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Planar pentacoordinate carbon in a sulphur-surrounded boron wheel: the global minimum of CB₅S₅⁺†

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We report a $\sigma + \pi$ double aromatic $CB_5S_5^+$ cluster, the first global minimum unusually having a planar hypercoordinate carbon inside a boron wheel. Five peripheral sulfur atoms stabilize the carbon-centered boron wheel by weakening the electron deficiency of the boron atoms through strong S \rightarrow B π back-bonding.

Having intrigued chemists for more than half a century, studies on exotic planar hypercoordinate carbon (phC) are still confronted by difficulties in experimental realization.¹ Specifically, since Hoffmann and co-workers pioneered the project in 1970 to achieve planar tetracoordinate carbon (ptC) in equilibrium structures,² a large number of phC species have been computationally designed.^{1,3} Nevertheless, few of them have been realized experimentally due to the issue of thermodynamic stability.⁴ The majority of computationally designed phC species are not the lowest-lying isomers on their potential energy surfaces (PESs), and are hard, if not impossible, to synthesize and characterize in experiments. This common knowledge is based on the results from joint experimental and computational studies, in which the computational works found that only when the phC structures are the global-minimum (GM) can they be experimentally realized.⁵ Therefore, it is highly desired to discover GM structures with the phC arrangement.

In phC chemistry, the GM structures generally have amphoteric metals, such as Be and Al, as the key ligand atom.^{1b,6} Remarkably, the ptC clusters $C_2Al_4^{-7}$ and $C_5Al_5^{-}$,⁸ first predicted to be the GM and a highly competitive isomer of the GM, were experimentally realized by Dong *et al.*^{5e} and Zhang *et al.*,⁹ respectively. These two excellent experimental achievements

uster, the first global dinate carbon inside stabilize the carbonron deficiency of the ording. Here a century, studies (phC) are still contation.¹ Specifically, the project in 1970 of thermodynamic difference for thermodynamic difference for thermodynamic have been compuof thermodynamic have been compution to design phC structures, chemists are keener on using boron than amphoteric metals because carbon-boron bonding is more covalent than carbon-metal bonding. Nevertheless, almost all phC structures having boron atom(s) are not the GMs, because their competitive isomers with a planar hypercoordinate boron (phB) are more stable in energy due to the electron-deficiency of boron, which leads to a higher preference for multicentre bonding than carbon. This common knowledge is demonstrated by experimental studies on an array of binary boron-carbon clusters CB_6^- , CB_6^{2-} , CB_7^- , and CB_8^- , 5^h none of which actually contain phC.

Consequently, a big challenge in phC chemistry is to achieve thermodynamically stable phC structures with boron atom(s) as the ligand(s). Currently, only CB_4^+ , CAl_3B^{2-} , CB_2Al_2Mg , CB₂Ga₂Mg, and CB₃Mg₂⁻ clusters¹⁰ have been confirmed to be boron-containing GMs with a perfect phC. These clusters are achieved by the charge effect, the electron localization effect, or favourable electrostatic interactions. Nonetheless, the boron atoms in these clusters never compose an integrated wheel. Given that boron wheels with a planar hypercoordinate transition metal have been successfully characterized in photoelectron spectroscopy,¹¹ it is natural to ask whether a carbon atom can stay stably inside a boron wheel. The answer is positive! In this contribution, we report the CB₅S₅⁺ star, a GM cluster with the desired ppC in a B_5 wheel (1a in Fig. 1). We note that a recent M.A. thesis has studied the $CB_5S_5^+$ species, but it was optimized to a non-planar structure with C₁ symmetry,¹² which is potentially different from the perfect ppC structure reported in our work.

This study has been inspired by both previously reported boraplane¹³ and our recently reported ppC $CAl_5O_5^+$ cluster.^{6a} The perfect ptC in boraplane was achieved by replacing ligand carbon atoms in the octaplane with boron atoms, which adjusted the electronic structure of the ptC centre, while the ppC in $CAl_5O_5^+$ was designed by bridging the Al–Al edges of a milestone ppC CAl_5^+ cluster¹⁴ with O atoms, which not only

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Fig. 1 B2PLYP-D3(BJ)/aug-cc-pVTZ-optimized structures of CB₅O₅⁺ ($\mathbf{0}$, $C_{5\nu}$), CB₅S₅⁺ ($\mathbf{1a}$, D_{5h}) and the concerned isomers of $\mathbf{1a}$. The bond lengths (in Å) and Wiberg bond orders are given in black and italic red fonts, respectively. The relative energies (ΔE , in kcal mol⁻¹) are reported at both CCSD(T) + ZPE_{B2PLYP-D3(BJ)} and B2PLYP-D3(BJ) levels.

protected the active low valent Al atoms, but also made the Al atoms in $CAl_5O_5^+$ less electron-deficient than those in CAl_5^+ . Can this type of change in electronic properties happen to boron? To answer this question, we tried to replace Al atoms in $CAl_5O_5^+$ with B atoms. However, the corresponding $CB_5O_5^+$ cluster (0, see Fig. 1) adopts a non-planar structure in C_{5v} symmetry at the B2PLYP-D3(BJ)¹⁵/aug-cc-pVTZ level, which may be due to the geometric mismatch between the carbon centre and the small B5O5 ring. Interestingly, 0 has a rather wide HOMO-LUMO gap of 9.94 eV at the B2PLYP-D3(BJ)/ aug-cc-pVTZ level, hinting at a well-defined electronic structure. So, it is worth modifying the structure of **0** to achieve a perfect ppC system. Herein, we choose to replace O atoms with larger S atoms, thus leading to the $CB_5S_5^+$ cluster (1a, see Fig. 1). At the B2PLYP-D3(BJ)/aug-cc-pVTZ level, 1a is perfectly planar. The C-B distances in 1a are 1.644 Å, short enough for each boron atom to be counted as a coordination to carbon, suggesting that 1a is an eligible ppC cluster. Note that the Wiberg bond order for C–B bonding (WBI_{C–B}) is 0.62 in 1a, indicating the obvious covalency.

Since boron commonly prefers the planar hypercoordinate central position more than carbon, it is of interest to compare the stability of **1a** with its isomer **1b** (Fig. 1) having a phB. The relative energies are assessed at the CCSD(T)/aug-cc-pVTZ level considering the zero-point energy (ZPE) corrections at B2PLYP-D3(BJ)/aug-cc-pVTZ (abbreviated as CCSD(T) + ZPE_{B2PLYP-D3(BJ)}). Surprisingly and remarkably, **1b** is 61.2 kcal mol⁻¹ higher than **1a** at this level of theory. The PES of CB₅S₅⁺ is further explored here using the stochastic search algorithm¹⁶ as coded in the GXYZ 2.0 program.^{7,17} The results indicate that **1a** is the true GM of the CB₅S₅⁺ system and the second lowest isomer **1c** (Fig. 1) locates 1.1 kcal mol⁻¹ higher. **1c** has a ptC and can be built from **1a** by breaking one C–B connection. Other isomers are higher in energy than **1a** by at least 17.2 kcal mol⁻¹ (see **1d** in Fig. 1), and thus we shall focus on **1a** in the following.

To evaluate the dynamic stability of **1a**, 100 ps Born–Oppenheimer molecular dynamic (BOMD) simulations¹⁸ were performed at four selected temperatures, including 4, 298, 500, and 1000 K and at the PBE/DZVP level, where **1a** is an energy minimum ($\nu_{\min} = 26 \text{ cm}^{-1}$). Shown in Fig. 2 are plots describing



Fig. 2 RMSD (in Å) *versus* simulation time (in ps) for cluster **1a** during the BOMD simulations at 4, 298, 500, and 1000 K, respectively.

structural evolution during the simulations using the root-meansquare deviation (RMSD) relative to the optimized geometry. The RMSD plots at 4 and 298 K have no upward jump and the fluctuations are also small, suggesting that **1a** is dynamically very rigid. As a comparison, those at 500 and 1000 K all show reversible upward jumps. Detailed structural sampling indicates the reversible isomerization to **1c**. Nevertheless, in the majority of the simulation time at 500 K, the structure of **1a** is maintained. Thus, though **1a** is not dynamically rigid at this temperature, it should determine the spectroscopic features in future experimental studies. In contrast, the structures of both **1a** and **1c** account for about half of the simulation time at 1000 K. In all BOMD simulations, the planarity of the system is maintained. Cluster **1a** possesses a well-defined electronic structure, as reflected by a wide HOMO–LUMO gap of 7.47 eV at the B2PLYP-D3(BJ)/aug-cc-pVTZ level and high vertical detachment energy (VDE) of 13.22 eV and rather low vertical electron affinity (VEA) of 4.31 eV at the OVGF/aug-cc-pVTZ level.¹⁹ The wide HOMO–LUMO gap, high VDE and low VEA suggest a low trend for **1a** to excite, lose and gain electron. Thus, **1a** is electronically robust.

To better understand the electronic structure of **1a**, adaptive natural density partitioning (AdNDP) analysis²⁰ is performed. As shown in Fig. 3, **1a** has five lone pairs of S atoms (bonding element **A**) with an occupation number (ON) of 1.95 |e|, ten B-S 2c-2e σ bonds (element **B**, ON = 1.94 |e|), and five B-S-B 3c-2e π bonds (element **C**, ON = 1.99 |e|). Such π bonds show obvious S \rightarrow B back-bonding characters. Since each B atom is involved in two of these π bonds and each S atom forms one such bond with two B atoms, the B atoms would accept a substantial amount of electrons from S atoms. As a result, the electron deficiency of the B atoms in **1a** is significantly weakened, which should be the key reason why carbon can stay favorably inside the planar pentacoordinate center. The remaining four pairs of electrons form three 6c-2e σ bonds (element **G**, ON = 1.97-1.99 |e|) and one 11c-2e π bond (element **G**,



Fig. 3 Chemical bonding patterns of clusters **1a** and **1b** according to the AdNDP analysis. Occupation numbers (ONs) are denoted.

ON = 2.00 |e|). These four delocalized σ/π bonds are crucial for its planarity and contribute to stabilizing the ppC structure. Indeed, they not only let the bonding around the central carbon meet the octet rule, but also offer double $6\sigma/2\pi$ aromaticity to **1a**.

Since the structural difference between 1a and 1b only lies in the position of carbon, one would wonder why 1b is much less stable than **1a**. AdNDP analysis suggests that exchanging the position of carbon with one of the boron atoms significantly affects the σ -bonding framework. As shown in Fig. 3, the delocalized CB₅ 6c-2e σ bonds (elements D-F) in 1a are absent in 1b. Instead, there is one C-B 2c-2e σ bond (element S, ON = 1.93 |e|) and two B_3 3c-2e σ bonds (element T, ON = 1.94 |e|). Therefore, the less stability of **1b** (relative to **1a**) may be attributed to the loss of σ electron delocalization within the CB₅ moiety. Other bonding elements in 1b are similar to those in 1a, as exemplified by five 1c-2e lone pairs of S atoms (elements H-J, ON = 1.94-1.97 |e|), ten B-S or C-S $2c-2e \sigma$ bonds (elements K-O, ON = 1.89-1.98 |e|), five B-S-B or B-S-C 3c-2e π bonds (elements **P-R**, ON = 1.91–1.99 |e|), and one 11c–2e π bond (element U, ON = 2.00 |e|).

To independently verify the existence of aromaticity, we have performed the nucleus-independent chemical shift (NICS) calculations.²¹ The results are presented in the form of colorfilled cross sections of NICS (CS-NICS).²² As shown in Fig. 4, CS-NICS(0) and CS-NICS(1) correspond to the NICS distribution in the molecular plane (approximate plane for **1b**) and that in the plane parallel to and located 1 Å above the molecular plane, which are employed to assess σ and π aromaticity, respectively. The ring-like light blue region within the CB₅ moiety of **1a** (Fig. 4A) indicates strong aromatic electron circulation, which is consistent with three evenly distributed delocalized 6c–2e



Fig. 4 NICS results for clusters **1a** and **1b**. Panels **A** and **C** correspond to the molecular planes, while panels **B** and **D** correspond to the planes parallel to and located 1 Å above the molecular planes. The NICS values that are negative, positive, and close to zero denote aromaticity, anti-aromaticity, and non-aromaticity, respectively.

 σ bonds, as revealed from AdNDP analysis. In contrast, the light blue regions distribute separately within the CB₅ moiety of **1b** (Fig. 4C). These consist of two B₃ triangles adjacent to a carbon atom, as well as a mid-point region in the C–B connection, which are divided by yellow or light green regions (non-aromaticity) in the B₃ triangle opposite to the carbon atom and two C–B–B triangles. Consequently, σ electrons do not fully delocalize in the CB₅ moiety of **1b**, which is in line with one C–B 2c–2e σ bond and two B₃ 3c–2e σ bonds, as generated by AdNDP analysis. In short, **1b** does not possess σ aromaticity. The π aromaticity is not essentially different in **1a** and **1b**, as reflected by the CS-NICS(1) plots (Fig. 4B and D), in which the regions above the CB₅ moieties are largely filled with green, the sign for aromatic electron circulations.

In conclusion, we have demonstrated through the case of the ppC CB_5S_5^+ cluster that the carbon atom can be stabilized in the centre of an integrated boron wheel when the electron deficiency of boron is properly weakened. The isomer with a central planar pentacoordinate boron is 61.2 kcal mol⁻¹ less stable than the ppC cluster because of the loss of σ -aromaticity. Being a dynamically viable global energy minimum, the ppC CB₅S₅⁺ cluster should be promising for gas-phase generation and spectroscopic characterizations.

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Conflicts of interest

There are no conflicts to declare.

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