Pentagonal five-center four-electron π bond in ternary B₃N₂H₅ cluster: an extension of the concept of three-center four-electron ω bond†

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Boron-based heteroatomic rings can have exotic chemical bonding, in which the p lone-pairs of heteroatoms manage to participate in delocalized π bonding, compensating for boron’s electron-deficiency. We explore herein the bonding properties of ternary B–N–H systems with a pentagonal ring, using the B₃N₂H₅ clusters as examples. Computational structural searches lead to perfectly planar C₂ᵥ B₃N₂H₅ (1) and C₂ᵥ B₃N₂H₅− (2) as global minima for the neutral species and monoanion, which feature a pentagonal B₃N₂ ring. The corresponding dianion C₂ᵥ B₃N₂H₅²− (3) is a local minimum, whose global minimum adopts a chain-like open structure. Bonding analyses reveal a five-center four-electron (5c–4e) π system in 1, dubbed the 5c–4e o-bond. It is a 4π system in the bonding/nonbonding combination, originating from two N 2p lone-pairs, which can be considered as an extension of the concept of 3c–4e ω-bond. The extra electrons in 2 and 3 occupy a markedly destabilized π orbital. Thus, a 4π configuration, rather than a π sextet according to the (4n + 2) Hückel rule, is electronically robust for the B₃N₂H₅ clusters. Infrared and photoelectron spectra are predicted for 1 and 2, respectively. Structural evolution of ring-like and chain-like isomers with charge-state in B₃N₂H₅ clusters as examples. Computational structural searches lead to perfectly planar C₂ᵥ B₃N₂H₅⁻ clusters as analogs of naphthalene, bicyclobutadiene (C₄H₄), and antiaromatic cyclobutadiene (C₄H₄). Significant changes in the geometry of B₃N₂H₅⁻ upon substitution of the H terminals with three boronyl (BO) groups. Indeed, BO and H are isoelectronic, monovalent σ radicals. Similar to benzene, D₃h B₃O₃X₃ (X = O, N) in B₃N₂H₅ clusters are 4π systems in a bonding/nonbonding combination, in contrast to the bonding/antibonding combination in 4π-antiaromatic cyclobutadiene (C₄H₄).

1. Introduction

Boron as a neighbor of carbon in the periodic table is electron-deficient, resulting in unusual structural, electronic, and bonding properties for boron-based nanoclusters and nanomaterials. Theoretical and experimental studies have established an analogous relationship between boron-based clusters and aromatic hydrocarbons, including polycyclic aromatic hydrocarbons. Notably, classical inorganic benzene analogues, boroxine (B₃O₃H₃) and borazine (B₃N₃H₆), have received consistent attention. Both B₃O₃H₃ and B₃N₃H₆ possess a hexagonal B₃X₃ (X = O or N) ring...

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‡ D. Z. Li and L. Y. Feng contributed equally to this work.

† Electronic supplementary information (ESI) available: Alternative optimized low-lying structures of B₃N₂H₅ clusters at B3LYP/aug-cc-pVTZ level, along with their relative energies at B3LYP and single-point CCSD(T) (Fig. S1–S3); structure and bonding of chain-like open isomer of B₃N₂H₅ (Fig. S4 and S5); and optimized sandwich structures CₓB₃N₂H₅/Ni (1A₁) and CₓB₃N₂H₅/Ni (2A₁) at B3LYP level (Fig. S6). See DOI: 10.1039/c6cp07954g

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featuring twin B₃S₂ rings. Inspired by this finding, we further studied smaller B₃S₂H₃⁰⁻/– clusters, which were shown to be analogs of cyclopentadienyl and cyclopentadienyl anion (D₅h, C₅H₅⁻)¹,⁶,⁸

So, how far can we push the bonding analogy between heteroatomic B–X rings and cyclopentadienyl radical/cyclopentadienyl anion? Does the difference in electronegativity between B and X have a marked effect on the bonding nature of B–X rings? Does the Hückel rule govern the stability of B–X rings in extreme cases? Is the π sextet essential for pentagonal B–X rings? The current work attempts to address these issues. We have studied a series of boron–nitrogen hydride clusters, B₃N₃H₅⁰⁻/–, at three charge-states. The species are isovalent to C₅H₅⁻, C₅H₅⁻, and B₃S₂H₃⁰⁻/–, but differ from the latter systems in terms of electronegativity: 2.55 for C, 2.04/2.58 for B/S, and 2.04/3.04 for B/N. For the ternary B–N–H clusters, the neutral species and monoanion possess global-minimum structures with a pentagonal B₂N₂ ring: CᵥB₂N₂H₃ (1, ¹A₁) and CᵥB₂N₂H₅⁻ (2, ²B₁). The dianion has a pentagonal local minimum CᵥB₂N₂H₅⁰⁻ (3, ¹A₁), whose global minimum is chain-like. B₃N₃H₅ (1) has an energy gap of 5.42 eV between its highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO), which indicates a remarkably stable neutral cluster with a 4π system, in contrast to 6π aromaticity according to the (4n + 2) Hückel rule. The robust 4π system in 1 is proposed as a 5c–4e o-bond. It makes use of two N 2p lone-pairs for a completely bonding five-center π bond and a residual nonbonding one. The 5c–4e o-bond can be viewed as an extension of the 3c–4e o-bond in XeF₂.¹⁹

2. Computational methods

Global-minimum searches for the B₃N₃H₅ cluster were conducted at the density-functional theory (DFT) level using the Coalescence Kick (CK)²⁰,²¹ and Gradient Embedded Genetic Algorithm (GEGA)²²,²³ programs, further aided with manual structural constructions. Structures for B₃N₃H₅⁻ anion and B₃N₃H₅⁰⁻ dianion were computed primarily on the basis of low-lying isomers of B₃N₃H₅. Considering the connections of the potential energy surfaces in B₃N₃H₅⁰⁻/–, additional computer searches for B₃N₃H₅⁻ and B₃N₃H₅⁰⁻ do not seem necessary. Candidate low-lying structures were then fully optimized at the B3LYP/aug-cc-pVTZ level.²⁴,²⁵

Harmonic vibrational frequencies were calculated at the same level to verify that the reported structures are true minima. Relative energies for top low-lying isomers of B₃N₃H₅⁰⁻/– were refined using single-point CCSD(T) calculations²⁶–²⁸ at the B3LYP geometries. For the sandwich complexes, the Stuttgart relativistic small core basis set and effective core potential (Stuttgart RSC 1997 ECP)²⁹ were employed for Fe and Ni. Structural optimizations were performed for the complexes by taking into consideration different spin-multiplicity states.

Adaptive natural density partitioning (AdNDP)³⁰ and canonical molecular orbital (CMO) analyses, as well as nucleus-independent chemical shift (NICS)¹¹ calculations, were carried out to elucidate the nature of bonding and aromaticity in B₃N₃H₅⁰⁻/–. The NBO 5.0 program¹² was used to calculate natural atomic charges. The photoelectron spectrum of the B₂N₂H₅⁻ (2) monoanion cluster was simulated at the time-dependent B3LYP (TD-B3LYP)³³,³⁴ level and the infrared (IR) spectrum predicted for the B₃N₃H₅ (1) neutral species. All the calculations and analyses were performed using Gaussian 09.³⁵ Multiwfn³⁶ was used to perform the orbital composition analysis.

3. Results

Fig. 1 shows the Cᵥ global-minimum structures of B₃N₃H₅ (1, ¹A₁) and B₃N₃H₅⁻ (2, ²B₁), where 1 is identified from the CK and GEGA searches and 2 is obtained using low-lying isomers of B₃N₃H₅ as initial structures by adding one extra electron, followed by structural reoptimizations and energetics evaluation (including CCSD(T)). Also shown is a relevant Cᵥ local minimum for the dianion: B₂N₂H₅⁻ (3, ¹A₁). Alternative low-lying isomers of B₂N₂H₅⁰⁻/– within 30 kcal mol⁻¹ are presented in the ESI† (Fig. S1–S3).

3.1. B₃N₃H₅

As shown in Fig. 1 and Fig. S1 (ESI†), CᵥB₂N₂H₃ (1, ¹A₁) is global minimum for the neutral species. Structure 1 is perfectly planar and has a pentagonal heteroatomic B₂N₂ ring, terminated by H atoms akin to cyclopentadienyl. The closest competitive structure, CᵥB₂N₂H₃ (¹A₁), has a rhombic B₂N₂ core, which is terminated by three H atoms and one BH₂ group. It is marginally higher in energy by 0.56 kcal mol⁻¹ at B3LYP. In fact, the B₂N₂ ring is common in low-lying isomers of B₂N₂H₅⁰⁻/– (Fig. S1 and S2, ESI†). However, at single-point CCSD(T) level, 1 is better defined as

![Fig. 1](image-url) Global-minimum structures of CᵥB₂N₂H₃ (1, ¹A₁) and CᵥB₂N₂H₅⁻ (2, ²B₁) at the B3LYP/aug-cc-pVTZ level, along with a local minimum of CᵥB₂N₂H₅⁻ (3, ¹A₁). These structures possess a heteroatomic B₂N₂ five-membered ring. Selected bond distances are labeled in Angstroms. The B atom is in pink, N in blue, and H in gray.
global minimum, with alternative structures being at least 4.8 kcal mol$^{-1}$ higher in energy.

Recommended covalent radii$^{37}$ give the upper bound of B–B single, B–B double, and B–B triple bonds as 1.70, 1.56, and 1.46 Å, respectively. The B1–B3 distance in 1 (1.74 Å) is close to and somewhat longer than a single bond; we tentatively assign it as a single bond. The B–N distances are 1.42 and 1.45 Å, which are in between single (1.56 Å) and double (1.38 Å) bonds, suggesting a delocalized ring system. The calculated HOMO–LUMO gap of 1 is 5.42 eV at B3LYP, confirming a robust, closed-shell electronic system.

3.2. B$_3$N$_2$H$_5$\(^{-}\)

Adding one extra electron to the LUMO of 1, we reach the $C_{2v}$ $B_3N_2H_5$ (2, $^3B_1$) monoanion. It turns out to be the global minimum (Fig. S2, ESI$^\dagger$), which lies 9.66 and 18.09 kcal mol$^{-1}$ below the second isomer, $C_6$ ($^2A_1'$), at B3LYP and single-point CCSD(T) levels, respectively. Note that the rhombic isomer for the monoanion, $C_{2h}$ ($^3B_1$), is 17.36 kcal mol$^{-1}$ above the global minimum at B3LYP, in sharp contrast to the neutral system (0.56 kcal mol$^{-1}$; Fig. S1, ESI$^\dagger$).

The B1–B3 distance in 2 is 1.67 Å, being shorter by 0.07 Å than that in 1, suggesting that the former is probably beyond a single bond. The B–N bonds in 2 are 1.44 versus 1.47 Å, which both fall in between single and double bonds, similar to 1. However, the bottom B–N bonds (B1–N8 and B3–N7) expand by 0.05 Å from 1 to 2, whereas the upper ones shrink by 0.01 Å. The distance changes indicate that the extra electron in 2 is heavily located on B1–B3, and that there appears to be substantial intramolecular Coulomb repulsion even in the monoanion.

3.3. B$_3$N$_2$H$_5$\(^{2-}\)

A cyclic dianion cluster $C_{2v}$ $B_3N_2H_5$\(^{2-}\) (3, $^1A_1$) (Fig. 1) is located by adding one electron to the singly-occupied HOMO of 2. Structure 3 is a true minimum, which lies 20.65 and 12.19 kcal mol$^{-1}$ above a chain-like open structure $C_6$ ($^2A_1'$) (Fig. S3, ESI$^\dagger$) at B3LYP and CCSD(T), respectively. Structure-wise, 3 is rather similar to 2, and the B1–B3 distance expands slightly from 2 to 3 despite one more bonding electron in the latter. The potential energy surface of the $B_3N_2H_5$\(^{2-}\) dianion appears to be more complicated than those of the neutral species and monoanion, in particular at the CCSD(T) level, where three chain-like dianion structures are within 1.18 kcal mol$^{-1}$. Given the computational uncertainties in energetics for the dianion, these structures cannot be distinguished from each other. We thus choose to discuss only the first structure in the text.

4. Discussion

4.1. Structures and bonding in $B_3N_2H_5$\(^{6/-2/-}\): the importance of 4r electrons

The $C_{2v}$ $B_3N_2H_5$\(^{6/-2/-}\) (1–3) species have a five-membered $B_3N_2$ ring as the structural core, similar to the $C_5$ ring in $C_5H_5$ and $C_5H_5^*$. In terms of valence electrons, $B_3N_2H_5$ has one fewer than $C_5H_5$. Thus, 1–3 are formally isovalent to $C_5H_5$\(^{7/-0/-}\). Bonding analyses for 1–3 are relatively simple. For example, the bonding elements in 1 as revealed from AdNDP are illustrated in Fig. 2. It has 24 electrons, of which 10 are used for five terminal 2c–2e σ B–H bonds and another 10 for four 2c–2e σ B–N bonds and one 2c–2e σ B–B bond. In short, the σ framework consumes 20 electrons for classical, localized bonds. The remaining 4 electrons form the π framework with a completely bonding 5c–2e π bond, as well as a formally bonding/antibonding 5c–2e π bond (Fig. 2, bottom panels), which look similar in shape to two of the π CMOs in a typical π sextet, such as in benzene. All AdNDP bonds in 1 have nearly ideal occupation numbers (ONs) shown.

4.2. On the five-center four-electron (5c–4e) σ-bond in $C_{2v}$ $B_3N_2H_5$: a conceptual extension of the 3c–4e σ-bond

Electron-deficient compounds are known to form 3c–4e σ-bond.$^{19}$ For example, XeF$_2$ as a linear species is held together by a
For boron-based clusters, the 3c–4e oxygen bonding system in clusters with a rhombic B$_2$O$_2$ core was described as formally 5c–4e bonding/nonbonding combination of completely bonding CMO and a nonbonding one. Such a bonding/nonbonding combination of σ CMOs is called the 3c–4e σ-bond, leading to an effective Xe–F bond order of 0.5. For boron-based clusters, the 3c–4e σ-bond was recently extended to linear π systems (Fig. 4(a)). Furthermore, the 4π system in clusters with a rhombic B$_2$O$_2$ core was described as the 4c–4e σ-bond (Fig. 4(b)). The favorable 4π electron-counting in C$_{2v}$ B$_2$N$_2$H$_5$ 1–3 offers the possibility to further extend the concept of the 3c–4e σ-bond, this time from the linear three-center case to the pentagonal, heteroatomic B$_3$N$_2$ ring.

The key to validate this extension lies in the nature of two π CMOs in 1 (Fig. 4(c); Table 1). Here HOMO–4 is a completely bonding π CMO, being contributed by p atomic orbitals (AOs) of N7/N8 (72.8% in total) and yet with substantial contributions from p AOs of B1/B2/B3 (26.9% in total). On the other hand, HOMO–1 is dominated by 91.1% contributions from p AOs of N7/N8. Since the N–N distance (2.38 Å; compared with 1.42 Å for N–N single bond 13) is quite large, the N–N interaction is negligible and HOMO–1 can be practically viewed as nonbonding. In short, HOMO–4 and HOMO–1 in 1 represent a bonding/nonbonding combination of π CMOs, exactly in the spirit of the linear 3c–4e σ-bond 13 and rhombic 4c–4e σ-bond 14. Therefore, we propose to call the 4π system in B$_2$N$_2$H$_5$ (1) the 5c–4e σ-bond.

The 5c–4e σ-bond in 1 originates from two N 2p lone-pairs. It makes use of two of these electrons for a completely bonding π CMO owing to the covalent/ionic interaction of B/N centers; two “residual” electrons occupy a nonbonding CMO. The net bonding effect of the 4π electrons is dominated by HOMO–1 (2.14 eV at B3LYP; Table 1) allowing an estimation of the bond strength as ~ 4.3 eV for the 4π electrons, which is significant in particular considering the fact that they would otherwise be merely two lone-pairs. The concept of the 5c–4e σ-bond may be applicable to the o-bond19 and rhombic 4c–4e o-bond. Therefore, we propose to call the 4π system in B$_2$O$_2$H$_2$ (1Ag) but with substitution of one NH group by S.

The orbital energy difference between HOMO–1 and HOMO–4 in B$_2$N$_2$H$_5$ 1 is 2.14 eV, which is sufficiently large for the one-electron orbitals not to overlap significantly and can thus be practically viewed as nonbonding. However, this difference is too small compared to the one-electron bonding orbitals of the 4π electron system (aromatic at least 5h C$_5$H$_5^+$). The orbital energy difference between HOMO–1 and HOMO–4 in B$_2$O$_2$H$_2$ (1Ag) allows an estimation of the bond strength as ~ 4.3 eV for the 4π electrons, which is significant in particular considering the fact that they would otherwise be merely two lone-pairs.

The orbital energy difference between HOMO–1 and HOMO–4 in B$_2$O$_2$H$_2$ (1Ag) allows an estimation of the bond strength as ~ 4.3 eV for the 4π electrons, which is significant in particular considering the fact that they would otherwise be merely two lone-pairs.
Table 2  Nucleus-independent chemical shift, NICS(1) and NICSzz(1), for B_{11}N_{11}H_{19}^{2-} and B_{11}N_{11}H_{13} as well as their relevant B–S–H, B–N–S–H, and C–H species, at the B3LYP/aug-cc-pVTZ level. These values are calculated at 1 Å above the ring center.

<table>
<thead>
<tr>
<th>Species</th>
<th>NICS(1) (ppm)</th>
<th>NICSzz(1) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{2v} B_{3}N_{2}H_{5}^{2-} (A\textsubscript{1})</td>
<td>−0.16</td>
<td>−1.66</td>
</tr>
<tr>
<td>C\textsubscript{2v} B_{3}N_{2}H_{5} (A\textsubscript{1})</td>
<td>0.64</td>
<td>5.80</td>
</tr>
<tr>
<td>C\textsubscript{2v} B_{3}S_{3}H_{5}^{2-} (A\textsubscript{1})</td>
<td>−5.06</td>
<td>−13.64</td>
</tr>
<tr>
<td>C\textsubscript{2v} B_{3}S_{2}H_{3} (A\textsubscript{1})</td>
<td>0.24</td>
<td>6.71</td>
</tr>
<tr>
<td>C\textsubscript{2v} B_{3}NSH_{4}^{2-} (A\textsubscript{1})</td>
<td>−4.73</td>
<td>−11.15</td>
</tr>
<tr>
<td>D_{n1} C_{3}H_{3} (A\textsubscript{1})</td>
<td>−9.66</td>
<td>−34.54</td>
</tr>
<tr>
<td>C\textsubscript{2v} C_{3}H_{5} (A\textsubscript{1})</td>
<td>65.01</td>
<td>198.97</td>
</tr>
</tbody>
</table>

* The 6t systems are shown in boldface.

C\textsubscript{2v} B_{3}NSH_{4}^{2-} as a true minimum has calculated NICS(1) and NICSzz(1) values of −4.73 and −11.15 ppm, respectively, which are in between those of C\textsubscript{2v} B_{3}S_{2}H_{3}^{2-} and C\textsubscript{2v} B_{3}N_{2}H_{5}^{2-} (3). The least aromaticity of C\textsubscript{2v} B_{3}N_{2}H_{5}^{2-} (3) in all species discussed above makes the B_{3}N_{2}H_{5}^{2-}/− system an ideal candidate to validate the 4\textalpha{} electron-counting and the concept of 5c–4e o-bond.

4.3. Charge-state dependence of ring-like versus chain-like structures in B_{3}N_{2}H_{5}^{2−}/−

Ring-like C\textsubscript{2v} B_{3}N_{2}H_{5}^{0−}/− (1 and 2) have proved to be global minima (Fig. 1), whereas C\textsubscript{2v} B_{3}N_{2}H_{5}^{2−} (3) is only a local minimum, being ∼21 kcal mol\(^{-1}\) above a chain-like C\textsubscript{6} (A\textalpha{}) open structure. A relevant chain-like isomer can be traced back in B_{3}N_{2}H_{5}^{0−}/− as well. The energetics of these two sets of structures are compared in Fig. 5 at three charge-states; note that the open structure of B_{3}N_{2}H_{5} differs slightly from those of B_{3}N_{2}H_{5}^{2−}/− in the position of one H atom. From neutral species to monoanion, the ring-like isomer remains as global minimum. However, at the dianion charge-state, the chain-like isomer gains relative stability and becomes the global minimum, and indeed the top six isomers of B_{3}N_{2}H_{5}^{2−} are all chain-like (Fig. S3, ESI†). Since the frontier CMOs of 2 and 3 are the same, the reverse energy order from monoanion and dianion has to be attributed to the enhanced intramolecular Coulomb repulsion in dianion 3.

Calculated natural charges for 1–3 (Table 3) indicate that 84% of the first extra charge, and 97% of the second, are distributed on B1/B3/B2. In particular, the B1/B3 centers accept 65% and 48% of the first and second charges, respectively, which should impose substantial Coulomb repulsion in 3. Understandably, chain-like B_{3}N_{2}H_{5}^{2−} can better manage the charges. Coulomb repulsion has already a discernible structural effect in monoanion 2 (Fig. 1), for which the B1–N8/B3–N7 bonds are elongated. For dianion 3, the B1–B3 bond does not shrink despite the gain of electron in the vicinity, further manifesting the repulsive effect in the ring.

Fig. S4 (ESI†) illustrates the chain-like C\textsubscript{6} (A\textalpha{}) structure of B_{3}N_{2}H_{5}^{2−} at the B3LYP level. The B–N distances (from left to right) of 1.36/1.38, 1.27, and 1.50 Å are assigned to double B–N, triple B≡N, and single B–N bonds, respectively,\(^{37}\) which lead to a classical Lewis structure as shown in Fig. S4(b) (ESI†). The Lewis presentation is fully confirmed by the AdNDP data (Fig. S5, ESI†). The two extra charges are located primarily on two N centers (26% versus 43%).

4.4. Predicted infrared spectrum and photoelectron spectrum

To aid future experimental characterizations of the C\textsubscript{2v} B_{3}N_{2}H_{5} (1, A\textsubscript{1}) and B_{3}N_{2}H_{5} (2, B\textsubscript{2}) global-minimum clusters, we report their calculated infrared (IR) spectrum and photoelectron spectrum, respectively. The IR simulation of 1 is presented in Fig. 6. Three adjacent peaks are revealed at 2611–2647 cm\(^{-1}\), which correspond to B–H symmetric stretchings. Among them, the intense peak at 2627 cm\(^{-1}\) (a\textsubscript{1}) is associated with terminal B1–H and B3–H stretching. Another four adjacent peaks are present at 1273–1394 cm\(^{-1}\), mainly corresponding to B–H rocking vibrations. We also calculated the vertical ionization potential (VIP) of 1, which amounts to 10.06 eV at the B3LYP level (Table 4).
be much smaller than those of the isovalent B3S2H3.
0.25 and 0.38 eV at single-point CCSD(T). These values turn out to
are 0.37 and 0.51 eV, respectively, at B3LYP, which are refined to
simulated PES spectrum of C₆.
6
1.81 eV, VDE: 1.98 eV; single-point CCSD(T) data), 18
attempt to pursue sandwich-type complexes by using
4.5.
C₆
5c–4e o-bond (see Section 4.2.).
features an extremely low first VDE and a sizable energy gap
found with VDEs from 0.51 to 6.28 eV. This PES spectrum
calculations, is shown in Fig. 7. Nine detachment channels are
attributed to intramolecular Coulomb repulsion in
C₆
D
Ferrocene, Dsh (C₅H₅)₂Fe (17,18
4
C₆
[(B₃N₂H₅)₂Fe]²⁻ (6), C₂v
[(B₃N₂H₅)₂Fe]²⁻ (7), C₂v
[(B₃N₂H₅)₂FeLi]₂ (8), and C₂v
[(B₃N₂H₅)₂FeLi]₂ (9) complexes at the B3LYP level, as compared
with the cyclopentadienyl counterparts: Dsh (C₅H₅)₂Fe (4) and
Dsh (C₅H₅)₂Fe (5). Structural integrity of 2 is preserved in
complexes 6–9. Differing from staggered 4 and eclipsed 5, the
staggered 6 is a true minimum with the lowest vibrational
frequency of 57.68 cm⁻¹ and it is more stable with respect to
eclipsed 7 (Table 4). Complex 6 follows the 18-electron rule.
When two Li⁺ cations are attached to diamions 6 and 7, neutral
salt complexes C2h [(B₃N₂H₅)₂Fe]Li₂ (8) and C2v [(B₃N₂H₅)₂FeLi]₂
(9) with a planar B₃N₂H₅⁻ motif are obtained. Complex 8 is a true
minimum with the lowest frequency of 51.78 cm⁻¹. Both 7 and 9
are transition states. The calculated VIP of 8 is 5.77 eV at B3LYP, a
value that is slightly lower than that of 5 (7.06 eV).
To further evaluate the thermodynamic stability of sandwich
complexes 6 and 8, we have calculated their formation energies
(FEs) following the equations:
Fe (5A1g) + 2B₃N₂H₅⁻ (2, C₂v, ²B₁) = [(B₃N₂H₅)₂Fe]²⁻ (6, C₂h, ¹A₁g)
2Li⁺ (¹A₁g) + [(B₃N₂H₅)₂Fe]²⁻ (6, C₂h, ¹A₂g) = [(B₃N₂H₅)₂FeLi]₂
(8, C₂h, ¹A₂g)
In the calculations of FEs, free energy corrections are considered.
As shown in Table 4, the FEs are 3.60 and −113.24 kcal mol⁻¹ for 6
and 8, respectively. The FE for 8 is substantial, indicating that its
formation is highly exothermic. Note that the FEs of Dsh (C₅H₅)₂Fe
(5) and C2h [(B₃N₂H₅)₂FeLi]₂ (ref. 18b) at the same level are −192.56
and −87.60 kcal mol⁻¹, respectively. Thus, B₃N₂H₅⁻ (2) is probably
a more favorable ligand than B₃S₂H₅⁻. Similar to Dsh (C₅H₅)₂Fe,¹⁷
η⁴-heterocyclic (C₂P₂R₂)Ni sandwiches,⁴⁵,⁴⁶ and metal–benzene
complexes M₄(benzene)₆m (M = Sc to Cu),¹⁷ sandwiches 6 and 8
(especially 8) may be viable targets for synthetic efforts.
We have also attempted to use C₂v B₃N₂H₅ (1) as a ligand
to build sandwich complexes, for which the same metal Fe,

4.5. C₂v B₃N₂H₅⁻ (2) as a potential ligand in sandwich-type
complexes
Ferrocene, Dsh (C₅H₅)₂Fe, in which cyclopentadienyl C₅H₅
serves as ligand, was first prepared in the early 1950s.¹⁷,¹⁴–¹⁴⁴
C₂v B₃N₂H₅⁻ (2) is isovalent to cyclopentadienyl. We thus
attempt to pursue sandwich-type complexes by using 2 as ligand.
Fig. 8 depicts the optimized structures of C₂v [(B₃N₂H₅)₂Fe]²⁻ (6),
C₂v [(B₃N₂H₅)₂FeLi]₂ (7), C₂v [(B₃N₂H₅)₂FeLi]₂ (8), and C₂v
[(B₃N₂H₅)₂FeLi]₂ (9) complexes at the B3LYP level, as compared

Table 4 Calculated lowest vibrational frequencies (υₘₚₜ), vertical ionization potentials (VIPs), and formation energies (FEs) of C₂v B₃N₂H₅⁻ (1), C₂v B₃N₂H₅⁻ (2), and their relevant sandwich-type complexes (6–9). For comparison, those of the cyclopentadienyl counterparts, Dsh (C₅H₅)₂Fe (4) and Dsh (C₅H₅)₂Fe (5), have also been tabulated.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>υₘₚₜ (cm⁻¹)</th>
<th>VIP (eV)</th>
<th>FE (kcal mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂v B₃N₂H₅⁻ (1)</td>
<td>270.22</td>
<td>10.06</td>
<td></td>
</tr>
<tr>
<td>C₂v B₃N₂H₅⁻ (2)</td>
<td>374.74</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td>Dsh (C₅H₅)₂Fe (4)</td>
<td>−40.37</td>
<td>7.05</td>
<td>−192.17</td>
</tr>
<tr>
<td>Dsh (C₅H₅)₂Fe (5)</td>
<td>31.97</td>
<td>7.06</td>
<td>−192.56</td>
</tr>
<tr>
<td>C₂v [(B₃N₂H₅)₂Fe]²⁻ (6)</td>
<td>57.68</td>
<td>3.60</td>
<td></td>
</tr>
<tr>
<td>C₂v [(B₃N₂H₅)₂Fe]²⁻ (7)</td>
<td>−54.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂v [(B₃N₂H₅)₂FeLi]₂ (8)</td>
<td>51.78</td>
<td>5.77</td>
<td>−113.24</td>
</tr>
<tr>
<td>C₂v [(B₃N₂H₅)₂FeLi]₂ (9)</td>
<td>−10.77</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Free energy corrections are included in the FE calculations. The difference in FE between 6 and 8, as well as between 7 and 9, is attributed to intramolecular Coulomb repulsion in 6 and 7 due to the multiple charges.

Fig. 6 Simulated infrared (IR) spectrum of C₂v B₃N₂H₅⁻ (1) neutral species.

Fig. 7 Simulated photoelectron spectrum of C₂v B₃N₂H₅⁻ (2) cluster at the time-dependent B3LYP (TD-B3LYP) level with the aug-cc-pVTZ basis set. The simulation was done by fitting the distribution of calculated vertical detachment energies (VDEs) with unit-area Gaussian functions of 0.04 eV half-width.
basis set, and method are chosen. Sandwich-type \( \text{C}_{2v} \) \([\text{B}_3\text{N}_2\text{H}_5 \text{Fe}] \) complex (with 16 electrons) turns out to be a second order saddle point, with imaginary frequencies of complex (with 16 electrons) turns out to be a second order saddle point, with imaginary frequencies of 

5. Conclusions

We have reported theoretical predictions, at the B3LYP and single-point CCSD(T) levels, of boron-nitrogen hydride clusters \( \text{C}_{2v} \) \( \text{B}_3\text{N}_2\text{H}_5^{0/-} \) (1 and 2) as global minima via structural searches, as well as \( \text{C}_{2v} \) \( \text{B}_3\text{N}_2\text{H}_5^{2/-} \) (3) as a local minimum, and studied their electronic structure and chemical bonding. \( \text{C}_{2v} \) \( \text{B}_3\text{N}_2\text{H}_5 \) (1) with a pentagonal \( \text{B}_3\text{N}_2 \) core is a 4π system in a bonding/nonbonding combination, akin to that of a prototypical three-center four-electron \( \sigma \)-bond. We propose the concept of a five-center four-electron \( \sigma \)-bond, where the 4π electron-counting in 1 is robust. In contrast, 6π is not favorable for the \( \text{B}_3\text{N}_2\text{H}_5^{0/-/2/-} \) system. The concept may be applicable for other heteroatomic, pentagonal clusters and molecules.

Acknowledgements

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References

29  Stuttgart RSC 1997 ECP basis sets used in this work and the related references therein can be obtained from https://bse.pnl.gov/bse/portal.