

# Systematic Investigation of Electronic and Molecular Structures for the First Transition Metal Series Metallocenes $M(C_5H_5)_2$ ( $M = V, Cr, Mn, Fe, Co,$ and $Ni$ )

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The electronic structures of the first-row transition-metal metallocenes,  $MCp_2$  ( $M = V, Cr, Mn, Fe, Co,$  and  $Ni$ ), have been studied using a broad range of density functional methods with flexible double- $\zeta$  plus polarization (DZP) basis sets. Geometrical parameters of the  $D_{5h}$  and  $D_{5d}$  conformations (and structures of lower symmetry for  $CrCp_2$  and  $CoCp_2$ ) were fully optimized. For the ferrocene system, best characterized experimentally, the B3LYP, BLYP, and BP86 methods give structures in good agreement with experiment. For the  $D_{5h}$ – $D_{5d}$  energy difference, the same three methods predict 0.75 kcal/mol (B3LYP), 0.99 kcal/mol (BLYP), and 1.13 kcal/mol (BP86). The cyclopentadienyl rings are very nearly planar; the angles of the C–H bond out of the Cp ring are less than  $1^\circ$  for all metallocenes except ferrocene. The C–H bonds are bent slightly away from the metal for V and Mn, slightly toward the metal for Fe and Ni, and virtually not at all from chromocene. According to the energetic and vibrational analyses, the  $D_{5h}$  conformations are found to be the global minima, leaving open the possibility that the  $D_{5d}$  conformations may exist under certain conditions. However,  $MnCp_2$  probably exists as a mixture of both  $D_{5h}$  and  $D_{5d}$  conformations, because both are genuine minima with only a small energy difference. The predicted B3LYP energy differences ( $D_{5h}$ – $D_{5d}$ ) for the six metallocenes are 0.29 (V), 0.28 (Cr), 0.13 (Mn), 0.75 (Fe), 0.38 (Co), and 0.23 kcal/mol (Ni). A number of reassignments of experimental vibrational bands are suggested. The molecular orbital energy level diagrams and the electron configurations for the metallocenes are compared. This information, obtained in a consistent manner across the first transition metal series, is helpful for discussion of the bonding characters and the chemical reactivities of these metallocenes.

## Introduction

The compound dicyclopentadienyliron  $Fe(C_5H_5)_2$ , or  $FeCp_2$ , was discovered nearly simultaneously by two research groups in 1951.<sup>1,2</sup> Its sandwich structure was identified by Wilkinson, Rosenblum, Whiting, and Woodward<sup>3</sup> as well as Fischer and Pfab<sup>4</sup> in 1952, and was named ferrocene.<sup>5</sup> Since then, the ferrocene-like dicyclopentadienylmetal compounds, namely metallocenes, have attracted wide interest from both experimental and theoretical chemists. There are many studies of the structures and spectra of metallocenes. In early 1956 Dunitz, Orgel, and Rich<sup>6</sup> demonstrated a staggered structure for crystalline ferrocene by X-ray diffraction, and then in 1966 Bohn and Haaland<sup>7</sup> showed that the free molecule has an eclipsed equilibrium configuration by means of gas-phase electron diffraction. The geometric parameters and rotation barrier ( $0.9 \pm 0.3$  kcal/mol) of the free ferrocene molecule were also determined by Haaland and Nilsson.<sup>8</sup> The Raman and infrared spectra of ferrocene were reported by Lippincott and Nelson<sup>9</sup> as early as 1955 and 1958, and then by Bodenheimer and Low in 1969 and 1973.<sup>10</sup> Following the early experimental studies of ferrocene, the discoveries of other metallocenes for the first-row transition metals, such as  $VCp_2$ ,  $CrCp_2$ ,  $MnCp_2$ ,  $CoCp_2$ , and  $NiCp_2$ , appeared one after another,<sup>11–21</sup> and some experimental molecular properties were reported in these studies.

Early theoretical studies gave molecular orbital descriptions of ferrocene via semiempirical methods.<sup>22–25</sup> During the past

two decades, more reliable ab initio theoretical investigations of the first-row transition metal metallocenes have been published.<sup>26–35</sup> With the rapid development of information technology, these studies show that computational quantum chemistry is able to reveal the nature of the electronic structure of the metallocenes. In 1991, Park and Almlöf<sup>29</sup> predicted values of 1.65–1.67 Å (experimental value is 1.66 Å) for the Fe–ring distance in ferrocene using the MCPF (modified coupled-pair functional) approach with all 66 valence electrons correlated. And then in 1995 Pierloot, Persson and Roos<sup>30</sup> predicted an Fe–ring distance of 1.643 Å and bond energy of 32.3 kcal/mol (experimental value  $36.4 \pm 5$  kcal/mol) using the complete active space (CAS)SCF method followed by second-order perturbation theory (CASPT2). Thus far, the most accurate theoretical iron–cyclopentadienyl equilibrium distance in ferrocene was predicted by Koch, Jorgensen, and Helgaker in 1996.<sup>31</sup> They computed the Fe–ring distance to be 1.660 Å at the CCSD(T) level of theory employing a triple- $\zeta$  valence basis set augmented with a double set of polarization functions (TZV2P+f). This Koch/Jorgensen/Helgaker structure is in excellent agreement with experiment. Recently, density functional theory (DFT) methods have also been widely used to investigate transition metal complexes. Beginning in 1991, Ziegler and co-workers<sup>32</sup> applied the local-density approximation (LDA) and nonlocal (NL) correction methods to study the geometry of ferrocene. In 1997 Mayor-Lopez and Weber<sup>33</sup> optimized four metallocene structures ( $MCp_2$ ,  $M = V, Mn, Fe, Ni$ ) at the BPW91 level of theory. These studies show that the less costly DFT results are also in reasonable agreement with experiment.

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**TABLE 1: Structures, Total Energies, and the Relative Energies ( $\Delta E$ ) for the  $D_{5h}$  and  $D_{5d}$  Structures of Ferrocene**

	HF	BHLYP	B3LYP	BLYP	BP86	LSDA	expt <sup>c</sup>
	$D_{5h}$						
Fe–Cp, <sup>a</sup> Å	1.865	1.725	1.681	1.678	1.644	1.585	1.660
Fe–C, Å	2.219	2.105	2.077	2.082	2.053	1.999	2.064 ± 0.003
C–C, Å	1.413	1.418	1.434	1.448	1.446	1.432	1.440 ± 0.002
C–H, Å	1.074	1.077	1.085	1.093	1.094	1.095	1.104 ± 0.006
$\angle$ Cp,H, <sup>b</sup> deg	0.58	1.33	1.18	0.90	1.12	1.64	3.7 ± 0.9
<i>E</i> , hartree	–1646.84239	–1650.51995	–1650.88525	–1650.75354	–1651.09888	–1646.85498	
	$D_{5d}$						
Fe–Cp, <sup>a</sup> Å	1.866	1.726	1.684	1.682	1.649	1.591	
Fe–C, Å	2.220	2.106	2.080	2.085	2.057	2.003	
C–C, Å	1.413	1.418	1.433	1.448	1.445	1.431	
C–H, Å	1.074	1.077	1.085	1.093	1.094	1.095	
$\angle$ Cp,H, <sup>b</sup> deg	0.55	1.45	1.46	1.20	1.53	2.11	
<i>E</i> , hartree	–1646.84224	–1650.51932	–1650.88405	–1650.75196	–1651.09708	–1646.85254	
$\Delta E$ , kcal/mol	0.10	0.39	0.75	0.99	1.13	1.53	
$\Delta E$ , kcal/mol (with ZPVE)	0.04	0.27	0.63	0.83	0.97	1.29	0.9 ± 0.3

<sup>a</sup> Denotes the distance from the Fe atom to the center of cyclopentadienyl ring. <sup>b</sup> Denotes the angle of the C–H bond out of the cyclopentadienyl ring, and the angle is defined as positive if the H atom tilts toward the metal atom. <sup>c</sup> References 8 and 12.

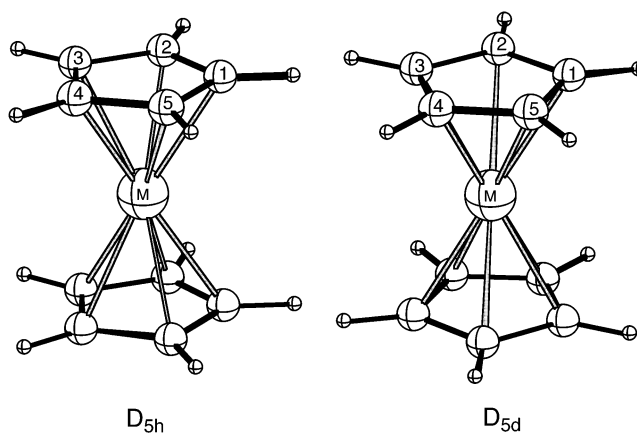
Despite so many experimental and theoretical investigations of the molecular structures of metallocenes, there is still controversy concerning the description of the electronic structures of these important systems.<sup>36,37</sup> There are almost no reliable orbital energies reported for the other metallocenes, and chemists usually discuss metallocene bonding and essential features on the basis of the molecular orbital diagram of ferrocene.<sup>38</sup> This may not be appropriate, because the other metallocenes have different numbers of valence electrons from ferrocene, and they could have somewhat different molecular orbital diagrams. The MO level differences could cause not only the necessary change of electron configuration but also possible changes in the symmetry of the molecular structures. Therefore, it is desirable to investigate the electronic structures of the metallocenes systematically to discuss the properties, bonding, and reactions of metallocenes.

In view of the good performance of DFT for ferrocene, we were instigated to investigate the electronic structures of the first-row transition-metal metallocenes using density functional theory. In the present study, we will report DFT results for six first-row transition-metal metallocenes, namely, VCp<sub>2</sub>, CrCp<sub>2</sub>, MnCp<sub>2</sub>, FeCp<sub>2</sub>, CoCp<sub>2</sub>, and NiCp<sub>2</sub>. The next section of this paper will describe the theoretical methods briefly, and the third section will give the theoretical results, including a discussion and comparison of the electronic structures of these six first-row transition-metal metallocenes.

### Theoretical Methods

In this study, double- $\zeta$  plus polarization (DZP) basis sets are used. For the carbon and hydrogen atoms, the DZP basis sets are Dunning's standard double- $\zeta$  contraction<sup>39</sup> of Huzinaga's primitive sets<sup>40</sup> with one set of pure spherical harmonic polarization functions added with orbital exponents  $\alpha_d(\text{C}) = 0.75$  and  $\alpha_p(\text{H}) = 0.75$ . For the first-row transition-metals V, Cr, Mn, Fe, Co, and Ni, Wachters' primitive sets<sup>41</sup> are used in our loosely contracted DZP basis set but augmented by two sets of p functions and one set of d functions and contracted following Hood, Pitzer, and Schaefer,<sup>42</sup> and designated (14s11p6d/10s8p3d).

Electron correlation effects were included employing density functional theory methods (DFT), which have been widely recommended as a practical and effective computational tool, especially for organometallic compounds.<sup>43</sup> Among the density functional approaches, the most reliable approximation is often thought to be the hybrid HF/DFT method using the combination of the three-parameter Becke functional with the Lee–Yang–



**Figure 1.** Two conformations of the metallocenes.

Parr nonlocal correlation functional known as B3LYP.<sup>44,45</sup> Also, to compare the various functionals, four other DFT methods, i.e., BHLYP,<sup>46</sup> BLYP,<sup>45,47</sup> BP86,<sup>47,48</sup> LSDA,<sup>49</sup> as well as the Hartree–Fock (HF) method, were also used for ferrocene.

We fully optimize the geometries of the six first-row transition-metal metallocenes, VCp<sub>2</sub>, CrCp<sub>2</sub>, MnCp<sub>2</sub>, FeCp<sub>2</sub>, CoCp<sub>2</sub>, and NiCp<sub>2</sub>, and evaluate the vibrational frequencies for both of their common conformations by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The corresponding infrared intensities are also evaluated analytically. For the open shell systems, unrestricted DFT methods are employed. All the computations were carried out with the Gaussian94 program,<sup>50</sup> in which the fine grid (75 302) is the default for evaluating integrals numerically, and the tight ( $10^{-8}$  hartree) designation is the default for the SCF convergence.

### Results and Discussions

**1. Geometry of Ferrocene.** To begin, we optimized the geometries of ferrocene by using six methods with the DZP basis set. Ferrocene is a closed shell system, which has two widely discussed conformations, i.e., eclipsed ( $D_{5h}$ ) and staggered ( $D_{5d}$ ). The electronic configurations were the accepted  $(a_1')^2(e_2')^4$  for  $D_{5h}$  and  $(a_{1g})^2(e_{2g})^4$  for  $D_{5d}$ . Figure 1 sketches the  $D_{5h}$  and  $D_{5d}$  conformations and the atom-numbering system. Table 1 lists the main geometric parameters and the energies for the  $D_{5h}$  and  $D_{5d}$  conformations of ferrocene. The  $D_{5h}$  structure is predicted to be the global minimum for the free

**TABLE 2: Harmonic Vibrational Frequencies ( $\text{cm}^{-1}$ ) and Infrared Intensities<sup>a</sup> ( $\text{km}^{-1}$ , in Parentheses) for the  $D_{5h}$  Structure of Ferrocene**

no.	sym	HF	BHLYP	B3LYP	BLYP	BP86	LSDA	expt <sup>b</sup>	expt <sup>c</sup>
6	$a_1''$	20 (0)	34 (0)	49 (0)	56 (0)	63 (0)	73 (0)		$\leq 20$
22	$e_1'$	144 (0)	159 (0)	161 (0)	157 (1)	166 (1)	174 (1)	179	180
4	$a_1'$	236 (0)	267 (0)	287 (0)	291 (0)	308 (0)	339 (0)	309	315
16	$e_1''$	304 (0)	350 (0)	355 (0)	345 (0)	367 (0)	404 (0)	389	391
11	$a_2''$	411 (28)	456 (0)	461 (13)	453 (26)	482 (37)	536 (62)	478	485
21	$e_1'$	404 (6)	462 (21)	472 (27)	463 (26)	491 (29)	540 (36)	492	504
34	$e_2''$	686 (0)	633 (0)	590 (0)	553 (0)	560 (0)	581 (0)	569	
28	$e_2'$	675 (0)	637 (0)	593 (0)	554 (0)	561 (0)	581 (0)	597	598
14	$e_1''$	888 (0)	854 (0)	812 (0)	775 (0)	779 (0)	789 (0)	844	
2	$a_1'$	899 (0)	863 (0)	826 (0)	794 (0)	800 (0)	803 (0)	814	
9	$a_2''$	893 (388)	862 (180)	827 (94)	797 (66)	804 (56)	813 (46)	820	820–860 <sup>e</sup>
33	$e_2''$	930 (0)	882 (0)	835 (0)	795 (0)	793 (0)	797 (0)	885 <sup>d</sup>	
19	$e_1'$	911 (2)	880 (5)	843 (6)	809 (6)	816 (7)	826 (9)	855	
27	$e_2'$	931 (0)	890 (0)	850 (0)	818 (0)	817 (0)	820 (0)	897 <sup>d</sup>	
31	$e_2''$	1034 (0)	945 (0)	890 (0)	840 (0)	843 (0)	856 (0)	1055 <sup>d</sup>	
25	$e_2'$	1014 (0)	957 (0)	895 (0)	846 (0)	849 (0)	860 (0)	1058 <sup>d</sup>	900 <sup>f</sup>
13	$e_1''$	1103 (0)	1059 (0)	1011 (0)	972 (0)	977 (0)	981 (0)	998	1010 <sup>g</sup>
18	$e_1'$	1108 (35)	1064 (29)	1017 (25)	980 (21)	985 (20)	990 (22)	1005	
30	$e_2''$	1164 (0)	1101 (0)	1060 (0)	1027 (0)	1026 (0)	1016 (0)	1189 <sup>d</sup>	1060
24	$e_2'$	1153 (0)	1109 (0)	1067 (0)	1035 (0)	1034 (0)	1025 (0)	1191 <sup>d</sup>	
3	$a_1'$	1220 (0)	1184 (0)	1130 (0)	1083 (0)	1095 (0)	1129 (0)	1102	
10	$a_2''$	1217 (0)	1183 (15)	1131 (28)	1085 (32)	1098 (32)	1134 (29)	1110	
7	$a_2'$	1394 (0)	1325 (0)	1267 (0)	1224 (0)	1214 (0)	1199 (0)	1250	
5	$a_1''$	1393 (0)	1324 (0)	1267 (0)	1224 (0)	1215 (0)	1199 (0)	1255	
32	$e_2''$	1585 (0)	1443 (0)	1386 (0)	1328 (0)	1346 (0)	1386 (0)	1351	
26	$e_2'$	1514 (0)	1469 (0)	1405 (0)	1348 (0)	1366 (0)	1406 (0)	1356	
15	$e_1''$	1594 (0)	1521 (0)	1446 (0)	1387 (0)	1389 (0)	1399 (0)	1410	
20	$e_1'$	1598 (0)	1522 (1)	1447 (1)	1388 (2)	1390 (2)	1402 (4)	1410	
29	$e_2''$	3396 (0)	3331 (0)	3228 (0)	3138 (0)	3147 (0)	3159 (0)	3085	
23	$e_2'$	3396 (0)	3332 (0)	3230 (0)	3139 (0)	3148 (0)	3160 (0)	3100	
12	$e_1''$	3412 (0)	3346 (0)	3242 (0)	3151 (0)	3160 (0)	3170 (0)	3086	
17	$e_1'$	3413 (20)	3347 (9)	3244 (13)	3153 (20)	3162 (22)	3172 (5)	3077	
8	$a_2''$	3425 (1)	3359 (0)	3254 (0)	3162 (2)	3171 (3)	3181 (0)	3103	
1	$a_1'$	3426 (0)	3360 (0)	3255 (0)	3164 (0)	3172 (0)	3182 (0)	3110	

<sup>a</sup> For the degenerate frequencies ( $e_1'$ ,  $e_1''$ ,  $e_2'$ ,  $e_2''$ ), the IR intensities in this table are for one component only. <sup>b</sup> Reference 10. <sup>c</sup> Reference 51. <sup>d</sup> These values were re-assigned by ref 34. See text. <sup>e</sup> These frequencies were assigned to the vibrational modes 2, 9, 14, 19, 27, and 33. See ref 51. <sup>f</sup> This frequency was assigned to the vibrational modes 14, 19, 25, and 33. See ref 51. <sup>g</sup> This frequency was assigned to the vibrational modes 13 and 18. See ref 51.

ferrocene molecule with the H–F and all the DFT methods. Compared with Haaland and Nilsson's experimental energy difference between the  $D_{5h}$  and  $D_{5d}$  conformations ( $\Delta E = 0.9 \pm 0.3$  kcal/mol),<sup>8</sup> the Hartree–Fock method predicts a value that is too small (0.1 kcal/mol). Along with the increasing the DFT component in the exchange functional, the energy difference  $\Delta E$  increases gradually. It is predicted to be 0.39 kcal/mol by the BHLYP method, 0.75 kcal/mol by B3LYP, and 0.99 kcal/mol by BLYP. The BP86 and LSDA methods predict an even larger energy difference, i.e., 1.13 and 1.53 kcal/mol, respectively. The correction for zero point vibrational energies (ZPVE) decreases the energy difference, and it becomes smaller, namely, 0.04, 0.27, 0.63, 0.83, 0.97, and 1.29 kcal/mol by the HF, BHLYP, B3LYP, BLYP, BP86, and LSDA methods, respectively. Among these methods, the B3LYP, BLYP, and BP86 results are in agreement with the Haaland–Nilsson experiment ( $0.9 \pm 0.3$  kcal/mol). With all six methods, the differences of bond distances between the  $D_{5h}$  and  $D_{5d}$  conformations are very small. For the C–C and C–H bond distances, they are almost identical (within 0.001 Å). For the Fe–C bond distance, those of the  $D_{5d}$  structure are slightly longer than those of  $D_{5h}$  (in the range 0.001–0.004 Å). The theoretical Fe–C bond lengths are evaluated by the different methods in the ordering HF > BHLYP > BLYP > B3LYP > BP86 > LSDA. Compared with experiment, the deviations are 0.155, 0.041, 0.018, 0.013, –0.011, and –0.065 Å, respectively. It is apparent that the theoretical distances at the B3LYP and BP86 levels are closest to the experimental values. For the C–C bond length, the theoretical values closest to the experiment are also the

B3LYP and BP86 methods, with the deviation of only –0.006 and +0.006 Å, respectively. Thus, the B3LYP and BP86 methods appear to be the most reliable for predicting the molecular structures of metallocenes.

## 2. Harmonic Vibrational Frequencies for Ferrocene. In

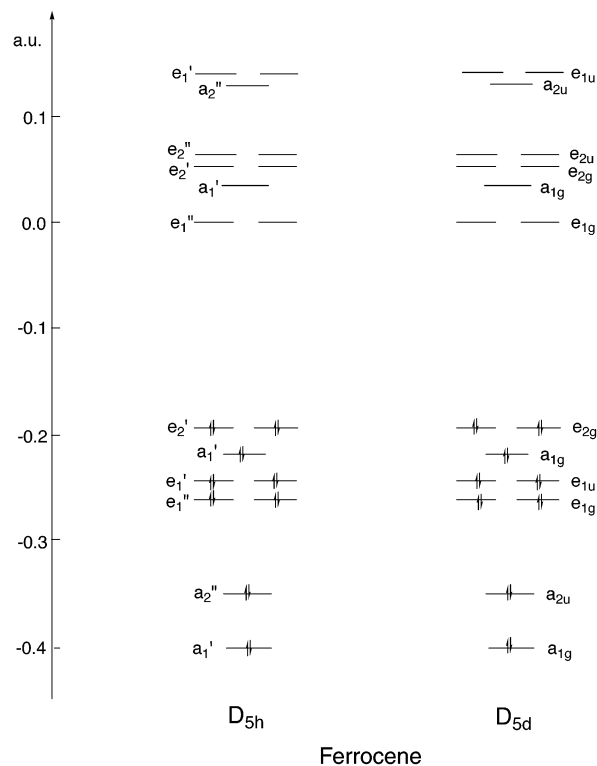
Table 2, the harmonic vibrational frequencies predicted by all six methods for  $D_{5h}$  ferrocene are listed and compared with experiment. The first column is the conventional numbering for the vibrational modes of the metallocenes suggested by Lippincott and Nelson<sup>9</sup> and by Bodenheimer and Low.<sup>10</sup> The far-right two columns are experimental assignments.<sup>10,51</sup> As early as the 1950s–1960s, some Raman and infrared spectra of ferrocene were reported,<sup>9</sup> and in 1973 comprehensive assignments of the vibrational modes for ferrocene were suggested by Bodenheimer and Low.<sup>10</sup> The latter are listed in Table 2. The present DFT vibrational frequencies are in fairly good agreement with the experimental assignments. Among the theoretical methods, B3LYP and BP86 predict the vibrational frequencies closest to experiment. However, for the in-plane CH bending (modes 24 and 30), CH wagging (modes 25 and 31), and in-plane ring distortion (modes 27 and 33), the experimental assignments appear too large. These deviations were previously pointed out by Berces, Ziegler, and Fan (1994) in their important theoretical study.<sup>32</sup> They suggested the reassignment of 1058 and 1055  $\text{cm}^{-1}$  to the modes 24 and 30 (C–H bending), and 897 and 885  $\text{cm}^{-1}$  to the modes 25 and 31 (C–H bending), but did not assign the observed 1191 and 1189  $\text{cm}^{-1}$  bands to fundamentals. After the reassignments, the comparison between the theoretical results and the experimental

**TABLE 3: Harmonic Vibrational Frequencies ( $\text{cm}^{-1}$ ) and Infrared Intensities<sup>a</sup> ( $\text{km}^{-1}$ , in Parentheses) for the  $D_{5d}$  Structure of Ferrocene**

no.	sym	HF	BHLYP	B3LYP	BLYP	BP86	LSDA
6	$a_{1u}$	12i	46i	56i	61i	64i	73i
22	$e_{1u}$	143 (0)	159 (0)	166 (0)	162 (0)	172 (1)	178 (1)
4	$a_{1g}$	236 (0)	268 (0)	289 (0)	292 (0)	309 (0)	340 (0)
16	$e_{1g}$	303 (0)	352 (0)	366 (0)	363 (0)	385 (0)	422 (0)
11	$a_{2u}$	411 (29)	455 (0)	458 (12)	448 (26)	476 (37)	526 (63)
21	$e_{1u}$	403 (6)	455 (21)	451 (30)	430 (32)	455 (36)	498 (45)
34	$e_{2u}$	686 (0)	639 (0)	602 (0)	565 (0)	572 (0)	593 (0)
28	$e_{2g}$	675 (0)	631 (0)	583 (0)	544 (0)	551 (0)	568 (0)
14	$e_{1g}$	887 (0)	849 (0)	808 (0)	771 (0)	776 (0)	785 (0)
2	$a_{1g}$	899 (0)	862 (0)	828 (0)	794 (0)	802 (0)	802 (0)
9	$a_{2u}$	893 (388)	858 (181)	820 (95)	787 (67)	794 (57)	800 (48)
33	$e_{2u}$	930 (0)	882 (0)	834 (0)	794 (0)	791 (0)	793 (0)
19	$e_{1u}$	910 (2)	877 (5)	840 (6)	804 (6)	814 (8)	822 (10)
27	$e_{2g}$	931 (0)	888 (0)	850 (0)	816 (0)	816 (0)	820 (0)
31	$e_{2u}$	1034 (0)	952 (0)	890 (0)	839 (0)	839 (0)	857 (0)
25	$e_{2g}$	1009 (0)	943 (0)	888 (0)	837 (0)	842 (0)	852 (0)
13	$e_{1g}$	1103 (0)	1057 (0)	1011 (0)	973 (0)	978 (0)	982 (0)
18	$e_{1u}$	1108 (35)	1064 (28)	1017 (24)	978 (22)	982 (21)	987 (22)
30	$e_{2u}$	1166 (0)	1106 (0)	1065 (0)	1034 (0)	1033 (0)	1024 (0)
24	$e_{2g}$	1151 (0)	1105 (0)	1063 (0)	1030 (0)	1029 (0)	1018 (0)
3	$a_{1g}$	1220 (0)	1185 (0)	1132 (0)	1085 (0)	1098 (0)	1132 (0)
10	$a_{2u}$	1217 (0)	1183 (15)	1132 (29)	1086 (34)	1100 (35)	1135 (31)
7	$a_{2g}$	1393 (0)	1323 (0)	1264 (0)	1221 (0)	1212 (0)	1196 (0)
5	$a_{1u}$	1393 (0)	1323 (0)	1265 (0)	1222 (0)	1212 (0)	1196 (0)
32	$e_{2u}$	1584 (0)	1470 (0)	1402 (0)	1341 (0)	1359 (0)	1399 (0)
26	$e_{2g}$	1514 (0)	1443 (0)	1390 (0)	1337 (0)	1356 (0)	1398 (0)
15	$e_{1g}$	1594 (0)	1520 (0)	1447 (0)	1389 (0)	1392 (0)	1404 (0)
20	$e_{1u}$	1597 (0)	1522 (1)	1445 (1)	1385 (1)	1387 (1)	1397 (3)
29	$e_{2u}$	3395 (0)	3332 (0)	3230 (0)	3139 (0)	3149 (0)	3160 (0)
23	$e_{2g}$	3396 (0)	3332 (0)	3230 (0)	3140 (0)	3149 (0)	3160 (0)
12	$e_{1g}$	3412 (0)	3347 (0)	3243 (0)	3153 (0)	3162 (0)	3172 (0)
17	$e_{1u}$	3413 (20)	3347 (9)	3244 (13)	3153 (20)	3162 (21)	3172 (5)
8	$a_{2u}$	3425 (1)	3359 (0)	3255 (1)	3164 (2)	3173 (3)	3182 (1)
1	$a_{1g}$	3425 (0)	3360 (0)	3256 (0)	3165 (0)	3173 (0)	3182 (0)

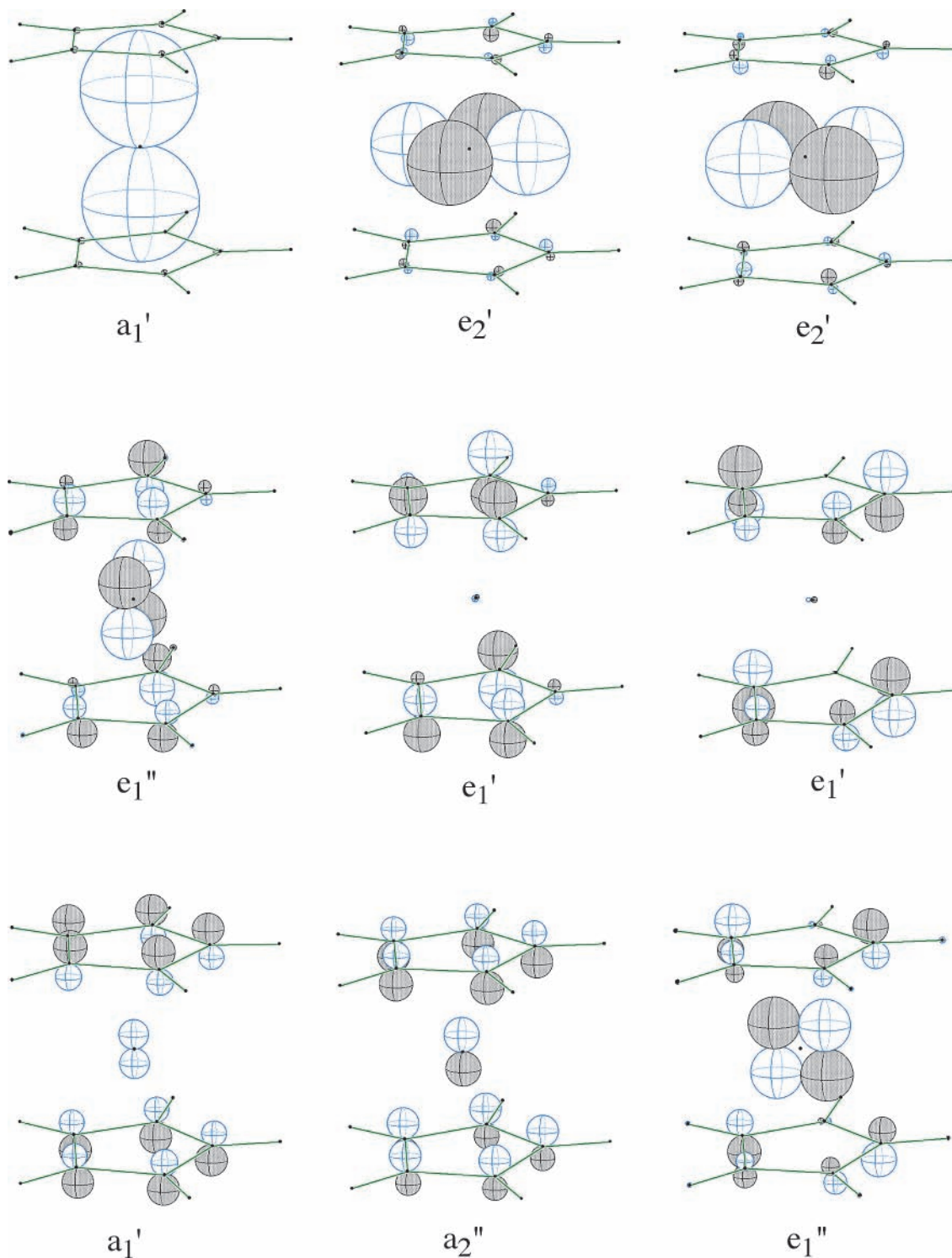
<sup>a</sup> For the degenerate frequencies ( $e_1'$ ,  $e_1''$ ,  $e_2'$ ,  $e_2''$ ), the IR intensities in this table are for one component only.

assignments is much improved. However, modes 27 and 33 (ring torsion) have no experimental assignments. In 2000, Kemner et al. reported vibrational spectra from inelastic neutron scattering (INS).<sup>51</sup> They suggested that the frequency for the torsion mode ( $\nu_6$ ) is less than  $20 \text{ cm}^{-1}$ , a feature not assigned in ref 10. They assigned the feature at  $1060 \text{ cm}^{-1}$  to modes 24 and 30 (C–H bending),  $1010 \text{ cm}^{-1}$  to modes 13 and 18 (also C–H bending), and  $900 \text{ cm}^{-1}$  to modes 14, 19, 25, and 31 (C–H wagging). They also assigned a strong and very broad peak ( $820\text{--}860 \text{ cm}^{-1}$ ) in the INS spectrum roughly to the contributions of six vibrational modes, which are modes 2, 9, 14, 19 (C–H wagging), 27, and 33 (ring distortion). These assignments make for a closer concordance with our predictions, but the resolution of the INS spectra is so low that the assignments to the vibrational fundamentals for ferrocene have not yet been completed. Our theoretical prediction may thus provide useful assistance for further experimental studies. Our theoretical harmonic vibrational frequencies for the eclipsed ( $D_{5h}$ ) ferrocene are all real (Table 2), indicating it is a genuine minimum. Our theoretical harmonic vibrational frequencies for the staggered ( $D_{5d}$ ) ferrocene (Table 3) are very similar to those of the  $D_{5h}$  structure, but all six methods predict a small imaginary frequency, indicating that the staggered structure of the free ferrocene molecule is a transition state. The normal mode related to the imaginary vibrational frequency is the expected ring rotation, which leads to the  $D_{5h}$  structure. However, in light of the very small energy difference between the  $D_{5d}$  and  $D_{5h}$  structures, and the very small magnitude of the imaginary frequency of  $D_{5d}$ , the  $D_{5d}$  structure might be observed in the condensed phase, as apparently shown by the Dunitz/Orgel/Rich crystal structure.<sup>6</sup>

**Figure 2.** Molecular orbital energy level diagram for ferrocene.

**3. Geometries for the Metallocenes  $M(\text{Cp})_2$  ( $M = \text{V, Cr, Mn, Co, Ni}$ ).** Because the B3LYP method predicts properties for ferrocene in reasonable agreement with available experi-





**Figure 3.** Sketches of the valence molecular orbitals for ferrocene.

ments, only the B3LYP method was used to investigate the other metallocenes in this research. For the other first-row transition metal metallocenes, our theoretical structures and total energies at the B3LYP DZP level of theory, along with the available experimental results, are displayed in Table 4. Unlike ferrocene, all the other metallocenes are open shell systems. As seen in Table 4, three of the open-shell metallocenes ( $M = V, Mn, Ni$ ) have two very low-lying conformations: eclipsed ( $D_{5h}$ ) and staggered ( $D_{5d}$ ), just like ferrocene. The total energies of the  $D_{5h}$  structures are uniformly lower than their corresponding  $D_{5d}$  structures, but the energy differences are smaller than that of ferrocene at the same B3LYP level of theory. These  $\Delta E$  values

are 0.29 kcal/mol for  $V Cp_2$ , 0.13 kcal/mol for  $Mn Cp_2$ , 0.75 kcal/mol for  $Fe Cp_2$ , and 0.23 kcal/mol for  $Ni Cp_2$ . Therefore, we can view the  $D_{5h}$  structures of the metallocene as somewhat more stable than the  $D_{5d}$  structures. However, because these energy differences between  $D_{5h}$  and  $D_{5d}$  are so small, the  $D_{5d}$  conformation may be observed under certain conditions. As we mentioned above, ferrocene is found to be a  $D_{5h}$  molecule in the gas phase<sup>8</sup> but apparently favors the  $D_{5d}$  conformation in the condensed phase.<sup>6</sup>

The geometric parameters of the  $D_{5h}$  and  $D_{5d}$  conformations are very similar. The bond lengths ( $M-C$ ) between the metal atom and the carbon atoms for the eclipsed  $D_{5h}$  conformations

**TABLE 4: Structures, Total Energies, and the Relative Energy ( $\Delta E$ ) of Metallocenes Optimized at the B3LYP DZP Level of Theory<sup>a</sup>**

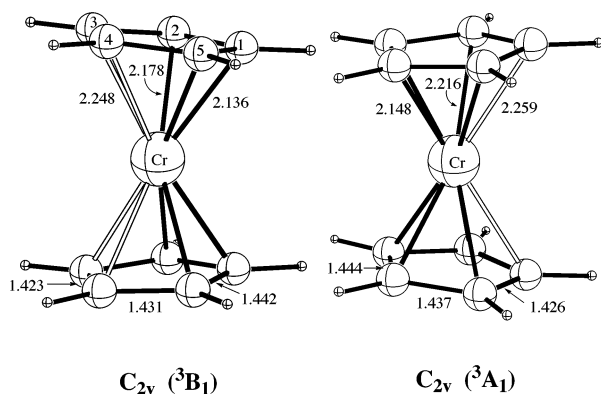
	VCp <sub>2</sub>			MnCp <sub>2</sub>			NiCp <sub>2</sub>		
	<i>D</i> <sub>5h</sub> <sup>4</sup> A <sub>1</sub> '	<i>D</i> <sub>5d</sub> <sup>4</sup> A <sub>1g</sub>	expt <sup>b</sup>	<i>D</i> <sub>5h</sub> <sup>6</sup> A <sub>1</sub> '	<i>D</i> <sub>5d</sub> <sup>6</sup> A <sub>1g</sub>	expt <sup>c</sup>	<i>D</i> <sub>5h</sub> <sup>3</sup> A <sub>1</sub> '	<i>D</i> <sub>5d</sub> <sup>3</sup> A <sub>1g</sub>	expt <sup>d</sup>
M–Cp, Å	1.965	1.967	1.928(6)	2.082	2.083	2.046(8)	1.867	1.868	1.828
M–C, Å	2.310	2.312	2.280(5)	2.411	2.412	2.380(6)	2.228	2.229	2.196(8)
C–C, Å	1.429	1.428	1.434(3)	1.429	1.429	1.429(8)	1.429	1.429	1.430(3)
C–H, Å	1.086	1.086	1.133(14)	1.086	1.086	1.125(10)	1.085	1.085	1.083(19)
∠Cp,H, deg	–0.1	–0.1	–1.5(1.6)	–0.8	–0.8	0(3)	0.5	0.5	0.3(2.9)
<i>E</i> , hartree	–1331.18584	–1331.18538		–1538.15552	–1538.15532		–1895.47856	–1895.47820	
Δ <i>E</i> , kcal/mol	0.00	0.29		0.00	0.13		0.00	0.23	
Δ <i>E</i> , kcal/mol (with ZPVE)	0.00	0.02		0.00	0.04		0.00	0.15	
CrCp <sub>2</sub>									
	symmetry constrained		<i>C</i> <sub>2v</sub>			<i>C</i> <sub>2h</sub>			expt <sup>e</sup>
	<i>D</i> <sub>5h</sub> <sup>3</sup> A <sub>1</sub> '	<i>D</i> <sub>5d</sub> <sup>3</sup> A <sub>1g</sub>	<sup>3</sup> B <sub>1</sub>	<sup>3</sup> A <sub>1</sub>	<sup>3</sup> A <sub>g</sub>	<sup>3</sup> B <sub>g</sub>			
Cr–Cp, Å	1.896	1.897						1.798(4)	
Cr–C <sub>1</sub> , Å	2.251	2.252	2.136	2.259	2.255	2.147		2.169(4)	
Cr–C <sub>2</sub> (C <sub>5</sub> ), Å			2.178	2.216	2.216	2.183			
Cr–C <sub>3</sub> (C <sub>4</sub> ), Å			2.248	2.148	2.157	2.244			
C <sub>1</sub> –C <sub>2</sub> (C <sub>1</sub> –C <sub>5</sub> ), Å	1.427	1.427	1.442	1.426	1.426	1.441		1.431(2)	
C <sub>2</sub> –C <sub>3</sub> (C <sub>5</sub> –C <sub>4</sub> ), Å			1.431	1.437	1.437	1.431			
C <sub>3</sub> –C <sub>4</sub> , Å			1.423	1.444	1.443	1.423			
C <sub>1</sub> –H, Å	1.086	1.086	1.085	1.086	1.086	1.085		1.108(7)	
C <sub>2</sub> (C <sub>5</sub> )–H, Å			1.085	1.086	1.086	1.085			
C <sub>3</sub> (C <sub>4</sub> )–H, Å			1.086	1.085	1.085	1.086			
∠Cp,H, deg	0.00	0.04						2.9(1.1)	
<i>E</i> , hartree	–1431.61860	–1431.61815	–1431.62699	–1431.62684	–1431.62580	–1431.62579			
Δ <i>E</i> , kcal/mol	5.26	5.55	0.00	0.09	0.75	0.75			
Δ <i>E</i> , kcal/mol (with ZPVE)			0.00	–0.15	0.49	0.43			
CoCp <sub>2</sub>									
	symmetry constrained		<i>C</i> <sub>2v</sub>		<i>C</i> <sub>2h</sub>		expt <sup>e</sup>	expt <sup>f</sup>	
	<i>D</i> <sub>5h</sub> ( <sup>2</sup> E <sub>1</sub> '')	<i>D</i> <sub>5d</sub> ( <sup>2</sup> E <sub>1g</sub> )	<sup>2</sup> B <sub>2</sub>	<sup>2</sup> A <sub>2</sub>	<sup>2</sup> A <sub>g</sub>	<sup>2</sup> B <sub>g</sub>			
Co–Cp, Å	1.774	1.777						1.739(2)	
Co–C <sub>1</sub> , Å	2.151	2.153	2.176	2.106	2.177	2.111		2.119(3)	
Co–C <sub>2</sub> (C <sub>5</sub> ), Å			2.117	2.175	2.119	2.178			
Co–C <sub>3</sub> (C <sub>4</sub> ), Å			2.166	2.143	2.168	2.143			
C <sub>1</sub> –C <sub>2</sub> (C <sub>1</sub> –C <sub>5</sub> ), Å	1.431	1.430	1.427	1.438	1.426	1.438		1.429(2)	
C <sub>2</sub> –C <sub>3</sub> (C <sub>5</sub> –C <sub>4</sub> ), Å			1.447	1.417	1.447	1.416		1.430(3)	
C <sub>3</sub> –C <sub>4</sub> , Å			1.412	1.450	1.412	1.450			
C <sub>1</sub> –H, Å	1.085	1.085	1.085	1.086	1.085	1.086		1.111(8)	
C <sub>2</sub> (C <sub>5</sub> )–H, Å			1.086	1.085	1.086	1.085		1.095(16)	
C <sub>3</sub> (C <sub>4</sub> )–H, Å			1.085	1.085	1.085	1.085			
∠Cp,H, deg	0.86	0.91						2.1(0.8)	
<i>E</i> , hartrees	–1769.92553	–1769.92493	–1769.92895	–1769.92894	–1769.92835	–1769.92833		3.70(3.31)	
Δ <i>E</i> , kcal/mol	2.15	2.52	0.00	<0.01	0.38	0.39			
Δ <i>E</i> , kcal/mol (with ZPVE)			0.00	–0.06	0.27	0.12			

<sup>a</sup> M–Cp denotes the distance from the metal atom to the center of cyclopentadienyl ring. ∠Cp,H denotes the angle of the C–H bond out of the cyclopentadienyl ring; this angle is defined to be positive when the C–H bonds are bent toward the metal atom. <sup>b</sup> Reference 13. <sup>c</sup> Reference 12. <sup>d</sup> Reference 11. <sup>e</sup> Reference 15. <sup>f</sup> Reference 14.

are always slightly shorter (by only 0.001–0.002 Å) than those for the staggered *D*<sub>5d</sub> conformations. Necessarily, the distances (Cp–M) between the cyclopentadienyl ring center and the metal atom for the *D*<sub>5h</sub> conformations are also slightly shorter than those for the *D*<sub>5d</sub> conformations. There are even smaller differences between the *D*<sub>5h</sub> and *D*<sub>5d</sub> conformations for the C–C and C–H bond lengths (less than 0.001 Å). The differences in the angle of the H atoms out of the ring plane (∠Cp,H) are also predicted to be very small (less than 0.1°). In Table 4 the out-of-plane angle ∠Cp,H is defined to be positive when the C–H bonds are bent toward the metal atom. The C–H bonds are slightly bent away from the metal atom for vanadocene (VCp<sub>2</sub>) and manganocene (MnCp<sub>2</sub>) and toward the metal for

ferrocene (FeCp<sub>2</sub>) and nickelocene (NiCp<sub>2</sub>). The ground state of MnCp<sub>2</sub> is predicted to have high spin (sextet). We have also considered the lower spin (doublet) state, but the lowest doublet state (<sup>2</sup>B<sub>1</sub> with *C*<sub>2v</sub> symmetry) lies energetically higher than sextet state by 4.4 kcal/mol.

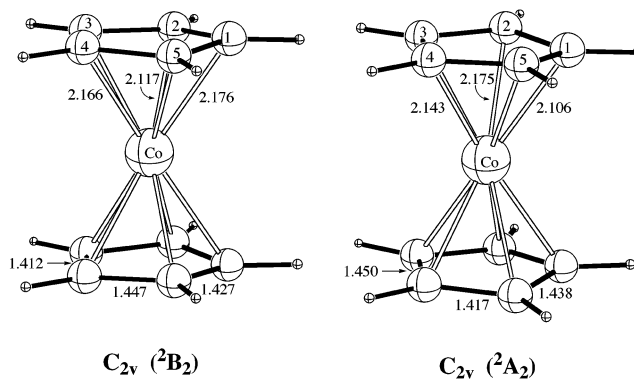
For CrCp<sub>2</sub>, there are local minima with both *D*<sub>5h</sub> (<sup>3</sup>A<sub>1</sub>') and *D*<sub>5d</sub> (<sup>3</sup>A<sub>1g</sub>) symmetries. The electron configurations are (a<sub>1</sub>')<sup>2</sup>-(a<sub>2</sub>'')<sup>2</sup>(e<sub>1</sub>'')<sup>4</sup>(e<sub>1</sub>')<sup>4</sup>(e<sub>2</sub>')<sup>2</sup>(a<sub>1</sub>')<sup>2</sup> and (a<sub>1g</sub>)<sup>2</sup>(a<sub>2u</sub>)<sup>2</sup>(e<sub>1g</sub>)<sup>4</sup>(e<sub>1u</sub>)<sup>4</sup>(e<sub>2g</sub>)<sup>2</sup>(a<sub>1g</sub>)<sup>2</sup>, respectively (Table 10). The *D*<sub>5h</sub> structure has a lower energy than the *D*<sub>5d</sub> structure by 0.3 kcal/mol. However, the distorted structures with *C*<sub>2v</sub> and *C*<sub>2h</sub> symmetries are energetically lower-lying by ~5 kcal/mol. The global minimum is the <sup>3</sup>B<sub>1</sub> state with the *C*<sub>2v</sub> structure (Figure 4 and Table 4). Its electron configu-



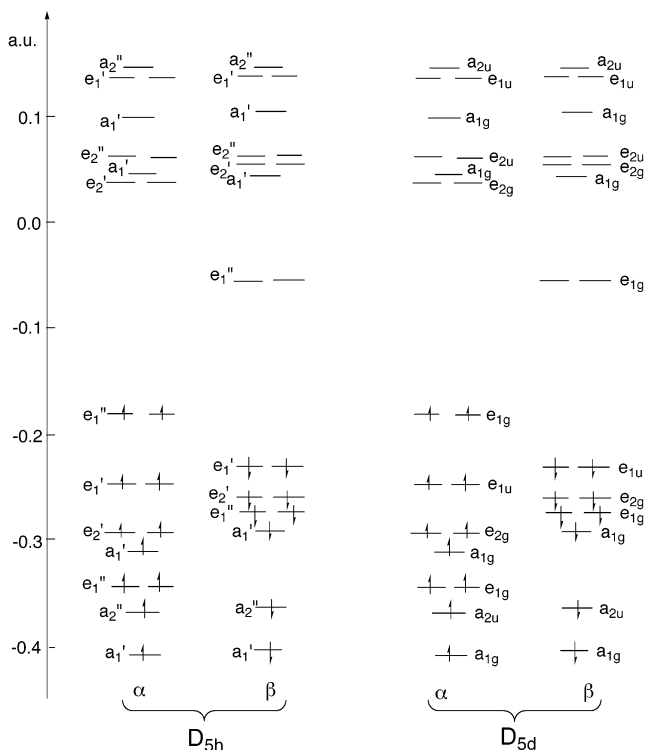
**Figure 4.** Distorted (from  $D_{5h}$  symmetry) equilibrium structures of chromocene. The  ${}^3B_1$  and  ${}^3A_1$  states are equally probable candidates for the global minimum.

ration is  $[\dots](a_1)^2(a_1)(b_1)$ . The  ${}^3A_1$  state with  $[\dots](b_1)^2(a_1)(a_1)$  configuration has an almost identical energy, but its geometry distorts from  $D_{5h}$  in the opposite direction (Figure 4). The distance between the  $C_1$  atom and the center of the  $C_3$ – $C_4$  bond is 2.203 Å for the  ${}^3A_1$  state, whereas that for the  ${}^3B_1$  state is 2.211 Å. Our  $C_{2v}$  structures appear to be in reasonable agreement with results mentioned briefly in an earlier theoretical study by Green and Jardine.<sup>52</sup> We also found other two states ( ${}^3A_g$  and  ${}^3B_g$ ) with  $C_{2h}$  structure, and their geometrical parameters are also shown in Table 4. Their energies are slightly higher than those of the  $C_{2v}$  structures (Table 4).

Because of the singly occupied degenerate orbital ( $e_1''$  for  $D_{5h}$ ;  $e_{1g}$  for  $D_{5d}$ ), the doublet cobaltocene ( $\text{CoCp}_2$ ) should have a lower symmetry than  $D_{5h}$  or  $D_{5d}$ , due to the Jahn–Teller effect. Nevertheless, we started our geometry optimization under the constraint of the  $D_{5h}$  or  $D_{5d}$  symmetry. The total energy of the constrained  $D_{5h}$  structure is predicted to be lower than that of  $D_{5d}$  by 0.38 kcal/mol. The geometric parameters of these two stationary points are very similar (Table 4). The Co–C bond distances of the  $D_{5d}$  structure are slightly longer, and the C–C bond distances are slightly shorter. The C–H bond distances of these two structures are almost the same. The hydrogen atoms are out of the ring plane and tilt toward the cobalt atom by about  $0.9^\circ$ . However, because this doublet state is degenerate, the  $D_{5h}$  and  $D_{5d}$  structures of cobaltocene will distort to remove the degeneracy, according to the well-known Jahn–Teller effect. This effect reduces the  $D_{5h}$  symmetry to  $C_{2v}$  and reduces  $D_{5d}$  to  $C_{2h}$ . For each of the  $C_{2v}$  or  $C_{2h}$  structures of  $\text{CoCp}_2$ , there are two possible electronic states. With  $C_{2v}$  symmetry, these are the  ${}^2B_2$  state with electron configuration  $[\dots](b_1)^2(a_1)^2(b_2)$  and the  ${}^2A_2$  state with electron configuration  $[\dots](b_1)^2(a_1)^2(a_2)$ . Their geometries are shown in Figure 5 and Table 4. The distance between the atom  $C_1$  and the center of bond  $C_3$ – $C_4$  for the  ${}^2B_2$  state is 2.225 Å, but this distance for the  ${}^2A_2$  state is decreased to 2.180 Å. The energies of the  ${}^2B_2$  and  ${}^2A_2$  electronic states are almost identical and lower than that of the constrained  $D_{5h}$  structure by 2.15 kcal/mol, which may be regarded as a consequence of the Jahn–Teller effect. Similarly, with  $C_{2h}$  symmetry, there are two states:  ${}^2A_g$  and  ${}^2B_g$ . The distance between atom  $C_1$  and the  $C_3$ – $C_4$  side is 2.224 Å for the  ${}^2A_g$  state, whereas it is 2.180 Å for the  ${}^2B_g$  state. The energies of the  ${}^2A_g$  and  ${}^2B_g$  states are almost identical too, but the energies of the  $C_{2v}$  structures are about 0.38 kcal/mol lower than those of the  $C_{2h}$  structures. Thus the high-symmetry eclipsed-staggered energy difference carries over to the Jahn–Teller distorted symmetries. Because the cyclopentadienyl rings are no longer regular pentagons but twisted from a plane, there are no unique



**Figure 5.** Distorted (from  $D_{5h}$  symmetry) equilibrium structures of chromocene. The  ${}^2B_2$  and  ${}^2A_2$  states are equally probable candidates for the global minimum.



**Figure 6.** Molecular orbital energy level diagram for nickelocene.

out-of-plane angles available for the  $C_{2v}$  and the  $C_{2h}$  structures in Table 4.

Table 4 also lists the experimental (constrained)  $D_{5h}$  structures determined by electron diffraction for the gas-phase samples.<sup>11–15</sup> Compared with the electron diffraction experiments, the theoretical M–C bond distances are slightly longer, whereas the theoretical C–C or C–H bond distances are slightly shorter. The deviations for the M–C bond lengths between the theoretical  $D_{5h}$  structures and the latest experimental results are +0.030, +0.031, +0.013, and +0.032 Å for  $\text{VCp}_2$ ,  $\text{MnCp}_2$ ,  $\text{FeCp}_2$ , and  $\text{NiCp}_2$ , respectively. The deviations of the average theoretical M–C bond lengths for the  $C_{2v}$  structures from the experimental results are +0.029, and +0.029 Å for  $\text{CrCp}_2$  and  $\text{CoCp}_2$ , respectively. The deviations for the C–C bond lengths are quite small, namely,  $-0.005$ ,  $-0.004$ ,  $0.000$ ,  $-0.006$ ,  $-0.001$ , and  $-0.001$  Å for  $\text{VCp}_2$ ,  $\text{CrCp}_2$ ,  $\text{MnCp}_2$ ,  $\text{FeCp}_2$ ,  $\text{CoCp}_2$ , and  $\text{NiCp}_2$ , respectively. If the experimental error bars are taken into account, our theoretical C–C bond distances are perfectly matched with experiment. The comparison for the theoretical

**TABLE 5: Harmonic Vibrational Frequencies (cm<sup>-1</sup>) and Infrared Intensities (km/mol, in Parentheses) for Vanadocene Predicted at the B3LYP/DZP Level of Theory, Compared with Experiment**

no.	<i>D</i> <sub>5h</sub>		<i>D</i> <sub>5d</sub>		expt <sup>a</sup> IR	expt <sup>b</sup>	
						Raman	IR
6	a <sub>1</sub> '	40 (0)'	a <sub>1u</sub>	24i			
22	e <sub>1</sub> '	102 (0)	e <sub>1u</sub>	87 (0)	180	183 (w)	
4	a <sub>1</sub> '	237 (0)	a <sub>1g</sub>	235 (0)		258 (m)	
16	e <sub>1</sub> ''	290 (0)	e <sub>1g</sub>	291 (0)		331 (m)	
21	e <sub>1</sub> '	360 (4)	e <sub>1u</sub>	350 (4)	426		426 (s)
11	a <sub>2</sub> ''	414 (11)	a <sub>2u</sub>	412 (11)	380		380 (s)
34	e <sub>2</sub> '	606 (0)	e <sub>2u</sub>	602 (0)			610 (vw)
28	e <sub>2</sub> '	611 (0)	e <sub>2g</sub>	609 (0)			
14	e <sub>1</sub> ''	782 (0)	e <sub>1g</sub>	782 (0)			
9	a <sub>2</sub> '	791 (248)	a <sub>2u</sub>	790 (246)	780		780 (vs)
2	a <sub>1</sub> '	801 (0)	a <sub>1g</sub>	793 (0)			
19	e <sub>1</sub> '	802 (0)	e <sub>1u</sub>	794 (0)	824		803 (sh)
33	e <sub>2</sub> ''	845 (0)	e <sub>2u</sub>	846 (0)			880 (br)
27	e <sub>2</sub> '	851 (0)	e <sub>2g</sub>	849 (0)			
31	e <sub>2</sub> ''	882 (0)	e <sub>2u</sub>	879 (0)			
25	e <sub>2</sub> '	892 (0)	e <sub>2g</sub>	880 (0)			
13	e <sub>1</sub> ''	1018 (0)	e <sub>1g</sub>	1017 (0)			
18	e <sub>1</sub> '	1021 (37)	e <sub>1u</sub>	1020 (38)	1005		1005 (vs)
30	e <sub>2</sub> ''	1067 (0)	e <sub>2u</sub>	1067 (0)			1047, 1055 (m)
24	e <sub>2</sub> '	1070 (0)	e <sub>2g</sub>	1069 (0)		1055 (w)	
10	a <sub>2</sub> ''	1131 (8)	a <sub>2u</sub>	1131 (8)	1107		1107 (s)
3	a <sub>1</sub> '	1132 (0)	a <sub>1g</sub>	1132 (0)		1106 (s)	
5	a <sub>1</sub> '	1271 (0)	a <sub>2u</sub>	1269 (0)			1260 (m)
7	a <sub>2</sub> '	1271 (0)	a <sub>2g</sub>	1270 (0)			
32	e <sub>2</sub> ''	1392 (0)	e <sub>2u</sub>	1393 (0)			1350 (m)
26	e <sub>2</sub> '	1398 (0)	e <sub>2g</sub>	1396 (0)		1345 (m)	
15	e <sub>1</sub> ''	1456 (0)	e <sub>1g</sub>	1456 (0)			
20	e <sub>1</sub> '	1457 (1)	e <sub>1u</sub>	1456 (1)	1420		1425 (m)
29	e <sub>2</sub> ''	3224 (0)	e <sub>2u</sub>	3222 (0)			
23	e <sub>2</sub> '	3225 (0)	e <sub>2g</sub>	3223 (0)			
12	e <sub>1</sub> ''	3239 (0)	e <sub>1g</sub>	3237 (0)			
17	e <sub>1</sub> '	3239 (6)	e <sub>1u</sub>	3238 (6)			3080 (w)
1	a <sub>1</sub> '	3252 (0)	a <sub>1g</sub>	3251 (0)			
8	a <sub>2</sub> ''	3252 (0)	a <sub>2u</sub>	3251 (0)			3090 (w)

<sup>a</sup> Reference 54. Infrared spectra in solution. <sup>b</sup> Reference 53. Raman and infrared spectra in solid at ~90 K.

C–H bond lengths is not as excellent as the C–C bonds, but the error bars pertaining to the electron diffraction experiment for the C–H bonds are also much larger.

**4. Harmonic Vibrational Frequencies for Metallocenes MCP<sub>2</sub> (M = V, Cr, Mn, Co, Ni).** Tables 5–9 list the harmonic vibrational frequencies of the five metallocenes excluding ferrocene. The mode numbers in Tables 5–9 are the same as in Table 2 for ferrocene.<sup>9,10</sup> The first feature seen in these tables is that for each metallocene the vibrational frequencies of the *D*<sub>5h</sub> structure and those of the *D*<sub>5d</sub> structure are nearly identical. (For chromocene and cobaltocene in Tables 6 and 8, we take the *C*<sub>2v</sub> structure and the *C*<sub>2h</sub> structure for the parallel comparison.) For most frequencies, the difference between *D*<sub>5h</sub> and *D*<sub>5d</sub> is just a few wavenumbers. The only eye-catching difference is that, except for MnCp<sub>2</sub>, the *D*<sub>5d</sub> structures (or the <sup>2</sup>A<sub>g</sub> state for cobaltocene and <sup>3</sup>A<sub>g</sub> state for chromocene) have one small imaginary frequency  $\nu_6$  (<50i cm<sup>-1</sup>). This implies that the *D*<sub>5d</sub> conformations are transition states. And this mode leads to the expected rotation of the cyclopentadienyl rings, as noted earlier for ferrocene. Thus the *D*<sub>5d</sub> conformations fall down energetically to the *D*<sub>5h</sub> conformations, consistent with the above comparison of the energies. For manganocene (MnCp<sub>2</sub>), however, both *D*<sub>5h</sub> and *D*<sub>5d</sub> conformations are minima and their energy difference (0.13 kcal/mol) is less than those predicted for the other metallocenes; i.e., *MnCp<sub>2</sub> has a flat double-well potential energy curve with respect to the ring rotation.* Thus

it is concluded that both *D*<sub>5h</sub> and *D*<sub>5d</sub> conformations exist in the gas phase. Another feature of Tables 5–9 is that all the five metallocenes have the same pattern for their infrared spectra. For the intra-ring modes, the vibrational frequencies of the different metallocenes are similar, and the corresponding IR intensities are all comparable. This indicates that the cyclopentadienyl rings in different metallocenes inhabit very similar environments.

However, for the six lowest frequencies, which are related to the inter-ring modes, the differences among the metallocenes are substantial. This is expected, because different transition metal atoms are involved. In Tables 5–9 the experimental results are also listed.<sup>21,53–56</sup> For the high frequencies (intra-ring modes), our B3LYP/DZP results are in good agreement with the available experimental data, with the average relative deviation being only about 3%, except for cobaltocene, which will be discussed below. For the low frequencies, i.e., those related to the inter-ring modes, the situation is more complicated. There are no experimental assignments for the ring rotation mode ( $\nu_6$ ) except for nickelocene. The  $\nu_6$  frequency for NiCp<sub>2</sub> is reported<sup>21</sup> to be 50 cm<sup>-1</sup>, which is somewhat larger than the B3LYP prediction (30 cm<sup>-1</sup>). Our theoretical predictions for  $\nu_{22}$  (ring–M–ring bending mode) seem too low for all the metallocenes compared with the available experimental data. For the modes  $\nu_4$  (the M-ring stretch mode) and  $\nu_{16}$  (ring tilt mode), our B3LYP frequencies are about 10–20% lower than the experimental assignments based on the Raman spectra.<sup>53</sup> For modes  $\nu_{11}$  and  $\nu_{21}$ , our B3LYP results have the reverse ordering compared with the IR spectra reported by refs 53 and 54 but are in agreement with the IR spectra reported in ref 21. By comparing experiment<sup>54</sup> with our theoretical IR intensities, we suggest the reversal of the experimental assignments of  $\nu_{11}$  and  $\nu_{21}$  in ref 54. Overall, after this modification, the B3LYP method predicts quite reasonable vibrational frequencies for the metallocenes compared with the available experimental results. For chromocene and cobaltocene, because the structures distort to *C*<sub>2v</sub> and *C*<sub>2h</sub>, the degenerate vibrational modes split. But in Tables 6 and 8, we still use the same mode numbering as those for *D*<sub>5h</sub> and *D*<sub>5d</sub>, for convenient comparison with the previous studies. So the mode numbers appear twice in Tables 6 and 8 if a mode is corresponding to a degenerate mode in *D*<sub>5h</sub> or *D*<sub>5d</sub>. The available experimental infrared spectra for cobaltocene were reported in 1975.<sup>55</sup> For most modes, the deviations are small (<10%), but some are quite large. Note especially that the experimental assignment for  $\nu_{21}$  (500 cm<sup>-1</sup> for the ring-tilt mode) is 4 times larger than our B3LYP prediction, and that for  $\nu_{31}$  (1040 cm<sup>-1</sup> for C–H wag) is 20% too large. The deviation for  $\nu_{34}$  (468 cm<sup>-1</sup> for ring torsion) is ~20% too small. These experimental assignments are suspicious to us, and further work is suggested. To our knowledge, there are no complete vibrational frequency assignments for the metallocenes except for ferrocene. Thus our present theoretical vibrational frequencies may be helpful for future studies.

**5. Electron Configurations for Ferrocene.** The molecular orbital energy levels for ferrocene at the B3LYP DZP level of theory may be seen in Figure 2. There are 18 electrons in the metal–ligand bonding orbitals of ferrocene, five from the  $\pi$  orbitals of each of the cyclopentadienyl rings, and eight from the iron atom. The bonding between the Fe atom and the rings in ferrocene is necessarily dominated by the iron 3d orbitals and the cyclopentadienyl  $\pi$  orbitals. From Figure 2, it may be seen that the 18 electrons occupy orbitals in the order a<sub>1</sub>' < a<sub>2</sub>'' < e<sub>1</sub>'' < e<sub>1</sub>' < a<sub>1</sub>' < e<sub>2</sub>' for the *D*<sub>5h</sub> conformation or, accordingly, a<sub>1g</sub> < a<sub>2u</sub> < e<sub>1g</sub> < e<sub>1u</sub> < a<sub>1g</sub> < e<sub>2g</sub> for the *D*<sub>5d</sub> conformation.



**TABLE 6: Harmonic Vibrational Frequencies (cm<sup>-1</sup>) and Infrared Intensities (km/mol, in Parentheses) for Chromocene Predicted at the B3LYP DZP Level of Theory, Compared with Experiment**

no.	$C_{2v}$				$C_{2h}$				expt <sup>a</sup> IR	expt <sup>b</sup>	
	${}^3B_1$		${}^3A_1$		${}^3A_g$		${}^3B_g$			Raman	IR
28	b <sub>1</sub>	35 (12)	b <sub>1</sub>	46i	b <sub>g</sub>	44 (0)	b <sub>g</sub>	41i			
6	a <sub>2</sub>	43 (0)	a <sub>2</sub>	25 (0)	a <sub>u</sub>	45i	a <sub>u</sub>	45i			
22	a <sub>1</sub>	121 (0)	a <sub>1</sub>	109 (0)	a <sub>u</sub>	113 (0)	a <sub>u</sub>	114 (0)	175		
22	b <sub>1</sub>	210 (32)	b <sub>1</sub>	201 (32)	b <sub>u</sub>	112 (0)	b <sub>u</sub>	112 (0)			
4	a <sub>1</sub>	262 (0)	a <sub>1</sub>	261 (0)	a <sub>g</sub>	261 (0)	a <sub>g</sub>	261 (0)		273 (s)	
11	b <sub>2</sub>	317 (1)	b <sub>2</sub>	315 (1)	b <sub>u</sub>	389 (15)	b <sub>u</sub>	391 (15)			408 (m)
16	a <sub>2</sub>	323 (0)	a <sub>2</sub>	321 (0)	a <sub>g</sub>	329 (0)	a <sub>g</sub>	329 (0)		370 (vw)	
21	a <sub>1</sub>	423 (9)	a <sub>1</sub>	423 (9)	a <sub>u</sub>	406 (11)	a <sub>u</sub>	406 (11)	433		435 (m)
34	b <sub>2</sub>	426 (1)	b <sub>2</sub>	424 (1)	b <sub>u</sub>	426 (0)	b <sub>u</sub>	425 (0)	412		
34	a <sub>2</sub>	595 (0)	a <sub>2</sub>	590 (0)	a <sub>u</sub>	588 (0)	a <sub>u</sub>	591 (0)			
16	b <sub>2</sub>	593 (0)	b <sub>2</sub>	594 (0)	b <sub>g</sub>	599 (0)	b <sub>g</sub>	602 (0)			
28	a <sub>1</sub>	600 (0)	a <sub>1</sub>	601 (0)	a <sub>g</sub>	602 (0)	a <sub>g</sub>	599 (0)			620 (vw)
21	b <sub>1</sub>	602 (0)	b <sub>1</sub>	595 (0)	b <sub>u</sub>	592 (0)	b <sub>u</sub>	588 (0)			
14	b <sub>2</sub>	765 (40)	b <sub>2</sub>	763 (38)	b <sub>g</sub>	731 (0)	b <sub>g</sub>	731 (0)			800 (sh)
14	a <sub>2</sub>	778 (0)	a <sub>2</sub>	775 (0)	a <sub>g</sub>	776 (0)	a <sub>g</sub>	764 (0)			
19	b <sub>1</sub>	778 (1)	b <sub>1</sub>	766 (0)	b <sub>u</sub>	774 (78)	b <sub>u</sub>	770 (76)	774		
2	a <sub>1</sub>	781 (0)	a <sub>1</sub>	790 (1)	a <sub>g</sub>	807 (0)	a <sub>g</sub>	784 (0)			765 (vs)
19	a <sub>1</sub>	797 (1)	a <sub>1</sub>	809 (0)	a <sub>u</sub>	796 (0)	a <sub>u</sub>	797 (0)			
9	b <sub>2</sub>	803 (102)	b <sub>2</sub>	801 (106)	b <sub>u</sub>	809 (66)	b <sub>u</sub>	810 (67)	792		
27	a <sub>1</sub>	816 (0)	a <sub>1</sub>	850 (0)	a <sub>g</sub>	849 (0)	a <sub>g</sub>	811 (0)			
27	b <sub>1</sub>	851 (0)	b <sub>1</sub>	784 (0)	b <sub>g</sub>	778 (0)	b <sub>g</sub>	849 (0)			
33	b <sub>2</sub>	836 (2)	b <sub>2</sub>	842 (0)	b <sub>u</sub>	844 (0)	b <sub>u</sub>	837 (2)			
33	a <sub>2</sub>	842 (0)	a <sub>2</sub>	834 (0)	a <sub>u</sub>	836 (0)	a <sub>u</sub>	843 (0)			
31	b <sub>2</sub>	860 (1)	b <sub>2</sub>	889 (1)	b <sub>u</sub>	891 (0)	b <sub>u</sub>	857 (1)			
25	a <sub>1</sub>	869 (0)	a <sub>1</sub>	895 (0)	a <sub>g</sub>	893 (0)	a <sub>g</sub>	862 (0)			
31	a <sub>2</sub>	895 (0)	a <sub>2</sub>	856 (0)	a <sub>u</sub>	857 (0)	a <sub>u</sub>	892 (0)			
25	b <sub>1</sub>	903 (0)	b <sub>1</sub>	864 (0)	b <sub>g</sub>	862 (0)	b <sub>g</sub>	894 (0)			
13	b <sub>2</sub>	1006 (7)	b <sub>2</sub>	1005 (7)	b <sub>g</sub>	989 (0)	b <sub>g</sub>	989 (0)		985 (w, br)	992 (vs)
13	a <sub>2</sub>	1007 (0)	a <sub>2</sub>	1006 (0)	a <sub>g</sub>	1007 (0)	a <sub>g</sub>	1008 (0)			
18	b <sub>1</sub>	996 (49)	b <sub>1</sub>	995 (49)	b <sub>u</sub>	1010 (42)	b <sub>u</sub>	1011 (42)	994		
18	a <sub>1</sub>	1011 (33)	a <sub>1</sub>	1010 (33)	a <sub>u</sub>	1010 (37)	a <sub>u</sub>	1010 (36)			
24	b <sub>1</sub>	1062 (2)	b <sub>1</sub>	1062 (1)	b <sub>g</sub>	1061 (0)	b <sub>g</sub>	1061 (0)		1048, 1055 (m)	1040, 1055 (w)
24	a <sub>1</sub>	1063 (1)	a <sub>1</sub>	1061 (2)	a <sub>g</sub>	1061 (0)	a <sub>g</sub>	1062 (0)			
30	a <sub>2</sub>	1057 (0)	a <sub>2</sub>	1065 (0)	a <sub>u</sub>	1068 (2)	a <sub>u</sub>	1059 (2)			
30	b <sub>2</sub>	1066 (0)	b <sub>2</sub>	1056 (0)	b <sub>u</sub>	1058 (2)	b <sub>u</sub>	1068 (2)			
10	b <sub>2</sub>	1120 (30)	b <sub>2</sub>	1120 (30)	b <sub>u</sub>	1120 (30)	b <sub>u</sub>	1120 (30)	1096		
3	a <sub>1</sub>	1122 (0)	a <sub>1</sub>	1121 (0)	a <sub>g</sub>	1122 (0)	a <sub>g</sub>	1123 (0)		1094 (vs)	1095
5	a <sub>2</sub>	1265 (0)	a <sub>2</sub>	1265 (0)	a <sub>u</sub>	1264 (0)	a <sub>u</sub>	1264 (0)			
7	b <sub>1</sub>	1266 (0)	b <sub>1</sub>	1265 (0)	b <sub>g</sub>	1262 (0)	b <sub>g</sub>	1262 (0)			1252 (w)
32	a <sub>2</sub>	1366 (0)	a <sub>2</sub>	1390 (0)	a <sub>u</sub>	1401 (3)	a <sub>u</sub>	1377 (2)			
26	b <sub>1</sub>	1378 (2)	b <sub>1</sub>	1401 (2)	b <sub>g</sub>	1392 (0)	b <sub>g</sub>	1369 (0)		1335 (m, br)	
32	b <sub>2</sub>	1391 (0)	b <sub>2</sub>	1365 (0)	b <sub>u</sub>	1377 (2)	b <sub>u</sub>	1402 (3)			
26	a <sub>1</sub>	1403 (3)	a <sub>1</sub>	1378 (2)	a <sub>g</sub>	1369 (0)	a <sub>g</sub>	1394 (0)			1340 (br)
20	a <sub>2</sub>	1445 (0)	a <sub>2</sub>	1446 (0)	a <sub>g</sub>	1447 (0)	a <sub>g</sub>	1449 (0)			
20	b <sub>2</sub>	1448 (3)	b <sub>2</sub>	1445 (4)	b <sub>g</sub>	1433 (0)	b <sub>g</sub>	1431 (0)			
15	b <sub>1</sub>	1435 (1)	b <sub>1</sub>	1437 (1)	b <sub>u</sub>	1446 (4)	b <sub>u</sub>	1449 (4)	1420	1408 (m, br)	1408
15	a <sub>1</sub>	1451 (0)	a <sub>1</sub>	1448 (0)	a <sub>u</sub>	1447 (0)	a <sub>u</sub>	1445 (0)			
29	a <sub>2</sub>	3226 (0)	a <sub>2</sub>	3231 (0)	a <sub>u</sub>	3230 (0)	a <sub>u</sub>	3226 (0)			
29	b <sub>2</sub>	3232 (0)	b <sub>2</sub>	3226 (0)	b <sub>u</sub>	3226 (0)	b <sub>u</sub>	3230 (0)			
23	b <sub>1</sub>	3227 (0)	b <sub>1</sub>	3230 (0)	b <sub>g</sub>	3229 (0)	b <sub>g</sub>	3227 (0)			
23	a <sub>1</sub>	3231 (0)	a <sub>1</sub>	3226 (0)	a <sub>g</sub>	3227 (0)	a <sub>g</sub>	3228 (0)			
12	b <sub>2</sub>	3243 (0)	b <sub>2</sub>	3242 (0)	b <sub>g</sub>	3242 (0)	b <sub>g</sub>	3241 (0)			
12	a <sub>2</sub>	3244 (0)	a <sub>2</sub>	3243 (0)	a <sub>g</sub>	3242 (0)	a <sub>g</sub>	3242 (0)			3086 (m)
17	a <sub>1</sub>	3244 (6)	a <sub>1</sub>	3243 (6)	a <sub>u</sub>	3243 (5)	a <sub>u</sub>	3243 (5)			
17	b <sub>1</sub>	3244 (3)	b <sub>1</sub>	3243 (3)	b <sub>u</sub>	3243 (6)	b <sub>u</sub>	3242 (6)			
8	b <sub>2</sub>	3257 (0)	b <sub>2</sub>	3256 (0)	b <sub>u</sub>	3256 (0)	b <sub>u</sub>	3255 (0)			
1	a <sub>1</sub>	3257 (0)	a <sub>1</sub>	3256 (0)	a <sub>g</sub>	3256 (0)	a <sub>g</sub>	3255 (0)		3105 (m)	3097 (m)

<sup>a</sup> Reference 54. Infrared spectra in solution. <sup>b</sup> Reference 53. Raman and infrared spectra in solid at ~90 K.

This ordering is different from the qualitative diagrams in refs 36a and 37, in which the highest occupied molecular orbital (HOMO) is a<sub>1</sub>' , but in agreement with that in ref 36b. Actually, an experimental ESR study in 1970 suggested that the ordering of the highest occupied MOs of ferrocene (*D*<sub>5d</sub>) is e<sub>1g</sub>(π-Cp) < e<sub>1u</sub>(π-Cp) < a<sub>1g</sub>(3d) ≅ e<sub>2g</sub>(3d).<sup>57</sup> The authors explicitly stated "they (a<sub>1g</sub> and e<sub>2g</sub> orbitals) lie close together". Because the ground state of the Fe<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub><sup>+</sup> cation was determined with

ESR by Prins<sup>57</sup> to have the <sup>2</sup>E<sub>2g</sub>[(e<sub>2g</sub>)<sup>3</sup>(a<sub>1g</sub>)<sup>2</sup>] configuration, i.e., an electron was lost from the e<sub>2g</sub> orbital, our theoretical orbital ordering is quite reasonable. The electronic states <sup>1</sup>A<sub>1</sub>' (a<sub>1</sub>')<sup>2</sup>-(e<sub>2</sub>')<sup>4</sup> for *D*<sub>5h</sub> symmetry or <sup>1</sup>A<sub>1g</sub> (a<sub>1g</sub>)<sup>2</sup>(e<sub>2g</sub>)<sup>4</sup> for *D*<sub>5d</sub> symmetry are of course consistent with the observed photoelectron spectra.<sup>58a</sup>

On the basis of the coefficients of the (Kohn–Sham) MO's, we can roughly describe the characteristic of each bonding MO

**TABLE 7: Harmonic Vibrational Frequencies (cm<sup>-1</sup>) and Infrared Intensities (km/mol, in Parentheses) for Manganocene Predicted at the B3LYP DZP Level of Theory, Compared with Experiment**

no.	<i>D</i> <sub>5h</sub>		<i>D</i> <sub>5d</sub>		expt <sup>a</sup> IR	expt <sup>b</sup>	
						Raman	IR
6	a <sub>1</sub> ''	32 (0)	a <sub>1u</sub>	20 (0)			
22	e <sub>1</sub> '	26 (3)	e <sub>1u</sub>	23 (3)			
16	e <sub>1</sub> ''	116 (0)	e <sub>1g</sub>	114 (0)		153 (m)	
21	e <sub>1</sub> '	189 (0)	e <sub>1u</sub>	185 (0)			
4	a <sub>1</sub> '	219 (0)	a <sub>1g</sub>	219 (0)		203 (m)	
11	a <sub>2</sub> ''	350 (85)	a <sub>2u</sub>	348 (85)			
34	e <sub>2</sub> ''	607 (0)	e <sub>2u</sub>	607 (0)			620 (w)
28	e <sub>2</sub> '	615 (0)	e <sub>2g</sub>	613 (0)		580 (m)	
14	e <sub>1</sub> '	750 (0)	e <sub>1g</sub>	748 (0)		807 (w)	
19	e <sub>1</sub> '	769 (0)	e <sub>1u</sub>	766 (0)	775		830 (w)
9	a <sub>2</sub> '	774 (429)	a <sub>2u</sub>	773 (427)	740		767 (vs)
2	a <sub>1</sub> '	784 (0)	a <sub>1g</sub>	784 (0)		760 (w)	
33	e <sub>2</sub> '	849 (0)	e <sub>2u</sub>	849 (0)			
27	e <sub>2</sub> '	850 (0)	e <sub>2g</sub>	850 (0)			
31	e <sub>2</sub> '	868 (0)	e <sub>2u</sub>	867 (0)			
25	e <sub>2</sub> '	877 (0)	e <sub>2g</sub>	872 (0)			
13	e <sub>1</sub> '	1017 (0)	e <sub>1g</sub>	1017 (0)			
18	e <sub>1</sub> '	1019 (49)	e <sub>1u</sub>	1019 (49)	1008		995, 1005s
30	e <sub>2</sub> '	1065 (0)	e <sub>2u</sub>	1065 (0)			1055 (w)
24	e <sub>2</sub> '	1068 (0)	e <sub>2g</sub>	1067 (0)		1065 (m)	
10	a <sub>2</sub> '	1132 (1)	a <sub>2u</sub>	1132 (1)	1100		1105 (w)
3	a <sub>1</sub> '	1134 (0)	a <sub>1g</sub>	1134 (0)		1108, 1113 (s)	
5	a <sub>1</sub> '	1269 (0)	a <sub>2u</sub>	1268 (0)			
7	a <sub>2</sub> '	1269 (0)	a <sub>2g</sub>	1269 (0)		1230(w, br)	
32	e <sub>2</sub> '	1382 (0)	e <sub>2u</sub>	1382 (0)			1345 (w)
26	e <sub>2</sub> '	1384 (0)	e <sub>2g</sub>	1384 (0)		1345 (m)	
15	e <sub>1</sub> '	1453 (0)	e <sub>1g</sub>	1453 (0)		1405 (w)	
20	e <sub>1</sub> '	1457 (0)	e <sub>1u</sub>	1456 (0)	1420		1425 (w)
29	e <sub>2</sub> '	3218 (0)	e <sub>2u</sub>	3218 (0)			
23	e <sub>2</sub> '	3219 (0)	e <sub>2g</sub>	3218 (0)			
12	e <sub>1</sub> '	3234 (0)	e <sub>1g</sub>	3234 (0)		3075 (m)	
17	e <sub>1</sub> '	3234 (6)	e <sub>1u</sub>	3234 (6)			3075 (m)
8	a <sub>2</sub> '	3248 (1)	a <sub>2u</sub>	3248 (1)			3090 (m)
1	a <sub>1</sub> '	3248 (0)	a <sub>1g</sub>	3248 (0)		3095 (m)	

<sup>a</sup> Reference 54. Infrared spectra in solution. <sup>b</sup> Reference 53. Raman and infrared spectra in solid at ~90 K.

with the atomic basis functions, and sketches for the ferrocene orbitals are shown in Figure 3. For the *D*<sub>5h</sub> structure, the lower a<sub>1</sub>' molecular orbital is a bonding orbital, combining the π orbitals of the cyclopentadienyl rings with mainly the 4s and 3d<sub>z<sup>2</sup></sub> orbitals of the Fe atom. The a<sub>2</sub>' molecular orbital is essentially a nonbonding orbital,<sup>36</sup> and it arises mainly from the π orbitals of the cyclopentadienyl rings and the 4p<sub>z</sub> orbital of the Fe atom. The degenerate e<sub>1</sub>' molecular orbitals are effective bonding molecular orbitals because they are mainly formed with the well-matched orbital interaction between the cyclopentadienyl p orbitals and the Fe 3d<sub>xz</sub> or 3d<sub>yz</sub> orbitals. The e<sub>1</sub>' bonding molecular orbitals arise mainly from the cyclopentadienyl π orbitals and the Fe 4p<sub>x</sub> or 4p<sub>y</sub> orbitals.

The higher occupied a<sub>1</sub>' orbital is almost the pure component of the Fe 3d<sub>z<sup>2</sup></sub>, so it is essentially a nonbonding orbital. The highest occupied molecular orbital (HOMO) e<sub>2</sub>', which is doubly degenerate, is a δ-type weakly bonding orbital containing small a contribution of the cyclopentadienyl π orbital interacting with either the Fe d<sub>x<sup>2</sup>-y<sup>2</sup></sub> orbital or the d<sub>xy</sub> orbital. The lowest empty molecular orbital (LUMO) e<sub>1</sub>' is the counterpart antibonding orbital containing a cyclopentadienyl π orbital interacting with the Fe 3d<sub>xz</sub> or 3d<sub>yz</sub> orbital. For the *D*<sub>5d</sub> conformation of ferrocene, the molecular orbitals from the B3LYP DZP treatment are analogous to those for the *D*<sub>5h</sub> conformation. The orbital energies of the LUMO and HOMO for the *D*<sub>5h</sub> conformation are -0.006 and -0.194 au, respectively, and for the *D*<sub>5d</sub> conformation are

-0.006 and -0.193 au, respectively. Ferrocene is obviously quite stable because it is a closed-shell system satisfying the 18 electron rule, and the gap between its LUMO and HOMO is substantial.

We should note here that the ferrocene orbital energies are sensitive to the theoretical methods, and they are *not* in close agreement with the photoelectron spectra. For example, the ionization energies of e<sub>2g</sub> and a<sub>1g</sub> orbitals were assigned to be 6.88 and 7.23 eV, respectively, on the basis of the photoelectron spectra,<sup>58</sup> but the corresponding Kohn-Sham orbital energies predicted by the B3LYP method are only -5.28 and -6.17 eV, respectively, and those predicted by BP86 are even worse, namely, -4.22 and -4.41 eV, respectively. As pointed out by Haaland,<sup>18</sup> Koopman theorem does not hold in these cases.

**6. Electron Configurations for Other Metallocenes MCp<sub>2</sub> (M = V, Cr, Mn, Co, and Ni).** The ground states of vanadocene, chromocene, and manganocene have 3, 2, and 1 electrons less than ferrocene, and the ground states of cobaltocene and nickelocene have 1 and 2 electrons more than ferrocene, respectively. The changes of the electron numbers could alter the energetic ordering of the molecular orbitals. In other words, the electron configurations of the first-row transition-metal metallocenes may not simply load the electrons into the orbitals on the basis of the ferrocene MO diagram.

For example, compared with ferrocene, triplet nickelocene (<sup>3</sup>A<sub>1</sub>' for *D*<sub>5h</sub> and <sup>3</sup>A<sub>1g</sub> for *D*<sub>5d</sub>) has two more electrons, which occupy the antibonding e<sub>1</sub>' orbitals with parallel spins. The occupied e<sub>1</sub>' orbital lies above the e<sub>2</sub>' orbital in the *D*<sub>5h</sub> conformation of nickelocene with the nonbonding orbitals filled by two spin-parallel electrons, and the same situation takes place in the *D*<sub>5d</sub> conformation of nickelocene. The energy gap between the LUMO and HOMO with α spin in *D*<sub>5h</sub> conformation nickelocene is 0.22 au, and that with β spin is 0.18 au. In the *D*<sub>5d</sub> conformation, the energy gap is almost the same. It is obvious that the NiCp<sub>2</sub> molecule should exhibit greater reactivity because the effect of the e<sub>1</sub>' bonding orbitals is counteracted to some extent by the two additional electrons of the e<sub>1</sub>' antibonding orbitals.

The DFT molecular orbital energy level diagrams for the ground-state vanadocene, chromocene, manganocene, and cobaltocene are shown in Supporting Information, and their electron configurations are listed in Table 10. Vanadocene has a quartet electronic ground state, <sup>4</sup>A<sub>1</sub>' for the *D*<sub>5h</sub> structure and <sup>4</sup>A<sub>1g</sub> for the *D*<sub>5d</sub> structure. The DFT energy ordering of the vanadocene occupied orbitals (Figure S1) is the same as that for ferrocene. Three unpaired parallel spin electrons occupy the orbitals e<sub>2</sub>' and a<sub>1</sub>' in the *D*<sub>5h</sub> conformation, or e<sub>2g</sub> and a<sub>1g</sub> in the *D*<sub>5d</sub> conformation. The energy gaps between the LUMO and HOMO are 0.19 au for both the *D*<sub>5h</sub> and *D*<sub>5d</sub> conformations, still quite large.

Chromocene has a triplet electronic ground state <sup>3</sup>B<sub>1</sub> for the *C*<sub>2v</sub> structure distorted from *D*<sub>5h</sub> symmetry. The <sup>3</sup>A<sub>1</sub> state (*C*<sub>2v</sub>) has almost the identical energy. The degenerate orbitals for *D*<sub>5h</sub> and *D*<sub>5d</sub> should split. The e<sub>1</sub>' orbital components of the *D*<sub>5h</sub> structure split into the b<sub>2</sub> and a<sub>2</sub> orbitals of *C*<sub>2v</sub> symmetry. Interestingly, the doubly occupied a<sub>1</sub> orbital is the HOMO; i.e., it lies higher than the near-degenerate singly occupied orbitals a<sub>1</sub> and b<sub>1</sub>. In the case of chromocene, the energy gap between the LUMO and HOMO is 0.18 au for α orbitals, but it is only 0.11 au for β orbitals. So we can reasonably conceive that the β electron in the HOMO a<sub>1</sub> might be easily excited or lost to make some chemical reaction occur. The *C*<sub>2h</sub> structures (distorted from *D*<sub>5d</sub>) have slightly higher energy, and they have very similar MO energy level diagrams (Figure S2). Because the energies

**TABLE 8: Harmonic Vibrational Frequencies (cm<sup>-1</sup>) and Infrared Intensities (km/mol) of Cobaltocene Predicted at the B3LYP DZP Level of Theory**

no. <sup>a</sup>	<i>C</i> <sub>2v</sub>				<i>C</i> <sub>2h</sub>				exp <sup>b</sup> IR (20 °C, 77 K)	
	<sup>2</sup> B <sub>2</sub>		<sup>2</sup> A <sub>2</sub>		<sup>2</sup> B <sub>g</sub>		<sup>2</sup> A <sub>g</sub>			
6	a <sub>2</sub>	28 (0)	a <sub>2</sub>	24 (0)	a <sub>u</sub>	35i	a <sub>u</sub>	32i		
28	b <sub>1</sub>	70 (2)	b <sub>1</sub>	72i	b <sub>g</sub>	92i	b <sub>g</sub>	96 (0)		
21	a <sub>1</sub>	137 (0)	a <sub>1</sub>	142 (0)	a <sub>u</sub>	134 (0)	a <sub>u</sub>	136 (0)	500	500 (m)
21	b <sub>1</sub>	143 (0)	b <sub>1</sub>	139 (0)	b <sub>u</sub>	132 (0)	b <sub>u</sub>	134 (0)	500	500 (m)
16	b <sub>2</sub>	210 (0)	b <sub>2</sub>	299 (0)	b <sub>g</sub>	234 (0)	b <sub>g</sub>	304 (0)		
16	a <sub>2</sub>	297 (0)	a <sub>2</sub>	208 (0)	a <sub>g</sub>	301 (0)	a <sub>g</sub>	209 (0)		
4	a <sub>1</sub>	254 (0)	a <sub>1</sub>	255 (0)	a <sub>g</sub>	253 (0)	a <sub>g</sub>	254 (0)		
22	a <sub>1</sub>	316 (5)	a <sub>1</sub>	370 (8)	a <sub>u</sub>	300 (5)	a <sub>u</sub>	363 (8)		
22	b <sub>1</sub>	377 (6)	b <sub>1</sub>	332 (3)	b <sub>u</sub>	362 (8)	b <sub>u</sub>	298 (5)		
11	b <sub>2</sub>	392 (1)	b <sub>2</sub>	391 (1)	b <sub>u</sub>	388 (1)	b <sub>u</sub>	388 (1)	430	430 (w, br)
34	b <sub>2</sub>	586 (2)	b <sub>2</sub>	587 (2)	b <sub>u</sub>	584 (3)	b <sub>u</sub>	585 (3)	468	468 (s)
34	a <sub>2</sub>	587 (0)	a <sub>2</sub>	587 (0)	a <sub>u</sub>	586 (0)	a <sub>u</sub>	586 (0)	468	468 (s)
28	a <sub>1</sub>	600 (0)	a <sub>1</sub>	601 (0)	a <sub>g</sub>	597 (0)	a <sub>g</sub>	599 (0)		
14	b <sub>2</sub>	752 (1)	b <sub>2</sub>	826 (1)	b <sub>g</sub>	781 (0)	b <sub>g</sub>	821 (0)		
19	a <sub>1</sub>	779 (5)	a <sub>1</sub>	800 (0)	a <sub>u</sub>	774 (5)	a <sub>u</sub>	838 (0)	820	820 (w)
27	b <sub>1</sub>	783 (0)	b <sub>1</sub>	781 (5)	b <sub>g</sub>	747 (0)	b <sub>g</sub>	782 (0)		
9	b <sub>2</sub>	786 (153)	b <sub>2</sub>	785 (152)	b <sub>u</sub>	782 (155)	b <sub>u</sub>	783 (154)	782	780 (s)
2	a <sub>1</sub>	799 (0)	a <sub>1</sub>	847 (2)	a <sub>g</sub>	794 (0)	a <sub>g</sub>	749 (0)		
14	a <sub>2</sub>	823 (0)	a <sub>2</sub>	751 (0)	a <sub>g</sub>	847 (0)	a <sub>g</sub>	797 (0)		
19	b <sub>1</sub>	849 (4)	b <sub>1</sub>	783 (1)	b <sub>u</sub>	841 (3)	b <sub>u</sub>	775 (6)	820	820 (w)
33	a <sub>2</sub>	838 (0)	a <sub>2</sub>	838 (0)	a <sub>u</sub>	838 (0)	a <sub>u</sub>	844 (3)	860	865 (s)
33	b <sub>2</sub>	838 (15)	b <sub>2</sub>	838 (14)	b <sub>u</sub>	838 (17)	b <sub>u</sub>	838 (18)	860	865 (s)
27	a <sub>1</sub>	848 (0)	a <sub>1</sub>	851 (2)	a <sub>g</sub>	820 (0)	a <sub>g</sub>	847 (0)		
31	a <sub>2</sub>	883 (0)	a <sub>2</sub>	884 (0)	a <sub>u</sub>	884 (1)	a <sub>u</sub>	886 (0)	1040	1040 (m)
31	b <sub>2</sub>	888 (7)	b <sub>2</sub>	891 (8)	b <sub>u</sub>	888 (6)	b <sub>u</sub>	892 (6)	1040	1040 (m)
25	b <sub>1</sub>	891 (0)	b <sub>1</sub>	890 (0)	b <sub>g</sub>	877 (0)	b <sub>g</sub>	878 (0)		
25	a <sub>1</sub>	900 (1)	a <sub>1</sub>	902 (0)	a <sub>g</sub>	884 (0)	a <sub>g</sub>	889 (0)		
13	a <sub>2</sub>	998 (0)	a <sub>2</sub>	1025 (0)	a <sub>g</sub>	997 (0)	a <sub>g</sub>	1025 (0)		
13	b <sub>2</sub>	1024 (1)	b <sub>2</sub>	998 (0)	b <sub>g</sub>	1022 (0)	b <sub>g</sub>	996 (0)		
18	b <sub>1</sub>	1001 (28)	b <sub>1</sub>	1026 (37)	b <sub>u</sub>	1001 (28)	b <sub>u</sub>	1028 (39)	998	1000 (s)
18	a <sub>1</sub>	1028 (39)	a <sub>1</sub>	1002 (27)	a <sub>u</sub>	1028 (38)	a <sub>u</sub>	1001 (28)	998	1000 (s)
24	b <sub>1</sub>	1045 (0)	b <sub>1</sub>	1047 (3)	b <sub>g</sub>	1043 (0)	b <sub>g</sub>	1041 (0)		
30	b <sub>2</sub>	1059 (5)	b <sub>2</sub>	1059 (6)	b <sub>u</sub>	1061 (4)	b <sub>u</sub>	1062 (4)	1140	1140 (w)
30	a <sub>2</sub>	1060 (0)	a <sub>2</sub>	1061 (0)	a <sub>u</sub>	1064 (0)	a <sub>u</sub>	1063 (0)	1140	1140 (w)
24	a <sub>1</sub>	1065 (0)	a <sub>1</sub>	1065 (0)	a <sub>g</sub>	1063 (0)	a <sub>g</sub>	1064 (0)		
10	b <sub>2</sub>	1133 (10)	b <sub>2</sub>	1133 (10)	b <sub>u</sub>	1133 (11)	b <sub>u</sub>	1133 (11)	1100	1100 (m)
3	a <sub>1</sub>	1133 (0)	a <sub>1</sub>	1133 (0)	a <sub>g</sub>	1134 (0)	a <sub>g</sub>	1134 (0)		
5	a <sub>2</sub>	1268 (0)	a <sub>2</sub>	1269 (0)	a <sub>u</sub>	1268 (0)	a <sub>u</sub>	1268 (0)	1255	1255 (m)
7	b <sub>1</sub>	1269 (0)	b <sub>1</sub>	1269 (0)	b <sub>g</sub>	1267 (0)	b <sub>g</sub>	1268 (0)		
26	b <sub>1</sub>	1344 (1)	b <sub>1</sub>	1344 (2)	b <sub>g</sub>	1333 (0)	b <sub>g</sub>	1334 (0)		
32	a <sub>2</sub>	1377 (0)	a <sub>2</sub>	1378 (0)	a <sub>u</sub>	1388 (2)	a <sub>u</sub>	1387 (0)	1370	1370 (m) <sup>c</sup>
32	b <sub>2</sub>	1385 (35)	b <sub>2</sub>	1385 (34)	b <sub>u</sub>	1394 (30)	b <sub>u</sub>	1395 (32)	1370	1370 (m) <sup>c</sup>
26	a <sub>1</sub>	1400 (2)	a <sub>1</sub>	1399 (0)	a <sub>g</sub>	1391 (0)	a <sub>g</sub>	1392 (0)		
20	b <sub>1</sub>	1435 (6)	b <sub>1</sub>	1472 (0)	b <sub>u</sub>	1437 (0)	b <sub>u</sub>	1474 (2)	1410	1410 (m)
15	a <sub>2</sub>	1438 (0)	a <sub>2</sub>	1470 (0)	a <sub>g</sub>	1438 (0)	a <sub>g</sub>	1472 (0)		
15	b <sub>2</sub>	1471 (1)	b <sub>2</sub>	1437 (2)	b <sub>g</sub>	1470 (0)	b <sub>g</sub>	1436 (0)		
20	a <sub>1</sub>	1474 (0)	a <sub>1</sub>	1438 (7)	a <sub>u</sub>	1474 (0)	a <sub>u</sub>	1437 (7)	1410	1410 (m)
29	b <sub>2</sub>	3228 (0)	b <sub>2</sub>	3227 (0)	b <sub>u</sub>	3228 (2)	b <sub>u</sub>	3228 (1)		
29	a <sub>2</sub>	3228 (0)	a <sub>2</sub>	3228 (0)	a <sub>u</sub>	3229 (1)	a <sub>u</sub>	3229 (2)		
23	b <sub>1</sub>	3228 (2)	b <sub>1</sub>	3228 (1)	b <sub>g</sub>	3228 (0)	b <sub>g</sub>	3228 (0)		
23	a <sub>1</sub>	3229 (1)	a <sub>1</sub>	3228 (2)	a <sub>g</sub>	3228 (0)	a <sub>g</sub>	3228 (0)		
12	a <sub>2</sub>	3240 (0)	a <sub>2</sub>	3249 (0)	a <sub>g</sub>	3241 (0)	a <sub>g</sub>	3249 (0)		
12	b <sub>2</sub>	3248 (0)	b <sub>2</sub>	3239 (0)	b <sub>g</sub>	3248 (0)	b <sub>g</sub>	3241 (0)		
17	b <sub>1</sub>	3241 (10)	b <sub>1</sub>	3250 (5)	b <sub>u</sub>	3241 (10)	b <sub>u</sub>	3249 (6)		
17	a <sub>1</sub>	3249 (6)	a <sub>1</sub>	3241 (10)	a <sub>u</sub>	3249 (6)	a <sub>u</sub>	3241 (10)		
8	b <sub>2</sub>	3257 (1)	b <sub>2</sub>	3258 (1)	b <sub>u</sub>	3258 (1)	b <sub>u</sub>	3258 (1)		
1	a <sub>1</sub>	3258 (0)	a <sub>1</sub>	3259 (0)	a <sub>g</sub>	3258 (0)	a <sub>g</sub>	3258 (0)		

<sup>a</sup> For comparison with other work, the numbering here is taken from *D*<sub>5h</sub> and *D*<sub>5d</sub> symmetry. Some numbers appear twice if they correspond to the degenerate modes in *D*<sub>5h</sub> and *D*<sub>5d</sub> symmetry. <sup>b</sup> Reference 55. Some frequencies repeat in this table because the mode number appears twice. <sup>c</sup> In ref 55, there are three bands (1335 (w), 1350 (m), and 1370 (m)) for this assignment.

for the <sup>3</sup>B<sub>1</sub> and <sup>3</sup>A<sub>1</sub> states are so close, experimentalists may observe a *D*<sub>5h</sub> structure, which is the average of these two equilibrium structures.

Though manganocene is only one electron short of ferrocene, it has five unpaired electrons in its <sup>6</sup>A<sub>1</sub>' electronic ground state for *D*<sub>5h</sub> and <sup>6</sup>A<sub>1g</sub>' for *D*<sub>5d</sub> (Figure S3). (As mentioned above, the doublet manganocene is predicted to lie energetically higher than the sextet by more than 5 kcal/mol.) The degenerate

antibonding orbital e<sub>1</sub>' in *D*<sub>5h</sub> (or e<sub>1g</sub> in *D*<sub>5d</sub>) is occupied by two electrons, and the bonding orbitals (a<sub>1</sub>' and e<sub>2</sub>') are similarly half-occupied. Compared with ferrocene in Figure 2, the order of the α orbitals e<sub>2</sub>' and a<sub>1</sub>' in *D*<sub>5h</sub> (or e<sub>2g</sub> and a<sub>1g</sub> in *D*<sub>5d</sub>) is exchanged. The energy gaps in the *D*<sub>5h</sub> conformation of manganocene between LUMO and HOMO are 0.19 au for α orbitals, and 0.18 au for β orbitals. These energy gaps in the *D*<sub>5d</sub> conformation are comparable to those in *D*<sub>5h</sub>. Because the

**TABLE 9: Harmonic Vibrational Frequencies (cm<sup>-1</sup>) and Infrared Intensities (km/mol, in Parentheses) of Nickelocene Predicted at the B3LYP DZP Level of Theory, Compared with Experiment**

no.	$D_{5h}$	$D_{5d}$	expt <sup>a</sup> IR	expt <sup>b</sup> IR	expt <sup>d</sup> IR or Raman
6	a <sub>1</sub> ''	30 (0)	a <sub>1u</sub>	25i	50
22	e <sub>1</sub> '	116 (0)	e <sub>1u</sub>	115 (0)	132, 135
16	e <sub>1</sub> '	171 (0)	e <sub>1g</sub>	169 (0)	205, 213
4	a <sub>1</sub> '	234 (0)	a <sub>1g</sub>	234 (0)	252
21	e <sub>1</sub> '	249 (1)	e <sub>1u</sub>	246 (1)	270
11	a <sub>2</sub> '	358 (20)	a <sub>2u</sub>	356 (20)	358
34	e <sub>2</sub> '	596 (0)	e <sub>2u</sub>	597 (0)	
28	e <sub>2</sub> '	609 (0)	e <sub>2g</sub>	606 (0)	500 (w)
14	e <sub>1</sub> '	768 (0)	e <sub>1g</sub>	766 (0)	
9	a <sub>2</sub> '	780 (253)	a <sub>2u</sub>	778 (254)	780 810 (s)
2	a <sub>1</sub> '	791 (0)	a <sub>1g</sub>	790 (0)	
19	e <sub>1</sub> '	793 (2)	e <sub>1u</sub>	789 (2)	800 842 (w)
33	e <sub>2</sub> '	844 (0)	e <sub>2u</sub>	844 (0)	
27	e <sub>2</sub> '	850 (0)	e <sub>2g</sub>	849 (0)	
31	e <sub>2</sub> '	874 (0)	e <sub>2u</sub>	876 (0)	
25	e <sub>2</sub> '	888 (0)	e <sub>2g</sub>	878 (0)	
13	e <sub>1</sub> '	1017 (0)	e <sub>1g</sub>	1017 (0)	
18	e <sub>1</sub> '	1020 (39)	e <sub>1u</sub>	1019 (39)	1005 1000 (s)
30	e <sub>2</sub> '	1061 (0)	e <sub>2u</sub>	1063 (0)	1052 (m)
24	e <sub>2</sub> '	1066 (0)	e <sub>2g</sub>	1065 (0)	
10	a <sub>2</sub> '	1136 (1)	a <sub>2u</sub>	1136 (1)	1110 1110 (m)
3	a <sub>1</sub> '	1137 (0)	a <sub>1g</sub>	1138 (0)	
5	a <sub>1</sub> '	1270 (0)	a <sub>2u</sub>	1270 (0)	1252 (m)
7	a <sub>2</sub> '	1271 (0)	a <sub>2g</sub>	1270 (0)	
32	e <sub>2</sub> '	1376 (0)	e <sub>2u</sub>	1378 (0)	1335 (w)
26	e <sub>2</sub> '	1383 (0)	e <sub>2g</sub>	1381 (0)	
15	e <sub>1</sub> '	1456 (0)	e <sub>1g</sub>	1456 (0)	
20	e <sub>1</sub> '	1458 (1)	e <sub>1u</sub>	1458 (1)	1415 1422 (m)
29	e <sub>2</sub> '	3228 (0)	e <sub>2u</sub>	3229 (0)	3104, 3112 (s) <sup>c</sup>
23	e <sub>2</sub> '	3228 (0)	e <sub>2g</sub>	3229 (0)	
12	e <sub>1</sub> '	3243 (0)	e <sub>1g</sub>	3244 (0)	
17	e <sub>1</sub> '	3244 (7)	e <sub>1u</sub>	3245 (7)	3075 (m)
8	a <sub>2</sub> '	3256 (1)	a <sub>2u</sub>	3257 (1)	
1	a <sub>1</sub> '	3257 (0)	a <sub>1g</sub>	3257 (0)	

<sup>a</sup> Reference 54. Infrared spectra in solution. <sup>b</sup> Reference 56. Infrared spectra of polycrystalline,  $T = 20^\circ\text{C}$ . The fundamental modes that are forbidden in the gas phase by symmetry (e.g., e<sub>2</sub>' or e<sub>2u</sub>) appear in the solid state. <sup>c</sup> Reference 56. Infrared spectra of polycrystalline,  $T = 77\text{ K}$ . <sup>d</sup> Reference 21. Infrared and Raman spectra (at 300 K) of crystal.

molecule has so many unpaired electrons and the HOMO is antibonding, the chemical reactivity should be significant.

For the cobaltocene molecule, because the last electron occupies the  $D_{2h}$  e<sub>1</sub>'' antibonding orbital (or the e<sub>1g</sub> antibonding

orbital for the  $D_{5d}$  structure), the degenerate orbitals should split, and the molecule should appropriately lower its symmetry according to the Jahn–Teller effect. For the  $C_{2v}$  conformation of cobaltocene, this unpaired electron could occupy either the b<sub>2</sub> orbital or a<sub>2</sub>, and the electronic states would be accordingly either  ${}^2\text{B}_2$  or  ${}^2\text{A}_2$  (Figure S4). However, these two states are found to have almost the identical total energies, the  ${}^2\text{B}_2$  state lying lower by less than 0.006 kcal/mol. For the  ${}^2\text{B}_2$  state, the energy gap between the LUMO and HOMO of the  $\alpha$  orbitals is quite small (0.09 au) but is substantial (0.18 au) for the  $\beta$  orbitals. The  ${}^2\text{A}_2$  state has almost the same energy gap. Likewise, for the  $C_{2h}$  conformation, there are two near-degenerate electronic states:  ${}^2\text{A}_g$  and  ${}^2\text{B}_g$ . The  ${}^2\text{A}_g$  state has the slightly lower energy. The energy gap between the LUMO and HOMO for the  $\alpha$  orbitals is 0.10 au but is 0.18 au for the  $\beta$  orbitals. The  ${}^2\text{B}_g$  electronic state has a similar diagram with comparable energy gap between LUMO and HOMO. Compared with ferrocene, because the additional electron occupies the antibonding orbital and the energy gaps are smaller, cobaltocene could have considerable chemical reactivity. Because the energy difference between the  ${}^2\text{B}_2$  and  ${}^2\text{A}_2$  states is negligibly small ( $<0.006$  kcal/mol), they can transit to each other easily and may exist simultaneously. Practically, it should be hard to distinguish the  ${}^2\text{B}_2$  and  ${}^2\text{A}_2$  states in the laboratory. Like chromocene, the experimentalist may observe an average  $D_{5h}$  structure.

From the analysis of the electron configurations of metallocenes, we can predict some geometric characteristics for these compounds. The B3LYP method predicts the Fe–Cp distance of eclipsed ( $D_{5h}$ ) ferrocene to be 1.68 Å (Table 1), whereas the M–Cp distances for other metallocenes are all longer (Table 4). For the  ${}^2\text{B}_2$  state of  $\text{CoCp}_2$ , the Co–Cp distance is  $\sim 1.77$  Å (Table 4), which is 0.09 Å longer than that in ferrocene. This is because one more electron occupies the antibonding b<sub>2</sub> orbital (one of the splitting e<sub>1</sub>'' orbitals), which weakens the interaction between the Co atom and the rings. Similarly, for nickelocene there are two electrons on the antibonding e<sub>1</sub>'' orbital, which makes the Ni–Cp distance in  ${}^3\text{A}_1'$  NiCp<sub>2</sub> even longer (1.87 Å in Table 4). Compared with FeCp<sub>2</sub>, there are two electrons less on the bonding e<sub>2</sub>' orbitals for CrCp<sub>2</sub>, and one electron less occupies the weakly bonding a<sub>1</sub>' orbital for VCp<sub>2</sub>. This makes the Cr–Cp and V–Cp distances also longer (1.97 Å for  $D_{5h}$  VCp<sub>2</sub> and 1.90 Å for  $D_{5h}$  CrCp<sub>2</sub>). For  ${}^6\text{A}_1'$  manganocene, because there are three fewer electrons in the bonding orbitals (a<sub>1</sub>' and e<sub>2</sub>') and two more electrons in the antibonding orbitals

**TABLE 10: Electron Configurations for the Six Metallocenes (MCp<sub>2</sub>) Studied Here**

MCp <sub>2</sub>	symmetry	valence electrons	electronic state	electron configuration
VCp <sub>2</sub>	$D_{5h}$	15	${}^4\text{A}_1'$	(a <sub>1</sub> ') <sup>2</sup> (a <sub>2</sub> '') <sup>2</sup> (e <sub>1</sub> '') <sup>4</sup> (e <sub>1</sub> ') <sup>4</sup> (a <sub>1</sub> ')(e <sub>2</sub> ') <sup>2</sup>
	$D_{5d}$		${}^4\text{A}_{1g}$	(a <sub>1g</sub> ) <sup>2</sup> (a <sub>2u</sub> ) <sup>2</sup> (e <sub>1g</sub> ) <sup>4</sup> (e <sub>1u</sub> ) <sup>4</sup> (a <sub>1g</sub> )(e <sub>2g</sub> ) <sup>2</sup>
CrCp <sub>2</sub>	$D_{5h}$	16	${}^3\text{A}_1'$	(a <sub>1</sub> ') <sup>2</sup> (a <sub>2</sub> '') <sup>2</sup> (e <sub>1</sub> '') <sup>4</sup> (e <sub>1</sub> ') <sup>4</sup> (e <sub>2</sub> ') <sup>2</sup> (a <sub>1</sub> ') <sup>2</sup>
	$D_{5d}$		${}^3\text{A}_{1g}$	(a <sub>1g</sub> ) <sup>2</sup> (a <sub>2u</sub> ) <sup>2</sup> (e <sub>1g</sub> ) <sup>4</sup> (e <sub>1u</sub> ) <sup>4</sup> (e <sub>2g</sub> ) <sup>2</sup> (a <sub>1g</sub> ) <sup>2</sup>
	$C_{2v}$		${}^3\text{B}_1$	(a <sub>1</sub> ) <sup>2</sup> (b <sub>2</sub> ) <sup>2</sup> (a <sub>2</sub> ) <sup>2</sup> (b <sub>2</sub> ) <sup>2</sup> (a <sub>1</sub> ) <sup>2</sup> (b <sub>1</sub> ) <sup>2</sup> (a <sub>1</sub> ) <sup>2</sup> (a <sub>1</sub> )(b <sub>1</sub> )
	$C_{2h}$		${}^3\text{A}_1$	(a <sub>1</sub> ) <sup>2</sup> (b <sub>2</sub> ) <sup>2</sup> (a <sub>2</sub> ) <sup>2</sup> (b <sub>2</sub> ) <sup>2</sup> (a <sub>1</sub> ) <sup>2</sup> (b <sub>1</sub> ) <sup>2</sup> (b <sub>1</sub> ) <sup>2</sup> (a <sub>1</sub> )(a <sub>1</sub> )
			${}^3\text{A}_g$	(a <sub>g</sub> ) <sup>2</sup> (b <sub>u</sub> ) <sup>2</sup> (a <sub>g</sub> ) <sup>2</sup> (b <sub>g</sub> ) <sup>2</sup> (a <sub>u</sub> ) <sup>2</sup> (b <sub>u</sub> ) <sup>2</sup> (b <sub>g</sub> ) <sup>2</sup> (a <sub>g</sub> )(a <sub>g</sub> )
			${}^3\text{B}_g$	(a <sub>g</sub> ) <sup>2</sup> (b <sub>u</sub> ) <sup>2</sup> (a <sub>g</sub> ) <sup>2</sup> (b <sub>g</sub> ) <sup>2</sup> (a <sub>u</sub> ) <sup>2</sup> (b <sub>u</sub> ) <sup>2</sup> (a <sub>g</sub> ) <sup>2</sup> (a <sub>g</sub> )(b <sub>g</sub> )
MnCp <sub>2</sub>	$D_{5h}$	17	${}^6\text{A}_1'$	(a <sub>1</sub> ') <sup>2</sup> (a <sub>2</sub> '') <sup>2</sup> (e <sub>1</sub> '') <sup>4</sup> (e <sub>1</sub> ') <sup>4</sup> (e <sub>2</sub> ') <sup>2</sup> (a <sub>1</sub> ')(e <sub>1</sub> '') <sup>2</sup>
	$D_{5d}$		${}^6\text{A}_{1g}$	(a <sub>1g</sub> ) <sup>2</sup> (a <sub>2u</sub> ) <sup>2</sup> (e <sub>1g</sub> ) <sup>4</sup> (e <sub>1u</sub> ) <sup>4</sup> (e <sub>2g</sub> ) <sup>2</sup> (a <sub>1g</sub> )(e <sub>1g</sub> ) <sup>2</sup>
FeCp <sub>2</sub>	$D_{5h}$	18	${}^1\text{A}_1'$	(a <sub>1</sub> ') <sup>2</sup> (a <sub>2</sub> '') <sup>2</sup> (e <sub>1</sub> '') <sup>4</sup> (e <sub>1</sub> ') <sup>4</sup> (a <sub>1</sub> ') <sup>2</sup> (e <sub>2</sub> ') <sup>4</sup>
	$D_{5d}$		${}^1\text{A}_{1g}$	(a <sub>1g</sub> ) <sup>2</sup> (a <sub>2u</sub> ) <sup>2</sup> (e <sub>1g</sub> ) <sup>4</sup> (e <sub>1u</sub> ) <sup>4</sup> (a <sub>1g</sub> ) <sup>2</sup> (e <sub>2g</sub> ) <sup>4</sup>
CoCp <sub>2</sub>	$D_{5h}$	19	${}^2\text{E}_1''$	(a <sub>1</sub> ') <sup>2</sup> (a <sub>2</sub> '') <sup>2</sup> (e <sub>1</sub> '') <sup>4</sup> (e <sub>1</sub> ') <sup>4</sup> (a <sub>1</sub> ') <sup>2</sup> (e <sub>2</sub> ') <sup>4</sup> (e <sub>1</sub> '')
	$D_{5d}$		${}^2\text{E}_{1g}$	(a <sub>1g</sub> ) <sup>2</sup> (a <sub>2u</sub> ) <sup>2</sup> (e <sub>1g</sub> ) <sup>4</sup> (e <sub>1u</sub> ) <sup>4</sup> (a <sub>1g</sub> ) <sup>2</sup> (e <sub>2g</sub> ) <sup>4</sup> (e <sub>1g</sub> )
	$C_{2v}$		${}^2\text{B}_2$	(a <sub>1</sub> ) <sup>2</sup> (b <sub>2</sub> ) <sup>2</sup> (a <sub>2</sub> ) <sup>2</sup> (b <sub>2</sub> ) <sup>2</sup> (a <sub>1</sub> ) <sup>2</sup> (b <sub>1</sub> ) <sup>2</sup> (a <sub>1</sub> ) <sup>2</sup> (b <sub>1</sub> ) <sup>2</sup> (a <sub>1</sub> ) <sup>2</sup> (b <sub>2</sub> )
	$C_{2h}$		${}^2\text{A}_2$	(a <sub>1</sub> ) <sup>2</sup> (b <sub>2</sub> ) <sup>2</sup> (a <sub>2</sub> ) <sup>2</sup> (b <sub>2</sub> ) <sup>2</sup> (a <sub>1</sub> ) <sup>2</sup> (b <sub>1</sub> ) <sup>2</sup> (a <sub>1</sub> ) <sup>2</sup> (b <sub>1</sub> ) <sup>2</sup> (a <sub>2</sub> )
			${}^2\text{A}_g$	(a <sub>g</sub> ) <sup>2</sup> (b <sub>u</sub> ) <sup>2</sup> (a <sub>g</sub> ) <sup>2</sup> (b <sub>g</sub> ) <sup>2</sup> (a <sub>u</sub> ) <sup>2</sup> (b <sub>u</sub> ) <sup>2</sup> (a <sub>g</sub> ) <sup>2</sup> (b <sub>g</sub> ) <sup>2</sup> (a <sub>g</sub> )(a <sub>g</sub> )
			${}^2\text{B}_g$	(a <sub>g</sub> ) <sup>2</sup> (b <sub>u</sub> ) <sup>2</sup> (a <sub>g</sub> ) <sup>2</sup> (b <sub>g</sub> ) <sup>2</sup> (a <sub>u</sub> ) <sup>2</sup> (b <sub>u</sub> ) <sup>2</sup> (a <sub>g</sub> ) <sup>2</sup> (b <sub>g</sub> ) <sup>2</sup> (a <sub>g</sub> )(b <sub>g</sub> )
NiCp <sub>2</sub>	$D_{5h}$	20	${}^3\text{A}_1'$	(a <sub>1</sub> ') <sup>2</sup> (a <sub>2</sub> '') <sup>2</sup> (e <sub>1</sub> '') <sup>4</sup> (a <sub>1</sub> ') <sup>2</sup> (e <sub>2</sub> ') <sup>4</sup> (e <sub>1</sub> ') <sup>4</sup> (e <sub>1</sub> '') <sup>2</sup>
	$D_{5d}$		${}^3\text{A}_{1g}$	(a <sub>1g</sub> ) <sup>2</sup> (a <sub>2u</sub> ) <sup>2</sup> (e <sub>1g</sub> ) <sup>4</sup> (a <sub>1g</sub> ) <sup>2</sup> (e <sub>2g</sub> ) <sup>4</sup> (e <sub>1u</sub> ) <sup>4</sup> (e <sub>1g</sub> ) <sup>2</sup>



( $e_1''$ ) than ferrocene, the Mn–Cp distance is expected to be even longer. This is confirmed by our B3LYP Mn–Cp distance, which is very long (2.08 Å, Table 4).

Let us also examine the relationship between the electron configuration and the  $\angle\text{Cp,H}$  angles. To have more effective bonding between the metal atom and the cyclopentadienyl rings, all the  $p_z$  orbitals of the carbon atoms are no longer perpendicular to the ring planes but tilt slightly toward the molecular center, and the trigonal hybridization of the C atoms on the rings should be accordingly modified.<sup>18</sup> Consequently, the C–H bonds should tilt slightly toward the metal atom, and this is why the predicted  $\angle\text{Cp,H}$  angle ranges from 0.9° to 1.6° in ferrocene with the five DFT methods. For other metallocenes, the  $\angle\text{Cp,H}$  angle is less than that of ferrocene, due to less effective bonding between the metal atom and the rings. For the  $D_{5h}$  CoCp<sub>2</sub>, because of the electron in the antibonding  $e_1''$  orbital, the  $\angle\text{Cp,H}$  angle predicted by B3LYP decreases from 1.2° to 0.9° (Table 4). For the  $D_{5h}$  NiCp<sub>2</sub>, the  $\angle\text{Cp,H}$  angle further decreases to 0.5°, because there are two electrons in the  $e_1''$  antibonding orbitals. For  $D_{5h}$  CrCp<sub>2</sub>, two fewer electrons are on the bonding  $e_2'$  orbital than ferrocene, and the  $\angle\text{Cp,H}$  angle essentially goes to zero. The experimental result<sup>13</sup> (2.9°) for CrCp<sub>2</sub> thus seems too large, even when the substantial error bars (1.1°) are taken into account. The  $\angle\text{Cp,H}$  angle for VCp<sub>2</sub> becomes negative, because there are three fewer electrons in the bonding orbitals ( $e_2'$  and  $a_1'$ ), compared with ferrocene. For the  ${}^6A_1'$  MnCp<sub>2</sub> ground state, there are three electrons missing in the bonding orbitals ( $e_2'$  and  $a_1'$ ) and two electrons occupied in the antibonding orbital ( $e_1''$ ). This electronic configuration is quite different from that of ferrocene, and consequently the C–H bonds tilt away from the central Mn atom by 0.76° for the  $D_{5h}$  structure (or 0.84° for  $D_{5d}$ ).

### Concluding Remarks

Density functional studies for the first-row transition-metal metallocenes, MCp<sub>2</sub> (M = V, Cr, Mn, Fe, Co, and Ni), demonstrate that metallocenes slightly favor the  $D_{5h}$  conformations for the free molecules. The present theoretical vibrational analyses confirm that the  $D_{5h}$  conformations for the metallocenes are usually genuine minima and have lower energies than the  $D_{5d}$  conformations. But the  $D_{5d}$  conformations will be accessed because the energy differences between  $D_{5h}$  and  $D_{5d}$  are very small. For MnCp<sub>2</sub>, the  $D_{5h}$  and  $D_{5d}$  conformations are both minima and have almost identical total energies. In the cases of CrCp<sub>2</sub> and CoCp<sub>2</sub>, the  $D_{5h}$  structure distorts to  $C_{2v}$  and the  $D_{5d}$  structure distorts to  $C_{2h}$ , due to the Jahn–Teller effect. Each symmetry ( $C_{2v}$  or  $C_{2h}$ ) has two near-degenerate electronic states, distorted in opposite directions (the  ${}^3B_1$  and  ${}^3A_1$  states for CrCp<sub>2</sub>, and  ${}^2B_2$  and  ${}^2A_2$  for CoCp<sub>2</sub>). The states with  $C_{2v}$  symmetry (derived from  $D_{5h}$ ) lie lower energetically than those with  $C_{2h}$  structures.

In this work we have reported consistent DFT MO energy level diagrams (mostly in the Supporting Information) for the metallocenes. The MO energy level orderings are not necessarily the same as that for ferrocene. Table 10 lists the electron configurations for all the metallocenes. The electron configurations and the MO energy levels are important in discussing the bonding characteristics in the metallocenes, as well as their chemical reactivities. This of course raises the question, “What is known from experiment about the reactivities of metallocenes?” In his 1998 book,<sup>59</sup> Long gives a good review of the properties of metallocenes. The cyclopentadienyl rings in ferrocene are reactive in a manner much like benzene. Ferrocene is known to be relatively stable but reactive toward electrophilic

substitution, Friedel–Crafts acylation, and metalation reactions. Ferrocene is also readily oxidized to ferrocenium. The chemical reactivity of other metallocenes is greater but varies widely across the series and is dominated by the number of valence electrons each compound possesses, due to the absence of the stable 18-electron structure of ferrocene. Vanadocene has a high reactivity, acting like a carbene in some respects. It is very air sensitive in solution and in the solid state. Chromocene is unstable and air sensitive but upon survival undergoes a typical range of reactions. Manganocene possesses significant ionic character and as such is quite reactive toward atmospheric oxygen, and ferrocene is liberated from a reaction of manganocenes with FeCl<sub>2</sub> in THF. Cobaltocene acts as a powerful reducing agent. Electrophilic substitution reactions of cobaltocene lead to oxidation to form cobaltocenium salts, but milder electrophiles such as alkyl halides can lead to the formation of substituted cyclopentadiene complexes. Nickelocene is easily oxidized to the nickelocenium ion. The reactivity of nickelocene generally reflects the tendency of the Ni atom to achieve the 18-electron configuration. As nickelocene is easily oxidized, there is not the extensive aromatic substitution chemistry compared to ferrocene. Although it is not straightforward to compare the reactivity for all the metallocenes quantitatively on the basis of the experimental facts,<sup>59</sup> it is clear that the other five metallocenes are more reactive than ferrocene, the same conclusion drawn from theoretical studies.

We have also reported the harmonic vibrational frequencies for metallocenes. Because there are no complete assignments for these metallocenes except ferrocene, our theoretical assignments should be helpful for future laboratory studies.

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**Supporting Information Available:** Energy level diagrams. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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