

given elsewhere,^{26,28} and here we will concentrate on the results obtained.

Some of the results of the calculations for $\ln K$ are shown in Figure 4, from which the following principal features are apparent. (1) The effect of including the triple-body dispersion term is to raise the calculated values of K relative to the values obtained for this quantity using only two-body forces. (2) The relative influence of the three-body term on K increases in the order (He in Ar) < (Ne in Ar) < (Kr in Ar). The effect is so pronounced in the system Kr in Ar that it is unlikely that "effective" pair potentials (which are contaminated by nonadditive effects) could ever properly account for the thermodynamics of this or of any system with a large solute:solvent size ratio. (3) Inclusion of the three-body nonadditive term results in excellent agreement with experimental data in those systems for which data are available. For the system Ne in Ar, where inclusion of this term significantly alters the calculated values of K , the agreement with experiment is improved relative to what is obtained by assuming pairwise additivity. Similar conclusions are drawn by examining the effect of nonadditivity on the functions ΔH_s° and \bar{V}_2° .²⁶

What Next?

The next major challenge would seem to be the calculation, from a rigorous molecular basis, of solubilities and related functions in complex chemical systems, i.e., those in which anisotropic forces such as anisotropic overlap and dispersion forces, multipolar forces, and charge-transfer forces play a significant role. For example, a rigorous molecular interpretation of the solubility and the temperature and pressure derivatives of the

(28) J. K. Lee, D. Henderson, and J. A. Barker, *Mol. Phys.*, **29**, 429 (1975).

solubility of benzene in water is still not feasible. The barriers to such a calculation are of two types. First, the relevant, full angle-dependent intermolecular potentials are not available for complex polyatomic molecules. A considerably less severe, but still significant, restriction is the absence of a statistical-mechanical formalism capable of accommodating dense fluids wherein the intermolecular interactions are strongly anisotropic. There have been a number of attempts made recently to deal with this problem,²⁹⁻³³ the most promising of which is, in the opinion of the author, one due to Gray and Gubbins,³¹⁻³³ who use perturbation theory to express the free energy of an anisotropic fluid as an expansion around that of an isotropic (e.g., Lennard-Jones) reference state. These authors have applied their theory to investigate the role of anisotropic forces in phase separations and related phenomena. While the theory is in principle applicable to molecules with any degree of anisotropy, difficulties are encountered in the evaluation of the higher order terms in the expansion, which become increasingly important as the anisotropy becomes large. For example, a molecule such as benzene, which is moderately anisotropic in its shape, or water, which manifests strong multipolar anisotropy (i.e., hydrogen bonding), can only just barely, if at all, be accommodated by this theory. More highly anisotropic molecules cannot. It seems likely that improvements in this theory, which would increase the range of its applicability, will be developed in the near future.

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(30) L. R. Pratt and D. Chandler, *J. Chem. Phys.*, **67**, 3683 (1977).

(31) M. Flytzani-Stephanopoulos, K. E. Gubbins, and C. G. Gray, *Mol. Phys.*, **30**, 1649 (1975).

(32) C. G. Gray, K. E. Gubbins, and C. H. Twu, *J. Chem. Phys.*, **69**, 182 (1978).

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Molecular Structure and Bonding in the 3d Metallocenes

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The accidental and independent discovery of dicyclopentadienyliron, now better known as ferrocene, was reported by two research groups in 1951 and 1952.¹ This was the first pure hydrocarbon derivative of iron to be prepared, and its exceptional stability caused considerable excitement. Ferrocene is not only unaffected by air, moisture, and heat up to 470 °C, it can be boiled in concentrated hydrochloric acid or 10% caustic soda without decomposition. Even somebody

who had not completed his secondary education at the time can feel some of this excitement when reading the literature. Within months the then novel but now well-known sandwich model had been proposed by Wilkinson, Rosenblum, Whiting, and Woodward^{2a} in the United States and independently by Fischer and Pfab^{2b} in Germany, and confirmed by X-ray crystallography.³ During the following years the dicyclo-

(1) (a) T. J. Kealy and P. L. Pauson, *Nature (London)*, **168**, 1039 (1951); (b) S. A. Miller, J. A. Tebboth, and J. F. Tremaine, *J. Chem. Soc.*, 632 (1952).

(2) (a) G. Wilkinson, M. Rosenblum, M. C. Whiting, and R. B. Woodward, *J. Am. Chem. Soc.*, **74**, 2125 (1952); (b) E. O. Fischer and W. Pfab, *Z. Naturforsch. B*, **7**, 377 (1952).

(3) (a) P. F. Eiland and R. Pepinsky, *J. Am. Chem. Soc.*, **74**, 4971 (1952); (b) J. D. Dunitz and L. E. Orgel, *Nature (London)*, **177**, 121 (1953).

Arne Haaland received his Ph.D. with W. H. Eberhardt at Georgia Institute of Technology in 1962. Upon his return to Norway he joined the electron-diffraction group under the leadership of Otto Bastiansen at the University of Oslo, where he is now senior lecturer. His research interest centers on structure and bonding in organometallic compounds. He has been active in Amnesty International and spent the years 1975-1977 as visiting professor at the University of Dar es Salaam, Tanzania.

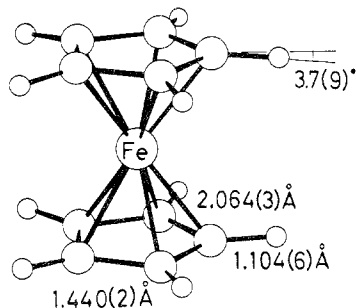


Figure 1. Molecular model of ferrocene.⁶

pentadienyl derivatives, Cp_2M , of the other metals in the first transition series from V to Ni were synthesized along with hundreds of cyclopentadienyl and arene complexes of the metallic elements, often by two or more groups simultaneously.⁴ In 1973 the two foremost workers in the field, E. O. Fischer and G. Wilkinson, were awarded the Nobel Prize in chemistry for their contributions.

Molecular Structure of Ferrocene

The main features of the structure of ferrocene were established through a three-dimensional X-ray analysis by Dunitz, Orgel, and Rich published in 1956.⁵ Electron density maps clearly showed the presence of cyclopentadienyl rings of approximate fivefold symmetry, lying one on top of the other with the iron atom in the middle. The C-C and Fe-C bond distances were about 1.40 and 2.05 Å, respectively. The iron atoms were lying at crystallographic symmetry centers, which—barring disorder—implies that the ligand rings are staggered. Since a staggered equilibrium conformation can be easily rationalized as the result of repulsion between C atoms in opposite rings, it came to be generally accepted. The hydrogen atoms could not be located in the X-ray study. But it seemed reasonable to expect the C-H bonds to be bent out of the plane of the C_5 ring away from the metal atom, as indicated, for instance, on the cover of the third edition of Pauling's book, "Nature of the Chemical Bond".

This was certainly the model of the ferrocene molecule that we expected to confirm when we initiated a gas-phase electron-diffraction (ED) investigation in 1964.⁶ The object of that study was primarily to obtain accurate values for the Fe-C and C-C bond distances for comparison with other metallocenes. This we obtained as indicated in Figure 1, but the investigation also gave two unexpected results: The equilibrium conformation in the gas phase was found to be eclipsed (D_{5h}) rather than staggered (D_{5d}), and the C-H bonds were bent about 5° out of the plane toward the metal atom. Subsequent refinement of a dynamic model^{6b} yielded a barrier to internal rotation of the Cp rings, $V_5 = 0.9(3) \text{ kcal mol}^{-1}$, and correction for thermal motion^{6c} ("shrinkage") reduced the angle between the C-H bonds and the ring plane to $\angle\text{C}_5\text{CH} = 3.7(9)^\circ$.

The barrier to internal rotation of the Cp rings is thus only about one-third of the rotational barrier in ethane. The equilibrium conformation of ferrocene is eclipsed, but an instantaneous picture of gaseous ferrocene would show a large number of molecules in staggered as well as intermediate conformations. If the dihedral angle ϕ is defined as zero when the rings are eclipsed, $\phi = 36^\circ$ corresponds to a staggered model. The number of gas-phase molecules with dihedral angle between ϕ and $\phi + d\phi$ is proportional to $\exp(-V(\phi)/RT)$ when $V(\phi)$ defines the shape of the restricting potential.^{6b} At 50°C the number of molecules in or near the eclipsed conformation is only four times the number of molecules in or near the staggered conformation.

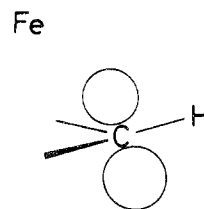
Over the years considerable evidence has accumulated that crystalline ferrocene is in fact disordered at room temperature. In particular, measurements of the heat capacity revealed a λ -point transition at 164 K which has been associated with the onset of rotational disorder of the Cp rings.⁷ The structure of crystalline ferrocene below the transition point has been the subject of a very careful X-ray investigation by Seiler and Dunitz.⁸ The unit cell is triclinic. If a centrosymmetric space group is assumed, the asymmetric unit consists of two molecules which show virtual D_5 symmetry and dihedral angles $\phi = 9^\circ$, that is, much closer to the eclipsed than to the staggered conformation. It seems reasonable to assume that the deviation from D_{5h} symmetry is due to packing forces. If $V(\phi)$ is assumed to vary in the simple way

$$V(\phi) = \frac{1}{2}V_5(1 - \cos 5\phi)$$

the observed distortion from D_{5h} symmetry requires about $0.1 \text{ kcal mol}^{-1}$, a small amount when compared with the heat of sublimation.

Very recent neutron and X-ray investigations of crystalline ferrocene at room temperature confirm that the ligand rings are disordered.⁹ Hence the conclusion that the molecules are staggered is no longer valid. The observed electron and nuclear scattering distributions may be interpreted by assuming that the crystal contains D_5 molecules with $\phi = 10^\circ$ in two different orientations randomly distributed throughout the crystal, but this interpretation is not unique.

The neutron diffraction data confirm that the H atoms have moved out of the C_5 plane and toward the metal atom, though the angle $\angle\text{C}_5\text{CH} = 1.6(4)^\circ$ is smaller than that obtained by gas-phase electron diffraction.^{9b} The deformation has been rationalized as a hybridization effect: the trigonal hybridization of the C atoms in the Cp^- ion is slightly modified to provide (approximate) $p\pi$ orbitals that are pointing more in the direction of the metal atom:¹⁰



(4) (a) E. O. Fischer and H. P. Fritz, *Adv. Inorg. Chem. Radiochem.*, **1**, 55 (1959); (b) G. Wilkinson and F. A. Cotton, *Prog. Inorg. Chem.*, **1**, 1 (1959).

(5) J. D. Dunitz, L. E. Orgel, and A. Rich, *Acta Crystallogr.*, **9**, 373 (1956).

(6) (a) R. K. Bohn and A. Haaland, *J. Organomet. Chem.*, **5**, 470 (1966); (b) A. Haaland and J. E. Nilsson, *Acta Chem. Scand.*, **22**, 2653 (1968); (c) A. Haaland, J. Lusztyk, D. P. Novak, J. Brunvoll, and K. B. Starowieyski, *J. Chem. Soc., Chem. Commun.*, 54 (1974).

(7) J. W. Edwards, G. L. Kington, and R. Mason, *Trans. Faraday Soc.*, **55**, 660 (1959).

(8) P. Seiler and J. D. Dunitz, *Acta Crystallogr., Sect. B*, **35**, 2020 (1979).

(9) (a) P. Seiler and J. D. Dunitz, *Acta Crystallogr., Sect. B*, **35**, 1068 (1979); (b) F. Takusagawa and T. F. Koetzle, *ibid.*, **35**, 1074 (1979).

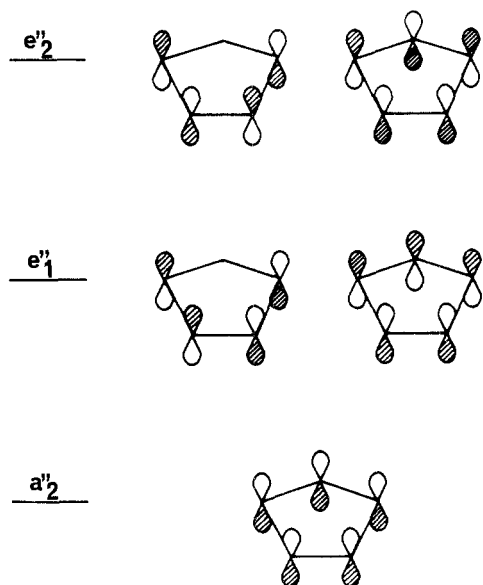


Figure 2. π molecular orbitals of the anion $(C_5H_5)^-$, symmetry D_{5h} . Reproduced with permission from ref 12c. Copyright 1975, North-Holland Publishing Co.

The M–C and C–C bond distances in decamethylferrocene, $(C_5Me_5)_2Fe$, obtained by ED or X-ray diffraction are indistinguishable from those of ferrocene.¹¹ However, the equilibrium conformation of gaseous $(C_5Me_5)_2Fe$ is staggered, D_{5d} , with a restricting barrier of $V_5 = 1.0$ (3) kcal mol⁻¹. Thus introduction of the ten methyl groups increases the energy of the eclipsed conformation relative to the staggered by about 2 kcal mol⁻¹. Moreover, the C(Cp)–C(Me) bonds are bent 3.4 (5)° out of the plane of the C_5 ring *away* from the metal atom. Both differences may be rationalized as the result of steric repulsion between Me groups.

Electronic Structure and Bonding

When first proposing the sandwich model for ferrocene, Wilkinson and co-workers noted that “the number of electrons available . . . for iron to carbon binding, is eighteen (five π electrons for each cyclopentadienyl unit, plus the eight electrons on the iron atom). Thus the effective atomic number of the central iron atom is thirty six (krypton structure)”.^{2a} Fischer and Pfab wrote: “Das zentrale Fe(II)-Ion bildet mit je 3 π -Elektronenpaaren der beiden parallel gegenüberstehenden, aromatischen Cyclopentadien-Anionen 6 oktaedrisch gerichtete, koordinative Kovalenzen und erreicht hierdurch Kryptonkonfiguration”.^{2b}

Rohmer and Veillard and their co-workers have carried out a series of *ab initio* LCAO–MO–SCF calculations on the ground and excited states of both ferrocene and the ferricenium ion, Cp_2Fe^+ , and correlated their results with a large amount of experimental information.¹² In the following we shall draw on their results and also on more recent calculations with a larger basis set.¹³

(10) M. Elian, M. M. L. Chen, M. P. Mingos, and R. Hoffmann, *Inorg. Chem.*, **15**, 1148 (1976).

(11) (a) A. Almendinger, A. Haaland, S. Samdal, J. Brunvoll, J. L. Robbins, and J. C. Smart, *J. Organomet. Chem.*, **173**, 293 (1979); (b) D. P. Freyberg, J. L. Robbins, K. N. Raymond, and J. C. Smart, *J. Am. Chem. Soc.*, **101**, 892 (1979).

(12) (a) M.-M. Coutiere, J. Demuyne, and A. Veillard, *Theor. Chim. Acta*, **27**, 281 (1972); (b) M.-M. Rohmer, A. Veillard, and M. H. Wood, *Chem. Phys. Lett.*, **29**, 466 (1974); (c) M.-M. Rohmer and A. Veillard, *Chem. Phys.*, **11**, 349 (1975).

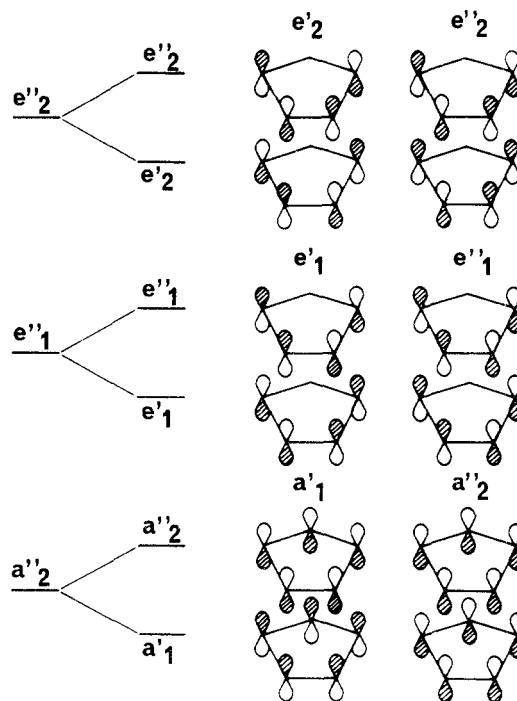


Figure 3. π symmetry orbitals for the $(C_5H_5)_2^{2-}$ ligand framework. Symmetry D_{5h} . Only one of each pair of degenerate orbitals is shown. Reproduced with permission from ref 12c. Copyright 1975, North-Holland Publishing Co.

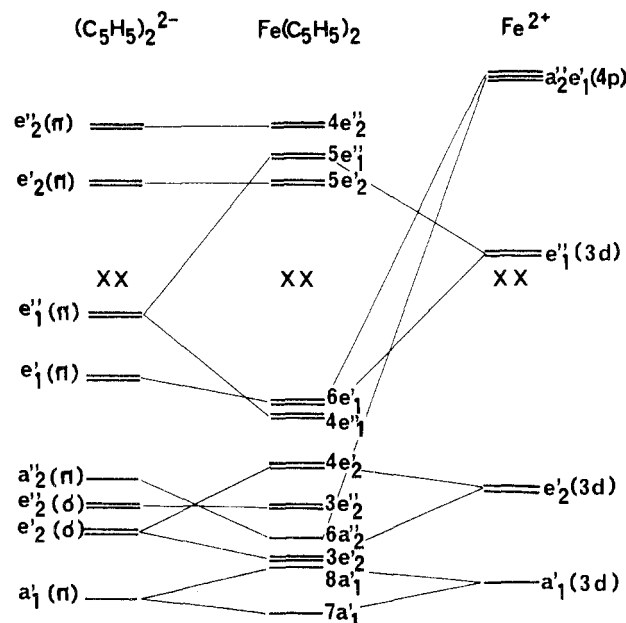


Figure 4. Orbital energies of the highest occupied and lowest virtual orbitals obtained by SCF calculations on the $(C_5H_5)_2^{2-}$ framework (left) and the $Fe(C_5H_5)_2$ molecule (center). (The zero points of the two diagrams do not coincide^{12c}.) Right: A schematic representation of the 3d and 4p orbital energies of the Fe^{2+} ion in the field of the ligand rings. The orbitals in each species are filled to the height indicated by XX.

It is instructive to begin the discussion by considering the five π molecular orbitals of the Cp^- ion (with D_{5h} symmetry) shown in Figure 2. The interaction between the two Cp groups in the Cp_2^{2-} ligand framework splits

(13) (a) P. S. Bagus, U. I. Wahlgren, and J. Almlöf, *J. Chem. Phys.*, **64**, 2324 (1976). (b) See also comments in J. H. Ammeter, H.-B. Bürgi, J. C. Thibault, and R. Hoffmann, *J. Am. Chem. Soc.*, **100**, 3686 (1978). (c) For a discussion in terms of ligand field theory see K. D. Warren, *Struct. Bonding*, **27**, 45 (1976).

Table I
Electron Configuration, Electron Imbalance, Average M-C Bond Distance, and Effective M-C Root Mean Square Vibrational Amplitudes (l) in the 3d Metallocenes^a

compound	electron configuration	electron imbalance	$R(M-C)$, Å	$l(M-C)$, Å	method
(C ₅ H ₅) ₂ Fe	¹ A ₁ '(a ₁ ' ² , e ₂ ' ⁴)	0	2.064 (3)	0.062 (1)	ED ⁶
(C ₅ H ₅) ₂ Co	² E ₁ '(a ₁ ' ² , e ₂ ' ⁴ , e ₁ ' ¹)	1	2.119 (3)	0.082 (1)	ED ²⁰
(C ₅ H ₅) ₂ Cr	³ E ₂ '(a ₁ ' ¹ , e ₂ ' ³)	2	2.169 (4)	0.078 (2)	ED ²⁴
(C ₅ H ₅) ₂ Ni	³ A ₂ '(a ₁ ' ² , e ₂ ' ⁴ , e ₁ ' ²)	2	2.196 (4)	0.084 (3)	ED ¹⁸
(C ₅ H ₅) ₂ V	⁴ A ₂ '(a ₁ ' ¹ , e ₂ ' ²)	3	2.280 (5)	0.058 (10)	ED ²⁴
(C ₅ H ₅) ₂ Mn	⁶ A ₁ '(a ₁ ' ¹ , e ₂ ' ² , e ₁ ' ²)	5	2.380 (6)	0.131 (6)	ED ²⁶
(C ₅ H ₄ Me) ₂ Mn	² E ₂ '(a ₁ ' ² , e ₂ ' ³)	1	2.144 (12)	0.160 (16)	ED ²⁷
(C ₅ H ₄ Me) ₂ Mn	⁶ A ₁ '	5	2.433 (8)	0.111 (8)	ED ²⁷
(C ₅ Me ₅) ₂ Fe	¹ A ₁ '	0	2.064 (3)	0.066 (2)	ED ^{11a}
(C ₅ Me ₅) ₂ Fe	¹ A ₁ '	0	2.050 (2)	-	X ^{11b}
(C ₅ Me ₅) ₂ Co	² E ₁ '	1	2.105 (2) ^b	-	X ²³
(C ₅ Me ₅) ₂ Mn	² E ₂ '	1	2.112 (2) ^b	-	X ^{11b}
[(C ₅ Me ₅) ₂ Co] ⁺	¹ A ₁ '	0	2.050 (2)	-	X ²³
[(C ₅ Me ₅) ₂ Fe] ⁺	² E ₂ '	1	2.097 (2) ^b	-	X ²³

^a Estimated standard deviations in parentheses in units of the last digit. ^b In these Jahn-Teller active species the estimated standard deviation of the mean M-C distance is given as the average esd of individual M-C distances.

each of these levels into two levels corresponding to the symmetric and antisymmetric combinations. (The words symmetric and antisymmetric refer to the horizontal symmetry plane of D_{5h}) (see Figure 3). The orbital energies of the highest occupied and lowest unoccupied (virtual) orbitals obtained by calculations on the Cp₂²⁻ framework are indicated in the diagram in Figure 4. It may be noted that the highest σ levels and the lowest π levels have similar energy. A schematic representation of the atomic orbitals of the Fe²⁺ ion in the field of the ligand rings is shown at the right hand side of Figure 4, and the orbital energies obtained by calculations on the ferrocene molecule¹² are displayed at the center.¹⁴ From the figure it is clear that the metal-ligand bonding is due mainly to the stabilization of the e₁' π orbitals of the ligands through combination with the e₁' metal atom d orbitals (3d_{xz} and 3d_{yz} when the z axis coincides with the fivefold symmetry axis). But there also appears to be a significant stabilization of the a₂' and e₁' ligand π orbitals through interactions with the appropriate 4p orbitals of the metal.

The orbital energies obtained by SCF calculations on a molecule may often serve as a guide to the energy required for electronic excitation or ionization. Thus, according to Koopman's theorem the ionization potential is equal to minus the orbital energy of the level from which the electron is removed:

$$IP = -\epsilon_j$$

The energy level diagram in Figure 4 then indicates that the first two bands in the photoelectron spectrum should be assigned to the processes where the electron is removed from the 6e₁' or the 4e₁' level. However, Prins has shown that the ground electronic state of the ferricinium ion, Cp₂Fe⁺, is ²E₂'¹⁵ and the first band in the photoelectron spectrum must consequently be assigned to the process where the electron is removed from the 4e₂' orbital. Similarly the second band in the PE spectrum has been assigned to the process when the electron is removed from the 8a₁' orbital, even though

calculations on Cp₂Fe yield higher energies for six other occupied orbitals.^{16a}

The apparent contradiction has been removed by Veillard and co-workers¹² who have pointed out that Koopman's theorem is derived under the assumption that all orbitals remain unaltered ("frozen") during the ionization process and that this condition is not satisfied in the case of ferrocene. When SCF calculations are carried out on the ion in the states obtained by removing electrons from the 4e₂' and 8a₁' orbitals, the electron distribution is found to be very different from that calculated under a frozen orbital assumption. The 4e₂' and 8a₁' orbitals of ferrocene are nearly pure metal 3d orbitals and removal of an electron with frozen orbitals would increase the formal charge on Fe by about +0.80 e in both cases. SCF calculations on the ionic species, however, show that the formal charge increases only by about 0.25 in either case. This redistribution of charge in the ion ("relaxation") is accompanied by an energy gain of 6 to 7 eV, and the ionization potential is reduced accordingly. When IP's are calculated according to

$$IP = E_{SCF}(\text{ion}) - E_{SCF}(\text{molecule})$$

the agreement with experiment is satisfactory. When electrons are removed from predominantly ligand orbitals, the relaxation energy is less than 1 eV, and Koopman's theorem remains valid as a first approximation.

The lowest frequency peaks in the electronic spectrum of ferrocene have been assigned to the transitions 8a₁' → 5e₁' and 4e₂' → 5e₁'', though 5e₁' is only the second lowest virtual orbital for FeCp₂ in the ground state.¹⁷ Again SCF calculations on several possible excited configurations indicate that ³E₁' is the lowest excited state. Calculations also indicate that the ground state of the anion, Cp₂Fe⁻, is ²E₁'.

If the "highest occupied molecular orbitals" of ferrocene are defined as those from which electrons are most easily removed, then all experimental evidence points to the 4e₂' and 8a₁' orbitals. Similarly, if the

(14) Following the advice of two referees we describe the symmetry of electronic states and individual molecular orbitals by the use of the irreducible representations of the D_{5h} point group, though the representations of the group D_{5d} have been in common use.

(15) R. Prins, *Mol. Phys.*, **19**, 603 (1970).

(16) (a) S. Evans, M. L. H. Green, B. Jewitt, A. F. Orchard, and C. F. Pygall, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1847 (1972); (b) S. Evans, M. L. H. Green, B. Jewitt, G. H. King, and A. F. Orchard, *ibid.*, **70**, 356 (1974).

(17) Y. S. Sohn, D. N. Hendrickson, and H. B. Gray, *J. Am. Chem. Soc.*, **93**, 3603 (1971).

"lowest unoccupied orbital" is defined as the one into which electrons are most easily accepted, all experimental evidence points to the $5e_1''$. (In the following we shall refer to these orbitals simply as e_2' , a_1' , and e_1'' .)

It is gratifying that the ground-state configurations of the other metallocenes from Cp_2V to Cp_2Ni can be obtained from the electronic configuration of Cp_2Fe by adding the required number of electrons to the e_1'' orbital or removing the required number from the e_2' or a_1' orbitals¹⁶ (see Table I).

Cobaltocene and Nickelocene. The ground-state electron configuration of Cp_2Co , $^2E_1''$, can be obtained from the configuration of ferrocene by adding one electron to the e_1'' orbital, and the ground state of Cp_2Ni , $^3A_2'$, by adding two electrons to the e_1'' orbital. The molecular structure of the latter compound in the gas phase has been determined by Hedberg and Hedberg.¹⁸ They found that the M-C bond distance was 0.13 Å longer and the M-C root mean square vibrational amplitude 0.02 Å larger than in ferrocene (see Table I). Since the atomic size is expected to decrease when going from Fe to Ni, the increase in these two parameters demonstrates that metal-ligand bonding is considerably weaker in Cp_2Ni . This weakening is easily rationalized as the result of the introduction of two electrons into the e_1'' molecular orbital, which is the antibonding combination of the e_1'' ligand π orbitals and the $3d_{xz}$ and $3d_{yz}$ orbitals of the metal.

The gas-phase electron-diffraction data were equally compatible with models with eclipsed and staggered rings, and refinement of D_{5h} and D_{5d} models led to larger values for the inter-ring vibrational amplitudes than in Cp_2Fe . Clearly the barrier to internal rotation of the ligand rings is lower than in ferrocene, not an unexpected result in view of the weaker M-Cp bonding and greater Cp-Cp distance. No significant deviation from planarity of the Cp ligands could be detected.

It may be noted that the C-C bond distance in Cp_2Ni as well as all the other Cp_2M compounds discussed below is 0.01 Å shorter than in ferrocene. The difference is small, but statistically significant.

The M-C bond distance in cobaltocene, which has only one electron in the antibonding e_1'' orbital, is intermediate between the bond distances in Cp_2Fe and Cp_2Ni . This compound, which contains one unpaired electron in a doubly degenerate molecular orbital, is expected to suffer Jahn-Teller distortion. A glance at Figure 2 or 3 suggests that the presence of one electron in the e_1'' orbital should lead to unequal amounts of CC π bonding around the rings. Indeed, calculations by Ammeter and co-workers suggest that the equilibrium geometry of Cp_2Co is one in which short and long CC bonds alternate around the rings, the deviations from the average value being about 0.03 Å.¹⁹ This difference is less than the root mean square vibrational amplitudes of the C-C bonds in Cp_2Fe and Cp_2Ni , $l = 0.046$ (1) and 0.044 (1₅) Å, respectively. The Jahn-Teller distortion is therefore dynamic: Individual bonds alternate between vibrations around shorter than average and longer than average positions as the unpaired electron alternates between the two e_1'' orbitals. In such a case refinement of a symmetrical D_{5h} model still leads to

satisfactory agreement between experimental and calculated ED data, but the dynamic Jahn-Teller effect manifests itself in larger-than-usual vibrational amplitudes. In fact two independent ED studies of Cp_2Co ²⁰ yielded C-C vibrational amplitudes, $l(C-C) = 0.055$ (1) and 0.056 (1₅) Å, that are significantly larger than in ferrocene or nickelocene and larger than calculated for Jahn-Teller inactive Cp_2Co from a molecular force field.^{20b}

The best fit to the ED data was obtained with a model of D_{5h} equilibrium ED symmetry, but a model with staggered rings could not be ruled out. The angle between the C_5 plane and the C-H bonds, $\angle C_5CH = 2.1$ (8)°, may be smaller than in ferrocene, but is significantly greater than zero at the 2% confidence level.

Cobalticinium and Ferricinium. The effect of removing the electron from the antibonding e_1'' orbital in Cp_2Co is demonstrated by the results of an X-ray diffraction investigation of $[(\eta-C_5H_5)(\eta-C_5H_4COOH)Co]PF_6$.^{21a} The mean Co-C bond distance in the carboxycobalticinium ion is 2.029 (9) Å, about 0.06 Å shorter than obtained for Cp_2Co ^{21b} by X-ray diffraction and similar to the M-C bond distance in ferrocene.

Removal of an electron from ferrocene has the opposite effect: the perpendicular Cp-Cp distances in four ferricinium salts studied by X-ray diffraction²² average 3.40 Å, about 0.06 Å longer than in neutral ferrocene derivatives studied by the same method. A recent very accurate X-ray study of $[(C_5Me_5)_2Fe]PF_6$ ²³ yielded an average M-C bond distance of 2.097 (2) Å, about 0.05 Å longer than in $(C_5Me_5)_2Fe$ studied by the same method and the same group.^{11b} Thus removal of an electron from the e_2'' orbital of ferrocene leads to an increase of the Fe-Cp distance, suggesting that the strength of the M-Cp bond has been reduced. This weakening may be due to the removal of the e_2'' electron per se or to the concurrent electronic rearrangement (relaxation). In any case the effect is the same, and we describe the e_2'' as a bonding orbital.

Chromocene, Vanadocene, and Manganocene. The ground-state electron configuration of Cp_2Cr , $^3E_2'$, can be obtained from that of ferrocene by removing one electron from the e_2' and one electron from the a_1' orbital.^{16b} The average M-C bond distance determined by ED is about 0.11 Å longer than in ferrocene.²⁴ A part of this increase is undoubtedly due to the increase in atomic size with decreasing nuclear charge. The magnitude of the size effect cannot be estimated by comparing the octahedral crystal radii of the M(II) ions, since these radii are themselves derived from observations on crystals where the energy level diagram is similar to that of the metallocenes with three stable t_{2g} and two unstable e_g orbitals. The size effect is best estimated by comparing the octahedral ionic radii of Ca(II)

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Table II
Symmetric (ν_4) and Antisymmetric (ν_{11}) M-Cp Stretching Modes of the 3d Metallocenes, M-Cp Force Constants, and Average Dissociation Energies

	n	$R(\text{M-C}),$ Å	$\nu_4, \nu_{11},^{29}$ cm^{-1}	$F_{\text{M-Cp}},$ mdyn Å^{-1}	$\overline{D}(\text{M-Cp}),^{31}$ kcal mol^{-1}	$\overline{D}_{\text{ion}}^-(\text{M}^{2+}\text{-Cp}^-),$ kcal mol^{-1}
$(\text{C}_5\text{H}_5)_2\text{Fe}$	0	2.06	303, 478	3.08	73	352
$(\text{C}_5\text{H}_5)_2\text{Co}$	1	2.12	-, 355	-	65	334
$(\text{C}_5\text{H}_5)_2\text{Cr}$	2	2.17	273, 408	2.34	68	318
$(\text{C}_5\text{H}_5)_2\text{Ni}$	2	2.20	255, 420	2.30	60	315
$(\text{C}_5\text{H}_5)_2\text{V}$	3	2.28	258, 380	2.05	88	292
$(\text{C}_5\text{H}_5)_2\text{Mn}$	5	2.38	212, -	<1.72	51	275

(3d⁰), high-spin Mn(II) (3d⁵), and Zn(II) (3d¹⁰), 1.00, 0.83, and 0.74 Å, respectively.²⁵ The average decrease in ionic radius from one element to the next is thus 0.025 Å, with the decrease being more rapid at the beginning of the series. We therefore estimate the size difference between Cr(II) (3d⁴) and Fe(II) (3d⁶) to be 0.05 Å or less. The rest of the observed elongation of the M-C bonds when going from Cp₂Fe to Cp₂Cr, about 0.06 Å or more, we attribute to the loss of bonding electrons.

The ground-state electron configuration of Cp₂V, ⁴A₂' can be obtained from that of ferrocene by removing two electrons from the e₂' and one electron from the a₁' orbital.^{16b} The M-C bond distance determined by ED is 2.28 Å, or 0.22 Å longer than in ferrocene,²⁴ and again we attribute the greater part of the elongation to the loss of bonding electrons.

We have therefore defined the "electron imbalance" of these metallocenes as the number of electrons in the antibonding e₁' orbital plus the number of vacancies in the bonding a₁' and e₂' levels.²⁴ In all the neutral metallocenes and ions discussed above the M-C bond distance increases monotonically with increasing electron imbalance. See Table I for a resumé. Though the agreement to some extent is fortuitous, it is also gratifying that the two complexes with electron imbalance $n = 2$, Cp₂Cr and Cp₂Ni, have very similar M-C bond distances.

In the gas phase at room temperature and above, manganocene, Cp₂Mn, is predominantly if not exclusively in the high-spin configuration ⁶A₁' (a₁'', e₂'², e₁'²).^{16b} The electron imbalance is thus $n = 5$, and the M-C bond distance determined by ED is larger than in any of the other metallocenes, about 0.32 Å longer than in ferrocene.²⁶ The weakness of Mn-Cp bonding is also demonstrated by the large M-C vibrational amplitude, $l = 0.131$ (6) Å, or twice as large as in ferrocene!

1,1'-Dimethylmanganocene and Decamethylmanganocene. In 1972 and 1974 Evans et al. published two articles on the He(I) PE spectra on the 3d metallocenes.¹⁶ The electron configurations listed in Table I have been taken from this work. Moreover Evans et al. noted that the PE spectrum of 1,1'-dimethylmanganocene, (C₅H₄Me)₂Mn, was much more complex than that of manganocene itself and suggested an interpretation in terms of a mixture of approximately equal amounts of high-spin (⁶A₁') and low-spin (²E₂', analogous to Cp₂Fe⁺) species.

Low-spin (C₅H₄Me)₂Mn would have an electron imbalance $n = 1$, equal to that of Cp₂Co, and would

therefore be expected to have an Mn-C bond distance of about 2.12 Å. It therefore seemed possible to determine the structure of both species simultaneously by gas-phase ED, and we immediately turned to Dr. M. L. H. Green at Oxford, asking for a sample. The study revealed that under the experimental conditions (nozzle temperature of about 100 °C) the gas consisted of two geometrically distinct species;²⁷ the most abundant with mole fraction $x = 0.62$ (4) had a Mn-C bond distance of 2.433 (8) Å, similar to, though significantly larger than, that of manganocene itself. The less abundant species had a bond distance of about 2.14 Å, close to the value expected for a low-spin manganocene.

In the meantime the presence of a high-spin/low-spin equilibrium had been confirmed by other workers.²⁸ The mole fractions in the gas phase are quite similar to the mole fractions of high- and low-spin species in toluene at 98 °C,^{28a} so the assignment of the $R(\text{M-C}) = 2.43$ Å species as high spin and the $R(\text{M-C}) = 2.14$ Å species as low spin appears quite secure. More recently an X-ray study of decamethylmanganocene,^{11b} which appears to be exclusively low spin, yielded an average Mn-C distance of 2.112 (2) Å, very similar to that of low spin (C₅H₄Me)₂Mn, particularly when it is recalled that correction for thermal motion would increase the X-ray value.

Finally it may be noted that the large Mn-C vibrational amplitude in low-spin (C₅H₄Me)₂Mn, $l = 0.160$ (16) Å, is in agreement with the existence of a dynamic Jahn-Teller effect involving the asymmetric ring-tilting mode as suggested by Ammeter and co-workers.¹⁹ This Jahn-Teller effect appears to be partly frozen out in crystalline (C₅Me₅)₂Mn.

M-Cp Force Constants. Lokshin, Aleksanyan, and co-workers²⁹ have assigned the symmetric and asymmetric M-Cp stretching modes (ν_4 and ν_{11}) of several metallocenes. Using a three-body model in which each Cp ring is approximated by a point mass equal to 65.10 amu, we have calculated the diagonal M-Cp stretch force constant, F_{MCP} , and the interaction force constants, F_{MCPM} , for M = Fe, Cr, Ni, and V.³⁰ The diagonal force constant of Cp₂Mn was calculated from

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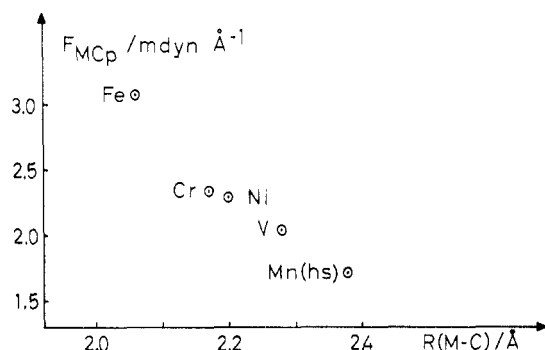


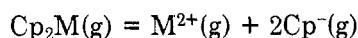
Figure 5. Diagonal M-Cp force constant of the 3d metallocenes as a function of the M-C bond distance.

ν_4 (observed for the melt) under the assumption that the interaction force constant is zero. The value obtained is thus an upper limit. For Cp_2Co no calculation is possible, since ν_4 has not been assigned. The force constants are listed in Table II, and in Figure 5 we plot the diagonal M-Cp stretching force constant as a function of the M-C bond distance. As expected, the force constant decreases monotonically as the bond distance—or electron imbalance—increases.

M-Cp Dissociation Energies. Tel'noi, Rabinovich, and co-workers³¹ have measured the heat of combustion of the 3d metallocenes and calculated the mean M-Cp dissociation energies as one-half the enthalpy of the reaction



The dissociation energies obtained are listed in Table II. It is seen that the dissociation energies only to a moderate degree reflect the variations in M-Cp bond strength as indicated in the discussion above. In particular Cp_2V has a higher dissociation energy than any of the other complexes. Using the data of the Russian workers we have calculated the mean ionic dissociation energies, $\bar{D}_{\text{ion}}(\text{M}^{2+} - \text{Cp}^-)$, as one-half the enthalpy of the reaction



with M^{2+} in the lowest state with the same number of unpaired electrons as the complex. The conversion requires knowledge of the electron affinity of the Cp ring (42.4 kcal mol⁻¹³²), the first and second IP of the metal atom, and the excess energy required to excite the M^{2+} ion to the lowest state with correct spin multiplicity.³³

Figure 6 shows a plot of \bar{D}_{ion} as a function of the M-C bond distance, and the ionic dissociation energies are seen to decrease monotonically with the bond distance.

"Covalent" and "Ionic" Metallocenes

Because of its high kinetic and thermodynamic stability, ferrocene has been commonly regarded as a "covalent" compound, while manganocene with its low stability and five unpaired electrons—reminiscent of the Mn^{2+} ion—has been considered "ionic". The other metallocenes have sometimes been arranged in sequence

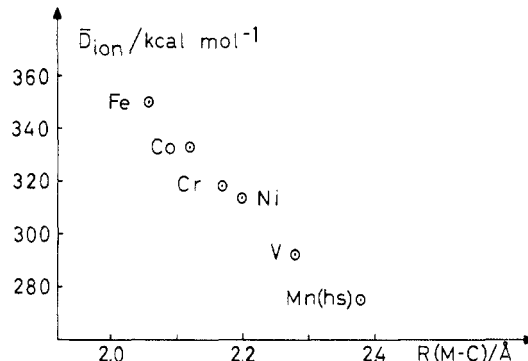


Figure 6. Mean ionic dissociation energy, $\bar{D}_{\text{ion}}(\text{M}^{2+} - \text{Cp}^-)$, of the 3d metallocenes as a function of the M-C bond distance.

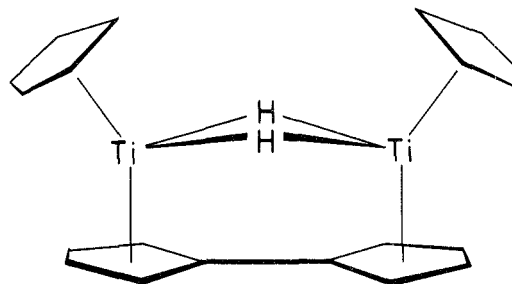
between these two extremes in order of "increasing ionic character", mostly on the basis of parameters reflecting the strength of the metal to ligand bond.

In fact very little is known about the charge distribution in these compounds. The C 1s core binding energies of the metallocenes from Cp_2V to Cp_2Ni obtained by high-energy PE spectroscopy indicate that in all these complexes the ligands carry negative—and the metal atom consequently positive—charge.³⁴ But significant differences in the core binding energies, reflecting differences in the ligand charge between the complexes, could not be found.

The concept "atomic charge" is itself not easy to define clearly. The formal charges obtained through Mulliken population analysis of wave functions obtained by ab initio molecular orbital calculations cannot be accepted at face value, since electron density which is actually in the ligand region may be assigned to the metal and vice versa. It may be noted, however, that the formal charges on Fe obtained in the two published SCF calculations on ferrocene,^{12,13a} +1.23 and +1.38, respectively, indicate that the charge separation is far from negligible.

There is, of course, no a priori reason to assume that there is a simple relationship between the strength of the M-Cp bond—as reflected in M-C bond distances, force constants or dissociation energies—and the magnitude of the charge separation.

Concluding Remarks. All attempts to prepare Cp_2Ti has led to the formation of the "titanocene dimer", $\text{Cp}_2\text{Ti}_2(\mu\text{-H})_2(\text{C}_5\text{H}_4\text{C}_5\text{H}_4)$, which has the structure³⁵



But decamethyltitanocene has been prepared and is moderately stable.³⁶ The compound has two unpaired electrons and must therefore be assigned one of the

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Table III
Metalloocene Ions of the First Row Transition Elements^a

d ²	d ³	d ⁴	d ⁵	d ⁶	d ⁷	d ⁸	d ⁹
V ⁺	Cr ⁺	V ⁻	Fe ⁺	Ni ²⁺	Ni ⁺	Co ⁻	Ni ⁻
		Mn ⁺	Cr ⁻	Co ⁺			
				Mn ⁻			

^a From ref 37. M⁺ and M⁻ stand for Cp₂M⁺ and Cp₂M⁻, respectively.

configurations a₁^{'1}, e₂^{'1}, or e₂^{'2}. In either case it has an electron imbalance of $n = 4$, and we predict an M-C bond distance of about 2.33 Å.

CaCp₂ has a polymeric structure with bridging cyclopentadienyl rings in the solid phase;³⁷ the gas-phase or solid-state structure of a monomeric Cp₂Ca derivative would show whether the simple relationship between M-C bond distance and electron imbalance extends to a 3d⁰ ($n = 6$) metalloocene. No neutral 3d⁹ metalloocene is known, but the structural characterization of the 3d¹⁰ ($n = 4$) compound Cp₂Zn would again be of interest.

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Turning to ionic derivatives, consultation of Table III shows that although 12 3d metalloocene ions are known,³⁸ only two, Cp₂Fe⁺ and Cp₂Co⁺, have had their structures determined.

Finally we wish to point out the fascinating possibility that one might be able to prepare some manganocene derivative for which an intermediate spin state (a₁^{'2}, e₂^{'2}, e₁^{'1}, or a₁^{'1}, e₂^{'3}, e₁^{'1}) is the most stable or for which an intermediate spin state is the most stable at a given Mn-C distance. Since the electron imbalance of an intermediate spin species would be $n = 3$, this bond distance should be in the neighborhood of 2.28 Å.

I am grateful for the help received from many able co-workers, whose names are found in the references, and to the Norwegian Research Council for Science and the Humanities for financial support. Finally I wish to express my gratitude to Drs. John Ammeter, V. T. Aleksanyan, J. D. Dunitz, T. F. Koetzle, and J. L. Robbins for their willingness to share the results of unpublished work, and to Dr. Jan Almlöf for helpful discussions.

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