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# Ferrocene analogues of sandwich $B_{12} \cdot Cr \cdot B_{12}$: A theoretical study

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The bowl $B_{12}$ cluster was previously reported to be analogous to benzene and predicted to be one of the best candidates to be new inorganic ligands. The structural stability and electronic properties of a new sandwich compound $Cr(B_{12})_2$ ($D_{3d}$) have been investigated by using density functional theory. It is found that the sandwich $Cr(B_{12})_2$ ($D_{3d}$) is a stable complex with large binding energy (−5.93 eV) and HOMO-LUMO gap (2.37 eV), as well as $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$, following the 18-electron principle. The detailed molecular orbitals and aromaticity analyses indicate that the sandwich compound $Cr(B_{12})_2$ ($D_{3d}$) is electronically very stable. The natural bond orbital analysis suggests that *spd*-$\pi$ interaction plays an important role in the sandwich compounds. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4773281]

## I. INTRODUCTION

The discovery in 1951 of the transition metal $\pi$-complex, ferrocene ($Fe(C_5H_5)_2$),[1,2] gave rise to great interest being shown in the possible structures of such compounds and in the nature of the metal-ring bonding. Subsequently, the sandwich type structures had been proposed.[3] Among these, $Fe(C_5H_5)_2$ (Refs. 4–14) and dibenzenechromium $Cr(C_6H_6)_2$ (Refs. 10, 11, and 15–27) as two typical sandwich clusters have been studied extensively. For $Fe(C_5H_5)_2$, a cyclopentadienyl anion ($C_5H_5^-$) contributes six $\pi$ electrons as $\pi$-bonding ligand and the $Fe^{2+}$ ($3d^6$) contributes six electrons, which follows the 18-electron principle. Similarly, for $Cr(C_6H_6)_2$, a benzene molecule ($C_6H_6$) contributes six $\pi$ electrons as $\pi$-bonding ligand and the Cr ($3d^44s^2$) atom contributes six electrons, which also meets the 18-electron principle. With more studies on sandwich compounds, the ligands are various and include not only hydrocarbons, e.g., borane,[28,29] CO,[30] $PH_3$,[30] boron clusters,[31–35] etc. The spectroscopic and theoretical studies have shown that boron clusters have planar geometries and exhibit aromatic and antiaromatic electronic properties analogous to hydrocarbons,[36] so they are predicted to be promising molecules for coordination chemistry as potential new ligands and for materials science as new building blocks.[37] A series of small carborne molecules containing multiple aromatic $B_3$ and $B_4$ units have been reported by Berndt and co-workers.[38–41] Up to now, some theoretical confirmations have been reported to design potential sandwich-like complexes based on the pure boron units $B_3^-$,[31] $B_6^{2-}$,[32,42] $B_7^-$,[33] $B_8^{2-}$,[34] and $B_{8\text{-}14}$.[35] In particular, Zhai and co-workers[36] have demonstrated that $B_{12}$ can be viewed to be analogous to $C_6H_6$. Later, Alexandrova and co-workers[34] indicated that $B_{12}$ can represent a better candidate to be a new inorganic ligand and building block of solids because of its closed shell structure with $\sigma$ and $\pi$ aromaticity.

Therefore, we design a new sandwich compound $Cr(B_{12})_2$ based on $B_{12}$ ligand. In this paper, we investigate the structural stability and electronic properties of staggered $Cr(B_{12})_2$ by using density functional theory (DFT). We show that: (i) $B_{12}$ unit can be a stable ligand in the sandwich $Cr(B_{12})_2$ ($D_{3d}$); (ii) the sandwich $Cr(B_{12})_2$ ($D_{3d}$) is very stable, following the 18-electron principle, as well as $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$.

## II. COMPUTATIONAL METHODS

Initially, we optimized the geometries of $Fe(C_5H_5)_2$, $Cr(C_6H_6)_2$, and $Cr(B_{12})_2$ ($D_{3d}$ and $D_{3h}$) by using the TPSSh[43] functional. In the optimization procedure, the 6-31G* and lanl2dz basis sets are employed for ligands and metals, respectively. The calculations of the energies and HOMO-LUMO gaps are performed at the TPSSh/6-311+G* level. Ligands (including hydrocarbon/boron) are also studied at the TPSSh/6-311+G* level. The TPSSh functional was proven to give reasonably accurate energetic properties of small boron clusters.[44–46] The $E_b$ (sandwich compound) = $E$ (sandwich compound) − $E$ (neutral metal) − 2 × $E$ (neutral ligand) value is the binding energy of the sandwich compound. The energies, $E(M^+)$ and $E(M^-)$, of the ionic states of each system M were calculated at the TPSSh/6-311+G* level by using the geometry of the neutral system optimized at the TPSSh/6-31G* level. Then, the IP = $E(M^+) - E(M)$ and EA = $E(M) - E(M^-)$ values are the vertical ionization potential and vertical electron affinity, respectively. In order to justify the use of TPSSh functional for these sandwich compounds, a benchmark calculation (Table I) on $Fe(C_5H_5)_2$ compound is completed by B3LYP,[47–49] M06,[50] PBE0,[51] and TPSSh[43] functionals with 6-311+G* basis set, and the high-level MP2 method[52] with aug-cc-pvtz basis set. The results of the benchmark calculation and experimental data verify the reliability of the TPSSh functional for these systems. The calculations of vibrational frequencies and ultraviolet-visible (UV-vis) absorption spectra and natural bond orbital (NBO)[53] analysis were

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TABLE I. Comparison of computed and experimental energies for $C_5H_5 \cdot Fe \cdot C_5H_5$ (Figure 1).

| Method[a] | $E_b$ (eV)[b] | $\Delta E_{HL}$ (eV)[c] | VEA (eV)[d] | VIP (eV)[e] |
|---|---|---|---|---|
| B3LYP | − 5.98 | 5.24 | −0.30 | 7.15 |
| M06 | − 7.79 | 4.74 | −0.40 | 6.93 |
| PBE0 | − 7.34 | 5.76 | −0.31 | 7.06 |
| TPSSh | − 7.66 | 4.26 | −0.34 | 7.14 |
| MP2 | − 9.35 | | −0.33 | 6.26 |
| Expt. | − 6.37[f] | | | 7.05[g] |

[a] Method: the basis set of DFT is 6-311+G* and the one of MP2 method is aug-cc-pvtz.
[b] $E_b$ is binding energy.
[c] $\Delta E_{HL}$ is HOMO-LUMO gap.
[d] VEA is vertical electron affinity.
[e] VIP is vertical ionization potential.
[f] −6.37 eV is the experimental $E_b$ of $Fe(C_5H_5)_2$ (Ref. 56).
[g] 7.05 eV is the experimental VIP of $Fe(C_5H_5)_2$ (Ref. 15).

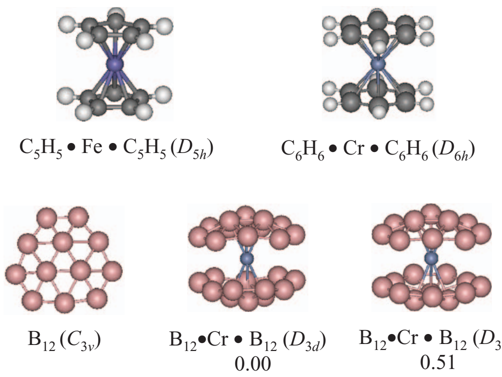
performed by TPSSh functional (ligands at 6-31G* and metals at lanl2dz levels). All calculations are carried out using the GAUSSIAN 09 package.[54]

## III. RESULTS AND DISCUSSION

### A. Energies and stability

The optimized geometries of $B_{12}$, $Cr(B_{12})_2$ ($D_{3d}$ and $D_{3h}$), $Cr(C_6H_6)_2$, and $Fe(C_5H_5)_2$ are shown in Figure 1. The XYZ coordinates of the $Cr(B_{12})_2$ ($D_{3d}$ and $D_{3h}$) compound can be found in the supplementary material.[55] $Fe(C_5H_5)_2$ is in $D_{5h}$ symmetry. $Cr(C_6H_6)_2$ is in $D_{6h}$ symmetry. $B_{12}$ is in $C_{3v}$ symmetry. $Cr(B_{12})_2$ in $D_{3d}$ symmetry is more stable than the one in $D_{3h}$ symmetry by 0.51 eV in energy. For $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$, the distances ($\exp_{M\text{-}C}$) between the metal and the carbon atoms experimentally are 2.064 ± 0.003 Å (Ref. 56) and 2.150 ± 0.002 Å,[57] respectively. At TPSSh/6-311+G* level, the calculated distances ($r_{M\text{-}C}$) are 2.042 Å and 2.138 Å, respectively, which are in agreement with experimental data. The computed $r_{M\text{-}B}$ of staggered $Cr(B_{12})_2$ is between 2.198 and 2.697 Å.

The binding energies ($E_b$), HOMO-LUMO gaps, vertical electron affinities (VEAs), and vertical ionization potentials (VIPs) of sandwich compounds $Fe(C_5H_5)_2$, $Cr(C_6H_6)_2$, and $Cr(B_{12})_2$ ($D_{3d}$ and $D_{3h}$) are listed in Table II. Comparing with the stable compounds $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$, we find that the staggered $Cr(B_{12})_2$ is also very stable. The calculated vibrational frequencies of $B_{12} \cdot Cr \cdot B_{12}$ (staggered and eclipsed) compound are shown in Figure 2. The vibrational frequencies of staggered $Cr(B_{12})_2$ are verified to be all positive, so it is indeed a local minimum. But there is a small imaginary vibrational frequency for eclipsed $Cr(B_{12})_2$ at 105 $cm^{-1}$, as labeled by arrow, so the eclipsed $Cr(B_{12})_2$ is a saddle point on the potential surface, which is the transition state for the rotation of the two $B_{12}$ moieties with respect to each and is 0.51 eV higher in energy. For $Fe(C_5H_5)_2$, the staggered $D_{5d}$ form is the transition state and the barrier to rotation from $D_{5d}$ to $D_{5h}$ is 0.04 eV (0.9 kcal/mol).[58] For $Cr(C_6H_6)_2$, the barrier to rotation from $D_{6d}$ to $D_{6h}$ is 0.03 eV (0.75 kcal/mol).[25] Therefore, the sandwich $Cr(B_{12})_2$ is analogous to $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$.



$C_5H_5 \bullet Fe \bullet C_5H_5$ ($D_{5h}$)
$C_6H_6 \bullet Cr \bullet C_6H_6$ ($D_{6h}$)
$B_{12}$ ($C_{3v}$)
$B_{12} \bullet Cr \bullet B_{12}$ ($D_{3d}$) 0.00
$B_{12} \bullet Cr \bullet B_{12}$ ($D_{3h}$) 0.51

FIG. 1. Optimized geometries of $C_5H_5 \cdot Fe \cdot C_5H_5$ ($D_{5h}$), $C_6H_6 \cdot Cr \cdot C_6H_6$ ($D_{6h}$), $B_{12}$ ($C_{3v}$), and $B_{12} \cdot Cr \cdot B_{12}$ ($D_{3d}$ and $D_{3h}$) at TPSSh/6-31G* and lanl2dz level, labeled are symmetry and relative energy of $B_{12} \cdot Cr \cdot B_{12}$ ($D_{3h}$) in eV to $B_{12} \cdot Cr \cdot B_{12}$ ($D_{3d}$) at TPSSh/6-311+G* level.

TABLE II. The binding energies, HOMO-LUMO gaps, vertical electron affinities (VEAs), and vertical ionization potentials (VIPs) of sandwich compounds $C_5H_5 \cdot Fe \cdot C_5H_5$, $C_6H_6 \cdot Cr \cdot C_6H_6$, and $B_{12} \cdot Cr \cdot B_{12}$ ($D_{3d}$ and $D_{3h}$).

| Compound | $E_b$ (eV)[a] | $\Delta E_{HL}$ (eV)[b] | VEA (eV) | VIP (eV) |
|---|---|---|---|---|
| $C_5H_5 \cdot Fe \cdot C_5H_5$ ($D_{5h}$) | −7.66 | 4.26 | − 0.34 | 7.14 |
| $C_6H_6 \cdot Cr \cdot C_6H_6$ ($D_{6h}$) | −2.83 | 3.30 | − 0.27 | 5.40 |
| $B_{12} \cdot Cr \cdot B_{12}$ ($D_{3d}$) | −5.93 | 2.37 | 2.31 | 7.72 |
| $B_{12} \cdot Cr \cdot B_{12}$ ($D_{3h}$) | −5.42 | 2.28 | 2.10 | 7.51 |

[a] $E_b$ is binding energy.
[b] $\Delta E_{HL}$ is HOMO-LUMO gap.

The calculated $E_b$ of $Fe(C_5H_5)_2$ is −7.66 eV, which is consistent with experimental $E_b$ = −6.37 eV (−147 kcal/mol).[56] The $E_b$ of $Cr(B_{12})_2$ ($D_{3d}$) is −5.93 eV, smaller than $Fe(C_5H_5)_2$ (−7.66 eV), but larger than $Cr(C_6H_6)_2$ (−2.83 eV). Moreover, the HOMO-LUMO gaps of $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$ are 4.26 eV and 3.30 eV, respectively, and the HOMO-LUMO gap of $Cr(B_{12})_2$ ($D_{3d}$) is also very large (2.37 eV). The optical band-edge of UV-vis absorption spectra (Figure S1 in the supplementary material[55]) is 2.29 eV, which is consistent with the computed the HOMO-LUMO gap (2.37 eV). In addition, the calculated VIPs of $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$ are 7.14 eV and 5.40 eV, which are in agreement with the experimental VIPs ($Fe(C_5H_5)_2$: 7.05 eV; $Cr(C_6H_6)_2$: 6.90 eV).[15] To further verify the reliability of the TPSSh functional for these systems, the VEA and VIP of $Fe(C_5H_5)_2$ are calculated by the high-level MP2 method with aug-cc-pvtz basis set and *ab initio* results (VEA = −0.33 eV and VIP = 6.26 eV) conform to the TPSSh results (VEA = −0.34 eV and VIP = 7.14 eV). Besides, the energy difference between VIP and VEA of $Cr(B_{12})_2$ ($D_{3d}$) is 5.41 eV (7.72 − 2.31), smaller than $Fe(C_5H_5)_2$ (7.14 + 0.34 = 7.48 eV), but near to $Cr(C_6H_6)_2$ (5.40 + 0.27 = 5.67 eV). In summary, the sandwich $Cr(B_{12})_2$ ($D_{3d}$) is indeed a very stable compound.

### B. Orbital analysis

To study the chemical bonding of these sandwich compounds $Fe(C_5H_5)_2$, $Cr(C_6H_6)_2$, and $Cr(B_{12})_2$) ($D_{3d}$) and ligands, molecular orbital (MO) analysis was given.

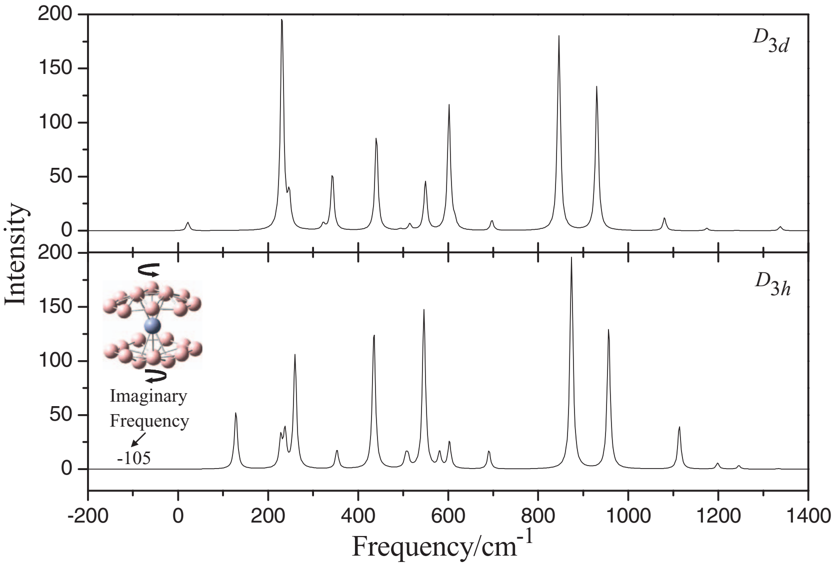


FIG. 2. Vibrational frequencies of $B_{12} \cdot Cr \cdot B_{12}$ ($D_{3d}$ and $D_{3h}$) compound, the arrow shows the imaginary frequency.

Here we first make detailed orbital analysis for each ligand as follows. From the MO diagrams (Figure S2 in the supplementary material[55]), the three delocalized $\pi$ orbitals can be identified easily (MO = 21, 27, and 28 in Figure 3), but it is difficult to identify the delocalized $\sigma$ orbitals. It is reported that $B_{12}$ is triply aromatic, i.e., $\pi$ aromatic and double $\sigma$ aromatic.[59] In order to gain insight into the nature of the bonding in $B_{12}$, we apply a new tool named adaptive natural density partitioning (AdNDP) to obtain patterns of chemical bonding. The method was recently developed by Zubarev and Boldyrev.[60–62] AdNDP is based on the concept of the electron pair as the main element of chemical bonding models, which recovers both Lewis bonding elements (1c–2e and 2c–2e objects) and delocalized bonding elements (*n*c–2e). In addition, we compare the results of AdNDP analysis of $B_{12}$ with the ones of hydrocarbon ligands (including $C_5H_5^-$ and $C_6H_6$). The results of AdNDP analysis are displayed in Figure 4. According to the results of AdNDP analysis, $C_5H_5^-$ (Figure 4(a)) has five peripheral 2c–2e C–C $\sigma$ bonds with occupation numbers ON = 1.98 |e| (superimposed on the single molecular framework), five 2c–2e C–H $\sigma$ bonds with ON = 1.99 |e| (superimposed on the single molecular framework), and three 5c–2e delocalized $\pi$ bonds with ON = 2.00 |e| responsible for the $\pi$ aromaticity of $C_5H_5^-$. $C_6H_6$ (Figure 4(b)) has six 2c–2e C–C $\sigma$ bonds with ON = 1.99 |e| (superimposed on the single molecular framework), six 2c–2e C–H $\sigma$ bonds with ON = 1.98 |e| (superimposed on the single molecular framework), and three 6c–2e delocalized $\pi$ bonds with ON = 2.00 |e| responsible for the $\pi$ aromaticity of $C_6H_6$. The quasi-planar $B_{12}$ (Figure 4(c)) has nine peripheral 2c–2e $\sigma$ bonds (three $\sigma$ bonds with ON = 1.93 |e| and six $\sigma$ bonds with ON = 1.89 |e|), three 4c–2e $\sigma$ bonds (ON = 1.96 |e|) delocalized mainly over the internal three-atomic cycle, which is responsible for $\sigma$ aromaticity satisfying Hückel's $4n+2$ rule, three 5c–2e $\sigma$ bonds with ON = 1.93 |e| responsible for the $\sigma$ aromaticity, and three 7c–2e $\pi$ bonds (ON = 1.97 |e|) binding the inner $B_3$ and the outer $B_9$ rings, which is responsible for the $\pi$ aromaticity of $B_{12}$. The above three distinct aromatic sextets ($4n+2$) of $B_{12}$ are shown clearly in Figure 4(c), which is in agreement with the previous study.[59] The delocalized $6\pi$-electron $B_{12}$ in staggered $Cr(B_{12})_2$ behaves analogous to the well-known $C_5H_5^-$ ligand in $Fe(C_5H_5)_2$ and $C_6H_6$ ligand in $Cr(C_6H_6)_2$.[36] All of them can contribute six $\pi$ electrons as effective $\pi$-bonding ligands in the sandwich compounds.

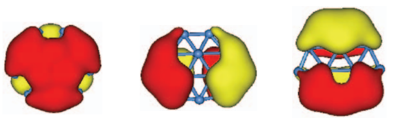

MO=21
(a)
MO=27
(b)
MO=28
(c)

FIG. 3. Delocalized $\pi$ orbitals of $B_{12}$ ($C_{3v}$) cluster (molecular visualization was performed using MOLEKEL 5.4).

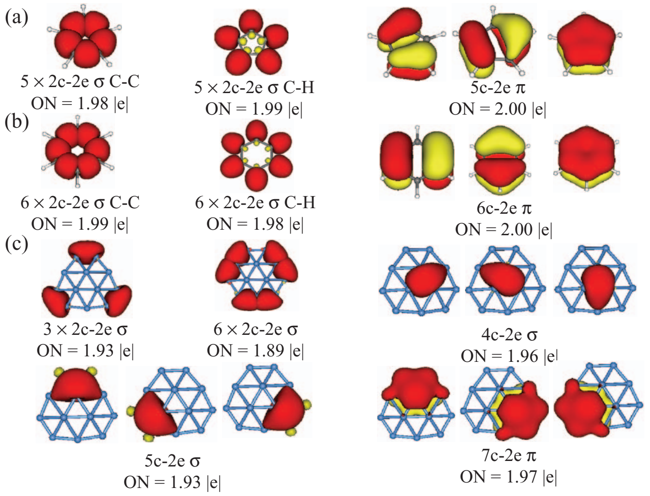


FIG. 4. The results of the AdNDP localization for cyclopentadienyl anion (a, $C_5H_5^-$), benzene (b, $C_6H_6$), and the quasi-planar $B_{12}$ cluster (c) (molecular visualization was performed using MOLEKEL 5.4).

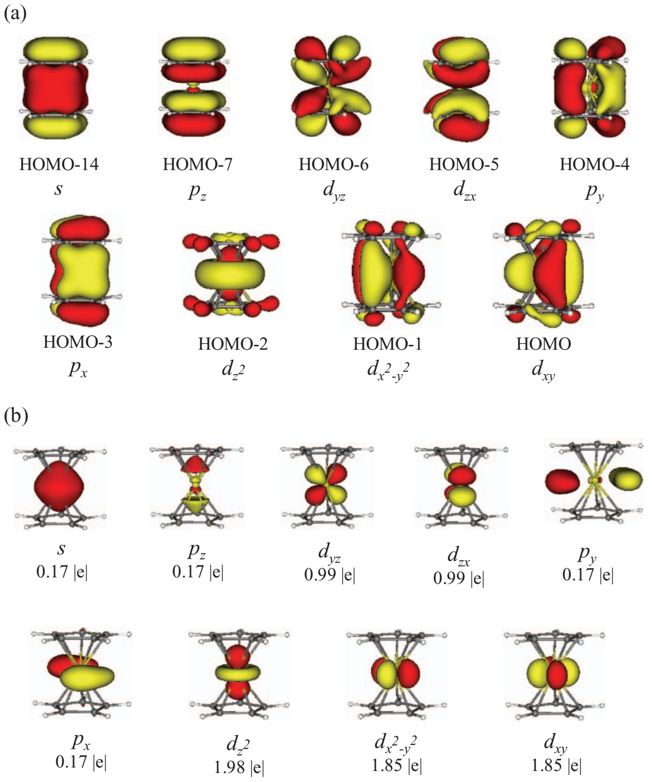


FIG. 5. The molecular orbitals (a) and the results of NBO analysis (b) of $C_5H_5 \cdot Fe \cdot C_5H_5$, the occupation numbers of lone pairs from Fe are labeled.

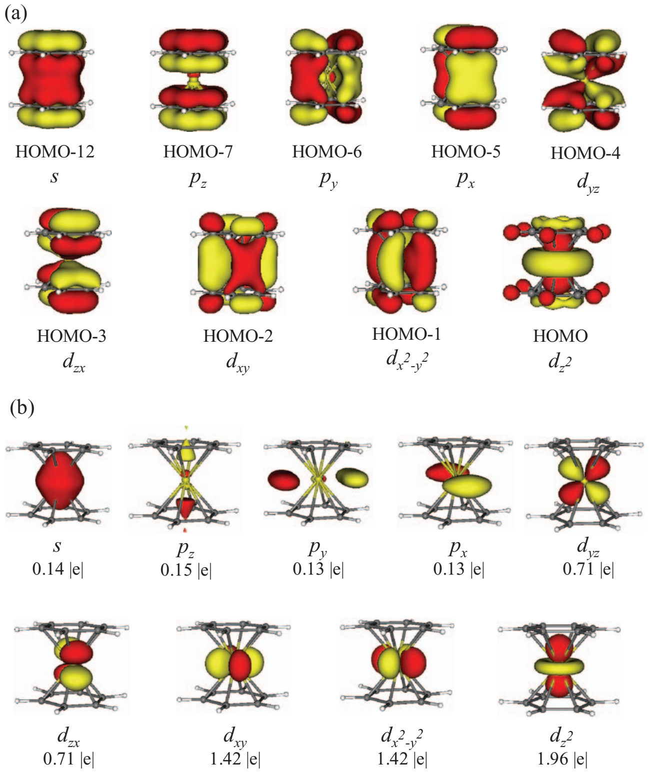


FIG. 6. The molecular orbitals (a) and the results of NBO analysis (b) of $C_6H_6 \cdot Cr \cdot C_6H_6$, the occupation numbers of lone pairs from Cr are labeled.

Next, we study the chemical bonding of the three sandwich compounds by MO analysis (all the canonical MOs can be found in the supplementary material.[55]). It is well known that sandwich $Fe(C_5H_5)_2$ is an electronic closed-shell structure, following the 18-electron principle. Curiously, why are the 18-electron complex series very stable? We think that the 18 valence electrons should occupy nine MOs and the electronic configuration should be $s^2p^6d^{10}$ for shell closure similar to the one of the inert gas Ar. As expected, the nine MOs (Figure 5(a)) are identified from the canonical MO diagrams. HOMO-14 can be viewed as a super $s$-$\pi$ orbital, formed from the 4$s$ orbital of metal and $\pi$ orbital of ligand. Similarly, HOMO-7 is a 4$p_z$-$\pi$ orbital, HOMO-6 (3$d_{yz}$-$\pi$) and HOMO-5 (3$d_{zx}$-$\pi$) are double-degenerate orbitals, HOMO-4 (4$p_x$-$\pi$) and HOMO-3 (4$p_y$-$\pi$) are double-degenerate orbitals. HOMO-2 is a 3$d_z{}^2$-$\pi$ orbital. HOMO-1 (3$d_x{}^2{}_{-y}{}^2$-$\pi$) and HOMO (3$d_{xy}$-$\pi$) are also double-degenerate orbitals. According to MO analysis, the sandwich $Fe(C_5H_5)_2$ has not only $d$-$\pi$ interaction, nine $spd$ orbitals of Fe atom corporately interact with the $\pi$ orbital of ligand, which is called "$spd$-$\pi$ interaction" in this work. From the shapes of orbitals we can see that the contributions of $\pi$ electrons are very small in HOMO-2, HOMO-1, and HOMO orbitals, so we presume that the three orbitals may be mainly occupied by six lone pair (LP) electrons on Fe (3$d^6$4$s^2$) atom.

To confirm the above supposition, we set a very low thresholds (ON = 0.1 |e|) in NBO analysis, and the MOs will be considered to be occupied by lone pair (LP) electrons from metal. In this way, we can evaluate the contributions of electrons from metal and ligand for each MO. Here, NBO analysis was used to calculate LP electron occupancies of MOs. For $s$, $p_x$, $p_y$, and $p_z$ orbitals of Fe (Figure 5(b)), the ONs of LPs are only 0.17 |e|. For $d_{yz}$ and $d_{zx}$ orbitals, the ONs of LPs are 0.99 |e|. For $d_z{}^2$ orbital, the ON of LP is high to 1.98 |e|. For $d_x{}^2{}_{-y}{}^2$ and $d_{xy}$ orbitals, the ONs of LPs are 1.85 |e|. From these data we can see that $spd$-$\pi$ interaction plays an important role in $Fe(C_5H_5)_2$ and HOMO-2 ($d_z{}^2$), HOMO-1 ($d_x{}^2{}_{-y}{}^2$), and HOMO ($d_{xy}$) orbitals are mainly occupied by LP electrons from Fe (3$d^6$4$s^2$) atom indeed. Thereby, the remaining two valence electrons on Fe atom are shared by Fe and two $C_5H_5$. Thus, Fe in the sandwich $Fe(C_5H_5)_2$ displays bipositive (+2) valence, which is in agreement with the previous study.[14,63]

Similarly, the nine $spd$-$\pi$ valence MOs of sandwich compound $Cr(C_6H_6)_2$ can also be found, as shown in Figure 6. The valence MOs of $Cr(C_6H_6)_2$ are analogous to the ones of $Fe(C_5H_5)_2$. According to the results of NBO analysis, HOMO-2 ($d_{xy}$, ON (LP) = 1.42 |e|), HOMO-1 ($d_x{}^2{}_{-y}{}^2$, ON (LP) = 1.42 |e|), and HOMO ($d_z{}^2$, ON (LP) = 1.96 |e|) are mainly occupied by six LP electrons from Cr (3$d^4$4$s^2$) atom, so Cr displays zero valence in the sandwich $Cr(C_6H_6)_2$, which is in agreement with the previous study.[63] In addition, the $spd$-$\pi$ interaction is also confirmed to exist in $Cr(C_6H_6)_2$.

As well as $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$, the nine $spd$-$\pi$ valence MOs (Figure 7(a)) of sandwich $Cr(B_{12})_2$ ($D_{3d}$) are identified from the canonical MO diagrams. HOMO-25 is a 4$s$-$\pi$ orbital. HOMO-19 is a 4$p_z$-$\pi$ orbital, HOMO-11 (4$p_y$-$\pi$) and HOMO-10 (4$p_x$-$\pi$) are double-degenerate orbitals, HOMO-9 (3$d_{yz}$-$\pi$) and HOMO-8 (3$d_{zx}$-$\pi$) are double-degenerate orbitals. HOMO-7 is a 3$d_z{}^2$-$\pi$ orbital. HOMO-3 (3$d_{xy}$-$\pi$) and HOMO-2 (3$d_x{}^2{}_{-y}{}^2$-$\pi$) are also double-degenerate

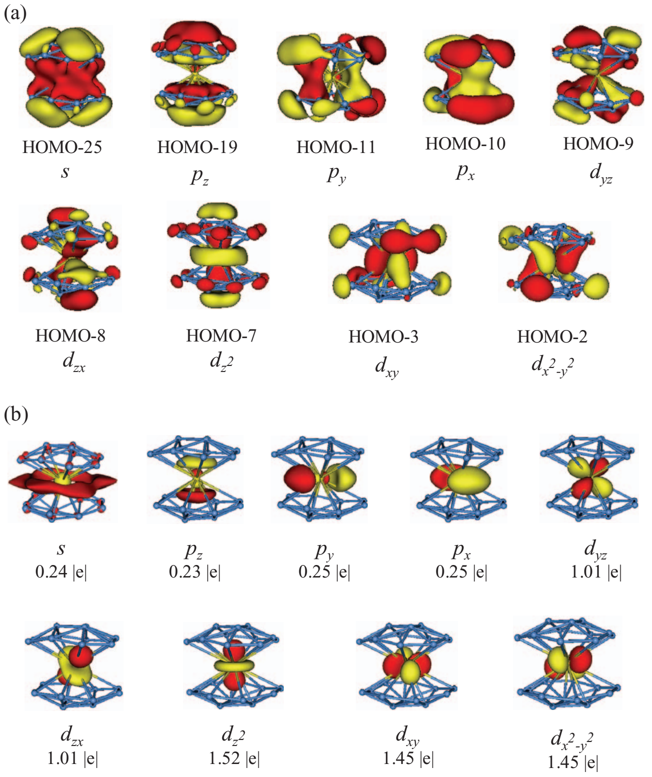


FIG. 7. The molecular orbitals (a) and the results of NBO analysis (b) of $B_{12} \cdot Cr \cdot B_{12}$, the occupation numbers of lone pairs from Cr are labeled.

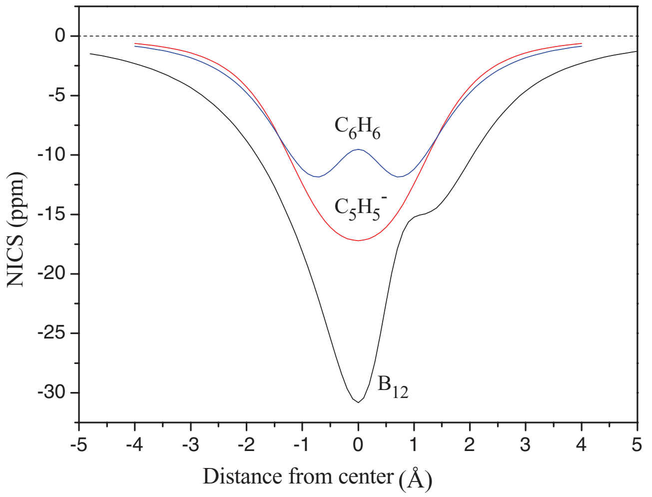


FIG. 8. The NICSzz-scan curves for $C_6H_6$, $C_5H_5^-$, and $B_{12}$, within the range of −5.0 to 5.0 Å above the geometric centers of the systems.

orbitals. The sandwich $Cr(B_{12})_2$ follows 18-electron principle with electronic configuration $s^2p^6d^{10}$. The shape of *s* orbital (Figure 7(b)) is exceptional due to molecular geometry. By NBO analysis, HOMO-7 ($d_z{}^2$, ON (LP) = 1.52 |e|), HOMO-3 ($d_{xy}$, ON (LP) = 1.45 |e|), and HOMO-2 ($d_{x^2-y^2}$, ON (LP) = 1.45 |e|) are mainly occupied by six LP electrons from Cr atom. In addition, from the MO diagrams of staggered $Cr(B_{12})_2$ (Figure S4 in the supplementary material[55]) we can find that some orbitals (MO = 53, 54, 55, 61, 62, 63, 66, 67, etc.) are occupied by delocalized $\sigma$ electrons of $B_{12}$ ligand and they are not involved in interacting with the orbitals of Cr atom. Thus, *spd*-$\pi$ interaction also plays an important role in staggered $Cr(B_{12})_2$.

In summary, $Fe(C_5H_5)_2$, $Cr(C_6H_6)_2$, and staggered $Cr(B_{12})_2$ all meet the 18-electron principle and have the similar MOs. In particular, the orbitals of staggered $Cr(B_{12})_2$ are almost same with the ones of $Cr(C_6H_6)_2$, thus we think that their stabilities should be almost same. In these sandwich compounds, *spd*-$\pi$ interaction plays an important role. The sandwich $Cr(B_{12})_2$ ($D_{3d}$) is a closed shell in electronic structure, as well as $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$.

### C. Aromaticity

"Aromaticity" is usually associated with the high stability,[31] so we analyze aromaticity of the sandwich compounds $Fe(C_5H_5)_2$, $Cr(C_6H_6)_2$, and $Cr(B_{12})_2$ ($D_{3d}$). Nucleus-independent chemical shift (NICS) value[64] is the most widely used as a quantitative measure for aromaticity (negative NICS values mean aromaticity and positive NICS values mean anti-aromaticity). Here, we first employ NICSzz-scan method[65,66] to analyze aromaticity of ligands $C_6H_6$, $C_5H_5^-$, and $B_{12}$. The NICSzz-scan analysis is analogous to the aromatic ring current shieldings approach,[67] which can provide a clear picture of the type of the ring current in aromatic and anti-aromatic systems[68] and can be used to characterize whether an inorganic system is aromatic, non-aromatic, and anti-aromatic.[69,70] Recently, the use of NICS to indicate aromaticity has been criticized by Lazzeretti group,[71,72] but currently it can be only used to monocyclic planar unsaturated molecules. $B_{12}$ is a bowl-like quasi-planar structure, so the formula given by Lazzeretti group is not applicable to our systems. And the NICS of our molecules are very large, which are less influenced by correction factor. Thus, we still apply the previous NICS to analyze the aromaticity.

Figure 8 plots the NICSzz-scan curves for $C_6H_6$, $C_5H_5^-$, and $B_{12}$, within the range of −5.0 to 5.0 Å above the geometric centers of the systems. From this figure, we can draw the following conclusions: (1) $B_{12}$ is more aromatic than $C_6H_6$ and $C_5H_5^-$, and the reason is that $B_{12}$ has triply aromaticity, namely, double $\sigma$ aromaticity and $\pi$ aromaticity.[59] (2) $B_{12}$ displays a narrow peak in the NICSzz-scan curve, because the $\sigma$ aromaticity decays more rapidly than $\pi$ aromaticity above the geometric centers of the systems. Note that the NICS calculated at 1 Å above the geometric center of the system (NICS(1)) describes the $\pi$ aromaticity.[31,65] (3) At the geometric centers of the systems, the NICSzz-scan curve of $C_6H_6$ displays a raised peak, but $C_5H_5^-$ is different. We think the reason may be that $C_6H_6$ has six C–C $\sigma$-bonds (12 electrons), which follows Hückel's 4*n* rule for $\sigma$ antiaromatic, but $C_5H_5^-$ has five C–C $\sigma$-bonds (10 electrons), which satisfies Hückel's 4*n*+2 rule for $\sigma$ aromatic. In a word, $B_{12}$ is a very stable ligand, as well as $C_5H_5^-$ and $C_6H_6$.

Then, Figure 9 depicts the NICSzz-scan curves for sandwich compounds $Cr(B_{12})_2$ ($D_{3d}$), $Cr(C_6H_6)_2$, and $Fe(C_5H_5)_2$, within the range of 0.3 to 4.0 Å above the geometric centers of the systems. From this figure we can see that the aromaticity of staggered $Cr(B_{12})_2$ is lower than the ones of $Cr(C_6H_6)_2$ and $Fe(C_5H_5)_2$, but the sandwich $Cr(B_{12})_2$ ($D_{3d}$) is still very aromatic (NICS ≈ −80 ppm). In addition, staggered $Cr(B_{12})_2$

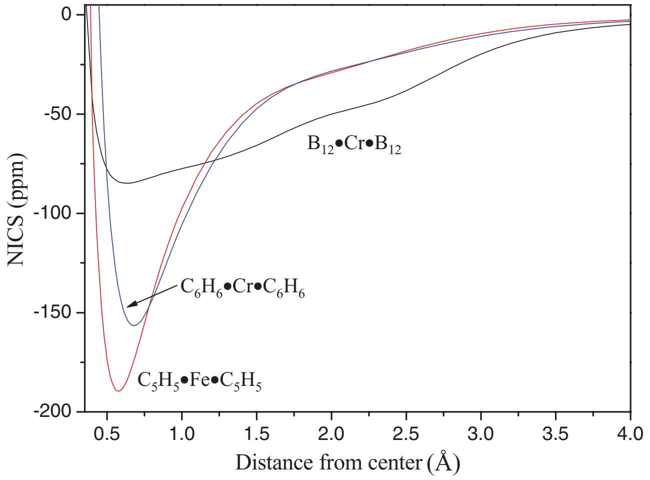


FIG. 9. The NICSzz-scan curves for $B_{12}\cdot Cr\cdot B_{12}$, $C_6H_6\cdot Cr\cdot C_6H_6$, and $C_5H_5\cdot Fe\cdot C_5H_5$, within the range of 0.3 to 4.0 Å above the geometric centers of the systems.

decays more slowly than $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$ in aromaticity. The reason may be that $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$ only have $\pi$ aromaticity, but staggered $Cr(B_{12})_2$ has $\pi$ aromaticity and the original double $\sigma$ aromaticity of ligand $B_{12}$. In brief, the sandwich compound $Cr(B_{12})_2$ ($D_{3d}$) has high aromaticity and stability.

## IV. CONCLUSIONS

In this work, we have studied structural stability and electronic properties of a new sandwich compound $Cr(B_{12})_2$ ($D_{3d}$) by using DFT. We found that the sandwich $Cr(B_{12})_2$ ($D_{3d}$) is a stable compound with large binding energy, HOMO-LUMO gap, and VIP-VEA gap, as well as $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$. The detailed MO and NBO analyses show that $B_{12}$ is a stable ligand and the sandwich compound $Cr(B_{12})_2$ ($D_{3d}$) meets the 18-electron principle and it is a close shell in electronic structure. The *spd*-$\pi$ interaction plays an important role in staggered $Cr(B_{12})_2$. The NICSzz-scan analysis indicates that the sandwich compound $Cr(B_{12})_2$ ($D_{3d}$) is very aromatic. In conclusion, theoretical confirmations have been provided on $B_{12}$ as a new ligand of the stable sandwich compound $Cr(B_{12})_2$ ($D_{3d}$). The bowl $B_{12}$ cluster will be one of the promising molecules for coordination chemistry as potential new ligands and for materials science as new building blocks. We hope that our work will lead to more studies on the synthesis of sandwich compound $Cr(B_{12})_2$ in experiments, which will further extend the rich boron and sandwich chemistry. If such compounds are synthesized, it will be significant in all-boron cluster coordination chemistry.

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