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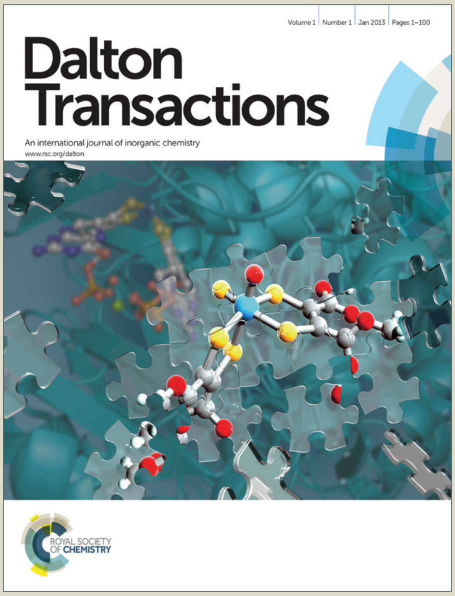

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Ferrocene Analogues of Sandwich $M(CrB_6H_6)_2$: A Theoretical Investigation[**]

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[**] Supplementary information (SI) available. The Figure S1 and Figure S2 include the partial canonical molecular orbitals and AdNDP localized bonding patterns of $[Mn(CrB_6H_6)_2]^+$ and $[Fe(CrB_6H_6)_2]^{2+}$; besides, the coordinates of $M(CrB_6H_6)_2$ (M = Cr, Mn^+, Fe^{2+}) (in angstrom) are listed in the SI.

The stability and electronic structures of the new sandwich compounds $M(CrB_6H_6)_2$ (M=Cr, Mn^+, Fe^{2+}) are investigated by density functional theory. All the investigated sandwich complexes are in D_{6d} symmetry and all of them are thermodynamics stable according to the large HOMO-LUMO gap, binding energy, vertical ionization potential and vertical electron affinity analysis, as well as $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$, following the 18-electron principle. The natural bond orbital, detailed molecular orbitals and adaptive natural density partitioning analyses suggests that the *spd*-π interaction plays an important role in the sandwich compounds. This work challenges the traditional chemical bonding of the inorganic metal compound, investigates firstly the bonding style of the *d* atom orbital interacting with π MO which formed by *p*-*d* atomic orbitals, and indicates that the metal-doped borane ring also be an ideal type π-electron donor ligand to stabilize the transition metal.

Key words: borane cluster; sandwich; ferrocene analogues; density functional theory

1. Introduction

Metallocenes have attracted much attention since the transition metal π-complex, ferrocene ($Fe(C_5H_5)_2$), has been discovered in 1951.[1,2] Lots of organometallic compounds are investigated experimentally and theoretically.[3-17] Warren[7] investigated the metal sandwich complexes by the charge transfer process and molecular orbitals. Clark et al.[8] studied the metal-ligand interaction in 3*d* sandwich complexes. As two typical sandwich clusters, $Fe(C_5H_5)_2$[18-29] and $Cr(C_6H_6)_2$[23,24,27 30-42] have been studied extensively. For $Fe(C_5H_5)_2$, the metal Fe atom contributes eight electrons ($3d^64s^2$) and each of the C atoms contributes one electron, which follows 18-electron principle. Similarly, the Cr atom of $Cr(C_6H_6)_2$ contributes six electrons ($3d^54s^1$) and each of the 12 carbons contributes one electron, which also meets 18-electron principle. With more studies on sandwich compounds, the ligands are various. The ferrocene analogues $[(\eta^5\text{-}E_5)_2M]$ (E = P, N, As, Sb, and Bi) have found important applications in both fundamental research and materials science.[1, 43-49] Besides, planar aromatic $[Al_4]^{2-}$,[50-54] $[N_5]^-$,[49] $[(P_5)_2Ti]^{2-}$,[55] borane,[56, 57] CO,[58] PH_3,[58] and boron clusters[59-63] can also be utilized as ligands to coordinate transition metals and form similar $[(\eta^n\text{-}E_n)_2M]$ complexes (n=4-6).

Recently, we have studied the chemical bonding and electron structure of $Cr@B_6H_6$ in C_{6v} symmetry, which features a Cr atom in a planar hexacoordinate environment out the center of a perfect B_6H_6 hexagon.[64]Inspired by the proposed 6-π electron aromatic $Cr@B_6H_6$, we present herein an investigation by density functional theory (DFT) of a new class of sandwich-type complexes, D_{6d} $M(CrB_6H_6)_2$ (M = Cr, Mn^+, Fe^{2+}). The compounds contain two parallel η^6-CrB_6H_6 hexagons centered with two nearly planar hexacoordinate Cr located along the sixfold molecular axis. These complexes are unique in that the delocalized π molecular orbitals (MOs) of the ligand, which interacted with the partially occupied *d* orbitals of the transition metal, possess the *d* orbital component of the Cr atom out the center of the planar B_6H_6 hexagon. To the best of our knowledge, there have been no investigations reported the metal-doped borane ligands in sandwich-type complexes. The results got in this work provide an important extension to the traditional concept of metallocenes-like complexes by incorporating hexacoordinate transition metal atoms in the systems.

2. Computational Details

The geometries of $M(CrB_6H_6)_2$ ($M = Cr, Mn^+, Fe^{2+}$) are optimized by using the TPSSh[65] functional. The optimization and the calculations of the energies and HOMO-LUMO gaps are performed at the TPSSh/6-311+G** level. We analyze the vibrational frequencies for checking the stability of structures at the same theoretical level. The TPSSh functional was proven to give reasonably accurate energetic properties of boron and boron-based clusters.[64, 66-69] The binding energy of the compound is defined as $E_b = E(M(CrB_6H_6)_2) - E(M) - E(CrB_6H_6)$. Then, the vertical ionization potential (VIP) of $Cr(CrB_6H_6)_2$ is calculated as $E([Cr(CrB_6H_6)_2]^+) - E(Cr(CrB_6H_6)_2)$, the vertical electron affinity (VEA) of $Cr(CrB_6H_6)_2$ is $E(Cr(CrB_6H_6)_2) - E([Cr(CrB_6H_6)_2]^-)$, and VEA of $[Mn(CrB_6H_6)_2]^+$ is $E([Mn(CrB_6H_6)_2]^+) - E(Mn(CrB_6H_6)_2)$. Natural bond orbital (NBO) analyses and adaptive natural density partitioning (AdNDP) analyses are implemented to gain insight into the bonding pattern of the complexes. All calculations are carried out by using the GAUSSIAN 09 package.[70]

3. Results and Discussion

We optimize $M(CrB_6H_6)_2$ ($M = Cr, Mn^+, Fe^{2+}$) at TPSSh/6-311+G** level. Figure 1 depicts the optimized staggered configurations of $M(CrB_6H_6)_2$. The binding energy, energy gap, VEA, VIP, rotation energy of $M(CrB_6H_6)_2$, $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$ are listed in Table 1, and also the natural atomic charges of $M(CrB_6H_6)_2$.

3.1. Structural and Chemical Stability

The staggered configurations of $M(CrB_6H_6)_2$ sandwich structures are all found to be true local minima by frequency check. The difference among the bond lengths of $Cr(CrB_6H_6)_2$, $[Mn(CrB_6H_6)_2]^+$ and $[Fe(CrB_6H_6)_2]^{2+}$ are little as shown in Figure 1. The lengths of B-B bond and Cr-B bond in the ligands (1.81 Å and 1.90 Å, respectively) become longer after forming sandwich compounds (1.84-1.85 Å and 1.94 Å, respectively). The bond lengths of the M-Cr bonds are 2.14-2.16 Å, and of the M-B bonds are 2.39-2.43 Å. As a comparison, the M-C bond lengths in D_{5h} $Fe(C_5H_5)_2$ and D_{6h} $Cr(C_6H_6)_2$ are 2.04 Å and 2.14 Å as calculated at the same theoretical level.[77] Figure 2 gives the energy of $Cr(CrB_6H_6)_2$, $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$ in different angle, which vividly shows that the most stable configuration of $Cr(CrB_6H_6)_2$ is staggered configuration and that of $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$ are eclipsed configuration. Although the energy differences between the staggered (D_{6d}) and the eclipsed (D_{6h}) conformations are very small (0.13-0.19 eV), the eclipsed $M(CrB_6H_6)_2$ complexes all turn out to be transition states with one imaginary located at 64i, 68i, and 69i cm^{-1}, respectively. When relaxed in the modes with the imaginary frequencies mentioned above, the eclipsed $M(CrB_6H_6)_2$ complexes are automatically transferred to the staggered conformation since the transition states are on rotational paths.

The stability of those compounds is evaluated theoretically. The fairly large HOMO-LUMO energy gaps (1.77-2.31 eV) and the binding energy (3.03-13.92 eV) of $M(CrB_6H_6)_2$ suggest high stability of those systems. Besides, the VIP values (7.38 eV) of $Cr(CrB_6H_6)_2$ and the VEA values (6.87 eV) of the cation $[Mn(CrB_6H_6)_2]^+$ are similar to the VIP values of ferrocene (7.14 eV) and dibenzenechromium (5.40 eV), and the VEA values (2.81 eV) of $Cr(CrB_6H_6)_2$ is small but larger than the values of ferrocene (-0.34 eV) and dibenzenechromium (-0.27 eV), which indicates that the natural molecules of $Cr(CrB_6H_6)_2$ and the cations of $Mn(CrB_6H_6)_2$ are stable. Moreover, the Wiberg bond indices (WBIs)[71] reveal that the strength of the B-H and B-B bonds in CrB_6H_6 ligands are well maintained and of the Cr-B bonds are decreased (0.99 in ligand and 0.79-0.80 in the sandwich complexes), when the introduction of a transition metal center, M, leads to two additional Cr-M bonds and twelve additional B-M bonds. The calculated total WBIs of the constituent atoms with WBI_H=1.00, WBI_B=3.31-3.43, WBI_{Cr}=6.30-6.36, and WBI_M=4.45-5.75 indicate that the center metal atoms interact strongly with the ligands.

3.2. Aromaticity

The ligand CrB_6H_6 is high aromatic analogues of benzene, and we suggest there may be delocalized electrons in $M(CrB_6H_6)_2$ as well as $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$. Since delocalization is always associated with aromaticity, we focus on the aromaticity of those systems. Nucleus-independent chemical shifts (NICS) value[72] is an easy and efficient criterion to identify aromatic nature. A large negative NICS implies the presence of diamagnetic ring currents. Hereby, we calculate NICS values along the X-axis of staggered $Cr(CrB_6H_6)_2$, eclipsed $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$ within the range of -6.0 to -1.0 Å and 1.0 to 6.0 Å (Figure 3). From this figure we can see that the variation tendency of the NICS value of $Cr(CrB_6H_6)_2$ is analogous to $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$. All of those curves decrease to the most large negative value from 1.0 to 6.0 Å and from -1.0 to -6.0 Å, which is influenced by the center nucleus. Besides, the aromaticity of $Cr(CrB_6H_6)_2$ is lower than the ones of $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$, but the sandwich complex $Cr(CrB_6H_6)_2$ is still aromatic (NICS = -7.11 ppm at X = 1.5 Å). The large negative NICS values suggest the strong interaction between the two parallel ligands and the center metal, which means that the sandwich complex is stable. Moreover, the Cr atom in the free ligand shifts only 0.07 Å after coordination, which indicates that the aromaticity of the ligand remains in

$M(CrB_6H_6)_2$.

3.3. Electronic structures

Why are these sandwich-type structures stable? In ferrocene, the center Fe in ferrocene is a +2 oxidation state, where the 2 electrons have been transferred to two $[C_5H_5]$s respectively. So the $[C_5H_5]$ has got the -1 chare state satisfying the Huckel 4*n*+2 rule.[73] Here we give the other answer NBO analyses. Although the π-MOs of the ligands overlap with the empty orbitals of the center Cr atom, which forming the coordination bonds from the CrB_6H_6 ligands to the center Cr, the natural atomic charges of the center Cr atom do not get negative charges (+0.67 |*e*|). The reason is that the electrons on 4*s* orbital of the neutral center Cr have been stripped away in $Cr(CrB_6H_6)_2$. The similar overlap is found in $[Mn(CrB_6H_6)_2]^+$ and $[Fe(CrB_6H_6)_2]^{2+}$. But the Mn^+ and Fe^{2+} have already lost electrons, so they should be positive charge, too. In order to get insight into the bonding style and delocalized orbital of those clusters, canonical molecular orbital (MO) analysis and the adaptive natural density partitioning (AdNDP) analysis is adopted. AdNDP is a new theoretical tool developed by Boldyrev group[74,75] for analyzing chemical bonding and has been successfully applied in organic and inorganic molecules and clusters.[64, 66, 67, 76-80] The size of basis sets does not affect much of the chemical bonding of the compounds, and thus in AdNDP analysis, the 6-31G* and lanl2dz basis sets are employed for nonmetals and transition metals. In the following we pick D_{6d} $Cr(CrB_6H_6)_2$ as examples to discuss their electronic structures.

The $Cr(CrB_6H_6)_2$ is an electronic closed-shell structure, following the 18-electron principle. Similar to $Fe(C_5H_5)_2$, $Cr(C_6H_6)_2$ and $Cr(B_{12})_2$,[66] nine *spd*-π MOs (Figure 4) are identified from the canonical MO diagrams. The MO(43) mainly represents the overlaps between the 4*s* orbital of center Cr and the π MO of the ligands, whereas the MO(48) reflects the interactions between the $3d_{z2}$ orbital of the center Cr and the π MO of the ligands. The MO(49) is formed by the $3p_z$ orbital of the center Cr and the π MO of the ligands. The MO(52) and MO(53), MO(54) and M(55) are double-degenerate orbitals, corresponding to p_x-π and p_y-π, d_{xz}-π and d_{yz}-π, respectively. The HOMOs (MO=56 and 57) are also double-degenerate orbitals, which result from the π MOs of the ligands and the $3d_{xy}^{1.33}$ and $3d_{x2-y2}^{1.33}$ of the center Cr.

AdNDP analysis gives more unambiguous details of the chemical bonding of the sandwich. As shown in Figure 5, AdNDP analysis reveals that there are twelve σ-BH bonds with occupy number (ON) of 1.93 |e|, twelve three-center two-electron (3c-2e) σ bonds and nine 15c-2e bonds of *spd*-π interaction (ON=1.96 and 2.00 |e|, respectively) in $Cr(CrB_6H_6)_2$. The results show that when the two C_{6v} CrB_6H_6 ligands fasten the Cr atom, only the 7c-2e π bonds of the ligands involve with the *spd* atom orbitals of center Cr, compared to the localized chemical bonding of the ligand.[64] Both the MO analysis and AdNDP analysis illustrate that the *spd*-π interaction plays an important role in stabilizing the sandwich.

3.4. Discussion

From the analysis above, we know that the bonding style of D_{6d} $Cr(CrB_6H_6)_2$ between the transition metal center and the ligands is nine *spd*-π interaction. When we replace the Cr with isoelectronic Mn^+ and Fe^{2+}, the bonding styles maintain the same (their partial MOs and AdNDP diagrams see Supplementary Information). As the nuclear charges number increasing, the natural charges of the Cr in the ligands are almost the same; the positive charges on the transition metal centers are raised remarkably; the negative electrons on the B atoms decrease and even turn to slightly positive charges, which shows that the attraction of the center M with positive charges to the π electrons of the ligands increase and well explains the large binding energy of $[Fe(CrB_6H_6)_2]^{2+}$.

4. Conclusion

In summary, we predict a new class of sandwich-type complexes D_{6d} M(CrB_6H_6)$_2$ (M=Cr, Mn^+, Fe^{2+}) by DFT calculations. Those sandwich compounds are thermodynamic stable according to their large HOMO-LUMO gap and binding energy, as well as $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$, following 18-electrons rule. The NBO analyses shows that when the electrons in 4*s* orbitals of the transition metal center is stripped, the π electrons of the two ligands enter the empty *dsp* atom orbitals of the center metal at the same time. The double interaction between the two ligands and the metal center is called *spd*-π interaction mentioned above, which plans an important role in stabilizing the sandwich. This interaction is confirmed by the MO analysis and AdNDP analysis. The 18 electrons involved in the interaction of the center metal and the two ligands are presented nine styles of s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, $d_{x^2-y^2}$, and d_{z^2} shape. The results obtained in this work provide an extension to the traditional concept of sandwich-type complexes, which have a central transition metal atom in the ligand.

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Table 1. Energy gap, ΔE_{HL} [eV]; binding energy, E_b [eV]; vertical ionization potential, VIP [eV]; vertical electron affinity, VEA [eV]; rotation energy, E_r [eV]; and natural atomic charges, q [|*e*|] for $M@(CrB_6H_6)_2$ (M = Cr, Mn^+) and $Cr@(C_6H_6)_2$ at TPSSh/6-311+G** level.

	ΔE_{HL}	E_b	VIP	VEA	E_r	q_{Cr}	q_B	q_M	q_H
$Cr@(CrB_6H_6)_2$	1.77	3.60	7.38	2.81	0.19	+0.38	-0.11	+0.67	-0.01
$[Mn@(CrB_6H_6)_2]^+$	2.31	3.03		6.87	0.14	+0.33	-0.05	+0.80	+0.01
$[Fe@(CrB_6H_6)_2]^{2+}$	2.24	13.92			0.13	+0.34	+0.01	+0.88	+0.03
$Cr@(C_6H_6)_2(D_{5h})$	3.30	2.83	5.40	-0.27					
$Fe@(C_5H_5)_2(D_{5h})$	4.26	7.66	7.14	-0.34					

Figure captions

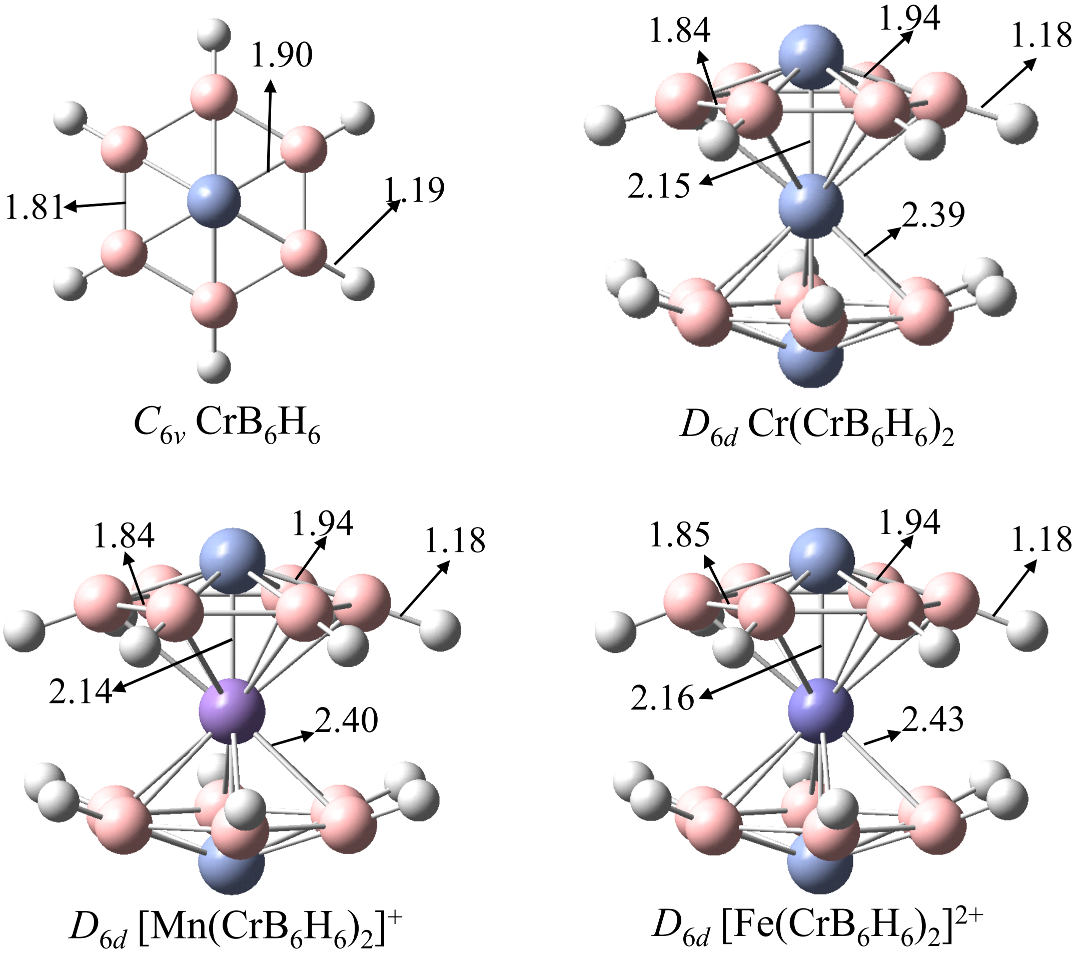
Figure 1 The optimized structures of the ligand CrB_6H_6 and the sandwich $M(CrB_6H_6)_2$ for M = Cr, Mn^+ and Fe^{2+}. The symmetry and bond lengths are labeled in figure; H-white, B-blue, Cr-light blue, Mn-purple, Fe-blue.

Figure 2 The energy of $Cr(CrB_6H_6)_2$, $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$ in different angle, the most higher energies are labeled in figure.

Figure 3 The NICSxx-scan curves for $Cr(CrB_6H_6)_2$, $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$ within the range of -7.0 to -1.0 Å and 1.0 to 7.0 Å in X-axis.

Figure 4 Partial canonical molecular orbitals of $Cr(CrB_6H_6)_2$.

Figure 5 AdNDP localized bonding patterns of $Cr(CrB_6H_6)_2$.



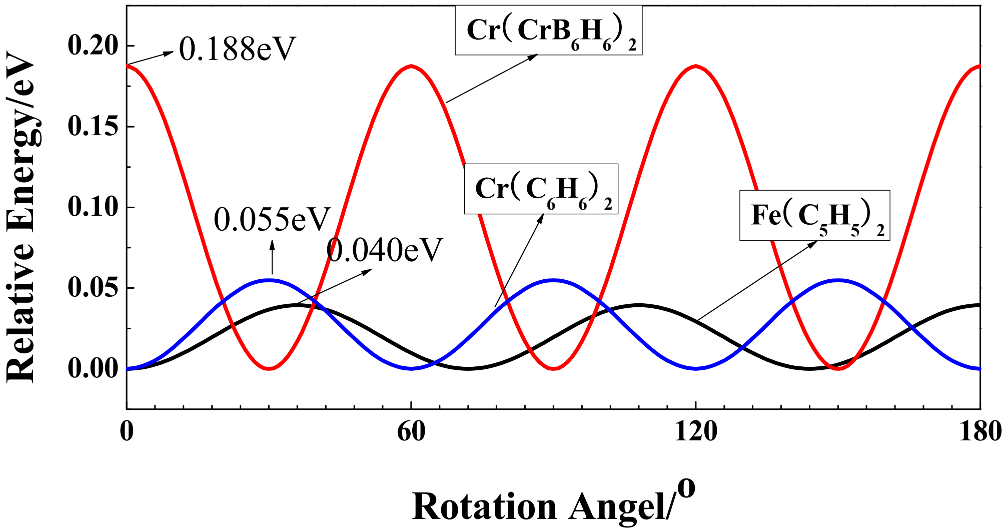
C_{6v} CrB_6H_6

D_{6d} $Cr(CrB_6H_6)_2$

D_{6d} $[Mn(CrB_6H_6)_2]^+$

D_{6d} $[Fe(CrB_6H_6)_2]^{2+}$

Fig. 1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0.10
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0.00
0
60
120
180
Rotation Angel/^{o}
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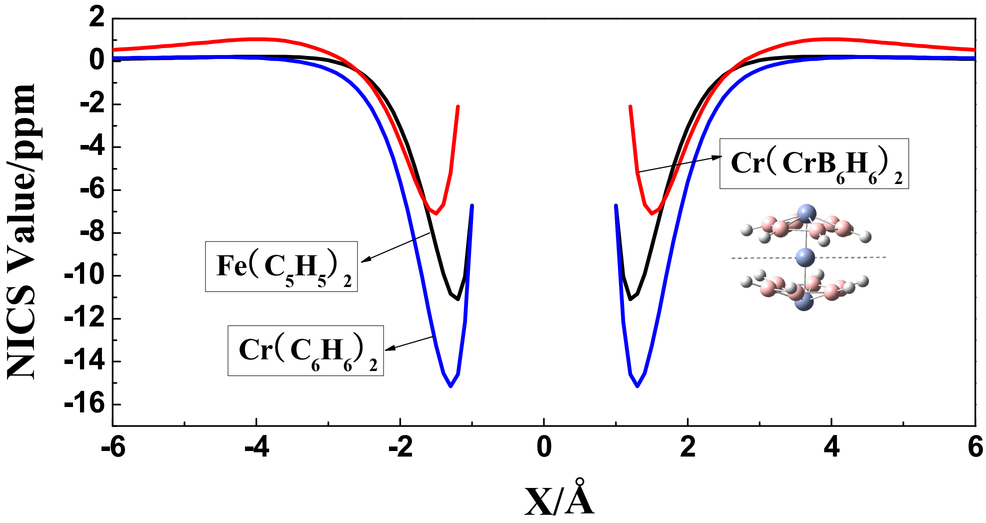
0.055eV
0.040eV
Cr(CrB$_6$H$_6$)$_2$
Cr(C$_6$H$_6$)$_2$
Fe(C$_5$H$_5$)$_2$

Fig. 2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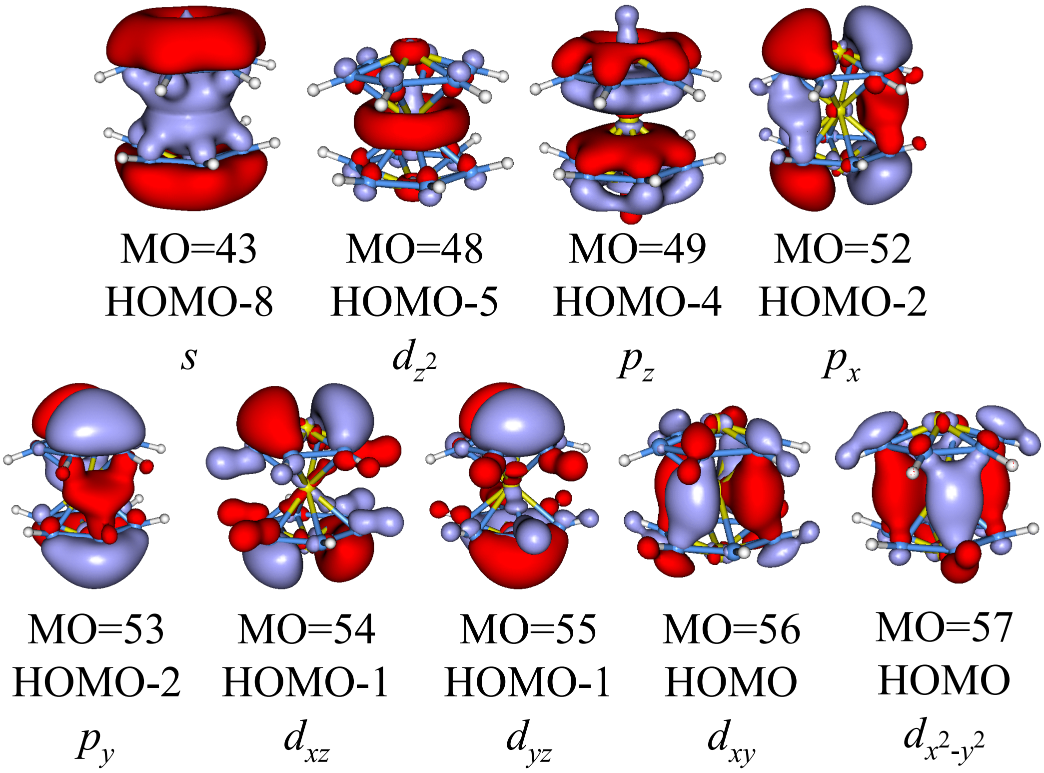
-6
-8
-10
-12
-14
-16
-6
-4
-2
0
2
4
6
X/Å
$Fe(C_5H_5)_2$
$Cr(C_6H_6)_2$
$Cr(CrB_6H_6)_2$

Fig. 3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MO=53 HOMO-2 p_y
MO=54 HOMO-1 d_{xz}
MO=55 HOMO-1 d_{yz}
MO=56 HOMO d_{xy}
MO=57 HOMO $d_{x^2-y^2}$

Fig. 4

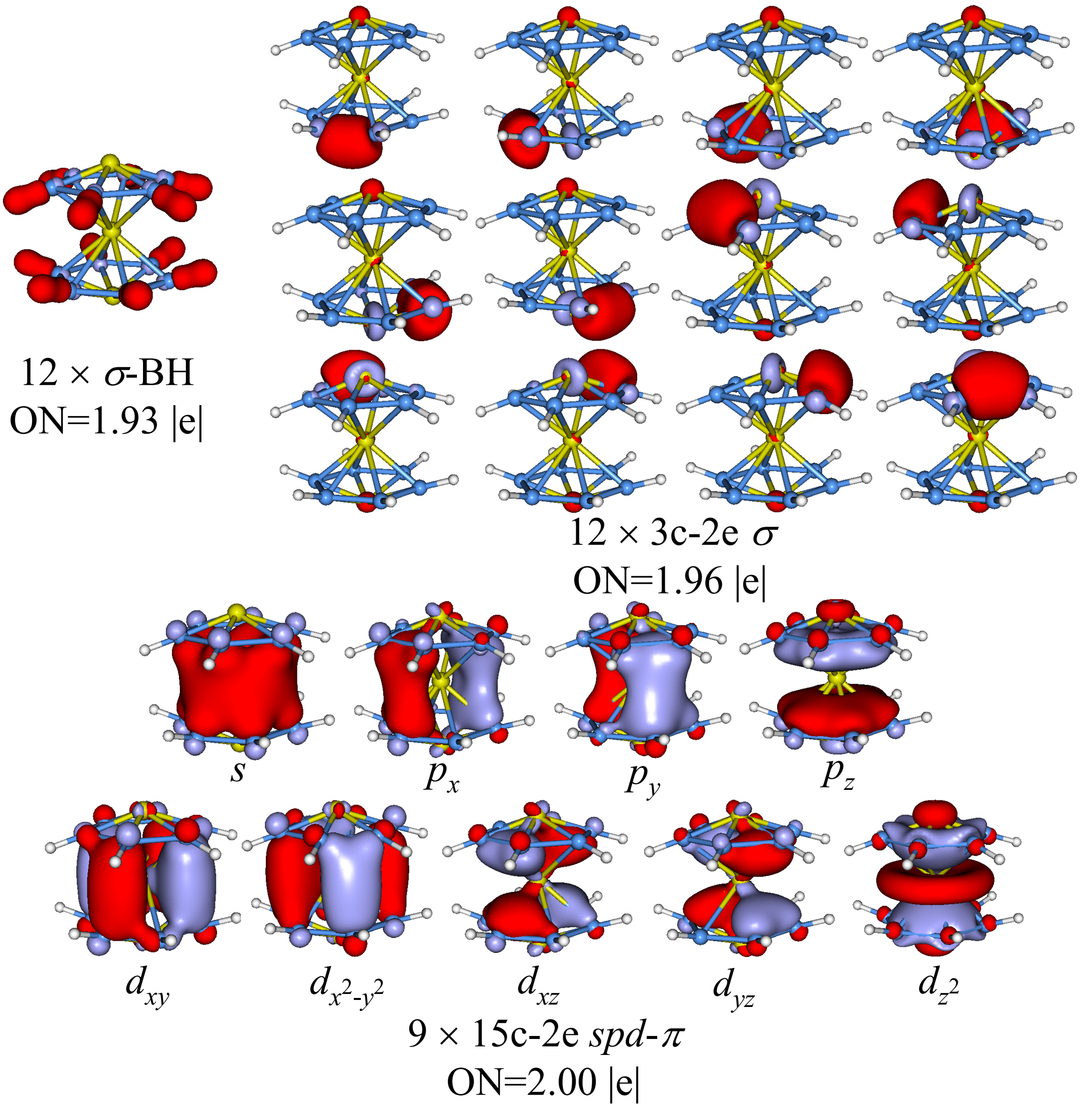
12 × σ-BH
ON=1.93 |e|
12 × 3c-2e σ
ON=1.96 |e|
s
p_x
p_y
p_z
d_{xy}
$d_{x^2-y^2}$
d_{xz}
d_{yz}
d_{z^2}
9 × 15c-2e *spd*-π
ON=2.00 |e|

Fig. 5