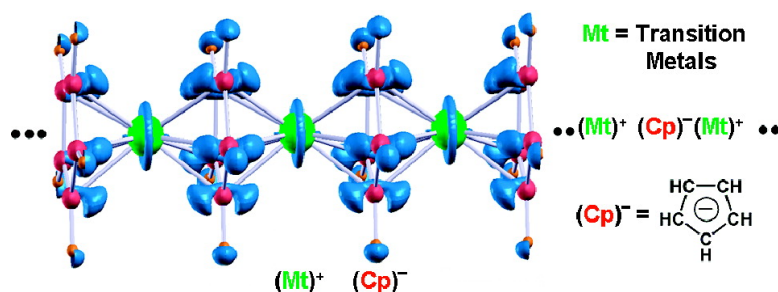


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*J. Am. Chem. Soc.*, **2008**, 130 (42), 13956-13960 • DOI: 10.1021/ja804053a • Publication Date (Web): 18 September 2008

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## Charge-Transfer-Based Mechanism for Half-Metallicity and Ferromagnetism in One-Dimensional Organometallic Sandwich Molecular Wires

Lei Shen,<sup>†,‡</sup> Shuo-Wang Yang,<sup>\*,†</sup> Man-Fai Ng,<sup>†</sup> Valeri Ligatchev,<sup>†</sup> Liping Zhou,<sup>§</sup> and Yuanping Feng<sup>‡</sup>

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**Abstract:** We present a systematic theoretical study on the mechanism of half-metallicity and ferromagnetism for one-dimensional (1-D) sandwich molecular wires (SMWs) constructed with altering cyclopentadienyl (Cp) and first-row transition metal (Mt). It is unveiled for the first time that, in (MtCp)<sub>∞</sub>, one valence electron would transfer from the Mt to the Cp ring, forming Cp<sup>-</sup> and Mt<sup>+</sup> altering structures. This electron transfer not only makes them more stable than the benzene analogues (MtBz)<sub>∞</sub> but also leads to completely different half-metallic and ferromagnetic mechanisms. We analyze such unusual half-metallicity and ferromagnetic behaviors and explain each SMW magnetic moment quantitatively. Finally, we indicate that a Peierls transition does not occur in these 1-D SMWs.

### Introduction

One-dimensional (1-D) vanadium–benzene (VBz)<sub>∞</sub> multidecker organometallic sandwich molecular wires (SMWs) have recently been extensively studied because they exhibit half-metallicity (one spin channel is metallic while the opposite spin channel is insulating<sup>1</sup>) and spin filter effects.<sup>2–9</sup> Their ferrocene analogues (FeCp)<sub>∞</sub> have been theoretically predicted to be the first unique 1-D molecules that possess half-metallicity, high spin filter effects, and negative differential resistance simultaneously.<sup>10</sup> Further examination of their magnetic properties show that the magnetic moment of (FeCp)<sub>∞</sub> is strikingly different from what can be expected, if we were to base our understandings entirely on the valence electron configuration of the Fe atom.

To illustrate this, we consider the d orbitals of Fe in (FeCp)<sub>∞</sub>. Under *D*<sub>5h</sub> or *D*<sub>6h</sub> symmetry of crystal field, the 3d orbitals of Fe split into a d<sub>3z<sup>2</sup>-r<sup>2</sup></sub> (a<sub>1</sub>) orbital and two sets of doubly degenerate d<sub>xy</sub>, d<sub>x<sup>2</sup>-y<sup>2</sup></sub> (e<sub>2</sub>) and d<sub>xz</sub>, d<sub>yz</sub> (e<sub>1</sub>) orbitals.<sup>4,5</sup> The valence electron configuration of Fe is 3d<sup>6</sup>4s<sup>2</sup>, and in such a situation the eight valence electrons occupy the d degenerate orbitals in (FeCp)<sub>∞</sub> as follows. Three minority (spin-down) electrons occupy the a<sub>1</sub> and e<sub>2</sub> orbitals, while five majority (spin-up) electrons occupy all five split d orbitals, resulting in two unpaired electrons in the doubly degenerate e<sub>1</sub> orbitals. In such a case, (FeCp)<sub>∞</sub> should in principle have a magnetic moment of 2.0 μ<sub>B</sub> per unit cell. However, our first principles calculation reveals a magnetic moment of 1.0 μ<sub>B</sub> per unit cell. One of the valence electrons in Fe seems to have disappeared. In contrast, (VBz)<sub>∞</sub> has five valence electrons: three spin-up electrons and two spin-down electrons, filling the a<sub>1</sub> orbital and one of the e<sub>2</sub> orbitals, leaving an unpaired electron in the e<sub>2</sub> orbital. Therefore, (VBz)<sub>∞</sub> should show a magnetic moment of 1.0 μ<sub>B</sub> per unit cell, which is exactly the same as the computed value.<sup>2,4,5</sup>

Although (FeCp)<sub>∞</sub> and (VBz)<sub>∞</sub> SMWs appear quite similar in geometry, the difference in magnetic moment between them implies that their electronic configurations and mechanism of half-metallicity and ferromagnetism could be intrinsically different. Furthermore, it is interesting to consider the following questions: (1) In addition to (FeCp)<sub>∞</sub>, are there any other transition metal (Mt) sandwich molecular wires, (MtCp)<sub>∞</sub>, that are half-metallic (HM)? (2) Since (FeCp)<sub>∞</sub> and (VBz)<sub>∞</sub> are found to be HM, how about their analogues (FeBz)<sub>∞</sub> and (VCp)<sub>∞</sub>, respectively? (3) What is the intrinsic mechanism of half-metallicity and ferromagnetism within these two types of SMW (i.e., (MtCp)<sub>∞</sub> and (MtBz)<sub>∞</sub>)? In this article, we aim to understand their half-metallicity and ferromagnetic properties and the mechanism behind them. Our study focuses on the first-

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**Table 1.** Optimized Lattice Constant ( $c$ ), Binding Energy ( $E_b$ ), Total Magnetic Moment per Unit Cell ( $M$ ), and the Energy Difference between the Ferromagnetic and Diamagnetic States ( $\Delta E$ ) for All (MtCp) $_{\infty}$  and (MtBz) $_{\infty}$ 

Mt	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Nb	Tc		
SMW	Cp	Cp	Cp	Bz	Cp	Cp	Bz	Cp	Cp	Cp	Cp	Bz	Bz	
$c$ (Å)	4.08	3.78	3.62	3.37	3.44	3.32	3.37	3.41	3.50	3.68	4.02	4.56	3.76	3.75
$^a E_b$ (eV)	-3.52	-4.23	-4.25	-4.96	-2.60	-2.41	-1.78	-4.38	-1.38	-1.16	-0.19	-0.14	-0.81	-0.11
$M$ ( $\mu_B$ )	0.00	0.89	2.00	0.88	1.00	0.00	1.00	1.00	0.00	0.00	0.00	0.00	0.57	1.00
$^b \Delta E$ (meV)	/	-48	-254	-113	-39	/	-351	-170	/	/	/	/	-25	-71
half-metallic	no	no	yes	yes (quasi)	yes	no	yes	yes	no	no	no	no	yes (quasi)	yes
100% spin-polarization	no	no	neg <sup>c</sup>	no	neg	no	pos	pos	no	no	no	no	no	pos
electron configuration	3d <sup>1</sup> 4s <sup>2</sup>	3d <sup>2</sup> 4s <sup>2</sup>	3d <sup>3</sup> 4s <sup>2</sup>	3d <sup>5</sup> 4s <sup>1</sup>	3d <sup>5</sup> 4s <sup>2</sup>	3d <sup>6</sup> 4s <sup>2</sup>	3d <sup>7</sup> 4s <sup>2</sup>	3d <sup>8</sup> 4s <sup>2</sup>	3d <sup>10</sup> 4s <sup>1</sup>	3d <sup>10</sup> 4s <sup>2</sup>	4d <sup>4</sup> 5s <sup>1</sup>	4d <sup>6</sup> 5s <sup>1</sup>		

<sup>a</sup>  $E_b = E_{SMW} - E_{Mt} - E_{Cp/Bz}$  where  $E_{SMW}$ ,  $E_{Mt}$ , and  $E_{Cp/Bz}$  are total energies of sandwich molecular wire, transition metal, and Cp or Bz rings, respectively. <sup>b</sup>  $\Delta E = E_{FM} - E_{DM}$  where  $E_{FM}$  and  $E_{DM}$  are the energies of ferromagnetic and diamagnetic states. <sup>c</sup> Neg = negative; pos = positive.

row transition metal (MtCp) $_{\infty}$  SMWs. Additionally, we also study (VBz) $_{\infty}$  and (MnBz) $_{\infty}$  and their two second-row Mt benzene analogues, (NbBz) $_{\infty}$  and (TcBz) $_{\infty}$ , because the former two were reported to be half-metallic.<sup>4</sup> Finally, on the basis of binding energy and half-metallic and ferromagnetic properties, we provide the electron configurations for these two types of SMW and account for their magnetic moments quantitatively. This is the first study to reveal the underlying mechanism of half-metallicity and ferromagnetism for these two types of SMW, and we believe the mechanism can be generally applied to similar 1-D SMWs.

## Methodology

A unit of SMW is placed within a unit cell of  $15 \times 15 \times c$  Å<sup>3</sup> as done in our previous study,<sup>10</sup> where  $c$  is the distance between two neighboring Cp or Bz units. Structure optimization, density of state (DOS), and band structure calculations are performed using Vienna ab initio simulation package.<sup>11</sup> The generalized gradient approximation (GGA)<sup>12</sup> scheme is used for electron exchange and correlation while the frozen-core projector augmented wave method is used to describe the interaction between ions and electrons.<sup>13</sup> The cutoff energy is set at 400 eV and a k-mesh of  $1 \times 1 \times 45$  is used for the infinite SMWs. A convergence of Hellmann–Feynman forces less than 0.01 eV/Å per atom has been achieved. Furthermore, we investigate the effect of doubling the unit cell size along the SMW direction to evaluate the ground state of ferromagnetic (FM), antiferromagnetic (AFM), and diamagnetic (DM) configurations in our spin-polarized calculations with structural optimization, and assess possibility of the Peierls transition.<sup>14,15</sup>

## Results and Discussion

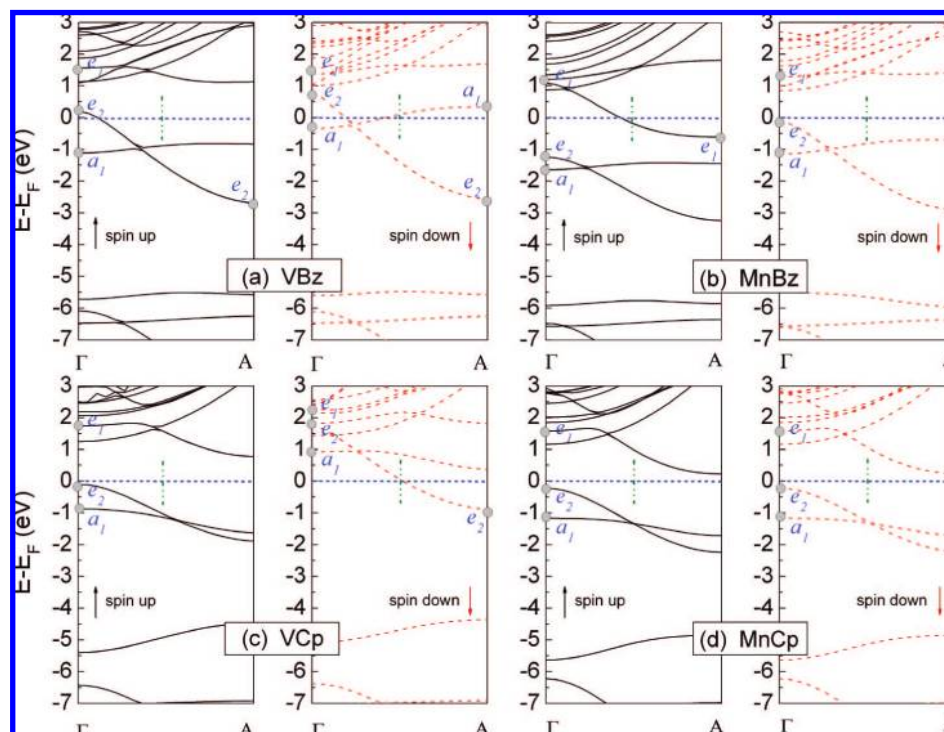
Table 1 summarizes the calculated results of binding energy ( $E_b$ ), magnetic moment per unit cell ( $M$ ), energy difference between FM and DM states ( $\Delta E$ ), half-metallicity, and spin-polarization<sup>16</sup> for the first-row (MtCp) $_{\infty}$  and additional two benzene analogues, (NbBz) $_{\infty}$  and (TcBz) $_{\infty}$ . It can be seen that

(MtCp) $_{\infty}$  with Mt from Sc to Fe is quite stable and its FM is energetically more favorable than its DM. Among them, (VCp) $_{\infty}$ , (CrCp) $_{\infty}$ , and (FeCp) $_{\infty}$  show HM and their magnetic moments are 2.0, 1.0, and 1.0  $\mu_B$ , respectively. For comparison, we also calculate their respective second-row Mt counterparts (i.e., (NbCp) $_{\infty}$ , (MoCp) $_{\infty}$ , and (RuCp) $_{\infty}$ ). It is found that (MoCp) $_{\infty}$  is not stable ( $E_b > 0$ ), whereas (NbCp) $_{\infty}$  and (RuCp) $_{\infty}$  are very fragile ( $E_b = -0.68$  and  $-0.98$  eV, respectively), and all of these three SMWs are nonmagnetic. These results suggest that strong stability (large bonding energy) is crucial or necessary for (MtCp) $_{\infty}$  to exhibit magnetic moment or HM property.

For the (MtBz) $_{\infty}$  systems, our calculation shows that (MnBz) $_{\infty}$  is HM and (VBz) $_{\infty}$  is quasi-HM, which agrees with that previously reported.<sup>4</sup> (VBz) $_{\infty}$  appears to be very stable, whereas (MnBz) $_{\infty}$  is moderately stable (Table 1). In comparison, their second-row Mt counterparts, (NbBz) $_{\infty}$  and (TcBz) $_{\infty}$ , are very unstable. Both of them are found to be HM and their magnetic moments are similar to that of their first-row Mt counterparts in the same group. The magnetic moments of (VBz) $_{\infty}$  and (NbBz) $_{\infty}$  are 0.88 and 0.57  $\mu_B$ , respectively, whereas both (MnBz) $_{\infty}$  and (TcBz) $_{\infty}$  have the same magnetic moment of 1.0  $\mu_B$ . Our results suggest that stability is not the main factor affecting the ferromagnetic and half-metallic properties for (MtBz) $_{\infty}$ . Instead, their ferromagnetic and HM properties are predominated by the valence electron configurations of Mt. Therefore, we can conclude that the mechanisms of ferromagnetism and half-metallicity in (MtCp) $_{\infty}$  and (MtBz) $_{\infty}$  are very different. Since only (VBz) $_{\infty}$  and (MnBz) $_{\infty}$  are HM among (MtBz) $_{\infty}$ , while in the case of the Cp analogues (VCp) $_{\infty}$  also shows HM properties, we plot their band structures (Figure 1) for a detailed analysis.

**(MnBz) $_{\infty}$  and (MnCbz) $_{\infty}$ .** As mentioned in the Introduction, under  $D_{5h}$  [for (MtCp) $_{\infty}$ ] or  $D_{6h}$  [for (MtBz) $_{\infty}$ ] structural symmetry, the 3d orbitals of Mt split into an  $a_1$  orbital and two sets of doubly degenerate  $e_2$  and  $e_1$  orbitals (Figure 2). In (MnBz) $_{\infty}$ , Mn has seven valence electrons ( $3d^5 4s^2$ ) due to filling of the 3d shell by the two s electrons.<sup>5</sup> Three minority valence electrons occupy the  $a_1$  and the degenerate  $e_2$  orbitals, while the  $e_1$  remains unoccupied and located above the Fermi level. Therefore, its minority channel is semiconducting. Furthermore, the four majority electrons occupy the  $a_1$ ,  $e_2$  orbitals and one of the  $e_1$  orbitals which cross the Fermi level and are occupied by only one unpaired electron (Figure 1), resulting in a metallic channel. Therefore, (MnBz) $_{\infty}$  appears 100% positive spin-polarization with a magnetic moment of 1.0  $\mu_B$ . The Mn valence electron configuration of (MnBz) $_{\infty}$  is presented schematically in Figure 2, together with that for its Cp analogy (MnCp) $_{\infty}$ . The band structure in Figure 1 clearly indicates that (MnCp) $_{\infty}$  is semiconducting and nonmagnetic (see also Table 1), which

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- (16) As shown by Mazin, I. I. *Phys. Rev. Lett.* **1999**, *83*, 1427, the degree of spin polarization,  $P$ , which eventually predetermines the “half-metallic” behavior of the condensed matter, could be defined in several different ways. In our study, we just followed the most intuitive (and probably simplest) definition:  $P = |N_{\uparrow} - N_{\downarrow}| / (N_{\uparrow} + N_{\downarrow})$ , where  $N_{\uparrow}$  and  $N_{\downarrow}$  are the electronic DOS at the Fermi level for the “up” and “down” spins, respectively. When only one of the DOS components remains positive (while another one equals zero), the above formula immediately yields  $P = 1$ , which predetermines 100% spin polarization of the material.



**Figure 1.** Band structures of  $(\text{MnBz})_\infty$ ,  $(\text{MnCp})_\infty$ ,  $(\text{VBz})_\infty$ , and  $(\text{VCp})_\infty$ . Vertical dashed lines in “spin down” panels represent wavevector  $k = \Pi/2c$  of the dimerized structure.

		$\begin{array}{c} - - e_1 \\ \uparrow \uparrow e_2 \\ \uparrow \uparrow a_1 \end{array}$		$\begin{array}{c} + - e_1 \\ \uparrow \uparrow e_2 \\ \uparrow \uparrow a_1 \end{array}$			
		(VBz) (2 $\mu_B$ )		(MnBz) (1 $\mu_B$ )			
$\begin{array}{c} - - e_1 \\ \circ - e_2 \\ \uparrow \uparrow a_1 \end{array}$	$\begin{array}{c} - - e_1 \\ \circ - e_2 \\ \uparrow \uparrow a_1 \end{array}$	$\begin{array}{c} - - e_1 \\ \uparrow \uparrow e_2 \\ \uparrow \uparrow a_1 \end{array}$	$\begin{array}{c} - - e_1 \\ \uparrow \uparrow e_2 \\ \uparrow \uparrow a_1 \end{array}$	$\begin{array}{c} \circ - e_1 \\ \uparrow \uparrow e_2 \\ \uparrow \uparrow a_1 \end{array}$	$\begin{array}{c} \uparrow \circ e_1 \\ \uparrow \uparrow e_2 \\ \uparrow \uparrow a_1 \end{array}$		
(ScCp) (0 $\mu_B$ )	(TiCp) (1 $\mu_B$ )	(VCp) (2 $\mu_B$ )	(CrCp) (1 $\mu_B$ )	(MnCp) (0 $\mu_B$ )	(FeCp) (1 $\mu_B$ )		

**Figure 2.** Valence electron configurations for  $(\text{MtCp})_\infty$ , where Mt = Sc, Ti, V, Cr, Mn, and Fe, and  $(\text{VBz})_\infty$  and  $(\text{MnBz})_\infty$ . The circle represents a hole that derives from an electron transfer from Mt to the Cp ring.

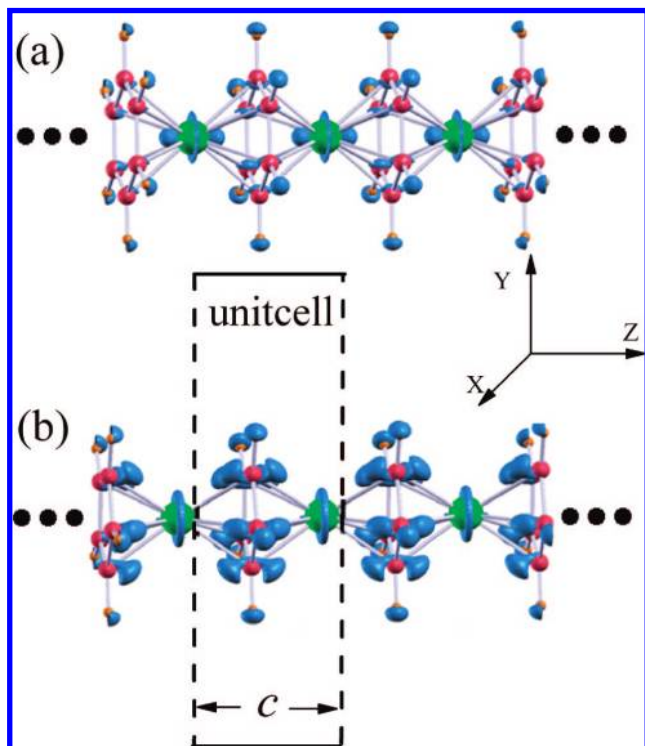
further indicates that the valence electron configurations of Mn in  $(\text{MnCp})_\infty$  and  $(\text{MnBz})_\infty$  must be different. One electron at the  $e_1$  level in  $(\text{MnBz})_\infty$  seems to be removed from Mn in  $(\text{MnCp})_\infty$ , so that its magnetic moment is zero.

**(VBz) $_\infty$  and (VCp) $_\infty$ .** For the case of  $(\text{VBz})_\infty$  and  $(\text{VCp})_\infty$ ,  $(\text{VBz})_\infty$  is quasi-HM while  $(\text{VCp})_\infty$  is fully HM. In  $(\text{VBz})_\infty$ , the majority spin-up bands have a very small density at the Fermi level, while the minority spin-down channel crosses the Fermi level, resulting in a quasi-HM  $(\text{VBz})_\infty$ . From Figure 2, we can clearly see that an unpaired electron of V occupies the  $e_2$  orbital. Therefore,  $(\text{VBz})_\infty$  should have a magnetic moment of 1.0  $\mu_B$ . However, our calculated value is only 0.88  $\mu_B$ . This is due to the semilocal GGA functional, which sometimes underestimates the magnetic moment for such SMWs as compared with the hybrid density functionals such as B3LYP.<sup>17</sup> It has been reported that, by using the B3LYP formalism, the magnetic moment of  $(\text{VBz})_\infty$  would be 1.0  $\mu_B$ .<sup>4</sup> However, this minor difference between B3LYP and GGA results will not affect the validity

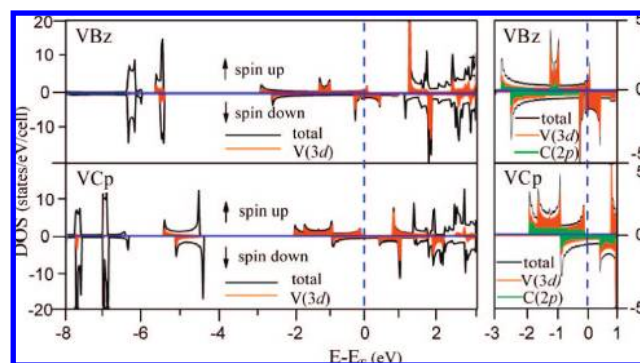
of our main conclusions. In fact, semilocal GGA had been effectively used to describe the electronic and magnetic properties of polymers without  $\Pi$ -conjugation.<sup>4</sup>

On the other hand,  $(\text{VCp})_\infty$  is half-metallic. The spin-up channel (three-electron) is semiconducting and spin-down channel (two-electron) is metallic. The five valence electrons occupy the  $a_1$  orbital but partially occupy the  $e_2$  orbitals, leaving only one unpaired electron in one of the  $e_2$  orbitals. But our calculated magnetic moment is 2.0  $\mu_B$ . This discrepancy motivates us to carefully examine the magnetic moment for all the first-row transition metals in  $(\text{MtCp})_\infty$  and their corresponding valence electron configurations as shown in Figure 2. It is found that  $(\text{MtCp})_\infty$  (Mt = Sc, Ti, V, Cr, Mn, Fe) behaves as if one valence electron has been moved away from Mt compared to their benzene analogues, and therefore the mechanism of their half-metallicity and ferromagnetism is very different. Let us take  $(\text{VCp})_\infty$  as an example, where Cp is a meta-stable radical, a five-member ring with five p electrons. According to the Hückel rule, Cp tends to capture an extra electron to form a stable aromatic configuration having  $4m + 2$  electrons (where  $m$  is an integer) like benzene. Actually, in  $(\text{VCp})_\infty$ , one valence electron of V has been transferred to the Cp ring, leaving four valence electrons in V and forming  $\text{V}^+$  and  $\text{Cp}^-$  alternating SMW structure. The  $a_1$  orbital is occupied with a pair of electrons of opposite spins, while each of the two degenerate  $e_2$  orbitals is occupied by a spin-up electron, resulting in two unpaired electrons. The resulting  $(\text{VCp})_\infty$  has a magnetic moment of 2.0  $\mu_B$  per unit cell, which agrees with our calculated result. Because of formation of the  $\text{V}^+$  and  $\text{Cp}^-$  alternating ionic structure, the electrostatic interactions within  $(\text{VCp})_\infty$  are strengthened and it becomes more stable. Therefore, the spin polarization of  $(\text{VCp})_\infty$  is due to the strong spin–spin exchange coupling between the valence electrons of  $\text{V}^+$  and the 2p electrons of  $\text{Cp}^-$ . We propose that the general mechanism for the formation of stable  $(\text{MtCp})_\infty$  involves the donation of one

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**Figure 3.** Iso-surfaces of electron charge density difference for (a)  $(\text{VBz})_\infty$  and (b)  $(\text{VCp})_\infty$ . The iso-value is  $0.084 \text{ e}/\text{\AA}^3$ . Green, red, and orange balls denote V, C, and H atoms, respectively. The dotted lines denote periodic unit cell, and  $c$  is lattice constant, which is double the distance between V and Cp.



**Figure 4.** DOS of  $(\text{VBz})_\infty$  and  $(\text{VCp})_\infty$ . Parts near the Fermi level are enlarged (right panel). Black line refers to the total DOS, while the orange and green areas are 3d and 2p electron projected DOS of V and Cp/Bz, respectively.

electron from Mt to the Cp ring to form  $\text{Mt}^+$  and aromatic  $\text{Cp}^-$  ring. The valence electron configurations for both  $(\text{MtBz})_\infty$  and  $(\text{MtCp})_\infty$  are shown in Figure 2.

The  $\text{V}^+$  and  $\text{Cp}^-$  alternating structure of  $(\text{VCp})_\infty$  can also be verified by its iso-surface of electron charge density difference (CDD) (Figure 3), which shows the electron charge transfer as compared to that of  $(\text{VBz})_\infty$ . It can be seen that the electron CDD around the Cp ring is much higher than that of benzene in  $(\text{VBz})_\infty$ . Furthermore, V in  $(\text{VCp})_\infty$  is surrounded by a lower charge density than that of V in  $(\text{VBz})_\infty$ . Figure 3 provides a clear picture to support the formation of the  $\text{V}^+$  and  $\text{Cp}^-$  alternating SMW. Meanwhile, the total and projected d and p electron DOS shown in Figure 4 could help us to further understand their intrinsic difference of magnetic mechanism.

The magnetism for  $(\text{MtBz})_\infty$  mainly comes from the open shell of d orbitals of Mt, which can be further confirmed from their PDOS near the Fermi level. Taking  $(\text{VBz})_\infty$  as an example, it can be observed that the 3d electrons of V disperse over a large area from  $-6$  to  $3 \text{ eV}$ , while the 2p electrons of benzene are localized within the range of  $-2.5$  to  $-0.5 \text{ eV}$ , meaning that the benzene ring is quite stable in  $(\text{VBz})_\infty$ . In fact, the 3d electrons of Mt dominate the spin polarization of  $(\text{MtBz})_\infty$  as well as the HM property. In such a situation, Mt with the same or similar electron configuration may have the same magnetic property. Therefore, both  $(\text{NbBz})_\infty$  and  $(\text{VBz})_\infty$  show quasi-HM while  $(\text{TcBz})_\infty$  and  $(\text{MnBz})_\infty$  are half-metallic, regardless of the very weak bonding in  $(\text{NbBz})_\infty$  and  $(\text{TcBz})_\infty$ . This phenomenon further proves that the d electrons in Mt predominate the magnetic property of  $(\text{MtBz})_\infty$  and the contribution from 2p electrons of benzene is very limited. Thus, the PDOS of 2p near the Fermi level is very small (Figure 4). The ferromagnetism of  $(\text{MtBz})_\infty$  is due to the double exchange mechanism,<sup>18</sup> a kind of direct spin exchange coupling between neighboring M's that extend over the whole wire.

However, in  $(\text{VCp})_\infty$ , one valence electron of V has been transferred to the Cp ring, forming  $\text{V}^+$  and  $\text{Cp}^-$  alternating structure, which results in very strong coupling between the valence electrons of  $\text{V}^+$  and the 2p electrons of  $\text{Cp}^-$ . Newly formed hybrid orbitals delocalize along the valence band of the V component and cross the Fermi level in the spin-down channel (Figure 1). Meanwhile, the spin-up channel still remains semiconducting, resulting in a HM SMW. Therefore, the ferromagnetism of  $(\text{MtCp})_\infty$  arises mainly from the spin exchange coupling interaction between the valence electrons of  $\text{Mt}^+$  and the 2p electrons of  $\text{Cp}^-$  hybridization.<sup>19</sup> It is an indirect spin exchange interaction mechanism, where the ferromagnetic coupling between the  $\text{Mt}^+$  ions is mediated by neighboring anionic  $\text{Cp}^-$  rings, which facilitates the long-range magnetic interactions between the magnetic moments of the  $\text{Mt}^+$  ions. Specifically, the anionic  $\text{Cp}^-$  rings are slightly spin-polarized. For example, in a unit cell of  $(\text{FeCp})_\infty$ , the magnetic moment of Fe is  $1.03 \mu_B$  while the  $\text{Cp}^-$  ring has a value of only  $-0.07 \mu_B$ . Both the ferromagnetic and antiferromagnetic couplings between neighboring  $\text{Mt}^+$  ions are indirect coupling that extend through the whole SMWs. Such intrinsic difference between  $(\text{MtBz})_\infty$  and  $(\text{MtCp})_\infty$  is revealed for the first time, which helps us to understand the mechanisms of half-metallicity and ferromagnetism for these two types of SMWs.

We also studied the stability of half-metallic property and assessed the possibility of Peierls transition for these one-dimensional molecular wires. Peierls pointed out that 1-D wires with a partially filled band would become unstable at low temperatures because of the strong electron-phonon interaction.<sup>14,15</sup> In 1-D metallic structures, the partially filled energy band may split into sub-bands when the Fermi level crosses the band exactly at wavevector  $k = \Pi/2c$  ( $c$  is the lattice constant or spatial periodicity of molecular wires). In the case of the 1-D molecular wires considered here, the Fermi level intersects more than one band for some molecular wires (Figure 1a). The Peierls transition is unlikely to occur in such a situation since it is impossible for the Fermi level to cross all three bands simultaneously at  $k = \Pi/2c$ . On the basis of Figure 1c, Peierls transition may occur in the  $(\text{VCp})_\infty$  molecular wires. Actually, we studied the possible dimerization for all seven HM SMWs:

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(VCp) $_{\infty}$ , (CrCp) $_{\infty}$ , (FeCp) $_{\infty}$ , (NbCp) $_{\infty}$ , (TcCp) $_{\infty}$ , (MnBz) $_{\infty}$ , and (VBz) $_{\infty}$ . In each case, we doubled the unit cell along the SMW direction and optimized the structures. Results of the calculations show that, for all seven SMWs considered, the ground states are ferromagnetic and the optimized lattice constants are exactly two times the original lattice constants, and there is no relative displacement between the two units in the supercell, even if we started with a distorted initial structure. It clearly indicates that the Peierls transition has not occurred in the above SMW system. This is because the bond lengths of Mt- $\eta^5$ Cp and Mt- $\gamma^6$ Bz are quite fixed along the 1-D SMWs.

Finally, we must indicate that the general mechanism is applied well to stable (MtCp) $_{\infty}$  ( $E_b > -2.4$  eV) where Mt = Sc, Ti, V, Cr, Mn, and Fe. We note that, for those relatively unstable (MtCp) $_{\infty}$  ( $E_b < -1.4$  eV) where Mt = Co (-1.38 eV), Ni (-1.19 eV), Cu (-0.19 eV), and Zn (-0.14 eV), the situation is different. All these SMWs are nonmagnetic. One possibility is that the Mt does not donate a valence electron to Cp completely in these SMWs; otherwise, the strong electrostatic interactions should generate large  $E_b$ . The electron CDD of (MtCp) $_{\infty}$  (Mt is Co to Zn) shows that Co, Cu, and Zn do not donate any electrons to Cp and their electron CDD is similar to that of (VBz) $_{\infty}$  (Figure 3), but the Cp in (NiCp) $_{\infty}$  does capture an extra electron from Ni and its electron CDD is like that of (VCp) $_{\infty}$ . The mechanisms of the HM and ferromagnetism for these four (MtCp) $_{\infty}$  seem quite complex and deviate from that

of the stable SMWs. It still remains unclear, and further investigation is necessary to gain insight in this area.

## Conclusions

In conclusion, we carried out a theoretical investigation on 1-D organometallic sandwich molecular wires (MtCp) $_{\infty}$  for first-row transition metals. For the first time, we show that for stable (MtCp) $_{\infty}$  (Mt = Sc, Ti, V, Cr, Mn, and Fe) one valence electron of Mt transfers to Cp to form an aromatic Cp $^-$  ring, which results in an alternating Mt $^+$  and Cp $^-$  ionic structure. Additionally, we describe the formation of local magnetic moment and collective ferromagnetism of (MtCp) $_{\infty}$  and compare it to the respective (MtBz) $_{\infty}$ . We also explain the magnetic moment of each (MtCp) $_{\infty}$  qualitatively. The long-range ferromagnetism of (MtCp) $_{\infty}$  mainly comes from the spin exchange coupling between the valence electrons of Mt $^+$  and the 2p electrons of Cp $^-$ . It is totally different from that of (MtBz) $_{\infty}$ , where magnetic moments mainly come from the open shell of d orbitals of Mt and the long-range ferromagnetism is caused by the double exchange mechanism, a kind of direct spin exchange coupling between Mts. Finally, we also evaluate seven SMWs that show HM and found that FM is a magnetic ground state. Additionally, we assessed that a Peierls transition does not occur in those 1-D SMWs.

**Acknowledgment.** We thank Dr. Ante Bilic, Dr. Yong Kian Soon, and Miss Emmeline Yeo for their helpful discussions.

JA804053A