

# Intercalation of Transition Metals into Stacked Benzene Rings: A Model Study of the Intercalation of Transition Metals into Bilayered Graphene

Il Seung Youn,<sup>†</sup> Dong Young Kim,<sup>†</sup> N. Jiten Singh,<sup>†</sup> Sung Woo Park,<sup>†</sup> Jihee Youn,<sup>†</sup> and Kwang S. Kim<sup>\*,†</sup>

<sup>†</sup>Department of Chemistry and Department of Physics, Pohang University of Science and Technology, Pohang 790-784, Korea

**S** Supporting Information

**ABSTRACT:** Structures of neutral metal–dibenzene complexes,  $M(C_6H_6)_2$  ( $M = Sc–Zn$ ), are investigated by using Møller–Plesset second order perturbation theory (MP2). The benzene molecules change their conformation and shape upon complexation with the transition metals. We find two types of structures: (i) stacked forms for early transition metal complexes and (ii) distorted forms for late transition metal ones. The benzene molecules and the metal atom are bound together by  $\delta$  bonds which originate from the interaction of  $\pi$ -MOs and d orbitals. The binding energy shows a maximum for  $Cr(C_6H_6)_2$ , which obeys the 18-electron rule. It is noticeable that  $Mn(C_6H_6)_2$ , a 19-electron complex, manages to have a stacked structure with an excess electron delocalized. For other late transition metal complexes having more than 19 electrons, the benzene molecules are bent or stray away from each other to reduce the electron density around a metal atom. For the early transition metals, the  $M(C_6H_6)$  complexes are found to be more weakly bound than  $M(C_6H_6)_2$ . This is because the  $M(C_6H_6)$  complexes do not have enough electrons to satisfy the 18-electron rule, and so the  $M(C_6H_6)_2$  complexes generally tend to have tighter binding with a shorter benzene–metal length than the  $M(C_6H_6)$  complexes, which is quite unusual. The present results could provide a possible explanation of why on the Ni surface graphene tends to grow in a few layers, while on the Cu surface the weak interaction between the copper surface and graphene allows for the formation of a single layer of graphene, in agreement with chemical vapor deposition experiments.

Bis( $\eta^6$ -benzene)chromium,  $Cr(C_6H_6)_2$ , is an 18-electron closed-shell compound including two benzene rings with a chromium atom at the center, which is one of the most well-known examples of organometallic sandwich complexes. Since its discovery by Fischer and Hafner,<sup>1</sup> numerous experimental and theoretical studies have been carried out to investigate how two benzene rings and a chromium atom interact and what kind of structure the complex forms.<sup>2–13</sup>  $Cr(C_6H_6)_2$  has the two eclipsed stacked forms of two benzene rings with the chromium atom placed at the midpoint of the two benzene centroids. On the basis of these studies, researchers have investigated electronic properties of the  $Cr(C_6H_6)_2$  complex and the related cation complexes for a possible use as spin trap device or for the extension to carbon nanotubes and graphene.<sup>14–37</sup> In addition, other similar molecules with transition metals have been studied for the same purpose,<sup>38–52</sup> and the analogs such as graphene–metal hybrid materials have been utilized for electronic devices, biosensors, and the removal of hazardous materials.<sup>53–56</sup> Nevertheless, the structure of the complexes of transition metals has not been properly studied at the high level of theory yet.

For  $Cr(C_6H_6)_2$ , the  $\pi$  character of each benzene interacts with d orbitals in the chromium atom;  $\pi$ -molecular orbitals (MOs) of benzene (Bz) molecules interact with the  $d(xy)$  and  $d(x^2 - y^2)$  orbitals in the chromium atom, forming the  $\delta$  bond. In this case, the  $\pi$ – $\pi$  interaction<sup>57–68</sup> between two benzene molecules is very small because of their large separation, while the metal– $\pi$  interaction<sup>69–74</sup> between a metal atom and benzene molecules is dominant. Here, we investigated the structures of

bis(benzene)–first-row transition metal complexes ( $Bz_2M$ ;  $M = Sc–Zn$ ) using ab initio calculations. Even though there have been many theoretical studies of  $Bz_2M$ , they used only density functional theory (DFT) methods,<sup>2,11,12,23,26,28,39,41,48,51</sup> which have not been well tested for the interactions between benzene and central metal atoms. Thus, we have carried out MP2 calculations using the aug-cc-pVDZ (aVDZ) and aug-cc-pVTZ (aVTZ) basis sets. Since the highest occupied molecular orbitals (HOMO) are doubly degenerate, the  $Bz_2M$  complexes maintain uniformly stacked structures for  $M = Sc–Cr$ . Those structures support the 18-electron rule in organometallics. Even though  $Bz_2Mn$  has 19 electrons, it has the same structure with  $Bz_2Cr$  due to the nature of the HOMO, which diffuses the extra electron. For  $Bz_2M$  where  $M = Fe–Zn$ , the complexes cannot have well-ordered stacking forms because of the instability caused by too many excess electrons. Hence, two benzene molecules stray from each other or one benzene molecule is bent, changing the electron donation type from  $\eta^6$  to  $\eta^4$  or  $\eta^2$ .

In order to compare the structural properties of the sandwiched complexes ( $Bz_2M$ ) with those of the corresponding complexes having only one benzene molecule ( $BzM$ ), we also examined their different natures in molecular bonding character. The critical interaction in  $BzM$  complexes is the one between  $\pi$ -MOs of benzene and  $d(xz)$  or  $d(yz)$  orbitals of the metal atom.<sup>10,33</sup> This type of  $\sigma$ -bonding itself is stronger than  $\delta$  bonding; yet, the  $BzM$

**Received:** September 20, 2011

**Published:** November 21, 2011

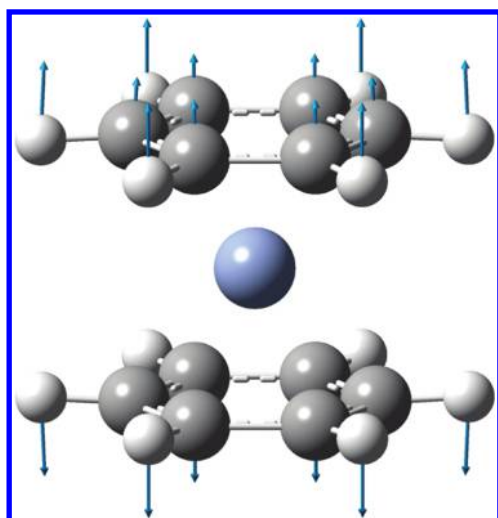


Figure 1. Breathing mode in  $Bz_2M$ .

complexes do not satisfy the 18-electron requirement because a ligand, benzene, donates electrons from only one side. On the other hand, two benzene molecules donate electrons, and then  $\pi$ -MOs interact with a metal atom from both above and below, satisfying the 18-electron requirement with stronger binding in  $Bz_2M$ . This results in a shorter distance between the metal atom and the benzene centroid ( $d_{M-Bz}$ ) in the  $Bz_2M$  complexes than in the corresponding  $BzM$  ones for  $M = Sc-Mn$ , except for  $Bz_2Ti$  and  $Bz_2Cr$ .

We performed ab initio calculations using the Gaussian 09 package.<sup>75</sup> To search for low-lying energy structures, we have dealt with several probable structures based on the structure of  $Cr(C_6H_6)_2$  with point group  $D_{6h}$ . In order to find the proper spin multiplicity of each metal atom in each complex, we optimized all structures with symmetry adaptation at each defined spin multiplicity by using MP2 with the aug-cc-pVDZ (aVDZ) basis set for carbon and hydrogen atoms and the CRENBL effective core potentials (ECP)<sup>76</sup> for transition metal atoms. The frequency analysis was done to confirm the minimum-energy structures. The structures were reoptimized with basis set superposition error (BSSE) correction. The single point energy calculations were performed at the MP2 level of theory with the aug-cc-pVTZ (aVTZ) and CRENBL ECP basis sets. The complete basis set limit energies<sup>77,78</sup> were not made because of possible errors arising from large BSSEs at the aVDZ level. We studied natural bonding orbital (NBO) charges, binding energies (negative value of the interaction energies:  $-\Delta E$ ), distances between the benzene and metal atom, and frequencies of a breathing mode (Figure 1).

## DETERMINATION OF THE MOST STABLE SPIN CONFIGURATIONS

The possible spin multiplicities of each metal complex are 2 and 4 for Sc and Co; 1, 3, and 5 for Ti and Fe; 2, 4, and 6 for V and Mn; 1, 3, 5, and 7 for Cr; 1 and 3 for Ni; 2 for Cu; and 1 for Zn in the complexes. In the  $Bz_2M$  case, each complex has the most stable structure in the lowest spin multiplicity. The singlet and the triplet Fe complexes have similar energies. The spin multiplicity of each  $BzM$  complex at the lowest energy is dependent on the kind of metal atom: Sc, V, and Fe prefer 4, 4,

Table 1. MP2/aVTZ Results for the  $BzM$  Complexes

metal	point group	spin multiplicity	$d_{M-Bz}$ (Å)	$\Delta E$ (kcal mol <sup>-1</sup> )	NBO charge of metals (a.u.) <sup>a</sup>
Sc	$C_{2v}$	4	1.923	-82.3	0.875
Ti	$C_{2v}$	1	1.604	-84.4	1.060
V	$C_1$	4	1.712	-37.4	0.996
Cr	$C_{3v}$	1	1.511	-208.7	0.697
Mn	$C_1$	2	1.887	-48.2	0.772
	$C_1$	4	1.610	-54.8	1.375
Fe	$C_1$	3	1.512	-30.8	1.239
Co	$C_{2v}$	2	1.503	-84.9	0.525
Ni	$C_{3v}$	1	1.441	-103.2	0.778
Cu	$C_1$	2	3.305	-1.9	-0.080
Zn	$C_s$	1	3.559	-2.0	-0.045

<sup>a</sup> NBO charges are calculated at the MP2/aVDZ level.

and 3, respectively, and the others prefer the lowest spin multiplicities (see Supporting Information).

## STRUCTURES OF $BzM$ COMPLEXES

In the  $BzM$  complexes, geometry optimization was performed for several different spin multiplicities. These data are summarized in Table 1 (MP2/aVTZ) and in Table S1 (MP2/aVDZ) in the Supporting Information. Several spin states of  $BzM$  ( $M = Sc, Ti, Cr, Mn$ , and  $Co$ ) show attractive interactions. The lowest spin multiplicities exhibit stronger binding for all  $BzM$ 's except for  $M = Sc, V, Mn$ , and  $Fe$ ; for  $M = Sc, V$ , and  $Fe$ , each spin multiplicity of 4, 4, and 3 shows stronger binding. The spin multiplicity of 2 in  $BzMn$  shows the strongest binding at the MP2/aVDZ level, but the spin multiplicity of 4 does at the MP2/aVTZ level. As shown in Figure 2, the structures of  $BzM$  complexes are based on the structure of point group  $C_{6v}$ . Only the  $BzV$  has a bent benzene molecule below the metal atom. Not only the shape of benzene but also the  $d_{M-Bz}$ 's differ from each other.

The primary interactions, which give bonding character to a complex, are benzene  $\pi$  orbitals with metal  $d(yz)$ ,  $d(xz)$ , and  $d(z^2)$  orbitals (Figure 3b 3 and 4). Other important interactions are ones between  $\pi^*$  orbitals (top orbitals in Figure 3a) and the rest, two d orbitals. While those interactions lead to a bonding property, one between the  $\pi$  orbital shown in the bottom of Figure 3a and an s orbital brings out antibonding character. The key point is that there are stabilization and destabilization of some orbitals during the formation of the molecular orbitals (MOs). Five d orbitals locate differently depending on a metal atom and its spin state. In the  $BzSc$  case, a scandium atom with a spin multiplicity of 4 has occupied frontier  $d(yz)$ ,  $d(z^2)$ , and s orbitals, and other vacant 3d orbitals. Thus, when they form the  $BzSc$  complex, high-lying  $d(xy)$  and  $d(x^2 - y^2)$  orbitals interact with  $\pi^*$  orbitals, which are in similar energy level, stabilizing the complex. A similar effect is caused from the formation of 3. On the other hand, the most stable  $\pi$  orbital is destabilized by interacting with the s orbital, forming the antibonding highest occupied molecular orbital (HOMO), 1. This antibonding HOMO causes relatively long distance  $d_{M-Bz}$ , 1.92 Å. The  $BzTi$  complex resembles the situation, but there is not a large advantage to forming 3 or forming 1 as the HOMO. This results in similar binding energies for  $BzSc$  and  $BzTi$ , but shorter  $d_{M-Bz}$  in  $BzTi$ , 1.60 Å. For  $BzV$ , a big energy loss comes from the

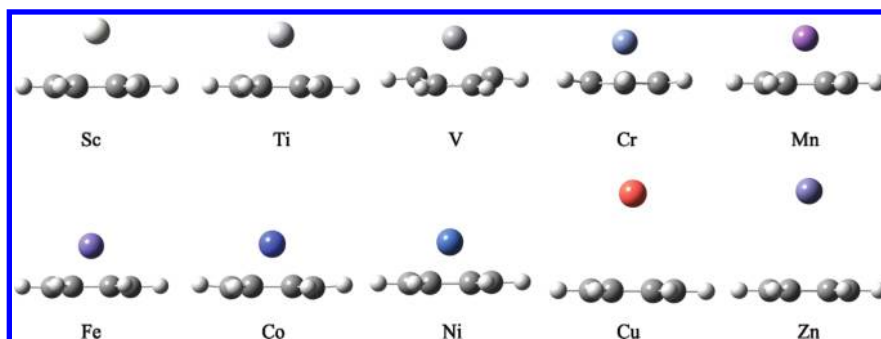


Figure 2. MP2/aVTZ predicted structures of BzM complexes.

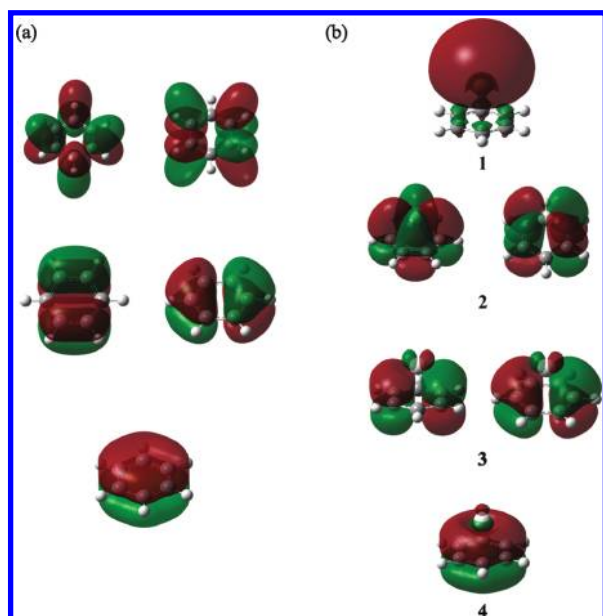


Figure 3.  $\pi$  orbitals of a benzene molecule (a) and important orbitals in BzM complexes (b).

formation of 3, which includes destabilization of  $d(yz)$  and  $d(zx)$  orbitals, leading to a small binding energy. All 2 and 3 orbitals with stabilization of  $\pi^*$ ,  $d(xz)$ ,  $d(yz)$ , and  $d(x^2 - y^2)$  orbitals are occupied in BzCr, and thus a benzene molecule and a chromium atom bind strongly. Some cases such as BzMn and BzFe cannot form bonding 2 or 3 orbitals due to a big difference in energy level between  $\pi^*$  and  $d$  orbitals, or they fail to gain big stabilization due to the same reason in spite of the formation of 2 and 3. A similar effect occurs intensively in BzCu and BzZn because their valence orbitals are fully occupied, so that extra electrons from a benzene molecule give rise to repulsion. Despite a big energy level difference, the Co and the Ni complexes form 2 and 3, which give great stabilization of the  $\pi^*$  orbitals and thus stronger binding energies than other BzM ( $M = \text{Mn, Fe, Cu, and Zn}$ ).

The above analysis explains why the  $d_{M-Bz}$  is small for  $M = \text{Sc–Ni}$  (1.4–1.9 Å), while the  $d_{M-Bz}$  is large for  $M = \text{Cu and Zn}$  (3.305 and 3.559 Å, respectively). The small  $d_{M-Bz}$ 's are from the bonding 2 and 3, but the large ones are from the electron repulsion and the antibonding 1. This indicates that on the Ni surface graphene tends to grow in a few layers, while on the Cu surface the weak interaction between the copper surface and graphene would lead to the formation of a single layer of

graphene, in agreement with chemical vapor deposition (CVD) experiments.<sup>78–80</sup> In addition, this significant difference in  $\pi$ –metal interactions between different metal atoms could be useful for ion sensing, such as conductance measurement through carbon-based electrodes such as graphene nanoribbons.<sup>81–83</sup>

### STRUCTURES OF Bz<sub>2</sub>M COMPLEXES

In Bz<sub>2</sub>M complexes, except for Bz<sub>2</sub>Sc of point group  $C_{2v}$ , the symmetry is broken in all complexes. Nevertheless, the structures of early transition metal complexes (Bz<sub>2</sub>Sc–Bz<sub>2</sub>Mn) are based on  $D_{6h}$ -like structures. On the other hand, the late transition metal complexes (Bz<sub>2</sub>Fe–Bz<sub>2</sub>Zn) have structures in which two distorted benzene rings stray away from each other (Figure 4). Notable points in structures of the Bz<sub>2</sub>M complexes are the  $d_{M-Bz}$  and the shape and arrangement of benzene molecules in each complex; while the Bz<sub>2</sub>M complexes of early transition metals have their benzene molecules intact, as in the corresponding BzM complexes, a benzene molecule in the late transition metal complexes stray away from each other or one of them is severely distorted, as compared to the corresponding BzM complexes (Figures 2 and 4). This is due to the well-known 18-electron rule, which indicates that the number of electrons from the ligands and the metal atom may be summed up toward 18 to form a stable metal complex. The ligands are two benzene molecules here, and the metal atoms are first row transition metals. In each Bz<sub>2</sub>M complex, one benzene ring donates six  $\pi$  electrons, and a metal atom has  $d$  electrons. Thus, the total number of electrons contributing to the bonding characters between two benzene rings and a metal is  $6 \times 2 + d$  electrons. Table 2 gives MP2/aVTZ results for the Bz<sub>2</sub>M complexes.

This analysis implies that in the range from Bz<sub>2</sub>Sc to Bz<sub>2</sub>Cr,  $d$  electrons occupying bonding orbitals lead to strong interactions. These bonding orbitals consist of  $\pi$  orbitals of the benzene molecules and  $d(xy)$  and  $d(x^2 - y^2)$  orbitals of the metal, resulting in  $\delta$  bonding orbitals, as shown in Figure 5. This explains why the Bz<sub>2</sub>Cr complex has the largest binding energy. This explanation is confirmed by comparing the calculation results of Bz<sub>2</sub>V<sup>−</sup>, Bz<sub>2</sub>Cr<sup>−</sup>, and Bz<sub>2</sub>Mn<sup>+</sup>; the MP2/aVDZ and MP2/aVTZ results show that Bz<sub>2</sub>V<sup>−</sup> (200 kcal mol<sup>−1</sup> and not converged) and Bz<sub>2</sub>Mn<sup>+</sup> (242 kcal mol<sup>−1</sup> and 241 kcal mol<sup>−1</sup>), which are isoelectronic to Bz<sub>2</sub>Cr (323 kcal mol<sup>−1</sup> and 342 kcal mol<sup>−1</sup>), have larger binding energies than Bz<sub>2</sub>V (173 kcal mol<sup>−1</sup> and 193 kcal mol<sup>−1</sup>) and Bz<sub>2</sub>Mn (181 kcal mol<sup>−1</sup> and 167 kcal mol<sup>−1</sup>), respectively, while Bz<sub>2</sub>Cr<sup>−</sup> (200 kcal mol<sup>−1</sup> and 213 kcal mol<sup>−1</sup>) has a smaller binding energy than its neutral form.



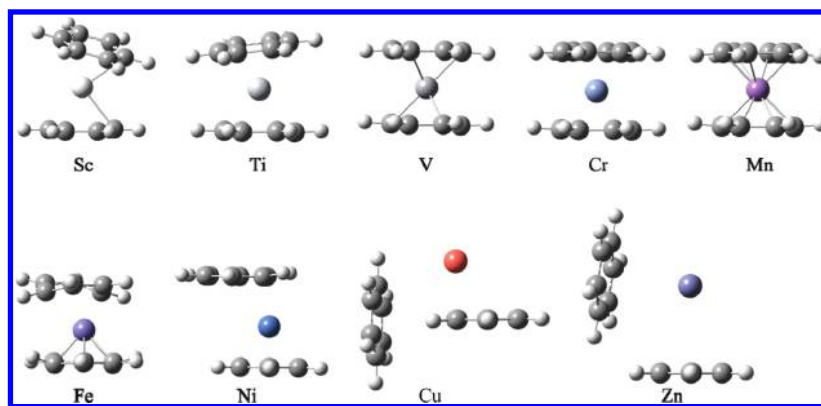


Figure 4. MP2/aVTZ predicted structures of the  $Bz_2M$  complexes.

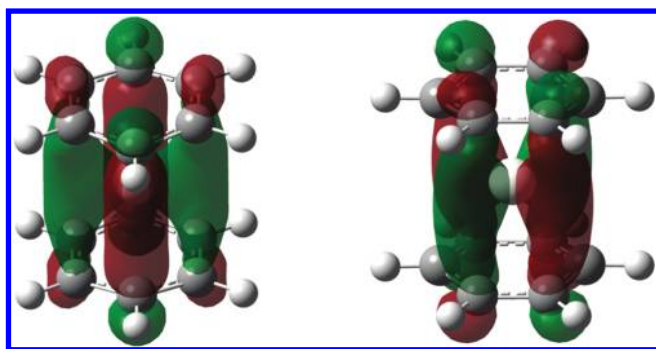


Figure 5.  $\delta$  bonding orbitals in  $Bz_2M$  complexes with point group  $D_{6h}$ .

According to the MO analysis, it is expected that the  $d_{M-Bz}$  is shorter in the  $Bz_2M$  than in the corresponding  $BzM$  for  $M = Sc-Cr$ . The  $Bz_2Ti$  and  $Bz_2Cr$ , however, show slightly longer  $d_{M-Bz}$  in the  $Bz_2M$ . In the  $Bz_2Ti$ , all 2 and 3 orbitals are formed and are fully occupied, while  $\delta$  bonding orbitals in  $Bz_2Ti$  are only partially occupied. Thus, even if  $Bz_2Ti$  shows stronger binding due to benzene stacking, it cannot obtain the full advantage of a decrease in  $d_{M-Bz}$ . It is also expected that the  $d_{M-Bz}$  in  $Bz_2M$  is the shortest in  $Bz_2V$  and  $Bz_2Cr$  due to the fact that 17 and 18 electrons fully occupy the orbitals in Figure 5. However, the  $d_{M-Bz}$  of  $Bz_2Cr$  is slightly longer than that of  $Bz_2V$ , even though the HOMO is a  $\delta$  bonding orbital. This slight deviation from the  $d_{M-Bz}$  tendency may arise from the slightly negative charge accumulated on the chromium atom due to its large electron affinity ( $65 \text{ kJ mol}^{-1}$ ) as compared with the smaller electron affinity of V ( $51 \text{ kJ mol}^{-1}$ ; Table 3). This negative charge of the metal repels the negative charges on carbon atoms in benzene molecules.

On the other hand, despite a 19-electron environment, the  $d_{M-Bz}$  of  $Bz_2Mn$  is the shortest among the five complexes, and the extent of the decrease for  $BzMn$  is also large. Of course, the structure itself is less stable than any  $Bz_2M$  of early transition metals, except for  $Bz_2Sc$ , based on the small binding energy of  $167 \text{ kcal mol}^{-1}$  for  $Bz_2Mn$ . As shown in Figure 6, a peculiar shape of the HOMO of  $Bz_2Mn$ , however, can dissipate electrons out of the central atom, and the complex is able to mitigate the electron repulsions. In fact, the positive NBO charge on the Mn atom in Table 3 supports the notion that  $Bz_2Mn$  dissipates electrons effectively (the electron affinity of Mn is  $\sim 0 \text{ kJ mol}^{-1}$ ).

The intercalation of  $FeCl_3$  inside the bilayer has recently been used for device fabrication.<sup>84</sup> It would be an interesting issue

Table 2. MP2/aVTZ Results for the  $Bz_2M$  Complexes<sup>a</sup>

metal	spin multiplicity	$d_{M-Bz}$ ( $d_{Bz2M} - d_{BzM}$ ) (Å)	$\Delta E$ ( $\text{kcal mol}^{-1}$ )	$\Delta\Delta E$ ( $\text{kcal mol}^{-1}$ ) <sup>b</sup>	freq. ( $\text{cm}^{-1}$ ) <sup>c</sup>
Sc	2	1.913 (−0.010)	−98.2	+66.4	234
Ti	1	1.732 (+0.128)	−191.0	−22.2	262
V	2	1.532 (−0.181)	−192.6	−117.8	395
Cr	1	1.589 (+0.078)	−341.7	+75.7	285
Mn	2	1.473 (−0.137)	−167.2	−57.6	337
Fe	1	1.377 (−0.135), 2.049 <sup>d</sup>	−234.8	−173.1	<i>e</i>
Ni	1	1.743 (+0.302), 2.251 <sup>d</sup>	−132.7	+73.7	<i>e</i>
Cu	2	2.437 <sup>f</sup> (−0.868), 3.672	−9.8	−6.0	<i>e</i>
Zn	1	3.462, <sup>g</sup> 3.448 <sup>g</sup> (−0.111)	−7.0	−3.0	<i>e</i>

<sup>a</sup>  $Bz_2Co$  was not optimized due to the convergence problem. <sup>b</sup> Cooperative binding energy difference:  $\Delta\Delta E = \Delta E(Bz_2M) - 2 \times \Delta E(BzM)$ . <sup>c</sup> Frequencies were calculated at the MP2/aVDZ level without BSSE correction. <sup>d</sup> Average distance between a metal and two nearest carbon atoms of the upper benzene. <sup>e</sup> The breathing mode is not defined. <sup>f</sup> Average distance between a metal and two nearest carbon atoms of each benzene. <sup>g</sup> Distance between Zn and each benzene centroid.

Table 3.  $d_{M-Bz}$ 's, Atomic Radii and NBO Charges of Metal in  $Bz_2M$  Complexes with Point Group of  $D_{6h}$  and  $BzM$  Complexes ( $M = Sc - Mn$ ).<sup>a</sup>

metal	atomic radius of metal atoms (Å)	$d_{M-Bz}$ ( $d_{Bz2M} - d_{BzM}$ ) (Å)	$Bz_2M$	$BzM$
Sc	2.090	1.913 (−0.010)	1.121	0.875
Ti	2.000	1.732 (+0.128)	0.829	1.060
V	1.920	1.532 (−0.180)	0.216	0.996
Cr	1.850	1.589 (+0.078)	−0.076	0.697
Mn	1.790	1.473 (−0.137)	0.015	1.375

<sup>a</sup> NBO charge of metal atoms (a.u.).

whether a single transition metal layer could be obtained inside bilayer graphene. In this regard, the metal–dibenzene structures could give interesting information for intercalated metal inside bilayered graphene.

The complexes of the late transition metals would be highly unstable if they maintain  $D_{6h}$ -like structure because in this case the number of electrons is larger than 18. Hence, the structures need to be distorted; one of benzene molecules strays so as not to donate all 6 electrons, donating fewer electrons to the central

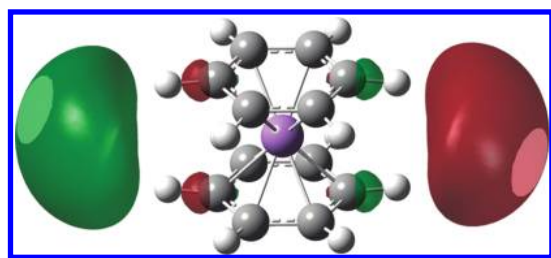


Figure 6. HOMO of  $Bz_2Mn$  with point group  $D_{6h}$ .

atom. Indeed, in the case of  $Bz_2Cu$ , it is interesting to note that since the interaction between Cu and Bz is very weak, the  $\pi$ -H interaction<sup>85,86</sup> is dominant between two benzene molecules, and the structure is no longer a stacked form.

### DISPERSION INTERACTION FOR $BzCu$ AND $BzZn$ COMPLEXES

Tables 1 and 2 present that Cu and Zn complexes show very weak binding ( $1.9$ – $9.8$  kcal mol<sup>−1</sup>) in both  $BzM$  and  $Bz_2M$  complexes. The origin of these weak binding energies can be deduced from the NBO charges of metals. The NBO charges of Cu and Zn are  $-0.08$  and  $-0.05$ , respectively, indicating that there is no charge transfer from a metal atom to a benzene molecule in each complex. Hence, these weak binding energies of  $BzCu$  and  $BzZn$  are mainly due to the dispersion interaction. Note that the dispersion interaction is overestimated at the MP2 level of theory. To clarify this problem, we further performed the calculation at the level of coupled cluster theory with the inclusion of single and double excitations and perturbative inclusion of triple excitations (CCSD(T)) with aVDZ basis set using the Molpro package<sup>87</sup> for  $BzM$  ( $M = Cu$  and  $Zn$ ). The binding energies with BSSE correction are  $1.3$  kcal mol<sup>−1</sup> for  $BzCu$  and  $1.0$  kcal mol<sup>−1</sup> for  $BzZn$  at the level of CCSD(T)/aVDZ. Note that the MP2/aVTZ calculation results give  $1.9$  and  $2.0$  kcal mol<sup>−1</sup> for  $BzCu$  and  $BzZn$ , respectively. Hence, in these cases, the MP2 level of theory gives a slightly overestimated dispersion interaction in comparison with the CCSD(T) level of theory.

In summary, we carried out a systematic study of  $Bz_2M$  complexes as compared with the corresponding  $BzM$  complexes. The results show sandwich structures for early transition metal complexes, while such sandwich structures are broken for late transition metal ones. The  $d_{M-Bz}$  in  $Bz_2M$  with doubly degenerate  $\delta$  bonding orbitals tends to decrease from  $M = Sc$  to  $M = V$ . It is quite interesting that even though the second coordination generally gives a longer coordination distance with smaller coordination energy than the first coordination, the present second coordination gives a shorter coordination distance with a larger coordination energy for the early transition metals because of the 18-electron rule. Unlike the  $Bz_2Cr$ , which gives some exception due to the negative NBO charge of Cr, the  $Bz_2Mn$  results in decreased  $d_{M-Bz}$  because of the diffuse HOMO. Structures of  $Bz_2M$  for late transition metals are distorted to avoid the instability caused by too many electrons around the central metal atom. As one of the two benzene molecules donates fewer electrons to a central atom, the whole structure is better stabilized. The present results provide a possible explanation of why graphene tends to grow in a few layers on the Ni surface, while on the Cu surface the weak interaction between the copper

surface and graphene allows for the formation of a single layer of graphene, in agreement with CVD experiments.

### ASSOCIATED CONTENT

**S Supporting Information.** Discussion on the MP2/aVDZ results for  $BzM$  and  $Bz_2M$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

### AUTHOR INFORMATION

#### Corresponding Author

\*E-mail: [kim@postech.ac.kr](mailto:kim@postech.ac.kr).

#### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENT

This work was supported by NRF (National Honor Scientist Program, 2010-0020414; WCU, R32-2008-000-10180-0) and KISTI (KSC-2011-G3-02).

### REFERENCES

- (1) Fischer, E. O.; Hafner, W. Z. *Naturforsch.* **1955**, *10b*, 665.
- (2) Rayón, D.; Frenking, G. *Organometallics* **2003**, *22*, 3304–3308.
- (3) Haaland, A. *Acta Chem. Scand.* **1965**, *19*, 41–46.
- (4) Albrecht, G.; Förster, E.; Sippel, D.; Eichkorn, F.; Kurras, E. Z. *Chem.* **1968**, *8*, 311.
- (5) Ngai, L. H.; Stafford, F. E.; Schäfer, L. J. *Am. Chem. Soc.* **1969**, *91*, 48–49.
- (6) Bochmann, M. *Organometallics 2, Complexes with TM-Carbon  $\pi$  bond*; Oxford Science Publication: Oxford, U.K., 1994.
- (7) Choi, K.-W.; Choi, S.; Sun, J. B.; Kim, S. K. *J. Chem. Phys.* **2007**, *126*, 034308.
- (8) Xiang, H.; Yang, J.; Hou, J. G.; Zhu, Q. *J. Am. Chem. Soc.* **2006**, *128*, 2310–2314.
- (9) Aspley, C. J.; Boxwell, C.; Buil, M. L.; Higgitt, C. L.; Long, C.; Perutz, R. N. *Chem. Commun.* **1999**, *11*, 1027–1028.
- (10) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J. *Chem. Rev.* **1982**, *82*, 499–525.
- (11) Rayane, D.; Allouche, A.-R.; Antoine, R.; Broyer, M.; Compagnon, I.; Dugourd, P. *Chem. Phys. Lett.* **2003**, *375*, 506–510.
- (12) Yasuike, T.; Yabushita, S. *J. Phys. Chem. A* **1999**, *103*, 4533–4542.
- (13) Jones, R. H.; Doerr, L. H.; Teat, S. J.; Wilson, C. C. *Chem. Phys. Lett.* **2000**, *319*, 423–426.
- (14) Ketkov, S. Y.; Selzle, H. L.; Schlag, E. W.; Domrachev, G. A. *Chem. Phys. Lett.* **2003**, *373*, 486–491.
- (15) Samuel, E.; Caurant, D.; Gourier, D.; Elschenbroich, Ch.; Agbaria, K. *J. Am. Chem. Soc.* **1998**, *120*, 8088–8092.
- (16) Calucci, L.; Cloke, F. G. N.; Englert, U.; Hitchcock, P. B.; Pampaloni, G.; Pinzino, C.; Puccinid, F.; Volpe, M. *Dalton Trans.* **2006**, 4228–4234.
- (17) Ketkov, S. Y.; Green, J. C.; Mehnert, C. P. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2461–2466.
- (18) Xiang, H.; Yang, J.; Hou, J. G.; Zhu, Q. *J. Am. Chem. Soc.* **2006**, *128*, 2310–2314.
- (19) Choi, K.-W.; Ahn, D.-S.; Lee, S.; Kim, S. K. *J. Phys. Chem. A* **2004**, *108*, 11292–11295.
- (20) Choi, K.-W.; Choi, S.; Ahn, D.-S.; Han, S.; Kang, T. Y.; Baek, S. J.; Kim, S. K. *J. Phys. Chem. A* **2008**, *112*, 7125–7127.
- (21) Choi, K.-W.; Choi, S.; Baek, S. J.; Kim, S. K. *J. Chem. Phys.* **2007**, *126*, 034308.

- (22) Han, S.; Singh, N. J.; Kang, T. Y.; Choi, K.-W.; Choi, S.; Baek, S. J.; Kim, K. S.; Kim, S. K. *Phys. Chem. Chem. Phys.* **2010**, *12*, 7648–7653.
- (23) Sahnoun, R.; Mijoule, C. *J. Phys. Chem. A* **2001**, *105*, 6176–6181.
- (24) Li, Y.; Baer, T. *J. Phys. Chem. A* **2002**, *106*, 9820–9826.
- (25) Yi, H.-B.; Lee, H. M.; Kim, K. S. *J. Chem. Theory Comput.* **2009**, *5*, 1709–1717.
- (26) Lyssenko, K. A.; Korlyukov, A. A.; Golovanov, D. G.; Ketkov, S. Y.; Antipin, M. Y. *J. Phys. Chem. A* **2006**, *110*, 6545–6551.
- (27) Sohnlein, B. R.; Yang, D.-S. *J. Chem. Phys.* **2006**, *124*, 134305.
- (28) Bérces, A.; Ziegler, T. *J. Phys. Chem.* **1994**, *98*, 13233–13242.
- (29) Kim, D.; Hu, S.; Tarakeshwar, P.; Kim, K. S.; Lisy, J. M. *J. Phys. Chem. A* **2003**, *107*, 1228–1238.
- (30) Meyer, F.; Khan, F. A.; Armentrou, P. B. *J. Am. Chem. Soc.* **1995**, *117*, 9740–9748.
- (31) Singh, N. J.; Min, S. K.; Kim, D. Y.; Kim, K. S. *J. Chem. Theory Comput.* **2009**, *5*, 515–529.
- (32) Perrier, A.; Gourier, D.; Joubert, L.; Adamo, C. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1337–1343.
- (33) Yi, H.; Diefenbach, M.; Choi, Y. C.; Lee, E. C.; Lee, H. M.; Hong, B. H.; Kim, K. S. *Chem.—Eur. J.* **2006**, *12*, 4885–4892.
- (34) Sohnlein, B. R.; Lei, Y.; Yang, D.-S. *J. Chem. Phys.* **2007**, *127*, 114302.
- (35) Philpott, M. R.; Kawazoe, Y. *Chem. Phys.* **2007**, *342*, 223–235.
- (36) Philpott, M. R.; Kawazoe, Y. *Chem. Phys.* **2008**, *348*, 69–82.
- (37) Singh, A. K.; Kumar, V.; Kawazoe, Y. *Eur. Phys. J. D* **2005**, *34*, 295–298.
- (38) Miyajima, K.; Nakajima, A.; Yabushita, S.; Knickelbein, M. B.; Kaya, K. *J. Am. Chem. Soc.* **2004**, *126*, 13202–13203.
- (39) Kandalam, A. K.; Rao, B. K.; Jena, P.; Pandey, R. *J. Chem. Phys.* **2004**, *120*, 10414–10422.
- (40) Béchamp, K.; Levesque, M.; Joly, H.; Manceron, L. *J. Phys. Chem. A* **2006**, *110*, 6023–6031.
- (41) Kua, J.; Tomlin, K. M. *J. Phys. Chem. A* **2006**, *110*, 11988–11994.
- (42) Philpott, M. R.; Kawazoe, Y. *J. Phys. Chem. A* **2008**, *112*, 2034–2042.
- (43) Kim, W. Y.; Kim, K. S. *Acc. Chem. Res.* **2010**, *43*, 111–120.
- (44) Kandalam, A. K.; Rao, B. K.; Jena, P.; Pandey, R. *J. Chem. Phys.* **2004**, *120*, 10414–10422.
- (45) Lee, E. C.; Choi, Y. C.; Kim, W. Y.; Singh, N. J.; Lee, S.; Shim, J. H.; Kim, K. S. *Chem.—Eur. J.* **2010**, *16*, 12141–12146.
- (46) Cho, Y.; Min, S. K.; Kim, W. Y.; Kim, K. S. *Phys. Chem. Chem. Phys.* **2011**, *115*, 6019–6023.
- (47) Kim, W. Y.; Choi, Y. C.; Min, S. K.; Cho, Y.; Kim, K. S. *Chem. Soc. Rev.* **2009**, *38*, 2319–2333.
- (48) Muhida, R.; Diño, W. A.; Rahman, M. M.; Kasai, H.; Nakanishi, H. *J. Phys. Soc. Jpn.* **2004**, *73*, 2292–2295.
- (49) Sceats, E. L.; Green, J. C. *Phys. Rev. B* **2007**, *75*, 245441.
- (50) Cho, W. J.; Cho, Y.; Min, S. K.; Kim, W. Y.; Kim, K. S. *J. Am. Chem. Soc.* **2011**, *133*, 9364–9369.
- (51) Rao, B. K.; Jena, P. *J. Chem. Phys.* **2002**, *116*, 1343–1349.
- (52) Valencia, H.; Gil, A.; Frapper, G. *J. Phys. Chem. C* **2010**, *114*, 14141–14153.
- (53) Myung, S.; Park, J.; Lee, H.; Kim, K. S.; Hong, S. *Adv. Mater.* **2010**, *22*, 2045–2049.
- (54) Myung, S.; Solanki, A.; Kim, C.; Park, J.; Kim, K. S.; Lee, K.-B. *Adv. Mater.* **2011**, *23*, 2221–2225.
- (55) Chandra, V.; Park, J.; Chun, Y.; Lee, J. W.; Hwang, I.-C.; Kim, K. S. *ACS Nano* **2010**, *4*, 3979–3986.
- (56) Chandra, V.; Kim, K. S. *Chem. Commun.* **2011**, *47*, 3942–3944.
- (57) Riley, K. E.; Pitok, M.; Jurečka, P.; Hobza, P. *Chem. Rev.* **2010**, *110*, 5023–5063.
- (58) Lee, E. C.; Kim, D.; Jurečka, P.; Tarakeshwar, P.; Hobza, P.; Kim, K. S. *J. Phys. Chem. A* **2007**, *111*, 3446–3457.
- (59) Sinnokrot, M. O.; Sherrill, C. D. *J. Phys. Chem. A* **2006**, *110*, 10656–10688.
- (60) Singh, N. J.; Min, S. K.; Kim, D. Y.; Kim, K. S. *J. Chem. Theory Comput.* **2009**, *5*, 515–529.
- (61) Lee, J. Y.; Hong, B. H.; Kim, W. Y.; Min, S. K.; Kim, Y.; Jouravlev, M. V.; Bose, R.; Kim, K. S.; Hwang, I.-C.; Kaufman, L. J.; Wong, C. W.; Kim, P.; Kim, K. S. *Nature* **2009**, *460*, 498–501.
- (62) Kim, K. S.; Tarakeshwar, P.; Lee, J. Y. *Chem. Rev.* **2000**, *100*, 4145–4185.
- (63) Ringer, A. L.; Sinnokrot, M. O.; Lively, R. P.; Sherrill, C. D. *Chem.—Eur. J.* **2006**, *12*, 3821–3828.
- (64) Špirko, V.; Hobza, P. *Chem. Phys. Chem.* **2006**, *7*, 640–643.
- (65) Timoshkin, A. Y.; Frenking, G. *Inorg. Chem.* **2003**, *42*, 60–69.
- (66) Sinnokrot, M. O.; Sherrill, C. D. *J. Am. Chem. Soc.* **2004**, *126*, 7690–7697.
- (67) Pitoňák, M.; Neogrády, P.; Řezáč, J.; Jurečka, P.; Urban, M.; Hobza, P. *J. Chem. Theory Comput.* **2008**, *4*, 1829–1834.
- (68) Sinnokrot, M. O.; Sherrill, C. D. *J. Phys. Chem. A* **2003**, *107*, 8377–8379.
- (69) Kim, D.; Hu, S.; Tarakeshwar, P.; Kim, K. S.; Lisy, J. M. *J. Phys. Chem. A* **2003**, *107*, 1228–1238.
- (70) Ihm, H.; Yun, S.; Kim, H. G.; Kim, J. K.; Kim, K. S. *Org. Lett.* **2002**, *4*, 2897–2900.
- (71) Yi, H.-B.; Lee, H. M.; Kim, K. S. *J. Chem. Theory Comput.* **2009**, *5*, 1709–1717.
- (72) Yi, H.-B.; Diefenbach, M.; Choi, Y. C.; Lee, E. C.; Lee, H. M.; Hong, B. H.; Kim, K. S. *Chem.—Eur. J.* **2006**, *12*, 4885–4892.
- (73) Rayón, V. M.; Frenking, G. *Chem.—Eur. J.* **2002**, *8*, 4693–4707.
- (74) Frunzke, J.; Lein, M.; Frenking, G. *Organometallics* **2002**, *21*, 3351–3359.
- (75) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, Y.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, R. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 09*, Revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.
- (76) Hurley, M. M.; Pacios, L. F.; Christiansen, P. A. *J. Chem. Phys.* **1986**, *84*, 6840–6853.
- (77) Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys.* **1997**, *106*, 9639–9646.
- (78) Min, S. K.; Lee, E. C.; Lee, H. M.; Kim, D. Y.; Kim, D.; Kim, K. S. *J. Comput. Chem.* **2008**, *29*, 1208–1221.
- (79) Kim, K. S.; Zhao, Y.; Jang, H.; Lee, S. Y.; Kim, J. M.; Kim, K. S.; Ahn, J. -H.; Kim, P.; Choi, J.-H.; Hong, B. H. *Nature* **2009**, *457*, 706–710.
- (80) Li, X.; Cai, W.; An, J.; Kim, S.; Nah, J.; Yang, D.; Piner, R.; Velamakanni, A.; Jung, I.; Tutuc, E.; Banerjee, S. K.; Colombo, L.; Ruoff, R. S. *Science* **2009**, *324*, 1312–1314.
- (81) Bae, S.; Kim, H.; Lee, Y.; Xu, X.; Park, J.-S.; Zheng, Y.; Balakrishnan, J.; Lei, T.; Kim, H. R.; Song, Y. I.; Kim, Y.-J.; Kim, K. S.; Özyilmaz, B.; Ahn, J.-H.; Hong, B. H.; Iijima, S. *Nat. Nanotechnol.* **2010**, *8*, 574–578.
- (82) Min, S. K.; Kim, W. Y.; Cho, Y.; Kim, K. S. *Nat. Nanotechnol.* **2011**, *6*, 162–165.
- (83) Kim, W. Y.; Kim, K. S. *Nat. Nanotechnol.* **2008**, *3*, 408–412.
- (84) Kim, N.; Kim, K. S.; Jung, N.; Brus, L.; Kim, P. *Nano Lett.* **2011**, *11*, 860–865.
- (85) Lee, E. C.; Hong, B. H.; Lee, J. Y.; Kim, J. C.; Kim, D.; Kim, Y.; Tarakeshwar, P.; Kim, K. S. *J. Am. Chem. Soc.* **2005**, *127*, 4530–4537.

(86) Tarakeshwar, P.; Choi, H. S.; Kim, K. S. *J. Am. Chem. Soc.* **2001**, *123*, 3323–3331.

(87) Werner, H.-J.; Knowles, P. J.; Manby, F. R.; Schütz, M.; Celani, P.; Knizia, G.; Korona, T.; Lindh, R.; Mitrushenkov, A.; Rauhut, G.; Adler, T. B.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Goll, E.; Hampel, C.; Hesselmann, A.; Hetzer, G.; Hrenar, T.; Jansen, G.; Köppl, C.; Liu, Y.; Lloyd, A. W.; Mata, R. A.; May, A. J.; McNicholas, S. J.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pflüger, K.; Pitzer, R.; Reiher, M.; Shiozaki, T.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T.; Wang, M.; Wolf, A. *MOLPRO*, version 2010.1; University College Cardiff Consultants Limited: Wales, U.K., 2010. <http://www.molpro.net> (accessed Nov. 2011).