because of the d−d band inversion from the Ta atoms, this class of nanosheets are intrinsic quantum spin Hall insulators with a large tunable band gap (>0.23 eV). Alexandrova and co-workers[32] explored the connection of ptC and Co or Ni atoms in 2D space and proposed that the Co_2C and Ni_2C monolayers are local minima featuring quasi-ptC and ptC, respectively. Both the Co_2C and Ni_2C monolayers are metallic, and the former has intrinsic ferromagnetism.

■ PLANAR PENTACOORDINATE OR HEXACOORDINATE CARBON IN 2D MATERIALS

The pursuit of 2D ptC-containing solids has encouraged scientists to develop more challenging extended planar carbon systems, i.e., ppC- and phC-containing 2D monolayers. A breakthrough in this arena came in 2014 with the prediction of the first 2D global minimum structure involving quasi-phC.[14] In this case, we utilized an isoelectronic substitution strategy (Figure 3A): the Be and B atoms of the BeB_2 monolayer were substituted with C and Be atoms, respectively. The substitution can yield an isoelectronic Be_2C monolayer, although every two neighboring Be atoms are prone to move into two planes after structure optimization (Figure 3B). It should be noted that the isoelectronic substitution strategy has played a key role in the discovery of planar hypercoordinate carbon and silicon molecules. One prominent example is that numerous ptC, ppC, and planar tetracoordinate silicon (ptSi) species were predicted via isoelectronic substitution with the number of valence electrons maintained (e.g., 16, 17, or especially 18), and some candidates, such as CAl_4^- and its relatives,[33] have been detected experimentally. In fact, the aforementioned Al_2C monolayer (Figure 2G)[26] is isoelectronic to the B_2C monolayer (Figure 2B).[22] It is highly recommended that the PES and the stability of the candidate be systematically explored after the isoelectronic substitution is performed.[8,14,34]

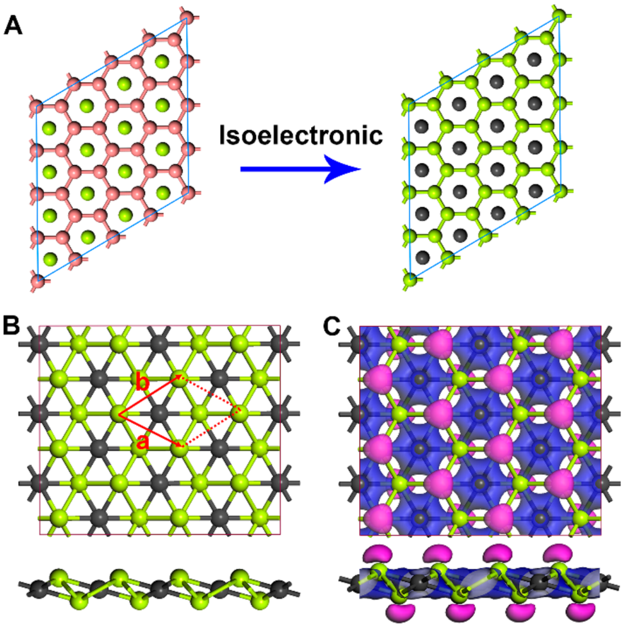


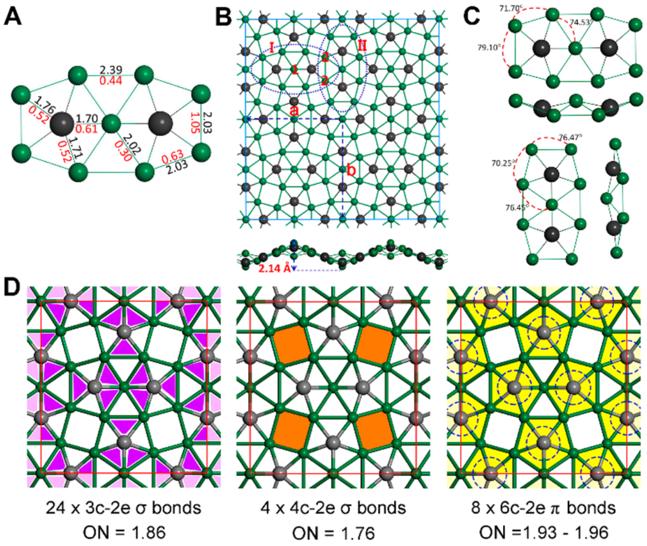
Figure 3. (A) Schematic of the isoelectronic substitution to go from BeB_2 to Be_2C. (B) Structure and (C) deformation charge density of the Be_2C monolayer (Be_2C−I). Blue and pink refer to electron-rich and -deficient areas, respectively. Reproduced with permission from ref 14. Copyright 2014 Wiley-VCH.

The Be_2C monolayer was identified with good thermal, mechanical, and dynamical stabilities. The deformation electronic density analysis demonstrated that the stabilization of quasi-phC originates from electron transfer from the p orbital of Be to the quasi-phC and back-donation of these electrons to the whole moiety (Figure 3C), a mechanism similar to that in the Al_2C monolayer. In addition to the exotic geometric structure, the Be_2C monolayer has a medium direct band gap of 2.34 eV and shows great potential as an anode material for high-performance lithium-ion batteries.[35] During the exploration of the PES, we also found a ptC-containing Be_2C isomer (Be_2C−II) that is 183 meV/atom higher in energy than the global minimum quasi-phC-containing Be_2C monolayer (Be_2C−I).

The discovery of the Be_2C−I monolayer inspired exploration of other 2D Be_2C phases. By means of a global minimum structure search without constraining the atoms in a plane, Qian et al.[36] found two new 2D Be_2C structures featuring quasi-phC, labeled as the β-Be_2C and γ-Be_2C monolayers. Though slightly higher in energy than Be_2C−I, both the β-Be_2C and γ-Be_2C monolayers exhibit considerable thermal and kinetic stabilities. Like Be_2C−I, β-Be_2C and γ-Be_2C are semiconductors with medium direct band gaps of 2.16 and 1.97 eV, respectively. The different Be−C patterns render β-Be_2C and γ-Be_2C unique mechanical properties different from those of Be_2C−I, i.e., a negative Poisson's ratio, and thus, the two metastable isomers are also fascinating. During the structure search, they found a Be_2C slab named α-Be_2C that contains a peculiar octacoordinated carbon moiety, probably a

2D material containing an octacoordinated carbon motif. Independently, Naseri et al.[37] also predicted the γ-Be_2C monolayer, denoted as Be_2C−III in their work, as it was motivated by a BeB_2 monolayer,[38] and pointed out that the band gap of the γ-Be_2C monolayer can be effectively modulated by external biaxial strains.

The first quasi-ppC-containing 2D material, namely, the Be_5C_2 monolayer,[15] was designed 2 years later after the discovery of the Be_2C−I monolayer. In that case, we also used the bottom-up strategy: a D_{2h} $Be_9C_2^{4-}$ building block featuring ppC was identified first (Figure 4A), followed by assembly of a Be_5C_2 monolayer with fusing of the Be_9C_4 moieties (Figure 4B). After exploration of PES, we found that this Be_5C_2 monolayer is the global minimum structure. Though the Be_5C_2 monolayer is remarkably buckled (2.14 Å), its quasi-ppC moieties do possess good planarity (Figure 4C). The sum of the five Be−C−Be angles in the two types of quasi-ppC moieties are 364.84° and 371.44°, which are close to the ideal value (360°). The stabilizing mechanism of the quasi-ppC in the Be_5C_2 monolayer is the same as that in the Be_2C[14] and Al_2C[26] monolayers. Such fascinating structural features bring the Be_5C_2 monolayer extraordinary properties. The Be_5C_2 monolayer is semimetallic and has an unusual negative Poisson's ratio.



24 x 3c-2e σ bonds
ON = 1.86
4 x 4c-2e σ bonds
ON = 1.76
8 x 6c-2e π bonds
ON =1.93 - 1.96

Figure 4. Structures of (A) $Be_9C_2^{4-}$, (B) Be_5C_2 monolayer, and (C) Be_9C_2 moieties in the Be_5C_2 monolayer. (D) Schematic of the SSAdNDP chemical bonding pattern. ON is short for occupation number. From ref 15. CC BY 4.0.

Understanding the nature of such unique chemical bonding is critical for developing planar hypercoordinate carbon chemistry. To decipher the rule-breaking planarity, it is a must to explore why the C atoms are prone to a planar configuration. Actually, it is well-established that electron delocalization plays an important role in the planarity of boron compounds.[39] The chemical bonding of the Be_5C_2 monolayer was explored using the SSAdNDP methodology,[17] which is a powerful tool for construing the nature of bond localization as well as delocalization in periodic solids and nanostructures. The SSAdNDP approach can intelligently partition the electron density matrix into n-center-two-electron (nc-2e) bonds, where n is the total number of atoms in the bond. Interestingly, for the Be_5C_2 monolayer (Figure 4D), there are no classical lone pairs or localized 2c-2e bonds; one unit cell contains 24 delocalized 3c-2e σ bonds (Be−C−Be triangles), four delocalized 4c-2e σ bonds (Be_4 squares), and eight delocalized 6c-2e π bonds (Be_5C moieties). Thus, the existence of significant electron delocalization could stabilize the quasi-ppC moieties in the Be_5C_2 nanosheet.

More recently, Zhu et al. identified entirely planar MC monolayers (M = Co, Ni, Cu) containing ppC moieties by comprehensive crystal structure searching.[40] Similar to the Be_5C_2 monolayer, these ppC motifs are stabilized by delocalized multicenter σ and π bonds. Although a few planar hypercoordinate carbon-containing 2D materials have been predicted theoretically in the last years, none has been synthesized experimentally to date. However, as the Be element seems to be a "magic" ligand, which can yield candidates with ptC, quasi-ppC, ppC, or quasi-phC moieties, we hope that some of the rule-breaking nanosheets based on Be ligands can be realized in the near future.

PLANAR HYPERCOORDINATE SILICON IN 2D MATERIALS

Silicon is in the same main group of elements as carbon, and accordingly, it is a key component of planar hypercoordinate chemistry. However, in sharp contrast, there are rare cases of planar hypercoordinate silicon in both molecules and 2D materials, though it seems easier for silicon to adopt the planar tetracoordination.[41]

A 2D system with ptSi, namely, a SiC_2 monolayer,[42] was designed in 2011, inspired by a ptSi-containing molecule, C_{2v} SiC_4 (Figure 5A). The fundamental stabilizing mechanism of ptSi in the SiC_2 monolayer is the removal of the unfavorable ptSi lone pair, which is different from ptC in the Al_2C and B_2C monolayers. Nevertheless, this SiC_2 monolayer is not a global minimum.[43] Another case in this arena came in 2018 with the prediction of a ptSi-containing SiC_8 monolayer by Sun and co-workers, which has good potential as an anode material for Li-ion batteries.[44]

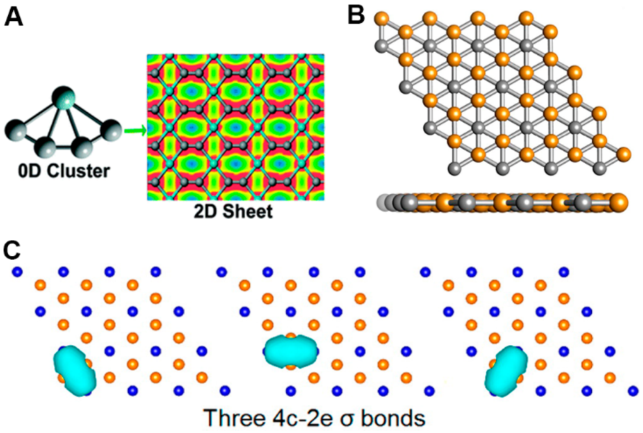


Figure 5. (A) Schematic from the inspiring SiC_4 molecule to the SiC_2 monolayer. (B) Structure and (C) SSAdNDP chemical bonding pattern of the Cu_2Si monolayer. Reproduced from (A) ref 42 and (B, C) ref 45. Copyright 2011 and 2015, respectively, American Chemical Society.

In 2014, Yang et al.[45] predicted a phSi-containing Cu_2Si monolayer that is a global minimum (Figure 5B). The phSi moiety is stabilized by the multicenter σ bonds; as revealed by SSAdNDP analysis, besides lone pairs on the Cu atom, the remaining electrons are delocalized as 4c-2e σ bonds over Cu–Si–Cu–Si rhombuses (Figure 5C).[45] Recently, Yan et al. predicted that this unique monolayer is an intrinsic superconductor ($T_c \approx 4.1$ K).[46] The experimental realization of 2D materials with planar hypercoodinate silicon motifs is ahead of that of the carbon counterparts. In around 2.5 years after Yang's theoretical prediction, Feng et al.[47] experimentally synthesized the Cu_2Si monolayer via direct evaporation of Si on a single-crystal Cu(111) plane in an ultrahigh vacuum. The joint angle-resolved photoemission spectroscopy and first-principles studies identified the unusual 2D Dirac nodal line fermions in the band structure of the Cu_2Si monolayer, which offer a platform to realize high-speed, low-dissipation nanodevices.

Besides Cu, other transition metals could serve as ligands to stabilize phSi in 2D nanosheets. For example, Yang et al.[48] predicted a nearly planar Ni_2Si monolayer by means of a global minimum search. Different from the Cu_2Si monolayer, the quasi-phSi moiety in the Ni_2S monolayer is stabilized by delocalized 3c-2e σ bonds over Ni–Si–Ni triangles. Recently, Sun et al.[49] proposed a quasi-phSi-containing Fe_2Si monolayer by extracting one stoichiometric layer from its bulk counterpart. This nanosheet is a ferromagnetic half-metal with a Curie temperature of over 780 K, and the Curie temperature can be further improved by applying biaxial strains. Using the same exfoliation strategy, Migas et al.[50] designed a series of alkaline-earth-metal based semiconducting 2D nanosheets containing quasi-phSi, namely, M_2Si monolayers (M = Mg, Ca, Sr, Ba). However, except for the Mg_2Si monolayer, these M_2Si monolayers have small imaginary frequencies near the Γ point.

In contrast to ptSi and phSi, no theoretical or experimental cases were reported for extending ppSi into periodic systems until 2018, most likely because of significant difficulty in finding an appropriate ligand to stabilize the quite unfavorable ppSi moiety in solids. Encouragingly, by using the bottom-up strategy, we demonstrated that quasi-ppSi is possible in a 2D material.[51] The building block is a ppSi-containing $Ca_4Si_2^{2-}$ species (Figure 6A), which follows the 18 valence electron rule.

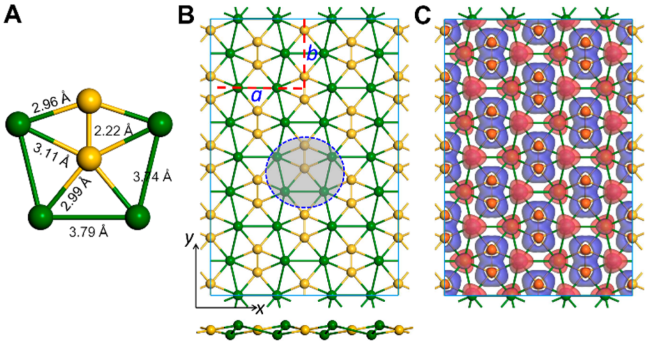


Figure 6. Structures of (A) $Ca_4Si_2^{2-}$ and (B) the Ca_2Si monolayer. (C) Deformation charge density of the Ca_2Si monolayer. Blue and red refer to electron-rich and -deficient areas, respectively. Adapted with permission from ref 51. Copyright 2018 Royal Society of Chemistry.

Fusing the Ca_4Si_2 moieties can result in a CaSi nanosheet (Figure 6B). In the optimized structure, each Si atom binds to four Ca ligands and another Si atom, forming a quasi-ppSi pattern with a buckling of 0.72 Å. The quasi-ppSi actually has good planarity due to strong electron transfer from Ca to Si and simultaneous back-donation (Figure 6C). The sum of the five angles around the quasi-ppSi center is 364.44°, which is close to the ideal value (360°). The moderate cohesive energy, all-positive phonon dispersions, good resistance to high temperature, and global minimum nature indicate its high stabilities.

The SSAdNDP analysis revealed that the existence of eight delocalized 3c-2e σ bonds (Ca–Si–Ca triangles) and two delocalized 4c-2e π bonds (Ca–Si–Ca–Si rhombuses) fundamentally contributes to stabilization of the quasi-ppSi moieties. Specially, this nanosheet has a negative Poisson's ratio and is a silicon-containing semiconductor with a desirable band gap for the semiconductor industry (0.50 eV) and good capacity for light harvesting. Interestingly, perfect ppSi was achieved when a biaxial tensile strain of 3.4% was applied.

PLANAR HYPERCOORDINATE NANOSHEETS BEYOND CARBON AND SILICON

The exploration of 2D materials with planar hypercoodinate atoms is not limited to carbon and silicon. Probably the most prominent example is 2D boron sheets with polymorphism. Numerous 2D boron layers have been theoretically predicted. Because of the natural electron deficiency of boron, planar tetracoordinate, pentacoordinate, and hexacoordinate boron are rather common. Specially, 2D boron nanosheets have been fabricated on the single-crystal Ag(111) plane via the molecular beam epitaxy approach.[52,53] The structures, properties, and applications of 2D boron were discussed in a recent review paper.[54]

The planar hypercoodination of boron is fundamentally different from the rule-breaking planar hypercoodinate carbon and silicon because it is an intrinsic characteristic of B due to the electron deficiency. However, the electron deficiency does make B a superior ligand for realizing other 2D planar hypercoordinate structures, such as the aforementioned ptC nanosheets[22,24,25] and the planar hypercoordinate transition-metal-containing monolayers discussed below.

Inspired by the bonding of the planar hexacoordinated Fe (phFe)-containing Fe©B_6H_6 cluster,[55] we recently described three 2D inorganic materials, namely, FeB_2 (Figure 7A),[56] β-FeB_6 (Figure 7B), and γ-FeB_6 (Figure 7C);[57] notably, the γ-FeB_6 monolayer is assembled from dehydrogenated Fe©B_6H_6 (isolated Fe©B_6 wheel). It was found that the FeB_2 monolayer

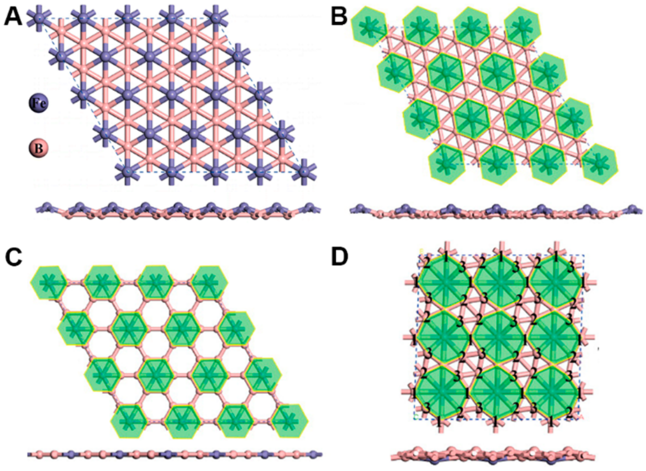


Figure 7. Structures of the (A) FeB_2, (B) β-FeB_6, (C) γ-FeB_6, and (D) α-FeB_6 monolayers. Reproduced from (A) ref 56 and (B–D) ref 57. Copyright 2016 American Chemical Society.

is a global minimum structure featuring quasi-phFe. This monolayer is a Dirac material with a high Fermi velocity (6.54 × 10^5 m s^{-1}), and its devices exhibit outstanding electrical conductivity.[58] Though β-FeB_6 and γ-FeB_6 are only local minima, they are charming semiconductors with excellent visible-light absorption. Besides, the scan of the PES of FeB_6 monolayer yielded an exotic α-FeB_6 phase (Figure 7D), which is a global minimum structure with quasi-planar octacoordinate iron. The SSAdNDP analysis revealed that there are no classic 2c-2e bonds in these Fe−B nanosheets and that delocalized multicenter σ and π bonds contribute significantly to the stability of the planar hypercoordinate iron moieties.

Recently, using the bottom-up strategy, Li et al.[59] proposed two metalloborophene layers featuring planar heptacoordinate cobalt and quasi-planar octacoordinate rhodium, of which the building blocks are CoB_{18}^- clusters[60] and RhB_{18}^- clusters,[61] respectively. By means of an intensive structural search, Tang et al.[62] predicted a ferromagnetic CoB_6 monolayer that contains planar hexacoordinate cobalt stabilized by the delocalized 3c-2e and 4c-2e σ bonds. They also proposed planar hexacoordinate nickel in a NiN_6 monolayer, which has a double Dirac cone near the Fermi level.[63] Furthermore, two recent theoretical studies based on global minimum searching demonstrated that the global minima of the MnB_6[64] and TiB_4 monolayers[65] contain planar octacoordinte manganese and titanium, respectively. More recently, Yang and co-workers[66] predicted an AlB_6 nanosheet with a planar tetracoordinate aluminum array in a tetragonal lattice by a comprehensive crystal structure search. Besides high stability, the AlB_6 monolayer exhibits triple Dirac cones and is a promising superconductor (T_c = 4.7 K, ranging up to 30 K at a tensile strain of 12%).

Planar hypercoordinate motifs also exist for some other atoms. For example, planar hexacoordinate germanium (phGe) and quasi-phGe can be stabilized as the global minima of Ni_2Ge[48] and Cu_2Ge monolayers,[67] respectively. Besides, most of the ligand elements can exhibit a planar hypercoodinate form, such as quasi-planar hexacoordinate beryllium in Be_5C_2 and Be_2C monolayers, planar hexacoordinate copper in the Cu_2Si monolayer, and quasi-planar heptacoordinate calcium in the CaSi monolayer.

CONCLUSIONS AND PERSPECTIVES

The discovery of each new 2D nanosheet with planar hypercoordinate carbon, silicon, and beyond is one solid step forward in fundamental chemistry and materials science. With the rule-breaking bonding, these exotic 2D structures do offer various exciting properties that are intriguing for a multitude of applications in electronics, optoelectronics, spintronics, mechanics, and energy conversion systems. In spite of the continuous efforts in designing such 2D systems, the successful cases in this arena, especially those featuring ideal planar moieties, are still very rare. While electron delocalization, including multicenter σ and π bonds, was identified to significantly contribute to the stabilization of the planar hypercoordinate moieties in 2D space, it remains very difficult to design a stable 2D material with these generally unstable species, and a systematic strategy for predicting such nanosheets has not been fully established. However, we strongly believe that the "bottom-up" and "isoelectronic substitution" concepts are very effective and helpful in the construction of new candidates. We foresee that more 2D materials featuring hypercoordinate motifs will appear in the coming years. Considering the tremendous progress in experimental techniques for the synthesis of 2D materials, we are optimistic that more rule-breaking nanosheets can be realized with some promising ligands (e.g., the "magic" Be or B) in the very near future.

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