

Bis(benzene)chromium Is a δ -Bonded Molecule and Ferrocene Is a π -Bonded Molecule[†]

Víctor M. Rayón and Gernot Frenking*

Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse,
D-35032 Marburg, Germany

Received November 26, 2002

The nature of the metal–ligand bonding in ferrocene and bis(benzene)chromium has been analyzed with the help of an energy partitioning scheme using the results of DFT calculations. The bonding analysis suggests that the Cr–Bz₂ bond is 37.9% electrostatic and 62.1% covalent. The binding interactions in ferrocene are predicted to be 51.1% electrostatic and 48.9% covalent if the charged species Fe²⁺ and (Cp⁻)₂ are used as interacting fragments, while they are 45.0% electrostatic and 55.0% covalent if neutral Fe and Cp₂ in the triplet states are used. The largest contributions to the orbital interactions in bis(benzene)chromium come from the Cr→Bz₂ δ -back-donation, while the most important orbital contribution in ferrocene comes from the Fe←Cp₂ π -donation. The larger contributions of the e_{1g}(π) orbitals in ferrocene are caused by better energy matching rather than better overlapping of the interacting orbitals.

Introduction

This work is our contribution to the 50th anniversary of the first synthesis of ferrocene [Fe(Cp)₂] by Kealy and Pauson in 1951¹ and the commemoration of the first rational synthesis of bis(benzene)chromium [Cr(Bz)₂] developed by Fischer and Hafner in 1955.² The syntheses of both compounds are considered as landmark events in organometallic chemistry which have recently been celebrated by retrospective accounts.^{3,4} The experimental findings set the stage for the development of the chemistry of metallocene⁵ and arene complexes,⁶ which now belong to the most important classes of organometallic compounds.⁷ The new molecules were not only a fruitful topic of experimental studies, but also a challenge to the theory of chemical bonding because the molecules exhibited a new kind of metal–ligand interactions. We do not want to review the early attempts to explain the nature of the chemical bonds in ferrocene and bis(benzene)chromium because this has been done before.^{3,4} The currently accepted bonding model for both compounds uses a molecular orbital correlation diagram where the symmetry-adapted occupied and vacant orbitals of the metal and the ligands

are combined. The covalent interactions are then usually explained in terms of donation and back-donation between the metal and the ligands. This will be discussed in more detail below.

The bonding situation in ferrocene and bis(benzene)chromium has already been analyzed with quantum chemical calculations in earlier theoretical work.^{8,9} The analysis of the orbitals led to the conclusion that the metal–ligand bonding comes mainly from the charge donation between the 3d π and 3d δ AOs of the metal and the π orbitals of the ligand. It was suggested after inspection of the metal population of the occupied orbitals that the Fe–Cp π orbitals in ferrocene are the most important components to the metal–ligand bonding, while in bis(benzene)chromium the δ bonds contribute more significantly than in [Fe(Cp)₂].^{9a,10} It would be helpful if the results of the orbital analysis were checked by a quantitative energy decomposition analysis that also considers electrostatic bonding.

We are currently working on a systematic investigation of different types of chemical bonds between atoms across the periodic system using a rigorously defined energy partitioning analysis of accurate quantum chemical calculations. It is our goal to estimate quantitatively the strength of the covalent and electrostatic bonding and the degree of multiple bonding, i.e., σ -, π -, and δ -bonding.^{11–13} In the course of this work we recently analyzed the metal–ligand interactions in [Fe(Cp)₂] and isostructural and valence isoelectronic heteroanalogues [Fe(E)₂] and [Fe(Cp)(E)] (E = N, P, As, Sb).¹² It was

[†] Theoretical Studies of Organometallic Compounds, Part 48. Part 47: Rayón, V. M.; Frenking, G. *Chem. Eur. J.* **2002**, *8*, 4693.

* Corresponding author.

(1) (a) Kealy, T. J.; Pauson, P. L. *Nature* **1951**, *168*, 1039. (b) Another paper that reported about the synthesis of ferrocene was submitted earlier than ref 1a, but it was published later: Miller, S. A.; Tebboth, J. A.; Tremaine, J. F. *J. Chem. Soc.* **1952**, 633.

(2) Fischer, E. O.; Hafner, W. *Z. Naturforsch.* **1955**, *10b*, 665.

(3) Articles in the special issue celebrating the 50th anniversary of the first synthesis of ferrocene in: *J. Organomet. Chem.* **2001**, 637–639.

(4) (a) Seyferth, D. *Organometallics* **2002**, *21*, 1520. (b) Seyferth, D. *Organometallics* **2002**, *21*, 2800.

(5) Togni, A.; Haltermann, R. L., Eds. *Metallocenes*; Wiley-VCH: New York, 1998.

(6) (a) Davis, R.; Kane-Maguire, L. A. P. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, UK, 1995; Vol. 5, pp 477–549.

(7) Elschenbroich, Ch.; Salzer, A. *Organometallics*, 2nd ed.; VCH: Weinheim, 1992.

(8) (a) Mayor-López, M. J.; Weber, J. *Chem. Phys. Lett.* **1997**, *281*, 226. (b) Pierloot, K.; Persson, B. J.; Roos, B. O. *J. Phys. Chem.* **1995**, *99*, 3465.

(9) (a) King, W. A.; Di Bella, S.; Lanza, G.; Khan, K.; Duncalf, D. J.; Cloke, F. G. N.; Fragala, I. L.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 627. (b) Osborne, J. H.; Trogler, W. C.; Morand, P. D.; Francis, C. G. *Organometallics* **1987**, *6*, 94. (c) Weber, J.; Kundig, P.; Goursot, A.; Penigault, E. *Can J. Chem.* **1985**, *63*, 1734. (d) Weber, J.; Geoffroy, M.; Goursot, A.; Penigault, E. *J. Am. Chem. Soc.* **1978**, *100*, 3995.

(10) Reference 7, p 347.

found that the calculated energy contributions of the different orbital interactions in ferrocene agree nicely with earlier suggestions that were based on MO correlation diagrams.^{12a} We extended this work to bis-(benzene)chromium. The results showed clearly that the dominant orbital interactions in the latter molecule come from orbitals having different (δ) symmetry than in ferrocene, where π orbitals yield the largest contributions to the orbital term. A second interesting result of the present work that has not been presented before is the comparison between the calculated interactions of charged and neutral moieties of ferrocene. The standard bonding model of $[\text{Fe}(\text{Cp})_2]$ considers the orbitals of Fe^{2+} and $(\text{Cp})_2^-$ because it is convenient to discuss the metal–ligand interactions in terms of donation and back-donation between closed-shell fragments. Another reason is that free Cp^- and the Cp ligand in ferrocene both have D_{5h} symmetry, while neutral Cp is subject to Jahn–Teller distortion, which yields two C_{2v} symmetric energy minima that are nearly degenerate.^{12a} The choice of the fragments has a strong influence on the results of the bonding analysis because Cp^- has energetically higher lying orbitals than Cp and the AOs of Fe^{2+} are much lower in energy than those of Fe. Thus, the previous conclusion that the metal–ligand donation is more important than the metal–ligand back-donation may be biased through the choice of the charged fragments. In this work we present for the first time a bonding analysis using neutral Fe and $(\text{Cp})_2$ as interacting fragments.

Methods

The calculations were performed at the nonlocal DFT level of theory using the exchange functional of Becke¹⁴ and the correlation functional of Perdew¹⁵ (BP86). Scalar relativistic effects have been considered using the zero-order regular approximation (ZORA).^{16,17} Uncontracted Slater-type orbitals (STOs) were used as basis functions for the SCF calculations.¹⁸ The basis sets for all atoms have triple- ζ quality augmented with one set of d-type and one set of f-type polarization functions for carbon and one set of p polarization functions for hydrogen. The $(1s2s2p)^{10}$ core electrons of the transition metals and the $1s^2$ core electrons of carbon were treated by the frozen core approximation.¹⁹ An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle.²⁰ All calculated data in this paper have been obtained at the BP86/TZP level of theory. The calculations were carried out with the program package ADF(2000.02).^{21,22}

- (11) (a) Diefenbach, A.; Bickelhaupt, F. M.; Frenking, G. *J. Am. Chem. Soc.* **2000**, *122*, 6449. (b) Uddin, J.; Frenking, G. *J. Am. Chem. Soc.* **2001**, *123*, 1683. (c) Chen, Y.; Frenking, G. *J. Chem. Soc., Dalton Trans.* **2001**, 434. (d) Doerr, M.; Frenking, G. *Z. Allg. Anorg. Chem.* **2002**, *628*, 843. (e) Loschen, C.; Voigt, K.; Frunzke, J.; Diefenbach, A.; Diedenhofen, M.; Frenking, G. *Z. Allg. Anorg. Chem.* **2002**, *628*, 1294. (f) Frenking, G.; Wichmann, K.; Fröhlich, N.; Grobe, J.; Golla, W.; Van, D. L.; Krebs, B.; Läge, M. *Organometallics* **2002**, *21*, 2921. (g) Rayón, V. M.; Frenking, G.; *Chem. Eur. J.* **2002**, *8*, 4693.
- (12) (a) Lein, M.; Frunzke, J.; Timoshkin, A. Y.; Frenking, G. *Chem. Eur. J.* **2001**, *7*, 4155. (b) Frunzke, J.; Lein, M.; Frenking, G. *Organometallics* **2002**, *21*, 3351.
- (13) Frenking, G.; Wichmann, K.; Fröhlich, N.; Loschen, C.; Lein, M.; Frunzke, J.; Rayón, V. M. *Coord. Chem. Rev.* **2003**, *238–239*, 55.
- (14) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
- (15) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.
- (16) Snijders, J. G. *Mol. Phys.* **1978**, *36*, 1789.
- (17) Snijders, J. G.; Ros, P. *Mol. Phys.* **1979**, *38*, 1909.
- (18) Snijders, J. G.; Baerends, E. J.; Vernooijs, P. *At. Nucl. Data Tables* **1982**, *26*, 483.
- (19) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41.

The bonding interactions between the metal and the ligands have been analyzed by means of an energy decomposition scheme that has been suggested by Morokuma²³ and independently by Ziegler.²⁴ The central quantity of the bonding analysis is the instantaneous interaction energy ΔE_{int} between the bonding fragments. It is calculated as the energy difference between the optimized molecule and the fragments with the frozen geometries of the complex. The choice of the fragments and the electron configurations of the metal are given in the discussion of the results. The interaction energy ΔE_{int} can be divided into three main components:

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}} \quad (1)$$

The three terms ΔE_{elstat} , ΔE_{Pauli} , and ΔE_{orb} can be interpreted in a physically meaningful way. ΔE_{elstat} gives the electrostatic interaction energy between the fragments that are calculated with the frozen electron density distribution of A and B in the geometry of the complex AB. The second term in the equation, ΔE_{Pauli} , refers to the repulsive interactions between the fragments that are caused by the fact that two electrons with the same spin cannot occupy the same region in space. The term comprises the four-electron destabilizing interactions between occupied orbitals. ΔE_{Pauli} is calculated by enforcing the Kohn–Sham determinant of AB, which results from superimposing fragments A and B, to obey the Pauli principle by antisymmetrization and renormalization. The stabilizing orbital interaction term, ΔE_{orb} , is calculated in the final step of the ETS analysis when the Kohn–Sham orbitals relax to their optimal form.²⁵ This term can be further partitioned into contributions by the orbitals that belong to different irreducible representations of the interacting system. It is thus possible to estimate the stabilizing contributions that come from orbitals having σ , π , or δ symmetry.

To calculate the bond dissociation energy D_e , it is necessary to add the preparation energy ΔE_{prep} , which is the energy difference of the fragments between the values calculated with the frozen geometry and with the electronic reference state and the electronic ground state at the equilibrium geometry, to the interaction energy ΔE_{int} given in eq 1:

$$\Delta E(= -D_e) = \Delta E_{\text{int}} + \Delta E_{\text{prep}} \quad (2)$$

Results

Figure 1 displays the most important geometrical parameters for bis(benzene)chromium (D_{6h}) and ferrocene (D_{5h} and D_{5d}) that have been calculated at the BP86/TZ2P level of theory. Frequency calculations show that, in agreement with experimental results, the eclipsed (D_{5h}) conformer of ferrocene is an energy minimum, while the staggered (D_{5d}) conformer is a transition state that is, however, only <0.1 kcal/mol

- (20) Krijn, J.; Baerends, E. J. *Fit Functions in the HFS-Method*, Internal Report (in Dutch); Vrije Universiteit Amsterdam: The Netherlands, 1984.

- (21) Bickelhaupt, F. M.; Baerends, E. J. *Rev. Comput. Chem.* **2000**, *15*, 1.

- (22) te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; van Gisbergen, S. J. A.; Fonseca Guerra, C.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931.

- (23) (a) Morokuma, K. *J. Chem. Phys.* **1971**, *55*, 1236. (b) Kitaura, K.; Morokuma, K. *Int. J. Quantum Chem.* **1976**, *10*, 325.

- (24) Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1.

- (25) It has been shown by Davidson²⁶ that the relaxation of the fragment orbitals is partly caused by the field effect of the other fragment in the geometry of the complex. However, to differentiate the field effect (which is an electrostatic effect) from the genuine orbital interactions, one has to consider the basis set superposition error (BSSE). This can be done in several ways,²⁶ which makes the results depend on the BSSE correction. We decided not to differentiate between the field effect and the orbital interaction effect, which both yield the ΔE_{orb} values.

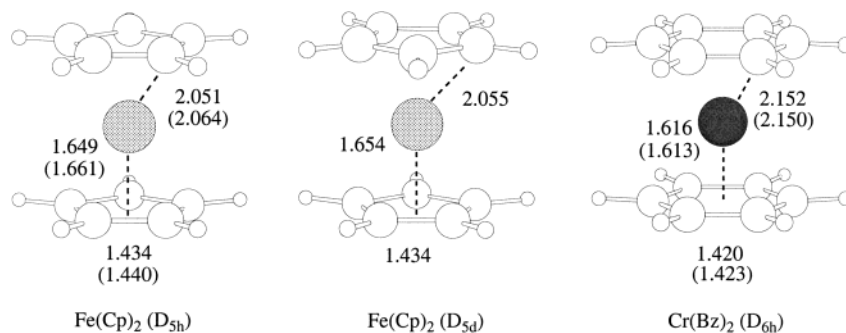


Figure 1. Optimized geometries of $[\text{Fe}(\text{Cp})_2]$ (D_{5h} and D_{5d}) and $[\text{Cr}(\text{Bz})_2]$ (D_{6h}) at BP86/TZ2P. Interatomic distances in Å. Experimental values^{27,28} are given in parentheses.

higher in energy than the D_{5h} form. The calculated Fe–C and C–C distances of the latter structure (2.051 and 1.434 Å) are in very good agreement with the gas phase electron diffraction data (2.064 and 1.440 Å, respectively).²⁷ The eclipsed (D_{6h}) conformation of bis(benzene)chromium is also an energy minimum. The computed Cr–C and C–C distances of $[\text{Cr}(\text{Bz})_2]$ (2.152 and 1.420 Å) are also in excellent agreement with the electron diffraction data (2.150 and 1.423 Å).²⁸ The longer metal–carbon bond distance in $[\text{Cr}(\text{Bz})_2]$ when compared to ferrocene is due to the larger size of the benzene ring and to the larger radius of the chromium atom. Note, however, that the distance from the metal atom to the center of the ligand ring in bis(benzene)chromium is ~ 0.04 Å shorter than in ferrocene.

The central part of this work is the analysis of the bonding situation in bis(benzene)chromium and ferrocene. The metal–ligand interactions in metallocenes and metal arene complexes are usually discussed in terms of qualitative MO correlation diagrams. Figure 2 shows a correlation diagram that gives the relevant orbitals of a d^6 transition metal with the reference electron configuration $(a_{1g})^2(e_{2g})^4(e_{1g})^0$ and a cyclic 12 π -aromatic sandwich ligand. The symmetry assignments of the orbitals are related to the D_{6h} conformation of $[\text{Cr}(\text{Bz})_2]$ and to the D_{5d} form of $[\text{Fe}(\text{Cp})_2]$. Most textbooks discuss the orbital interactions in ferrocene using the D_{5d} form because it is more convenient for comparison with other transition metal complexes.²⁹ We have also chosen to use the D_{5d} form of $[\text{Fe}(\text{Cp})_2]$ because the molecular orbitals have the same symmetry as those of $[\text{Cr}(\text{Bz})_2]$. Note that the a_{1g} and a_{2u} orbitals of the complexes have σ symmetry, the e_{1u} and e_{1g} orbitals have π symmetry, and the e_{2g} and e_{2u} orbitals have δ symmetry. According to the qualitative bonding model shown in Figure 2, the σ and π orbitals describe M–L donation, while the δ orbitals describe M→L back-donation.

The qualitative MO diagram shall now be discussed in the light of the results of the energy decomposition

(26) (a) Davidson, E. R.; Kunze, K. L.; Machado, F. B. C.; Chakravorty, S. J. *Acc. Chem. Res.* **1993**, *26*, 628. (b) Kunze, K. L.; Davidson, E. R. *J. Phys. Chem.* **1992**, *96*, 2129. (c) Machado, F. B. C.; Davidson, E. R. *J. Phys. Chem.* **1993**, *97*, 4397.

(27) (a) Haaland, A.; Nilsson, J. E. *Acta Chem. Scand.* **1968**, *22*, 2653. (b) Haaland, A. *Acc. Chem. Res.* **1979**, *12*, 415.

(28) Haaland, A. *Acta Chem. Scand.* **1965**, *19*, 41.

(29) See e.g.: (a) ref 7, p 320. (b) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; p 393. (c) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley: New York, 1999; p 686.

analysis of bis(benzene)chromium and ferrocene, which are given in Table 1. The first column gives the results for $[\text{Cr}(\text{Bz})_2]$ that were calculated using Cr atom with the valence electron configuration $(a_{1g})^2(e_{2g})^4(e_{1g})^0$ and $(\text{Bz})_2$ as fragments. The occupied valence orbitals of Cr are d_{z^2} , d_{xy} , and $d_{x^2-y^2}$. The calculations predict that the interaction energy between the excited chromium atom and the $(\text{Bz})_2$ ligand is $\Delta E_{\text{int}} = -268.5$ kcal/mol. The largest component of the interaction energy is the attractive orbital term $\Delta E_{\text{orb}} = -377.2$ kcal/mol. The electrostatic attraction $\Delta E_{\text{elstat}} = -230.5$ kcal/mol is clearly weaker than the covalent attraction. The energy partitioning analysis suggests that the metal–ligand bonding in bis(benzene)chromium is 62.1% covalent and 37.9% electrostatic. The largest contribution to the covalent interactions comes from the e_{2g} (δ) orbitals, which give 73.4%. Thus, the energy partitioning analysis shows that bis(benzene)chromium is a δ -bonded molecule.

The energy partitioning analysis of ferrocene has been carried out using two different fragmentation patterns. First we used the fragments that are isoelectronic with the fragments of $[\text{Cr}(\text{Bz})_2]$, i.e., Fe^{2+} with the valence electron configuration $(a_{1g})^2(e_{2g})^4(e_{1g})^0$ and $(\text{Cp}^-)_2$. Table 1 shows that the interaction energy of the charged fragments is much larger ($\Delta E_{\text{int}} = -893.9$ kcal/mol) than for bis(benzene)chromium. The largest contribution comes from the electrostatic term ($\Delta E_{\text{elstat}} = -599.9$ kcal/mol), but the covalent attraction is only slightly weaker ($\Delta E_{\text{orb}} = -573.9$ kcal/mol). Thus, the calculations indicate that the strength of the covalent bonding in ferrocene (48.9%) is nearly as high as the electrostatic bonding (51.1%). The large value for ΔE_{orb} can be explained with the energetically low-lying acceptor orbitals of Fe^{2+} , which strengthens the M–L donation. The calculated values for the orbitals with different symmetry show that the contributions of the M–L donor interactions (σ and π orbitals) are indeed stronger in $[\text{Fe}(\text{Cp})_2]$ than in $[\text{Cr}(\text{Bz})_2]$, while the M→L back-donation (δ orbitals) is weaker. The largest contribution to the covalent bonding in ferrocene comes from the e_{1g} (π) orbitals, which give 64.7% of ΔE_{orb} (Table 1).

The analysis of the bonding situation in ferrocene may be biased toward M–L donor interactions because of the choice of charged fragments Fe^{2+} and $(\text{Cp}^-)_2$. Therefore, we carried out a second energy partitioning analysis of $[\text{Fe}(\text{Cp})_2]$ using neutral Fe and Cp_2 as interacting fragments. We solved the problem of occupying the degenerate e_{1g} orbitals with only two electrons by choosing the triplet states of Fe, which has

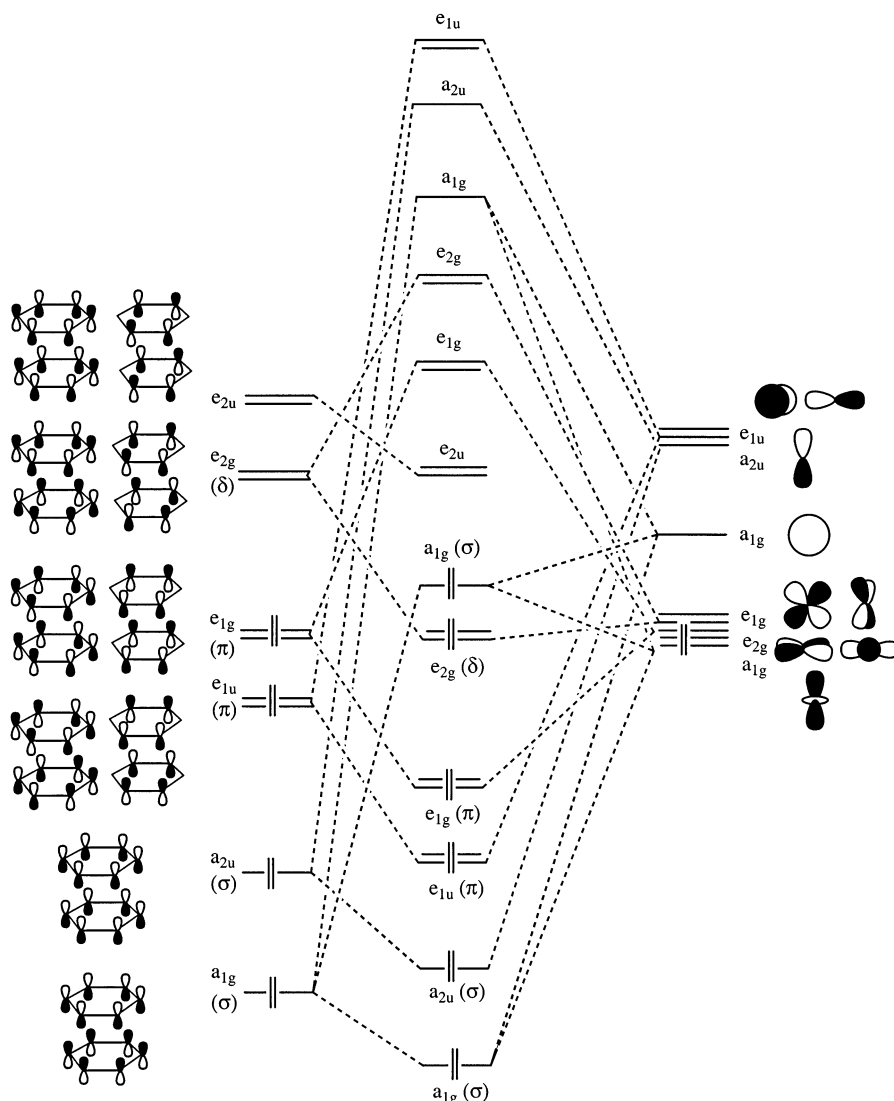


Figure 2. Qualitative orbital correlation diagram between a d^6 transition metal with the electron configuration $(a_{1g})^2(e_{2g})^4(e_{1g})^0$ and a cyclic 12 π -aromatic sandwich ligand. The shapes of the ligand orbitals have been taken from the B_{2v} ligand. The orbitals of the Cp_2 ligands look very similar. They are shown, for example, in reference ref 7, p 319. Note that the drawing of the energy levels is only qualitative.

a valence electron configuration $(a_{1g})^2(e_{2g})^4(e_{1g})^{\alpha\alpha}$, and Cp_2 , which has a the valence occupation $(a_{1g})^2(a_{2u})^2(e_{1u})^4(e_{1g})^{\beta\beta}$. Table 1 shows that the interaction energy ($\Delta E_{int} = -274.2$ kcal/mol) is much less than when the charged fragments are used. However, the *relative* contributions of ΔE_{elstat} and ΔE_{orb} are very similar in both analyses. The calculations show that the $Fe-(Cp)_2$ bonding between neutral Fe and Cp_2 is 45.0% electrostatic and 55.0% covalent. The breakdown of the latter term into orbitals having different symmetry indicates that the $e_{1g}(\pi)$ orbitals contribute 61.4% of ΔE_{orb} , which is not much less than the value of 64.7% that was calculated when charged fragments are used (Table 1). The contribution of the δ -bonding orbitals are larger when neutral fragments are used (29.7%) than in the case of charged fragments (8.3%), but the main conclusion remains that the covalent bonding in ferrocene comes mainly from π orbitals.

Please note that the calculated bond dissociation energies D_0 of $[Cr(Bz)_2]$ and $[Fe(Cp)_2]$ given in Table 1 are in good to reasonable agreement with the experimental values.

Table 1. Energy Decomposition Analysis of $[Cr(Bz)_2]$ and $[Fe(Cp)_2]$ at BP86/TZP (in kcal/mol; experimental values in square brackets)

term (D_{6h} , D_{5d})	$[Cr(Bz)_2]$ Cr $[d_{z^2}, d_{xy}, d_{x^2-y^2}]^6$	$[Fe(Cp)_2]$ Fe $^{2+}[d_{z^2}, d_{xy}, d_{x^2-y^2}]^6$	$[Fe(Cp)_2]$ ${}^3Fe[d_{z^2}, d_{xy}, d_{x^2-y^2}]^6[d_{xz}, d_{yz}]^{\alpha\alpha}$
ΔE_{int}	-268.5	-893.9	-274.2
ΔE_{pauli}	339.2	279.9	409.6
ΔE_{elstat}	-230.5 (37.9%)	-599.9 (51.1%)	-307.5 (45.0%)
ΔE_{orb}	-377.2 (62.1%)	-573.9 (48.9%)	-376.3 (55.0%)
$A_{1g}(\sigma)$	-35.4 (9.4%)	-48.6 (8.5%)	-24.6 (6.4%)
A_{2g}	0.0	0.0	0.0
B_{1g}	-0.1 (<1%)	<i>a</i>	<i>a</i>
B_{2g}	-0.2 (<1%)	<i>a</i>	<i>a</i>
$E_{1g}(\pi)$	-55.6 (14.7%)	-371.2 (64.7%)	-231.2 (61.4%)
$E_{2g}(\delta)$	-277.0 (73.4%)	-47.8 (8.3%)	-111.9 (29.7%)
A_{1u}	0.0	0.0	0.0
$A_{2u}(\sigma)$	-2.9 (<1%)	-28.3 (4.9%)	-2.9 (<1%)
B_{1u}	-0.2 (<1%)	<i>a</i>	<i>a</i>
B_{2u}	-0.1 (<1%)	<i>a</i>	<i>a</i>
$E_{1u}(\pi)$	-3.8 (<1%)	-61.5 (10.7%)	-4.8 (1.3%)
$E_{2u}(\delta)$	-1.8 (<1%)	-16.6 (2.9%)	-1.0 (<1%)
ΔE_{prep}	205.2	709.9	90.2
$\Delta E^{\ddagger} (= -D_e)$	-63.3	-184.0	-184.0
$-D_0$	-61.4 [-65.5] ^b	-175.9 [-158] ^b	-175.9 [-158] ^b

^a There is no representation of this symmetry in the point group D_{5d} . ^b Ref 32.

We analyzed the calculated data of the EDA in order to understand the reason the most important orbitals for ligand–metal bonding in ferrocene are the π orbitals, while in bis(benzene)chromium the dominant bonding contributions come from the δ orbitals. In the previous theoretical study by King et al.^{9a} it was reported that there is substantial M–L back-donation in $[M(\text{Bz})_2]$ ($M = \text{Ti, Zr, Hf, Cr, Mo, W}$) through the δ orbitals, which was estimated from the ligand atom contributions to the highest occupied $4e_{2g}$ orbital. In contrast, the $M \leftarrow L$ π donation via the $4e_{1g}$ and $5e_{1u}$ orbitals given by the metal population was much less. The results are supported by the EDA calculations, which suggest that only the $4e_{1g}$ orbitals are important. Inspection of the size of the overlap and the mixing coefficients of the highest lying fragment $e_{2g}(\delta)$ and $e_{1g}(\pi)$ orbitals of the metals and the ligands show that it is not the size of the overlap but the energy levels of the fragment MOs that mainly determine the strength of the interactions.³⁰ The $e_{2g}(\delta)$ orbital of $[\text{Cr}(\text{Bz})_2]$ has a slightly larger overlap integral (0.299) of the fragment orbitals than the $e_{1g}(\pi)$ orbital ($S = 0.240$), but the former orbital has a much larger mixing between the highest lying occupied orbital of Cr and the lowest lying vacant orbital of Bz_2 (55:42).^{31,32} The overlap integrals of the $e_{2g}(\delta)$ and $e_{1g}(\pi)$ fragment orbitals in ferrocene are nearly the same (0.161 and

0.167 for the charged fragments, 0.243 and 0.248 for the neutral fragments). However, the mixing of the e_{1g} fragment orbitals of the metal and ligand is much stronger (56:31 using neutral fragments and 55:30 using charged fragments) than that of the e_{2g} orbitals (80:15 using neutral fragments and 79:15 using charged fragments).

Summary

The energy partitioning analysis of the metal–ligand interactions in bis(benzene)chromium and ferrocene suggests that the bond in the former molecule is 37.9% electrostatic and 62.1% covalent. The binding interactions in the latter molecule are predicted to be 51.1% electrostatic and 48.9% covalent if the charged species Fe^{2+} and $(\text{Cp}^-)_2$ are used as interacting fragments, while they are 45.0% electrostatic and 55.0% covalent if neutral Fe and Cp_2 in the triplet states are used. The largest contributions to the orbital interactions in bis(benzene)chromium come from the $\text{Cr} \rightarrow \text{Bz}_2$ δ -back-donation, while the most important orbital contribution in ferrocene comes from the $\text{Fe} \leftarrow \text{Cp}_2$ π -donation. The larger contributions of the $e_{1g}(\pi)$ orbitals in ferrocene are caused by better energy matching rather than better overlapping of the interacting orbitals.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie. V.M.R. thanks the Secretaría de Estado de Educación y Universidades (MECD-Spain) for support via grant EX-01-09396368V. We thank Dr. Nikolaus Fröhlich for excellent support of the PC-Cluster 'Hückel'. Helpful service by the Hochschulrechenzentrum of the Philipps-Universität Marburg is gratefully acknowledged. Additional computer time was provided by the HHLR Darmstadt.

OM020968Z

(30) The lowest lying vacant $e_{2g}(\delta)$ acceptor orbital of the ligand Bz_2 is clearly lower in energy (-1.6 eV) than the $e_{2g}(\delta)$ acceptor orbital of the ligand Cp_2 ($+0.2$ eV), while the occupied $e_{2g}(\delta)$ donor AOs of Cr ($+0.8$ eV) and Fe ($+0.7$ eV) are energetically close together. A direct comparison of the energy levels of the $e_{1g}(\pi)$ fragment orbitals of $[\text{Cr}(\text{Bz})_2]$ and $[\text{Fe}(\text{Cp})_2]$ is hampered by the fact that, in the latter case, either the fragments are charged or both fragments have two electrons in the orbitals with the occupation $(e_{1g})^{\alpha\alpha}$ and $(e_{1g})^{\beta\beta}$.

(31) The remaining small contributions that then lead to 100% come from energetically lower lying occupied and higher lying unoccupied fragment orbitals.

(32) (a) FeCp_2 : Ryan, M. F.; Eyler, J. R.; Richardson, D. E. *J. Am. Chem. Soc.* **1992**, *114*, 8611. (b) CrBz_2 : Li, Y.; Baer, T. *J. Phys. Chem. A* **2002**, *106*, 9820.