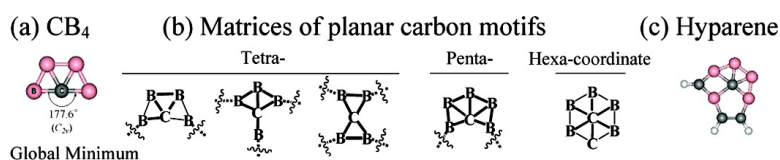


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Probing the Planar Tetra-, Penta-, and Hexacoordinate Carbon in Carbon–Boron Mixed Clusters

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Abstract: The concept of planar hypercoordinate (e.g., penta- and hexacoordinate) carbons is intriguing [Exner, K.; Schleyer, P. v. R. *Science* **2000**, *290*, 1937] as it is neither compatible with the standard rule of three-dimensional chemical bonding nor with the maximum tetracoordination. Herein we undertake a comprehensive study of the planar tetra- (ptC), penta- (ppC), and hexacoordinate carbon (phC) by covering the whole family of carbon–boron mixed clusters $C_{m=1-4}B_{n=4-8}$ and their anions. The potential energy surface of every carbon–boron cluster is sampled by using the basin-hopping global search algorithm coupled with *ab initio* geometry optimization. A large number of planar tetra-, penta-, and hexacoordinate carbon (local-minimum) structures are obtained. Several structures such as the phC consisting of C_2B_5 , $C_2B_5^-$, etc. are reported for the first time. In particular, a ptC corresponding to the *global minimum* of CB_4 is revealed, which appears to be highly stable for future synthesis. The boron-centered isomers are generally the more stable structures for planar multicoordinate carbons (ptC, ppC, and phC). The planar tetra-, penta-, and hexacoordinate boron are the prevalent structural motifs in low-lying isomers of the carbon–boron clusters. However, stability of the ptC and ppC units can be reinforced over the boron-centered isomers by attaching proper hydrocarbon unit $-(CH)_n-$ to form the so-called “hyparenes” [Wang, Z. X.; Schleyer, P. v. R. *Science* **2001**, *292*, 2465]. A new hyparene molecule is suggested for future synthesis of novel planar hypercoordinate carbon compounds.

1. Introduction

The spatial tetrahedral bonding of tetracoordinate carbon was first recognized by J. H. van't Hoff and J. A. Le Bel in 1874.^{1,2} Since then, tetracoordinate carbon has become a textbook concept. In 1970, R. Hoffmann et al.³ inquired whether it is conceivable to synthesize new coordination carbon geometry distinct from the tetracoordinate carbon, such as the planar tetracoordination carbon (ptC) (known as the anti-van't Hoff/Lebel compound). Because the concept of the planar tetracoordination carbon not only is of fundamental interest but also has important implication in developing new materials, molecular frameworks containing the anti-van't Hoff/Lebel unit has attracted intensive interests over the past 30 years.⁴ Despite of much efforts in both experimental and theoretical research,

realization of the anti-van't Hoff/Lebel complex in the laboratory remains a challenging task. This is largely because the conversion of a carbon from inherently tetrahedral coordination to planar tetracoordination is an energetically expensive process.^{3,5}

From analyzing the molecular orbital (MO) sequence of the planar methane (D_{4h}), Hoffmann suggested that the key to stabilizing ptC is to delocalize the lone pair electrons on the ptC center, known as the electronic stabilization mechanism.³ The introduction of σ -donating/ π -accepting substituents or the incorporation of lone pair into the π -electron delocalization system may stabilize the ptC center more efficiently.³ Motivated by this mechanism, a number of stable and simply structured ptC compounds were predicted theoretically.^{4h,i,6–10} A pioneer

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work was the design of a series of lithio-substituted ptC molecules by Schleyer, Pople, and co-workers in 1976.^{6a} The electropositive metal ligands (e.g., $-Li$) were found particularly effective to stabilize the ptC.^{4b} The first successful synthesis of molecules containing ptC was reported in 1977, where the ptC is coordinated with two vanadium (V) atoms.¹¹ To date, most ptC compounds synthesized in the laboratory are organometallic with transition metal. The group IVB transition-metal-based bent metallocenes, i.e., titanocene, zirconocene, and hafnocene, are found especially effective for making carbon compounds containing unusual coordinate structures.¹²

The smallest molecular system that can accommodate a planar tetracoordinate carbon is the penta-atomic molecule. A penta-atomic ptC molecule (CA_2Si_2) was proposed by Boldyrev and Schleyer in 1991.¹³ Later, the CA_2Si_2 , as well as CA_2Ge_2 and CGa_2Si_2 , were studied by Boldyrev and Simons using high-level *ab initio* calculations.¹⁴ It was concluded that the C atom in the global minimum structures of CA_2Si_2 , CA_2Ge_2 , and CGa_2Si_2 is in a planar tetracoordinate arrangement.¹⁴ Shortly after these findings, a joint theoretical/experimental study reported the CA_4^{2-} , CA_4^- , CA_3Si^- , and CA_3Ge^- species,¹⁵ the first ptC moieties confirmed by the experiment. A new family of pure carbon ptC systems, namely the dianion C_5^{2-} , were shown theoretically by Merino et al. in 2003.^{16,17} The C_5^{2-} can be further stabilized by binding with alkaline metals, such as the formation of $Li_2^{2+}C(C_4)^{2-}$ salt^{16a} in which the ptC moiety is intact. However, the dianion C_5^{2-} species is yet to be realized in the laboratory. Some ptC-containing one-, two-, and three-dimensional supermolecular structures were also proposed theoretically.^{6e,18,19}

Besides the electronic stabilization mechanism, an alternative way to stabilizing the planar tetracoordinate carbon is to incorporate a ptC moiety such as the CC_4 or CB_4 into a rigid steric system.^{20–28} However, it is challenging to realize this way of molecular design in the laboratory since the molecular skeleton would be under intense strain. The fenestranes might

be promising precursors toward the synthesis of anti-van't Hoff/Lebel structures.^{4d,22}

Besides the ptC, more fascinating forms of planar hypercoordinate carbon, e.g., the planar penta- and hexacoordinate carbon, were first suggested by Schleyer and co-workers based on high-level *ab initio* molecular orbital calculations.^{29,30} The CB_6^{2-} , CB_6H_2 , and three isomers of C_3B_4 were shown to be stable *local* minima, which contain planar hexacoordinate carbon (phC).²⁹ Moreover, an unusual heptacoordinate planar carbon structural unit, CB_7^- , was also proven to be a stable *local* minimum.³⁰ By linking the $-C_3B_3^-$, $-C_2B_4^-$, or $-CB_5^-$ unit with a hydrocarbon unit, $-(CH)_n-$, a new family of “hypanyrene” molecules that contain the ptC moiety was proposed.³⁰ Very recently, varieties of phC-containing molecules were also suggested.³¹ These previous studies have greatly advanced the notion of planar penta-, hexa-, and even heptacoordinate carbon and broadened the conventional view of the bonding capabilities of carbon atoms. Nevertheless, we are aware that the feasibility of the planar carbon structures is still based on theoretical prediction. Thus far, few experimental data are available on structures of carbon–boron mixed clusters.³² One recent experimental/theoretical photoelectron spectroscopy study showed that the planar heptacoordinate carbon structure (CB_7^-) is not the global minimum.³³

In this work, we undertake a systematic theoretical study to search for the planar tetra-, penta-, and hexacoordinate carbons by covering the whole family of small-sized carbon–boron mixed clusters C_mB_n and their anions $C_mB_n^-$ ($m = 1–4$ and $n = 4–8$). Toward this end, we combined a global minimum search technique (the basin-hopping algorithm)³⁴ with the density-functional theory (DFT)³⁵ geometry optimization. Previous theoretical studies have shown ample evidence of stable ptC, ppC, and phC structures in the clusters $C_{m=1–4}B_{n=4–8}$.^{29–31,36–38} Using the basin-hopping algorithm,³⁴ we obtained the lowest-energy structures (global minima) of every carbon–boron cluster, as well as all the low-lying and a number of high-lying metastable structures. Our major findings are summarized as

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follows: (i) A new global minimum ptC molecule, CB_4 , is revealed. It is predicted to be highly stable and thus a promising candidate for future synthesis. (ii) It is found that the planar tetra-, penta-, hexa-, and octacoordinate borons are dominant structural motifs in the global minima of $\text{C}_{m=1-4}\text{B}_{n=4-8}$ clusters and anions. (iii) More than 30 forms of ptC, ppC, and phC structural motifs are observed; most of them, however, have relatively high energy. (iv) A rule to describe the structural feature of boron in the ptC, ppC, and phC units is found. This general rule can be useful for the search of other planar multicoordinate carbon (pmC) structures. (v) The relative thermodynamic stabilities of carbon–boron mixed clusters containing pmC are evaluated for the first time. It is found that the exchange of the central C atom with a perimeter B atom in pmC can significantly lower the total energy (except for the CB_4). Further calculation, however, suggests that the stability of the ptC and ppC units can be significantly enhanced over the boron-centered isomers by attaching a proper hydrocarbon unit $-(\text{CH})_n-$ to form the hyparenes structures.³⁰

2. Computational Methods

We sample the potential energy surface of each carbon–boron cluster by means of the basin-hopping (BH) algorithm³⁴ combined with DFT geometry optimization.³⁵ Briefly, the BH algorithm removes relatively low barriers separating the local minima of the potential energy surface and thus effectively converts portions of the potential energy surface into a multidimensional staircase.³⁴ Effectiveness of the BH algorithm has been demonstrated previously.³⁹ Here we calculate the potential energy and energy gradient using a DFT method with a gradient-corrected functional, namely, the Perdew–Burke–Ezerhof (PBE) exchange-correlation functional⁴¹ implemented in the DMol3 program (a DFT program distributed by Accelrys, Inc., San Diego; see ref 40). The all-electron d-polarization function including double-numerical basis set (DND) is adopted. In the BH search, both the singlet and triplet energies for the close-shell clusters are examined.

We identify the lowest-energy isomer of a carbon–boron cluster in three steps: (1) all low-lying isomers (obtained from DMol3 total energy calculations) with their energy value within 46 kcal/mol (~ 2.0 eV) from the lowest-energy isomer are collected for further geometry optimization and frequency calculation at the B3LYP/6-311+G(d,p) level of theory using the *Gaussian03* package;^{42,43} (2) the single-point energies of top six lowest-lying isomers are calculated using a coupled-cluster method⁴⁴ [CCSD(T)/6-311+G(d,p)]; (3) those low-lying isomers with very close energies [less than 3 kcal/mol in energy difference in the CCSD(T)/6-311+G(d,p) calculation] are further examined via the CCSD(T)/cc-pVTZ calculation. We note that the mid-level CCSD(T)/6-311+G(d,p) calculation yields a qualitatively consistent energy

ranking compared to that from the CCSD(T)/cc-pVTZ calculation for the carbon–boron clusters (see Supporting Information).

3. Results and Discussion

Table 1 displays the predicted *global minima*, M1–M20 and $\text{M1}^-–\text{M20}^-$, for the 20 mixed carbon–boron clusters $\text{C}_{m=1-4}\text{B}_{n=4-8}$ and their anions. Here, the B:C ratio ranges from 1 to 8. It is found that all the lowest-energy structures of the close-shell species are in the singlet state. Almost all the lowest-energy structures [except for $\text{CB}_4^-(\text{M1}^-)$, $\text{CB}_6(\text{M3})$, and $\text{C}_3\text{B}_6^-(\text{M13}^-)$, and $\text{C}_4\text{B}_5^-(\text{M17}^-)$] are planar in geometry. It can be seen from Table 1 that the planar tetra-, penta-, and hexacoordinate boron are prevalent structural motifs for the carbon–boron clusters (M2–M20 and $\text{M1}^-–\text{M20}^-$). Only CB_4 (M1 in Table 1) contains a ptC unit. All other ptC, ppC, and phC structural isomers are local minima.

3.1. CB_4 : An Alternative Planar Tetracoordinate Carbon Compound. The CB_4 (M1) has a unique ptC structure. Although many ptC-containing compounds have been predicted theoretically,^{4h} only a few have been confirmed by experiment, such as CAL_4^{2-} , CAL_4^- , and CSiAl_3^- among others.¹⁵ The global minima of CAL_4^{2-} , CAL_4^- , and CSiAl_3^- exhibit the same structural feature, that is, the ptC center is stabilized by a closed four-membered ring, just like the Al_4 four-membered ring.^{13–15} The structure of CB_4 (M1) differs from that of CAL_4^{2-} , CAL_4^- , and CSiAl_3^- because the B–B bonds are too short to form a closed four-membered ring to accommodate the ptC center. The four boron atoms actually locate on one side of the carbon atom in the CB_4 . Hence, the CB_4 can be viewed as a cut from the CB_6^{2-} planar structure (where the six boron atoms form a six-membered ring to enclose the phC center)²⁹ by half.

Table 2 displays three low-lying isomers (A–C) of CB_4 along with the relative energies of the isomers at higher levels of theory. The coupled-cluster calculation at the CCSD(T)/cc-pVTZ level shows that the C_{2v} isomer **A** is the lowest-energy structure rather than the isomer **C** as suggested from the DFT/B3LYP calculation. Note that the isomer **C** is at triplet spin state. The relative energy of the T_d isomer of CB_4 is also shown in Table 2. One can see that the ptC structure greatly favors the spatial T_d isomer.

From an analysis of the molecular orbital of CAL_4^{2-} , Boldyrev et al. concluded that the unbalanced bonding and antibonding interactions among the $-\text{Al}$ ligands lead to the first-order Jahn–Teller distortion for the T_d structure.¹⁴ The 17- and 18-valence electron systems were suggested to be the most promising for the occurrence of planar structure.^{14,15c} In our case, the CB_4 only possesses 16-valence electrons. We attribute the electron-deficient nature of the boron to the stability of the neutral CB_4 . The delocalization of the lone pair has been considered as a key factor to stabilizing the central ptC.³ According to the molecular orbital pictures displayed in Figure 1, the lone pair on the central carbon atom of the CB_4 is delocalized by the surrounding boron atoms, as in the case of CAL_4^{2-15b} and $\text{C}(\text{C})_4^{2-17a}$. A significant contribution of the perpendicular p orbital of the central ptC atom to the highly delocalized π orbital (HOMO–4, $1b_1$) is seen (Figure 1). The total number of π -electrons in CB_4 is two, satisfying the Hückel ($4n + 2$) π -electron rule. The nucleus-independent chemical shift (NICS) values, which are -7.24 ppm at the molecular center and -20.06 ppm at 0.5 \AA above the molecular center [calculated at

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












































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Table 1. Lowest-Energy Structures of Carbon–Boron Clusters and Their Anions, C_mB_n and $C_mB_n^-$ ($m = 1-4$; $n = 4-8$)

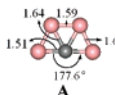

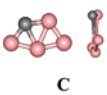

C_mB_n	$m=1$	$m=2$	$m=3$	$m=4$	
$n=4$	 (M1, C_{2v})	 (M6, C_{2v})	 (M11, C_s)	 (M16, C_{2v})	
	 (M1 ⁻ , C_1) ^a	 (M6 ⁻ , C_{2v})	 (M11 ⁻ , C_{2v})	 (M16 ⁻ , C_s)	
$n=5$	 (M2, C_s , 0.00)	 (M2-iso, C_{2v} , 0.23)	 (M7, C_s)	 (M12, C_s)	 (M17, C_s)
	 (M2 ⁻ , C_{2v})	 (M7 ⁻ , C_{2v} , 0.00)	 (M7 ⁻ -iso, C_s , 0.68)	 (M12 ⁻ , C_{2v})	 (M17 ⁻ , C_{2v})
$n=6$	 (M3, C_s)	 (M8, C_{2v} , 0.00)	 (M8-iso, C_{2v} , 0.32)	 (M13, D_{3h})	 (M18, C_s)
	 (M3 ⁻ , C_s)	 (M8 ⁻ , C_{2v})	 (M13 ⁻ , C_1 , 0.00)	 (M13 ⁻ -iso, C_s , 0.892)	 (M18 ⁻ , C_s)
$n=7$	 (M4, C_{2v})	 (M9, C_{2v})	 (M14, C_{2v})	 (M19, C_{2v})	
	 (M4 ⁻ , C_{2v})	 (M9 ⁻ , C_s)	 (M14 ⁻ , C_{2v} , 0.00)	 (M14 ⁻ -iso, C_s , 0.17)	 (M19 ⁻ , C_{2v})
$n=8$	 (M5, C_{2v})	 (M10, C_s)	 (M15, C_s)	 (M20, C_s)	
	 (M5 ⁻ , C_s)	 (M10 ⁻ , C_s)	 (M15 ⁻ , C_s)	 (M20 ⁻ , C_s)	

^a The side view of the nonplanar structure is given on the right side of the cluster.

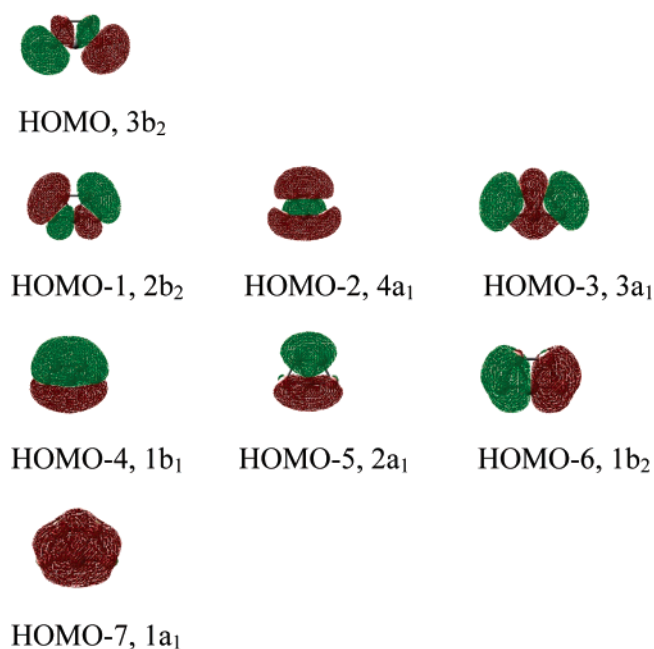
B3LYP/6-311+G(d,p) level], confirm the aromaticity nature of the CB_4 molecule. Furthermore, the large cohesive energy of 120.51 kcal/mol [calculated at the level of CCSD(T)/6-311+G(d,p)] suggests relatively high stability of the CB_4 molecule.

On the other hand, for the 17-electron anion CB_4^- , the ptC structure is not observed (cf. Table 1 and the Supporting Information for the low-lying energy isomers of the CB_4^-).

Table 2. Low-Energy Isomers of the CB₄ Cluster and Their Relative Energies

Methods	Low-lying Isomers A–C			Spatial Coordinate
				
	(C _{2v} , ¹ A ₁)	(C _s , ¹ A')	(C _n , ³ A)	(T _d , ¹ A ₁)
B3LYP/6-311+G(d,p)	0.00	-7.04	-8.97	109.15
MP2/cc-pVTZ	0.00	6.08	8.38	129.05
CCSD(T)/cc-pVTZ//MP2/cc-pVTZ ^a	0.00	1.67	4.84	103.61

^a The single-point CCSD(T) calculations are based on the geometries obtained from the second-order energy correction Møller–Plesset^{43c–g} (MP2)/cc-pVTZ optimizations. ^b The bond length and energy are in units of angstroms and kcal/mol, respectively. The geometry of CB₄ is obtained at the MP2/cc-pVTZ level calculation.

**Figure 1.** Molecular orbitals of the global minimum CB₄.

Although the bulk crystal of boron carbide CB₄ is a well-known hard material,⁴⁵ we are unaware of any structural data for the CB₄ molecule. Liu et al. recently observed structural conversion among various CB₄ isomers.³⁸ We certainly hope that the predicted lowest-energy CB₄ molecule can be isolated in future experiments. For that purpose, we present the calculated infrared spectrum of the CB₄ in the Supporting Information.

3.2. Structural Evolution of C_mB_n and C_mB_n[−] (m = 1–4; n = 4–8) Clusters. In the global minima M2–M20 and M1[−]–M20[−] (cf. Table 1), the carbon atom generally occupies the peripheral position of the clusters with only two- or three-fold coordination. A change of position of the peripheral carbon atom

will affect relative stabilities of the clusters. For example, the isomers M2-iso, M7[−]-iso, M8-iso, M13[−]-iso, and M14[−]-iso are slightly higher in energy than the global minima M2, M7[−], M8, M13[−], and M14[−], respectively (cf. Table 1).

The series of CB_n and C₂B_n (n = 4–8) are boron-rich carbon–boron clusters. It has been shown that the carbon-rich carbon–boron clusters, C_nB[−] (n = 1–13), have floppy linear or cyclic structures, similar to those of the pure carbon clusters (C_n[−]).^{46,47} Here, the neutral CB₄ (M1), CB₅ (M2), CB₆ (M3), CB₇ (M4), CB₈ (M5), C₂B₄ (M6), and C₂B₆ (M8) and anions CB₅[−] (M2[−]), CB₇[−] (M4[−]), C₂B₄[−] (M6[−]) show structural similarities to the pure boron clusters. For example, the lowest-energy structure CB₄ (M1) has the same skeleton structure as that of the B₅ cluster.⁴⁸ The lowest-energy structures CB₇ (M4), CB₇[−] (M4[−]), CB₈ (M5), and C₂B₆ (M8) are molecular-wheel like, similar to those of B₈, B₈^{2−}, and B₆[−], respectively.⁴⁹ Some other analogies, such as those between CB₅ (M2) and B₆,⁵⁰ CB₅[−] (M2[−]), C₂B₄ (M6), C₂B₄[−] (M6[−]), and B₆[−]⁵⁰ as well as between CB₆ (M3) and B₇⁴⁸ are also found, suggesting that the structures of the boron-rich carbon–boron clusters CB_n and C₂B_n are mainly dictated by the bonding capabilities of the boron. It is worth noting that the predicted lowest-energy structure CB₇[−] (M4[−]) is consistent with that from a recent experimental study.³³

With the increase of carbon composition in the mixed carbon–boron cluster, the lowest-energy structures of C₃B_n and C₄B_n (n = 4–8) become less compact. Some floppy ring structures are observed, such as those of M11[−] (C₃B₄[−]), M12[−] (C₃B₅[−]), M13 (C₃B₆), M16 (C₄B₄), M16[−] (C₄B₄[−]), M17 (C₄B₅), and M16[−] (C₄B₅[−]) (cf. Table 1). Another obvious structural perturbation due to the increase of carbon composition is that the coordination number of the central B atom is notably reduced. For example, the maximum coordination number of the central B atom is reduced to six in M12, M14, and M14[−] and five in M18, and M20, and even many tetracoordinate boron atoms show up in the C₄B_n (n = 4–8) series.

3.3. Molecular Wheels CB₇, CB₇[−], CB₈, C₂B₆ and Derivatives of Planar Tetra-, Penta-, and Hexacoordinate Boron Motifs. The global minima CB₇ (M4), CB₈ (M5), C₂B₆ (M8) and the anion CB₇[−] (M4[−]) are molecular wheel-like, where the central B atom is hepta- or octacoordinated, one less or equal to the maximum coordination number of the central B atom (octacoordinated⁴⁹) in the planar molecular wheel boron clusters. The hetero C atom occupies peripheral position in CB₇ (M4), CB₈ (M5), C₂B₆ (M8), and anion CB₇[−] (M4[−]). No B-centered molecular-wheel-like structures are found when the number of the peripheral C atom exceeds two.

These molecular-wheel-like structures CB₇ (M4), CB₈ (M5), C₂B₆ (M8), and CB₇[−] (M4[−]) possess relatively high stabilities. For the close-shell species CB₈ (M5), C₂B₆ (M8), and CB₇[−] (M4[−]), the energy differences (ΔE_{S–T}) between the singlet and the lowest triplet states are 16.75, 43.80, and 38.96 kcal/mol [calculated at the CCSD(T)/6-311+g(d) level], respectively. The CB₇ (M4), CB₈ (M5), and CB₇[−] (M4[−]) are much more stable

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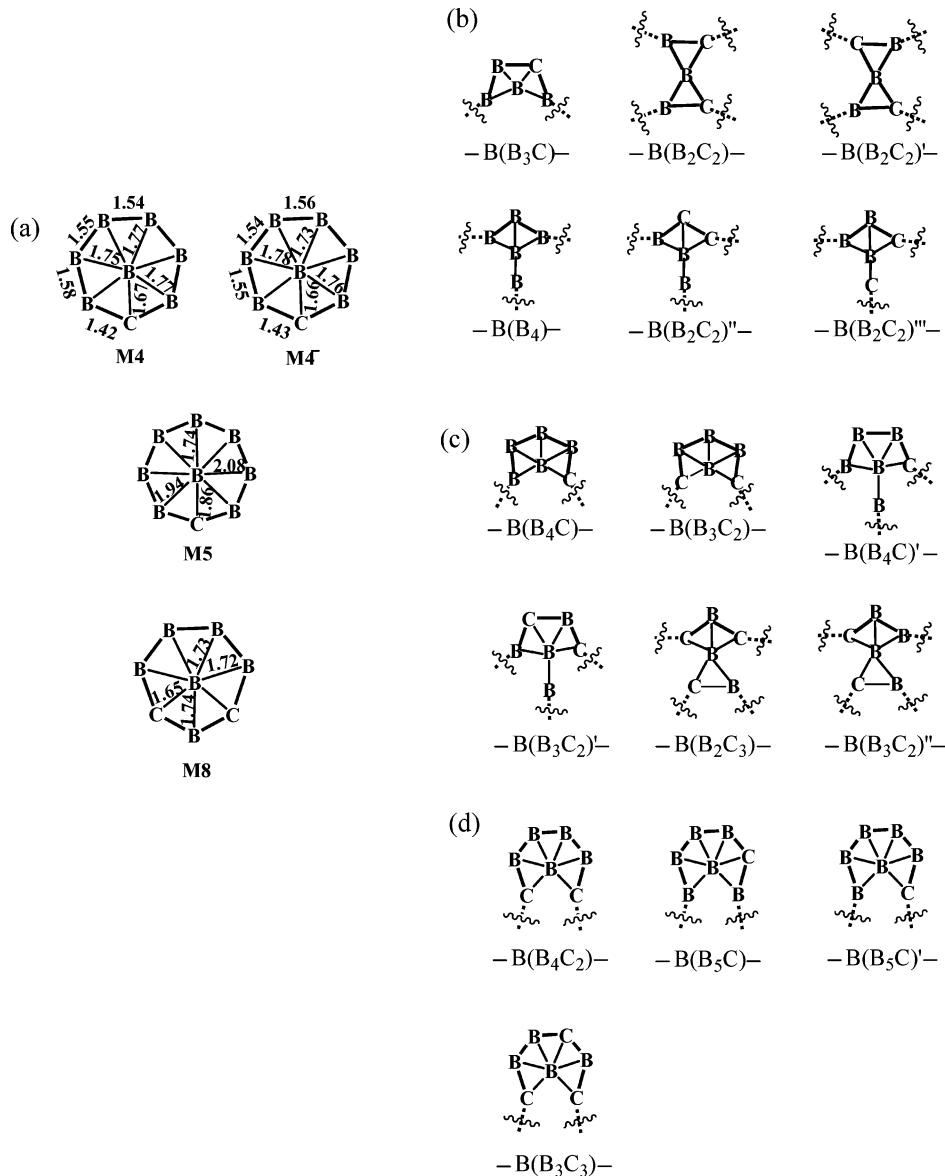
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Scheme 1. Schematic Illustrations of (a) Matrix Structure of Hepta- and Octacoordinate Boron Wheels: B_7C (**M4**), B_8C (**M5**), and B_6C_2 (**M8**) and Anion B_7C (**M4**⁻); (b) the Derivatives of Tetracoordinate Boron Structural Motifs: $-B(B_3C)-$ (in **M2**), $-B(B_2C_2)-$ (in **M18**⁻, **M19**, and **M19**⁻), $-B(B_2C_2)'\text{-}$ (in **M15**⁻), $-B(B_4)-$ (in **M3**⁻), $-B(B_2C_2)''\text{-}$ (in **M11**), and $-B(B_2C_2)'''\text{-}$ (in **M20**⁻); (c) the Derivatives of Pentacoordinate Boron Structural Motifs: $-B(B_4C)-$ (in **M5**⁻ and **M9**⁻), $-B(B_3C_2)-$ (in **M9**), $-B(B_4C)'\text{-}$ (in **M15**), $-B(B_3C_2)'\text{-}$ (in **M15**), $-B(B_2C_3)-$ (in **M18**), and $-B(B_3C_2)''\text{-}$ (in **M20**); (d) the Derivatives of Hexacoordinate Boron Structural Motifs: $-B(B_4C_2)-$ (in **M8**⁻), $-B(B_5C)-$ (in **M10**), $-B(B_5C)'\text{-}$ (in **M10**⁻), and $-B(B_3C_3)-$ (in **M12**)



compared to the second-lowest-energy structures by 27.09, 16.75, and 35.58 kcal/mol, respectively [calculated at the CCSD-(T)/6-311+g(d) level]. For the C_2B_6 , the second-lowest-energy structure **M8-iso** is nearly isoenergetic to the **M8**, which is also molecular wheel-like (cf. Table 1). The energy difference between **M8** and the third-lowest-energy structure of C_2B_6 is 15.51 kcal/mol (see the Supporting Information).

A main structural feature of the mixed carbon–boron clusters $C_{m=1-4}B_{n=4-8}$ and their anions is that the planar multicoordinate (tetra-, penta-, and hexacoordinate) boron is a prevalent structural motif. Scheme 1 summarizes various planar multicoordinate boron structural motifs seen in **M1**–**M20** and **M1**⁻–**M20**⁻. Indeed, the molecular wheel-like structures CB_7 (**M4**), CB_8 (**M5**), C_2B_6 (**M8**), and CB_7^- (**M4**⁻) may be viewed as a parent structure from which various planar tetra- (Scheme 1b), penta- (Scheme 1c), and hexacoordinate (Scheme 1d) boron can be derived. Apparent examples include the neutral molecular

wheels CB_8 (**M5**), C_2B_6 (**M8**), and their anions CB_8^- (**M5**⁻) and $C_2B_6^-$ (**M8**⁻). The attachment of one extra electron to the CB_8 (**M5**) or C_2B_6 (**M8**) leads to the reduction of the coordination number of the central B atom from the compact octa- or heptacoordination to the penta- or hexacoordination, respectively. For CB_7 (**M4**), CB_8 (**M5**), C_2B_6 (**M8**), and CB_7^- (**M4**⁻), the Wiberg bond indices (WBI) of the central B atom are analyzed by using the NBO program⁵¹ and are listed in Table 3. Although the coordination number of B atoms may increase up to eight, the WBI value of the central B atom is always less than four, suggesting that the octet rule is not violated. The bonds between the central B atom and the surrounding B and C atoms, $B_{\text{center}}-B$ and $B_{\text{center}}-C$, are electron-deficient multicenter bonds.

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Table 3. Calculated Properties of Molecular Wheel-Like Clusters CB_7 (**M4**), CB_7^- (**M4**⁻), CB_8 (**M5**), and C_2B_6 (**M8**), the Wiberg Bond Indices for the Central B Atom, and NICS Values (ppm) above the Mass Center of Cluster (B3LYP/6-311+G(d,p) Level of Theory)

molecules	total WBI for the central boron atom	NICS at a distance above the mass center of the cluster	
		(0.5 Å)	(1.0 Å)
C_2B_6	3.57	-12.22	-11.83
CB_7	3.63	-28.82	-22.30
CB_7^-	3.70	-28.92	-24.46
CB_8	3.50	-25.25	-24.32
CB_8^-	3.57	-24.48	-20.28

To gain more insights into the bonding nature of the planar multicoordinate boron structures, the molecular orbitals (MOs) of CB_7 (**M4**), CB_8 (**M5**), and C_2B_6 (**M8**) are further analyzed. An in-depth discussion of MOs of CB_7^- (**M4**⁻) has been given in ref 33. The neutral CB_7 (**M4**) possesses consistent electronic configurations and very similar shapes of MOs as those of CB_7^- (**M4**⁻). The removal of one electron from the CB_7^- results in little structural change (Scheme 1a). The electronic configurations and plots of MOs of the CB_7 (**M4**), CB_7^- (**M4**⁻), CB_8 (**M5**), and C_2B_6 (**M8**) are shown in Figure 2. A common feature of MOs in CB_7 (**M4**), CB_7^- (**M4**⁻), CB_8 (**M5**), and C_2B_6 (**M8**) is that both the σ and π electrons are highly delocalized above the molecular plane, which is responsible for relatively high stabilities of these species. All molecular-wheel-like structures are π -aromatic with three π -orbitals [HOMO, $1b_1$, HOMO-1, $1a_2$, and HOMO-5, $1b_1$ in C_2B_6 (**M8**); HOMO, $1a_2$, HOMO-1, $2b_1$, and HOMO-6, $1b_1$ in CB_7 (**M4**) and CB_7^- (**M4**⁻); HOMO, $1a_2$, HOMO-1, $2b_1$, and HOMO-5, $1b_1$ in CB_8 (**M5**)]. The π MOs of CB_7 (**M4**), CB_7^- (**M4**⁻), CB_8 (**M5**), and C_2B_6 (**M8**) are very similar in shape, composed mainly of the 2p orbitals of the perimeter boron atoms. The CB_7^- (**M4**⁻), CB_8 (**M5**), and C_2B_6 (**M8**) all have six π -electrons, satisfying the $(4n + 2)$ Hückel rule. The CB_7 (**M4**) has its highest π MO (HOMO, $1a_2$) half-filled, resulting in a $(4n + 1)$ π -electron system. It has been proposed that the CB_7^- (**M4**⁻) has doubly aromatic characters, namely, both π -aromatic and σ -aromatic.³³ We expect that the molecular wheel-like clusters CB_7 (**M4**), CB_8 (**M5**), and C_2B_6 (**M8**) are also doubly aromatic, similar to CB_7^- (**M4**⁻) even though the σ aromaticity is less pronounced. The three highly delocalized σ orbitals [HOMO-2, $6a_1$, HOMO-3, $4b_2$, and HOMO-6, $4a_1$ in C_2B_6 (**M8**); HOMO-2, $4b_2$, HOMO-3, $6a_1$, and HOMO-7, $4a_1$ in CB_7 (**M4**); HOMO-2, $5b_2$, HOMO-3, $6a_1$, and HOMO-7, $4a_1$ in CB_8 (**M5**)] are responsible for the bonding between the central B atom and the perimeter atoms, which is considered to confer the σ aromaticity for the molecular wheel-like clusters.³³ The aromaticities of CB_7 (**M4**), CB_7^- (**M4**⁻), CB_8 (**M5**), and C_2B_6 (**M8**) can be further evaluated via calculating the NICS values⁵² above the center of the cluster plane. The absolute NICS values (cf. Table 3) of these molecular wheel-like clusters are quite high [compared to that of the benzene whose NICS = -8.0 at the B3LYP/6-311+G(d,p) level]. The slightly smaller (absolute) NICS value of CB_7 (**M4**), compared to CB_7^- (**M4**⁻), may be rationalized by its inherent $(4n+1)$ π -electrons.

Taking CB_8^- (**M5**⁻) as an example, we further analyzed its bonding characteristic in the reduced planar pentacoordinate

boron system. The MOs of CB_8^- (**M5**⁻) in Figure 2c are compared with those of CB_8 (**M5**) in Figure 2d. CB_8^- (**M5**⁻) is also a planar structure with the central B atom having reduced pentacoordination. Although the structure of CB_8^- is not as compact as CB_8 , the shapes of π MOs (HOMO-1, $2a''$; HOMO-2, $12a'$; and HOMO-7, $1a''$) of CB_8^- are very similar to those of CB_8 (Figure 2c). However, the highly delocalized σ orbitals are no longer seen in CB_8^- due to change of the coordination environment. The negative NICS value (cf. Table 3) above the molecular plane of CB_8^- confirms its π aromaticity. The slightly smaller NICS value of CB_8^- (compared to that of CB_8) probably originates from less contribution of σ aromaticity, because of strongly fragmental σ orbitals (HOMO-3, $11a'$, HOMO-4, $10a'$, and HOMO-8, $7a'$ in Figure 2d).

We now draw some preliminary conclusions on the bonding and structural evolution of small-sized mixed carbon-boron clusters: (1) The planar multicoordinate (with tetra-, penta-, and hexacoordination) boron is the dominant structural unit in $\text{C}_{m=1-4}\text{B}_{n=4-8}$, which can be viewed as derivatives of the molecular wheel-like clusters CB_7 (**M4**), CB_8 (**M5**), C_2B_6 (**M8**), and CB_7^- (**M4**⁻); (2) the central B atom forms multicenter electron-deficient bonds with the perimeter atoms to stabilize the multicoordinate structures; (3) the 2p orbital of the peripheral boron atoms participates in the formation of the π molecular orbitals which are highly delocalized on the molecular plane and significantly enhance the stability of the clusters.

3.4. Planar Multicoordinate (Tetra-, Penta-, and Hexacoordinate) Carbons. It has been found that the B atom can assist the C atom to achieve unusual hypercoordination structure.⁵³ For example, the spatial penta- and hexacoordinate C atom has been observed in the carborane molecules via the formation of electron-deficient B-C bonds.⁵³ Schleyer and co-workers²⁹⁻³¹ were the first to put forth the idea of using B atoms as constituent parts to stabilize hypercoordinate C atom in a planar structure. A variety of planar penta- and hexacoordinate carbon compounds have been theoretically studied by Schleyer and co-workers.^{29-31,54} Most of the reported planar penta- and hexacoordinate carbon compounds are built upon prototype carbon-boron clusters, such as the CB_6^{2-} and CB_8 .^{29-31,54} In this study, besides the global minima shown in Table 1, we also obtained a large number of local minima through sampling the potential energy surface for each of $\text{C}_{m=1-4}\text{B}_{n=4-8}$ clusters. Notably, many local minima contain the planar tetra- (Table 4, **T1-T12**), penta- (Table 5, **P1-P9**), and hexacoordinate (Table 6, **H1-H6**) carbon units although they are metastable structures.

Planar Tetracoordinate Carbon (ptC). Table 4 collects various ptC structural motifs (**T1-T12**) and their corresponding metastable minima structures. We can classify the observed ptC structural motifs into three types: (I) **T1-T6**, the ptC center is surrounded by four atoms on one side; (II) **T7-T10**, the ptC center is stabilized by three and one atoms on each side; (III) **T11-T12**, the ptC center is stabilized by two atoms on each side. For ptC motifs **T1**, **T7**, and **T11**, the surrounding atoms are all boron. The other motifs, such as **T2-T6** (type I), **T8-T10** (type II), and **T12** (type III), can be viewed as derivatives of **T1**, **T7**, and **T11**, respectively, with one or two surrounding B atoms replaced by C atoms. This mechanism is somewhat

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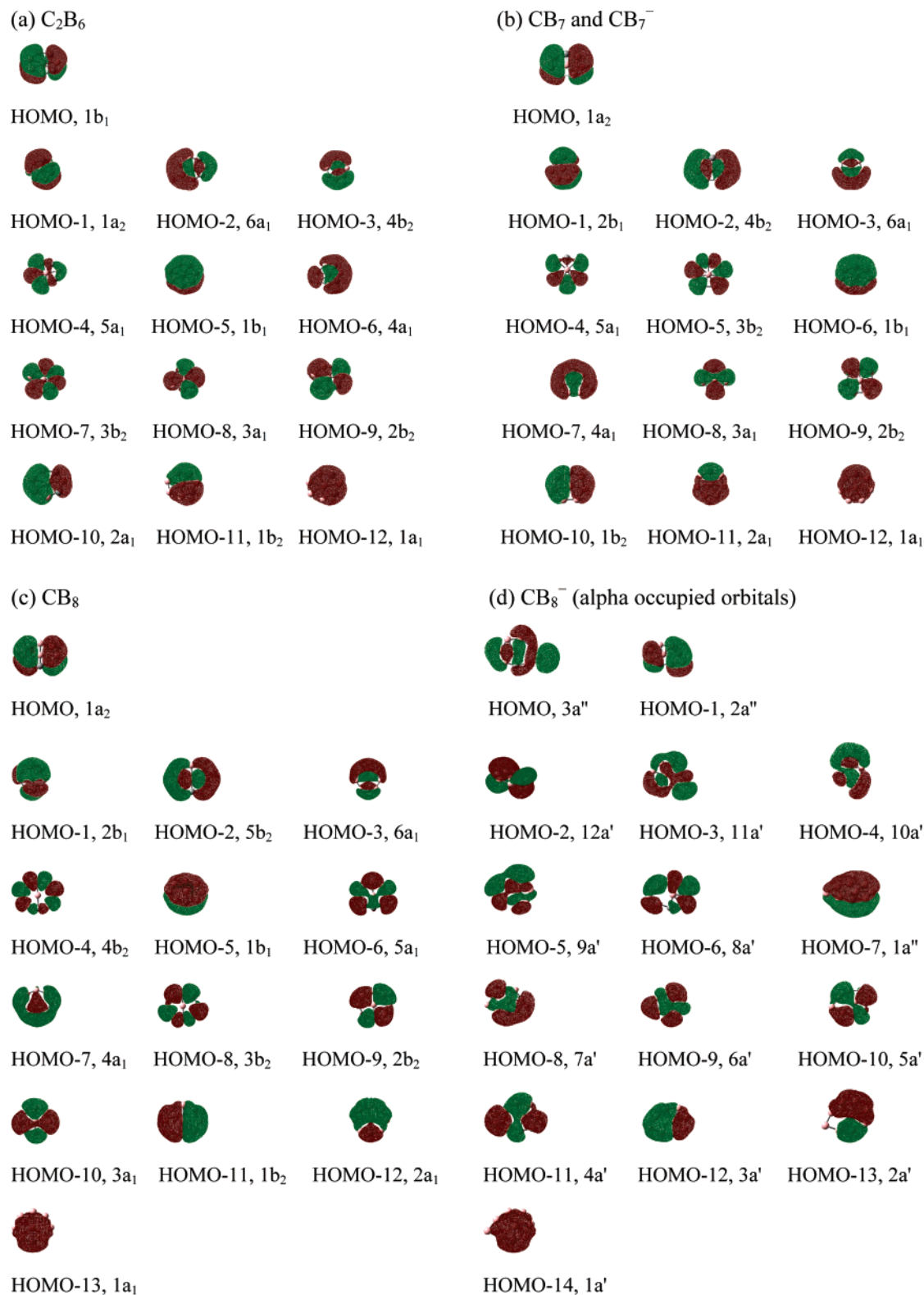


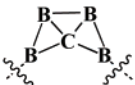
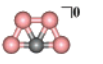

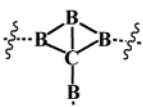
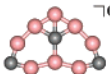
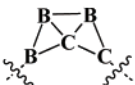
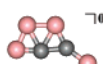

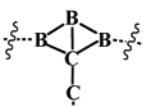
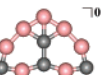
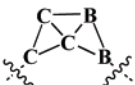
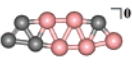
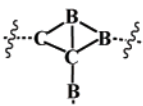
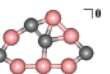
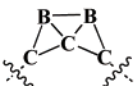
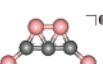

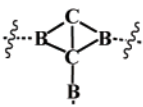
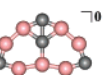
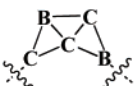
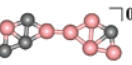
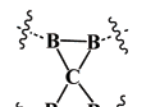
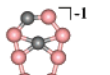
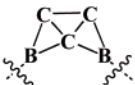
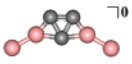
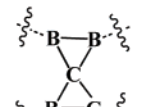
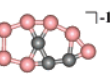
Figure 2. Molecular orbitals of molecular wheel-like clusters (a) C_2B_6 (**M8**), (b) CB_7 (**M4**) and CB_7^- (**M4⁻**), (c) CB_8 (**M5**), (d) CB_8^- (**M5⁻**).

similar to that in the ptC compounds CAI_4^{2-} and $CSiAl_3^-$, where the replacement of one of the surrounding Al atoms in the CAI_4^{2-} by a Si atom does not change the planarity of the cluster.¹⁵

Planar Pentacoordinate Carbon (ppC). Wang and Schleyer reported the first ppC structure.³⁰ The ppC structural units $-C_3B_3-$, $-C_2B_4-$, and $-CB_5-$ with three B atoms enclosed

were rationalized on the basis of the unique structure of CB_8 . Table 5 displays nine types of ppC structural motifs (**P1–P9**) observed in local minimum carbon–boron structures. The **P1** ($-CB_5-$), **P2** ($-C_2B_4-$), and **P8** ($-C_3B_3-$) are identical to those previously reported.³⁰ In particular, the ppC-containing carbon–boron clusters are abundant in nine-atom clusters, including the prototype motifs **P1** and **P4** (cf. Table 5). Like

Table 4. Collection of the ptC Structural Motifs (T1–T12) and Their Prototype Cluster Structures^a

Structural Motifs of ptC	Prototype Structures and Relative Energies (kcal/mol)		Structural Motifs of ptC	Prototype Structures and Relative Energies (kcal/mol)
 T1	 (0.00)	 (46.51)	 T7	 (9.11)
 T2	 (77.43)	 (54.13)	 T8	 (26.86)
 T3	 (59.82)		 T9	 (62.39)
 T4	 (73.57)	 (55.15)	 T10	 (38.66)
 T5	 (94.75)		 T11	 (54.13)
 T6	 (128.19)		 T12	 (56.73)

^a The relative stabilities of ptC clusters are evaluated via their energy difference (value in parentheses, calculated at CCSD(T)/6-311+G(d,p) level of theory) with respect to the lowest-energy isomer listed in Table 1.


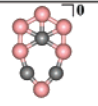
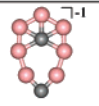
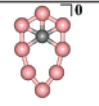

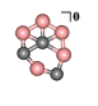
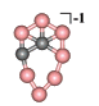
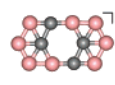

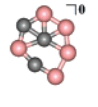
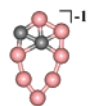

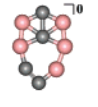
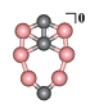

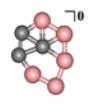
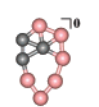

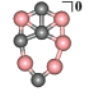
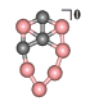

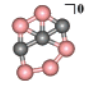
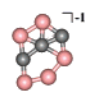
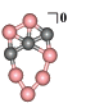

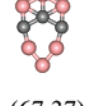
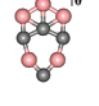

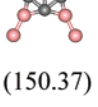
the ptC shown above, the structural motif **P1** can be considered as a matrix structure for all other motifs **P2–P9** with one or more perimeter B atoms replaced by C atoms. In addition, a local minimum structure containing two ppC motifs is also found (see the No. 3 prototype structure based on the motif **P2** in Table 5). This suggests that it is conceivable to build more complex structures containing more than one pmC units.

Planar Hexacoordinate Carbon (phC). Besides the ptC and ppC, some phC units are also revealed. Table 6 presents six types of phC structural motifs, **H1–H6**. Besides the known phC structures (C_3B_4 , **H4–H6**),³⁰ the neutral C_2B_5 (**H3**) and anions

$C_2B_5^-$ (**H3⁻**), $C_3B_4^-$ (**H6⁻**) are also phC-containing local minimum structures. Also, two new isomeric structural motifs $-C_3B_4-$ (**H1** and **H2**) are found in the C_3B_5 clusters.

Based on the ptC, ppC, and phC structural motifs listed in Tables 4–6, a simple rule may be outlined to understand the evolution of boron-stabilized planar multicoordinate carbon. From Tables 4–6, the structural motifs **T2–T6** and **P2–P9** can be viewed as derivatives of $-CB_4-$ (**T1**) and $-CB_5-$ (**P1**), respectively, with one or two surrounding boron atoms being replaced by the carbon atoms. The phC structural motifs **H1–H6** can actually be viewed as derivatives of the phC compound

Table 5. Collection of the ppC Structural Motifs (**P1–P9**) and Their Prototype Cluster Structures^a

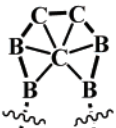
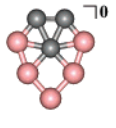
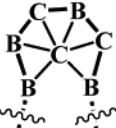
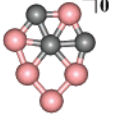

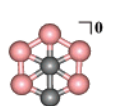
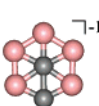

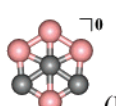
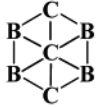
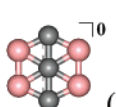

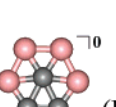
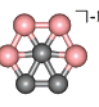
ppC Motifs	Prototype Structures and Relative Energies (kcal/mol)		
 P1	 (57.03)	 (27.57)	 (68.20) (Ref.30)
 P2	 (33.30)	 (55.92)	 (68.11)
 P3	 (59.36)	 (63.85)	
 P4	 (48.08)	 (57.86)	
 P5	 (75.25)	 (97.26)	
 P6	 (41.54)	 (91.30)	
 P7	 (66.87)	 (112.45)	 (80.76)
 P8	 (67.37)	 (31.43)	
 P9	 (150.37)		

^a The relative stabilities of ppC clusters are evaluated via their energy difference (value in parentheses, calculated at CCSD(T)/6-311+G(d,p) level of theory) with respect to the lowest-energy isomer listed in Table 1.

CB_6^{2-} .³⁰ According to this evolution rule, we are able to extrapolate more planar multicoordinate carbon motifs. Table 7 lists extrapolated ptC and ppC structural motifs, **T13–T16**

and **P10**, which are not observed during sampling of the potential energy surface, yet they can stably exist in the hypothetical carbon–boron hydrides.^{4h,56,57} Since only neutral

Table 6. Collection of the phC Structural Motifs (H1–H6) and Their Prototype Cluster Structures

Structural Motifs of PhC	Representative Structures and Relative Energies (kcal/mol)	
 H1	 (84.17)	
 H2	 (63.21)	
 H3	 (41.91)	 (42.89)
 H4	 (45.40)	
 H5	 (51.49)	
 H6	 (57.08)	 (125.29)

^a The relative stabilities of phC clusters are evaluated via their energy difference (value in parentheses, calculated at CCSD(T)/6-311+G(d,p) level of theory) with respect to the lowest-energy isomer listed in Table 1.

and anion clusters are studied here, it is possible to obtain more pmC structural motifs if the cation, dication, and dianion etc. are included, e.g., the $-CB_6^{2-}$.³¹

3.5. Stability Issues of the Planar Multicoordinate Carbon.

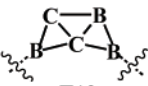
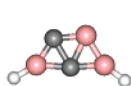
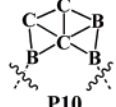
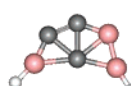
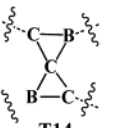

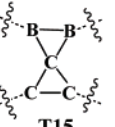
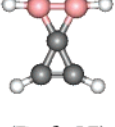
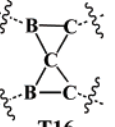
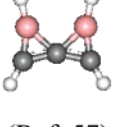
Although the results of various ptC, ppC, and phC local minimum structures are interesting, all these structures have relatively high energies, and most of them are 20 kcal/mol or 1.0 eV higher in energy than the predicted lowest-energy isomers

(55) Zhai, H. J.; Kiran, B.; Li, J.; Wang, L. S. *Nat. Mater.* **2003**, *2*, 827.

(56) Minyaev, R. M.; Gribova, T. N.; Minkin, V. I.; Starikov, A. G.; Hoffmann, R. J. *Org. Chem.* **2005**, *70*, 6693.

(57) Gribova, T. N.; Minyaev, R. M.; Minkin, V. I. *Collect. Czech. Chem. Commun.* **1999**, *64*, 1780.

Table 7. Extrapolated ptC and ppC Structural Motifs and Their Hydrides

Structural Motifs of PtC	Hydrides of ptC Motifs	Structural Motifs of ppC	Hydrides of ppC Motifs
 T13		 P10	
 T14			
 T15	 (Ref. 57)		
 T16	 (Ref. 57)		

^a The structures are optimized and frequencies are calculated at the B3LYP/6-311+G(d,p) level of theory.

(cf. Tables 4–6). In particular, the ppC- and phC-containing carbon–boron clusters (cf. Tables 5 and 6) all have relatively high energies. The high-energy characteristic of these clusters may be understood from different bonding behavior of C and B atoms even though boron and carbon are neighbor elements in the second row of the periodic table with similar valence electron structures $2s^22p^1$ and $2s^22p^2$. The formation of two-center/two-electron bond (2c/2e bond) is more favorable for C atom. In contrast, B atom tends to form electron-deficient bonds (such as the 3c/2e bond) which can lead to versatile tetra-, penta-, hexa-, hepta-, and even octacoordination boron.^{49,55} Hence, C atoms tend to occupy peripheral positions in the low-lying isomers of the carbon–boron clusters (cf. Table 1 and Supporting Information).

Can these ptC, ppC, and phC-containing (Tables 4–6) metastable structures be synthesized in the laboratory? This is still an open question. A necessary condition for realizing these novel structures in the laboratory is that intrinsically high rearrangement barriers exist for the pmC to prevent structural isomerization. For example, it has been shown that ~ 1.0 eV barrier height exists for the rearrangement of the C_3B_4 toward its lowest-energy isomer.²⁹ Some *ab initio* molecular dynamics simulations also confirm kinetic stabilities of some phC compounds.³¹ In any case, the energy data in Tables 4–6, as well as a recent photoelectron spectroscopy experiment,³³ suggest that direct synthesis of ptC, ppC, and phC-containing carbon–boron compounds will be very challenging.

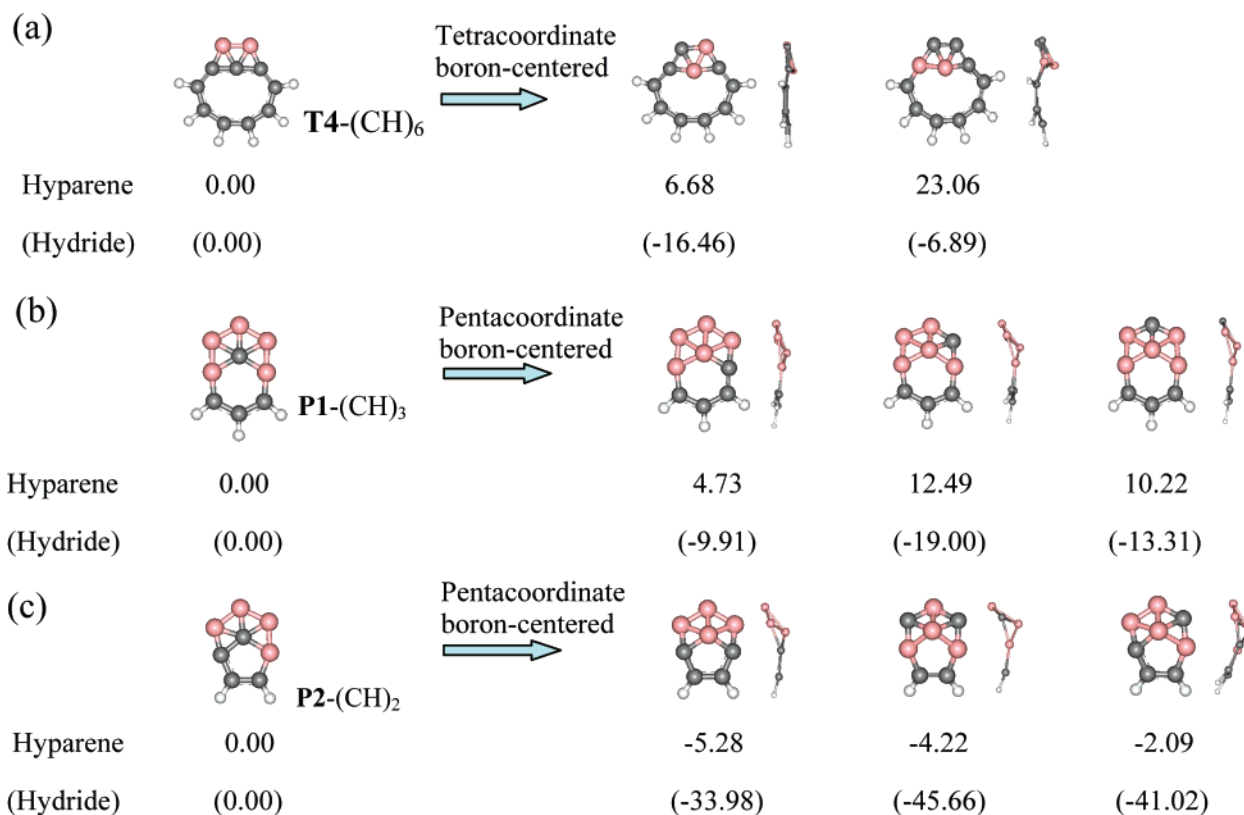


Figure 3. Relative stabilities of (a) ptC-containing hyparenes [**T4**-(CH)₆], hydrides and their boron-centered isomers; (b) ppC-containing hyparenes [**P1**-(CH)₃], hydrides and their boron-centered isomers; (c) ppC-containing hyparenes [**P2**-(CH)₂], hydrides and their boron-centered isomers. The relative energies of hydrides are given in the parentheses. All relative energies are in units of kcal/mol.

3.6. Relative Stabilities of ppC-Containing Hyparenes Molecules. As mentioned previously, it is possible to significantly enhance the stabilities of ptC and ppC species by making an *extended* molecular system, for example, by combining the ptC and ppC units with appreciable hydrocarbon units $-(CH)_n-$. An important feature of the ptC, ppC, and phC structural motifs is that they are extendable. Indeed, a family of ppC-containing hyparenes molecules have been theoretically proposed based on the structural units of $-CB_5-$ (**P1**), $-C_2B_4-$ (**P2**), and $-C_3B_3-$ (**P8**).³⁰ Moreover, myriad phC-containing molecules were also recently rationalized based on the building block $-CB_6^{2-}$.³¹

The pyramidal conversion has been shown to be a major isomerization mechanism in the boron-containing ptC system.⁵⁶ However, few studies have examined relative stabilities between carbon-centered and boron-centered isomers in the extended pmC systems.³¹ It has been shown that the exchange of the central C atom with a perimeter B atom in the phC systems can significantly lower the system energy,³¹ consistent with the stability tendency in the mixed carbon–boron cluster. Here, using three hypothetical monocyclic hyparene molecules, (**T4**-(CH)₆, **P1**-(CH)₃,³⁰ and **P2**-(CH)₂,³⁰), we confirm that it is possible to reduce the energy difference or even reverse the relative stabilities of the boron-centered and carbon-centered isomers by combining the ptC and ppC motifs with the hydrocarbon units $-(CH)_n-$. We can obtain *hydrides* by saturating the ptC (**T4**) and ppC (**P1** and **P2**) motifs with two hydrogen atoms, which are all stable *local* minima in the planar geometry. As expected, the exchange of the central C atom with a perimeter B atom in the *hydrides* significantly lowers the energy (see Figure 3, energy values in the parentheses).

Conversely, for the hyparene **T4**-(CH)₆, **P1**-(CH)₃,³⁰ and **P2**-(CH)₂,³⁰ the trend in the relative stabilities can be very different. In fact, one can see from Figure 3a and 3b that the ptC- and ppC-containing **T4**-(CH)₆ and **P1**-(CH)₃ are actually more stable than their boron-centered isomers by 6.68 and 4.73 kcal/mol, respectively. Also, the largest energy difference between the boron-centered isomer and the ppC isomer of the **P2**-C₂H₂ (Figure 3c) decreases to ~ 5 kcal/mol. The enhanced stabilities of these ptC- and ppC-containing *hyparenes* **T4**-(CH)₆, **P1**-(CH)₃, and **P2**-(CH)₂ are mainly due to their rigid coplanar structure. The replacement of the central C atom by B atom in **T4**-(CH)₆, **P1**-(CH)₃, and **P2**-(CH)₂ destroys the planarity of the system as shown in Figure 3. The B atom is pushed out of the molecular plane, which reduces relative stabilities the boron-centered isomers. Note that the phC would benefit less in relative stabilities from the formation of the hyparenes molecule $CB_6-(CH)_2$,³¹ because the exchange of the central C atom with the perimeter B atom will result in an energetically more favorable planar hexacoordinate boron center.

Finally, we remark that although the ptC- and ppC-containing *hyparenes* **T4**-C₆H₆ and **P1**-C₃H₃ appear to be very stable, they are still *local minimum* structures. For example, for the **P1**-(CH)₃, a lower energy [-13.86 kcal/mol at the B3LYP/6-311+G(d,p) level] ppC hyparene structure, **P1**-(CH)₃-iso, is found, which can be viewed as relocating the position of a $-CH-$ substituent, as shown in Figure 4a. Still, the exchange of the central C atom with a perimeter B atom in the **P1**-(CH)₃-iso raises the total energy, confirming the high stability of this new hyparene structure. However, a planar hexacoordinate boron-centered isomer structure (Figure 4b) is found to be more stable than both the ppC-containing hyparenes **P1**-C₃H₃ and **P1**-

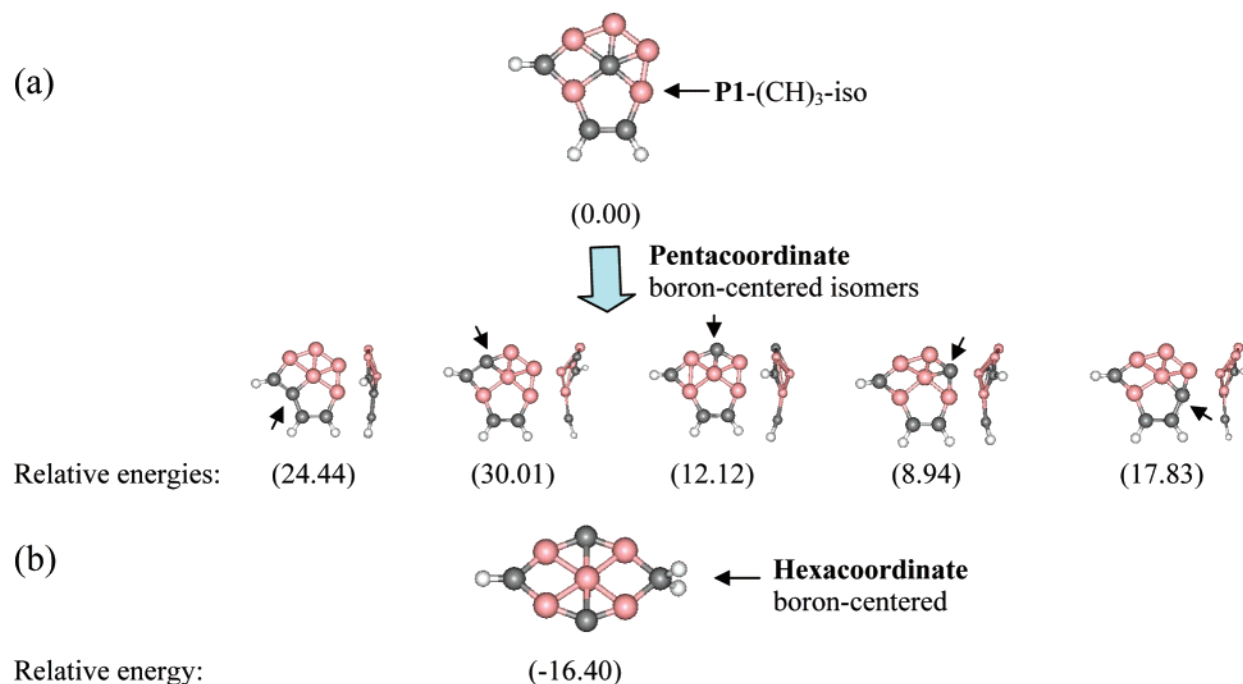


Figure 4. (a) A ppC-containing hyparene **P1-(CH)₃-iso** and its boron-centered isomers. (b) Low-energy phC-centered isomer. [Values in parentheses represent relative electronic energies calculated at the B3LYP/6-311+G(d,p) level and in units of kcal/mol.] The geometric data of hyparene **P1-(CH)₃-iso** and the hexacoordinate boron-centered isomer are given in Supporting Information.

C_3H_3 -iso by 30.26 and 16.40 kcal/mol [B3LYP/6-311+G(d,p) level], respectively. Despite the fact that the hyparenes (such as **P1-C₃H₃** and **P1-C₃H₃-iso**) are not necessarily the global minima, their unique rigid coplanar structure coupled with energetically favorable ppC motif provide a better hope for experimental isolation in the laboratory. It may be worthy of comparing the *hyparene* structures with other known constrained organic systems, such as *fenestranes*.^{4d,22} The latter systems are capable of possessing both relative high energies (because of the constraints) and structural rigidity.^{4d,22}

4. Conclusions

We report the first comprehensive study of the planar tetra-, penta-, and hexacoordinate carbons covering all the small-sized carbon–boron clusters $C_{m=1-4}B_{n=4-8}$ and their anions. A new boron-stabilized ptC molecule, CB_4 , is identified, which is stable enough for experimental synthesis. Besides the CB_4 , more than 30 forms of myriad ptC, ppC, and phC structural motifs are found. Although these are metastable structures, they enrich knowledge of bonding styles for the carbon atoms. We also showed that most ptC-, ppC-, and phC-containing carbon–boron clusters are energetically high-lying isomers. The more favorable structures are the planar tetra-, penta-, and hexacoordinate borons, which are the dominant structural units in the low-lying isomers of $C_{m=1-4}B_{n=4-8}$ and their anions. The exchange of the

planar-multicoordinate central C atom with the perimeter B atom in the $C_{m=1-4}B_{n=4-8}$ clusters generally results in isomers with much lower energies. This may explain why pmC clusters are hardly detectable in a recent photoelectron spectroscopy experiment. On the other hand, it is possible to significantly improve the stabilities of the ptC and ppC units by attaching them with appreciable hydrocarbon units, such as the $-(CH)_n-$ (forming the rigid hyparene structures).³⁰ Even though the hyparene structures are still not the global minima, the molecular design offers a synthetic route to realize pmC-containing compounds.

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Supporting Information Available: The complete reference 42, the geometries and relative energies of the top three low-lying isomer structures of carbon–boron clusters $C_{m=1-4}B_{n=4-8}$ and their anions, the geometrical data for structures given in Figure 4, and the infrared spectrum of the global minimum CB_4 . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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