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Electron-compensation: a valid strategy for chemically stabilizing boron-based clusters with hypercoordinate centres[†]

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To eliminate the chemical instability caused by the electron-deficiency of boron, two types of usual dative π bonds are recommended for compensating boron atoms in the computational design of boronbased clusters having hypercoordinate centres, which can lead to unusually stable targets for synthesis in the condensed phase.

Due to its electron-deficiency, boron shows high preference for multicentre σ bonds, which are different from that of carbon (localized σ bonds). The unique bonding preference not only leads to peculiar structures for small boron clusters,¹ but also supports the non-classical hypercoordinate centre (HC) in doped boron clusters, as illustrated by boron wheels² with a central planar hypercoordinate main group element or transition metal, and metal-boron binary clusters adopting novel half-sandwich,³ anti-sandwich,⁴ drum-like,⁵ cage-like,⁶ and other exotic structures.^{1c}

Previously, boron-based clusters with HCs were realized experimentally in the gas phase, while they were unknown in the condensed phase. The most probable reason could be the exposed electron-deficient boron atoms, which lead to the chemical instability that deters the corresponding clusters from being synthesized. Electronically, the clusters with exposed electron-deficient boron atoms are often related to narrow HOMO-LUMO gaps, low vertical detachment energies (VDEs), and/or high electron affinities (EAs). Chemically, such clusters are sensitive to nucleophilic attack, aggradation, oxidation, *etc.* Therefore, the boron-based clusters with HCs should be stabilized by weakening the electron-deficiency of boron and providing steric protection.

As a result, we propose in this work a strategy named "electron-compensation". We were inspired by our recently reported highly stable boron-containing clusters,⁷ including a $CB_5S_5^+$ cluster with a ppC, $MB_7O_7^+$ (M = Ni, Pd, Pt) clusters with a planar heptacoordinate transition metal, and [OB-(MB₇O₇)- BO^{-} (M = Fe, Ru, Os) clusters with a heptagonal bipyramidal nonacoordinate transition metal. Why are they so stable? The detailed analyses revealed that the boron atoms in these clusters were all surrounded by oxygen or sulphur atoms (X), which could form strong $X \rightarrow B$ dative π bonds to weaken the electron-deficiency of boron atoms. Simultaneously, the X atoms provide an inert outer shell for the steric protection of an active core boron-containing moiety. In this work, we call such electronic and steric stabilization effects provided by X atoms "electroncompensation", which is recommended for use in the rational design of boron-based clusters with HCs. In the following, we describe three aspects of the strategy, including the eligibility of X, the possible compensation model, and general requirements. In addition, the validity of the strategy was confirmed by an example application.

First, though our previous studies⁷ had proved the eligibility of oxygen and sulphur as X groups, we believe that the choice of X is not limited to them, but can be found in heavier chalcogens and other groups that can support the valence lone pair when forming the dative π bonds.

Second, we currently envisage two possible compensation models of $X \rightarrow B$ dative π bonds. Fig. 1a shows the bridging model, where each boron atom formally participates in two electron-sharing two-centre two-electron (2c-2e) σ bonds and two B $\leftarrow X \rightarrow B$ three-centre two-electron (3c-2e) dative π bonds. Fig. 1b shows the terminal model, where each boron atom formally participates in an electron-sharing 2c-2e σ bond, an electron-sharing π bond, and an X \rightarrow B 2c-2e dative π bond.

Third, to facilitate the synthesis in the condensed phase, a desired cluster should be neutral and it would be better if it was

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[†] Electronic supplementary information (ESI) available: Computational methods, the structures of CB₄X₄ (X = O, S, Se, Te, Po), Wiberg bond orders of **1a**, NBO charges (in |e|) of **1a**, full AdNDP bonding patterns of **1a**, the shapes of deformation densities ($\Delta \rho$) for EDA-NOCV analysis of **1a**, concerned isomers of **1a**, BOMD simulations of **1a**, and Cartesian coordinates for the clusters reported in this work. See DOI: https://doi.org/10.1039/d2cc05654b



ternary (containing only HCs, B, and X). Simultaneously, all boron atoms should be electronically saturated by electronegative X atoms/groups.

Electronically, the boron atoms in the proposed models are highly fixed by strong X-B bonding and their electron-deficiency is significantly lowered due to $X \rightarrow B \pi$ backdonation. Geometrically, the inert X atoms/groups are generally located at the outer-shell of the clusters, which can play a role in the stabilization via steric protection. Hence, though two electron-compensation models shown in Fig. 1 are usual in chemistry, the targeted applications in stabilizing the boron-based clusters are unusual because they may eliminate chemical instability at the source. The effectiveness of the strategy can be preliminarily proved by very recently reported ionic species.⁷ However, these examples are not enough for validation for two reasons: First, the corresponding clusters are not neutral and second, the symmetries of their structures are too high for experimental synthesis. Therefore, to give a more convincible validation, a strategy is applied in the following to design a neutral, ternary, and low symmetric global energy minimum (GEM) with a planar hypercoordinate carbon (phC).

We first try to meet the requirement of being neutral. The bridging model shown in Fig. 1a can be cyclized to give the B_nX_n rings, which can support *n* electrons for centripetal bonding. Hence, carbon with four valence electrons electronically fits a B_4X_4 ring to form a neutral CB_4X_4 cluster with a tetracoordinate carbon. To be concise, we initially examined chalcogens as X. However, as shown in Fig. S1 in the ESI,† though the clusters get close to a planar structure at the PBE0/BS1 level when

X goes from O to Po, the perfectly planar structure is not reached even for X = Po. So, the B_4 ring with only one chalcogen atom at each B–B edge is too small geometrically for a carbon to stay stably inside. Moreover, when the electronegativity of X atoms decreases from O to Po, the HOMO–LUMO gaps of CB₄X₄ clusters synchronously decrease from 6.33 eV to 3.84 eV, indicating that oxygen is the best choice in chalcogens for such types of structure. Therefore, we decided to modify the CB₄O₄ cluster by substituting the bridging oxygen atoms in CB₄O₄ with the larger B–O binary groups, which can enlarge the space inside the B₄ ring to achieve a planar tetracoordinate carbon (ptC) and simultaneously lower the symmetry of the cluster.

In this work, the previously reported $B_2O_2^8$ (Fig. 2) molecule was introduced onto each bridging O atom, leading to a new B₂O₃ bridging group. As shown in Fig. 2, the bonding environment of two boron atoms in the B₂O₃ group meets bridging and terminal models shown in Fig. 1, respectively. Correspondingly, introducing one or two B2O2 groups onto a CB4O4 cluster leads to new clusters with formulae of CB6O6 and CB8O8, respectively. As shown in Fig. 2, the CB₆O₆ cluster is still noticeably non-planar, but one CB_8O_8 cluster (1a) adopts a perfectly planar structure at the PBE0/BS1 level and the other one (1b) adopts a quasi-planar structure at the same level. The C-B distances in 1a are 1.500, 1.535, and 1.630 Å, respectively. Given that the sum of covalent radii of boron and carbon is 1.610 Å, these distances are short enough for the corresponding boron atoms to be counted as being coordinated to carbon, so the carbon atom in 1a should be a desired (neutral, ternary, and low-symmetry) cluster with a perfect ptC.

To prove the planar tetracoordination for carbon, we performed conventional natural bond orbital (NBO) analyses and the results are given in Fig. S2 (ESI[†]). As shown in the figure, the Wiberg bond orders for C–B bonding (WBI_{C–B}) range from 0.57 to 0.97 in **1a**, indicating the existence of significant covalent bonding. Simultaneously, the natural charge on carbon is -1.28 |e| and those on adjacent boron atoms range from



Fig. 2 Design of the CB_8O_8 cluster by modifying a CB_4O_4 cluster. All structures were optimized at the PBE0/BS1 level. The C-B distances in **1a** are given in Å.



Fig. 3 The key AdNDP bonding patterns of **1a**. For degenerate orbitals regarding molecular symmetries, only one orbital is shown for each pattern.

+1.07 to +1.11 |e|. Such a charge distribution pattern suggests the existence of strong attractive B–O electrostatic interactions. Therefore, four adjacent boron atoms are chemically bonded to carbon, consistent with the result of geometry analysis that carbon is planar tetracoordinate.

To give more details on chemical bonding in 1a, an adaptive natural density partitioning (AdNDP) analysis was performed. AdNDP can describe the chemical bonding through the n-centre two electron (nc-2e) bonds and thus is suitable for clusters with multicentre bonding. As shown in Fig. 3, and Fig. S3 in the ESI,† 1a possesses eight 1c-2e O lone pairs with an occupation number (ON) of 1.92–1.99 |e|, fourteen B–O 2c-2e σ bonds (ON = 1.94–1.99 |e|), two B–B 2c-2e σ bonds (ON = 1.98 |e|), four 2c-2e B–O π bonds (ON = 2.00 |e|, orbitals A and B), and six B-O-B 3c-2e π bonds (ON = 1.99 |e|, C-E). The B-O-B 3c-2e π bonds (ON = 1.99 |.99 |99 |ith ample: (a) W.-L.nation, which compensate the electron-deficient boron atoms. Regarding the bonding within the CB₄ moiety, there are three 5c-2e σ bonds (ON = 1.96 |e|, F-H) and one 5c-2e π bond (ON = 1.96 |e|, I). We analyzed the composition of these four AdNDP partitioned orbitals. The results reveal that the 2s, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals of carbon account for 54.3%, 72.1%, 72.7%, and 77.4% of orbitals F, G, H, and I, respectively, suggesting that carbon deeply participates in the bonding with four peripheral boron atoms, which is consistent with the above conclusions that carbon is in planar tetracoordination. In addition, these four orbitals fill six σ and two π delocalized electrons to the valence shell of the central carbon atom, not only meeting the octet rule, but also offering σ and π double aromaticity, which both stabilize the ptC arrangement.

To justify the dative nature of O–B π bonds, we performed the energy decomposition analysis (EDA) in combination with the natural orbitals for chemical valence (NOCV). **1a** was divided into two fragments in the EDA-NOCV analysis, including a neutral triplet O atom at the top of the cluster and the rest as a neutral triplet CB₈O₇ framework. As shown in Table 1, the results revealed that the energy for total orbital interactions (ΔE_{orb}) between two fragments is -671.6 kcal mol⁻¹, in which

Table 1 Results of EDA-NOCV calculations for the singlet state CB₈O₈ cluster at the PBE0/TZ2P level using a neutral O atom in the triplet reference state with a $2s^22p_x^{-1}2p_y^{-1}2p_z^{-2}$ electron configuration and CB₈O₇ (triplet) as interacting fragments. Energy values are given in kcal mol⁻¹

Energy terms	Assignments	Interaction energies for O (T) + CB_8O_7 (T)
$\Delta E_{\rm int}$		-265.8
ΔE_{Pauli}		635.4
$\Delta E_{\rm Attr}$		-901.2
$\Delta E_{\rm elstat}^{a}$		-229.6(25.5%)
$\Delta E_{\rm orb}{}^a$		-671.6 (74.5%)
$\Delta E_{\mathrm{orb}(1)}{}^{b}$	CB_8O_7 -O (2p _x) electron- sharing σ bond	-314.9 (46.9%)
$\Delta E_{\text{orb}(2)}{}^{b}$	CB_8O_7 –O (2p _y) electron- sharing σ bond	-311.4 (46.4%)
$\Delta E_{\mathrm{orb}(3)}{}^{b}$	$CB_8O_7 \leftarrow O(2p_z) \pi$ backdonation	-25.0 (3.7%)
$\Delta E_{\rm orb(rest)}^{l}$	5	-20.3 (3.0%)

^{*a*} The percentage values in the parentheses are the contribution to the total attractive interactions ($\Delta E_{\text{Attr}} = \Delta E_{\text{elstat}} + \Delta E_{\text{orb}}$). ^{*b*} The percentage values in the parentheses are the contribution to the total orbital interactions (ΔE_{orb}).

the energies for forming two O–B electron-sharing σ bonds $(\Delta E_{\text{orb}(1)} \text{ and } \Delta E_{\text{orb}(2)})$ are -314.9 and 311.4 kcal mol⁻¹, accounting for 46.9% and 46.4% of the total ΔE_{orb} , respectively. Nevertheless, though the energy for O \rightarrow B π backdonation $(\Delta E_{\text{orb}(3)})$ only accounts for 3.7% of the total ΔE_{orb} , the actual value for such π backdonation reaches 25.0 kcal mol⁻¹, suggesting the existence of a fairly strong dative bond. The deformation density of such a dative bond can be found in Fig. S4C in the ESI.†

To corroborate the aromaticity suggested by AdNDP analysis, we performed nucleus-independent chemical shift (NICS) calculations and presented the results in the form of colourfilled cross sections (CS) of NICS. The σ -aromaticity was described by the CS at the molecular plane [CS-NICS(0)], while the π -aromaticity was described by the CS parallel to and located 1 Å above the molecular plane [CS-NICS(1)]. As shown in Fig. 4A, the CS-NICS(0) for 1a shows a bright and evenly distributed blue region within a CB4 core moiety, a clue for strong σ aromatic electron circulation. Simultaneously, the CS-NICS(1) for 1a (Fig. 4B) exhibits an evenly distributed green region above the CB_4 moiety, suggesting the existence of π aromaticity. The NICS calculations indicate σ and π double aromaticity for 1a, consistent with the conclusions of AdNDP analysis. According to the request of a referee, we considered the contributions from core electrons to the total NICS for the point located 0.5 Å above ptC using both natural chemical shielding (NCS) and removing the valence electron $(RVE)^9$ methods. The results reveal that the contributions from core electrons are -4.40 and -0.11 ppm for NCS and RVE methods, respectively, which are much smaller than the contributions from $6\sigma + 2\pi$ delocalized electrons (-35.14 ppm). So, the core electrons do not significantly affect the NICS results.

To be synthesizable in the condensed phase, a cluster should be stable thermodynamically, dynamically, and chemically. According to our extensive exploration of the CB_8O_8



Fig. 4 The cross-sections (CSs) of NICS for **1a**. Panel **A** corresponds to the molecular planes, while panel **B** corresponds to the planes parallel to and located 1 Å above the molecular plane. The negative and positive NICS values indicate the aromatic and anti-aromatic ring circulations, respectively.

potential energy surface, 1a is the GEM, 1b is the second lowest isomer located 4.6 kcal mol⁻¹ higher (see ΔE in Fig. 2), while other isomers are less stable in energy than 1a by at least 22.3 kcal mol⁻¹ (see **1c-1e** in Fig. 2), so **1a** is thermodynamically stable. Note that though we can manually construct five isomers (see Fig. S5 in the ESI⁺) through exchanging the position of carbon with that of a boron in 1a, the lowest one (1f) is located 104.6 kcal mol^{-1} higher in energy than 1a, suggesting that the saturated boron atoms are more suitable to act as ligands than as planar tetracoordinate centres. The dynamic stability of 1a was studied by 100 picosecond Born-Oppenheimer molecular dynamics (BOMD) simulations at 4, 298, 500, and 1000 K and the plots for variation of rootmean-square deviation of structures (Fig. S6 in ESI⁺) revealed that 1a is dynamically stable against isomerization or dissociation. The chemical stability of **1a** is studied by examining its electronic robustness. The results reveal that 1a possessed a wide HOMO-LUMO gap of 6.16 eV, a high VDE of 10.35 eV and a positive EA of 0.10 eV, indicating that it is very difficult for 1a to excite, lose or gain an electron, so it should be chemically stable. Being thermodynamically, dynamically, and chemically stable, 1a would be a feasible target for experimental synthesis of ptC species in the condensed phase.

In conclusion, we have proposed a strategy named "electroncompensation" for chemically stabilizing boron-based clusters with non-classical hypercoordinate centres and have validated its effectiveness. Though the proposed dative π bonding models for our strategy are ordinary in chemistry, the applications of the strategy can be extraordinary because the widespread applications of our strategy in computational design may offer enough amounts of viable targets for experimental synthesis in the condensed phase. We invite the utilization of our strategy in the computational design of boron-containing clusters with non-classical hypercoordinate centres, which will significantly promote the development of both boron chemistry and nonclassical bonding chemistry.

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Conflicts of interest

There are no conflicts to declare.

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