0.09 G. Values for the spin polarization parameter with this coupling constant are $Q_\gamma = -0.87$ G with $\rho_\alpha = -0.103$; $Q_\gamma = -1.1$ G with $\rho_\alpha = -0.082$. The coupling of the γ hydrogens in radicals **3** and **4** is larger because of a contribution from a direct interaction with spin on the phenoxy ring. Compound **6** appears to be in a twisted conformation in which the γ protons are in close proximity to the aromatic ring. The nitrogen splitting from this radical is about a factor of 4.5 smaller than that observed from the other radicals, indicating a decrease in the spin density at the α carbon. The splitting from the γ protons of this compound is probably dominated by a direct interaction with spin at the *para* position of the phenoxy ring.

Lines from the ϵ protons of compounds **3** and **4** were not observed. Small negative couplings were observed from this position in the cyclic compounds. Contributions from spin polarization and from a direct interaction would have opposite signs for these protons. If the interactions are of a comparable magnitude, they would tend to cancel one another. In the case of the cyclic compounds, the geometry of the rings prohibits a direct interaction and these splittings are observable.

Conclusions

The nmr and esr spectra of a series of alkyl-substituted phenoxy radicals have been taken. Different interactions appear to be important in determining the coupling constants of the various aliphatic protons. The splitting constants of β protons seem to be dominated by a hyperconjugative mechanism. Both spin polarization and direct interaction appear to contribute to the longer range couplings.

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Electron Delocalization in Paramagnetic Metallocenes. II. Extended Huckel Molecular Orbital Calculations[1a,b]

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Abstract: Self-consistent charge extended Hückel molecular orbital calculations were carried out for vanadocene, methylvanadocene, cobaltocene, methylcobaltocene, nickelocene, and methylnickelocene. For these calculations, Basch, Gray, Viste VOIP's were used for the H_{ii}'s and the Wolfsberg–Helmholz approximation was used for the H_{ij}'s. The overlap matrices were computed using Clementi's SCF atomic functions. The molecular orbital calculation gives a generally good account of the experimental facts for the metallocenes, in particular the nmr contact shifts. It was found that the primary unpaired electron delocalization mechanism for vanadocene and chromocene involves σ MO's. This is in agreement with our earlier experimental conclusions. In cobaltocene and nickelocene, unpaired electron delocalization is dominated by the π contribution, but the σ effects are quite large. In all cases the magnitudes and signs of the coupling constants are well reproduced.

In the first paper of this series[3] the experimental results pertaining to the nmr contact shifts of the paramagnetic metallocenes were presented. It was suggested that the unpaired spin delocalization mainly involves cyclopentadiene σ orbitals in the vanadium and chromium metallocenes (by σ orbitals we mean the in-plane orbitals of the cyclopentadiene rings, it being recognized that there is no strict σ separation in this case). It was further argued that π delocalization probably is most important for cobalt and nickel metallocenes. In order to further clarify the experimental facts, we have carried out extended Hückel molecular orbital calculations for these metallocenes. The extended Hückel method was chosen because of the possibility of including all the valence orbitals of both the metal and the ligands.

Self-consistent field type molecular orbital calculations have been reported for various metallocenes by Shustorovich and Dyatkina[4-6] and Dahl and Ballhausen.[7] Unfortunately, all these calculations included only the cyclopentadienyl p_z orbitals and are therefore unsuitable for discussions of electron–proton hyperfine interaction constants.

The extended Hückel method has enjoyed considerable success in the treatment of various transition metal complexes. Cotton and coworkers have carried out extended Hückel calculations for $PtCl_4^{2-}$,[8] $ReCl_6^{2-}$, $OsCl_6^{2-}$, $IrCl_6^{2-}$, and $PtCl_6^{2-}$,[9] $Re_2Cl_8^{2-}$,[10] and bis(β-ketoenolate) complexes of Cu(II) and Ni(II).[11] It is

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(1) (a) Abstracted from the Ph.D. Thesis of M. F. Rettig, University of Illinois, 1967; (b) presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Paper M-42.

(2) National Science Foundation Predoctoral Fellow, 1963–1967.

(3) M. F. Rettig and R. S. Drago, *J. Am. Chem. Soc.*, **91**, 1361 (1969).

(4) E. M. Shustorovich and M. E. Dyatkina, *Zh. Strukt. Khim.*, **1**, 109 (1960).

(5) E. M. Shustorovich and M. E. Dyatkina, *Dokl. Akad. Nauk SSSR*, **131**, 113 (1960).

(6) E. M. Shustorovich and M. E. Dyatkina, *ibid.*, **133**, 141 (1960).

(7) J. P. Dahl and C. J. Ballhausen, *Kgl. Danske Videnskab. Selskab., Mat-Fys. Medd.*, **33** (5) (1961).

(8) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **6**, 369 (1967).

(9) F. A. Cotton and C. B. Harris, *ibid.*, **6**, 376 (1967).

(10) F. A. Cotton and C. B. Harris, *ibid.*, **6**, 924 (1967).

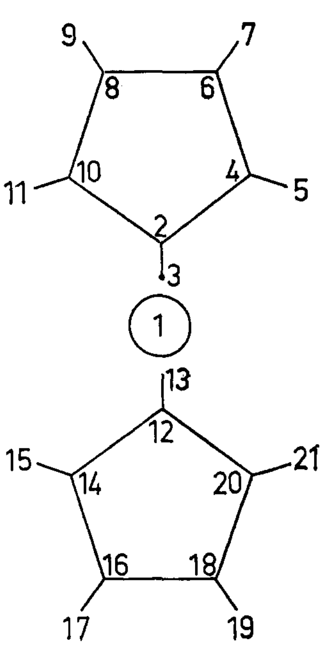

Figure 1. Numbering system for atoms in the metallocenes.

noteworthy that the degree of metal–ligand covalency (determined experimentally by chlorine nuclear quadrupole resonance) was in general well reproduced. In a series of papers, Gouterman and coworkers have used the extended Hückel method in calculations for metal-porphyrin complexes.[12–16] These workers were primarily interested in applying the extended Hückel method to calculation of uv and visible spectral parameters of the porphyrin complexes.

Extended Hückel calculations have also been very successful in the calculation of hyperfine coupling constants for various σ and π organic free radicals.[17] All these considerations suggested that the extended Hückel method would be useful in understanding the electron–proton coupling constants in the paramagnetic metallocenes. After this work had been completed, Schachtschneider, Prins, and Ros[18] reported results of extended Hückel calculations for vanadocene, ferrocene, and nickelocene. These workers did not, however, attempt calculations of electron–proton hyperfine coupling constants, nor did they carry out calculations for methyl-substituted metallocenes.

Experimental Section

Calculations. All calculations described below were carried out on the University of Illinois IBM 7094.

1. **Overlap Integrals.** In most cases the overlap matrix[19] was calculated using the multiexponential Slater-type basis sets of either Clementi[20a] or Richardson and coworkers.[20b,c] A single exponent of 1.20 was used for the hydrogen 1s orbital. Details for specific cases will be given below.

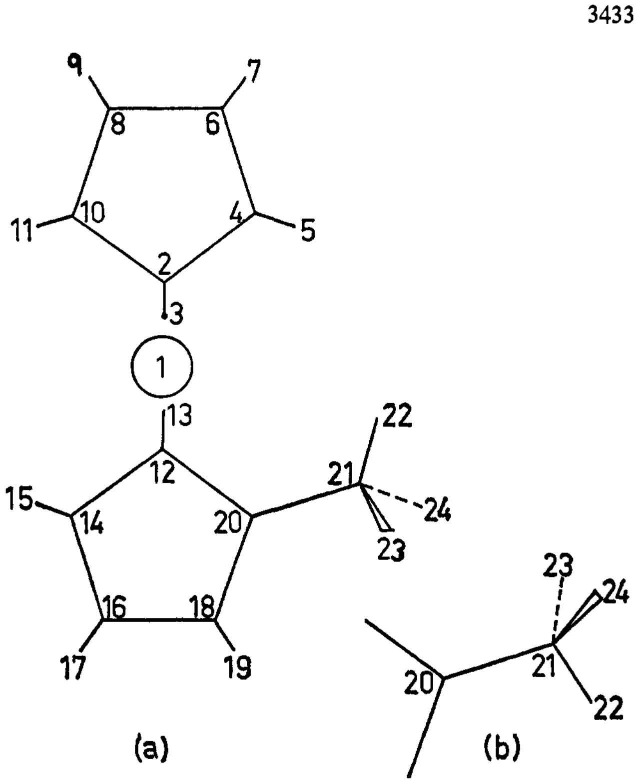

Figure 2. Numbering and substituent orientation in substituted metallocenes.

2. **Atomic Orbital Energies, H_{ii}'s.** The diagonal Hamiltonian matrix elements were determined according to the methods of Basch, Viste, and Gray.[21,22] The Basch, Viste, Gray expressions[21] were used for all the atoms. In this method of charge adjustment of H_{ii}, the metal 3d, 4s, and 4p energies are expressed as functions of charge and orbital occupations. The orbital occupations and atomic charges in this work were determined by a standard Mulliken population analysis.[23]

3. **H_{ij}'s.** The off-diagonal Hamiltonian matrix elements were calculated using the Wolfsberg–Helmholz approximation,[24] with K fixed at 1.75 (eq 1).

$$H_{ij} = KS_{ij}(H_{ii} + H_{jj})/2 \text{ with } K = 1.75 \qquad (1)$$

Calculations for vanadocene using the Cusachs' approximation[25] for H_{ij} (eq 1 with $K = (2 - |S_{ij}'|)$, where S_{ij}' is calculated in a local relative coordinate system) showed no appreciable differences from the Wolfsberg–Helmholz approximation.

4. **Molecular Geometry.** In all cases (both cyclopentadienide and monomethylcyclopentadienide) the atom coordinates of the cyclopentadienyl groups were taken or estimated from the recent electron diffraction study of ferrocene.[26] The following distances were used for coordinated $C_5H_5^-$: C–C, 1.429 Å; C–H, 1.116 Å. For methylcyclopentadienide, the ring carbon to methyl carbon distance was taken to be 1.52 Å, and the methyl carbon to hydrogen distance was 1.091 Å. Regular geometry was assumed throughout (rings strictly pentagonal, methyl groups with strictly tetrahedral angles). Figures 1 and 2 show the arrangement and numbering of

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(11) F. A. Cotton, C. B. Harris, and J. J. Wise, *Inorg. Chem.*, **6**, 909 (1967).

(12) M. Zerner and M. Gouterman, *Theoret. Chim. Acta*, **8**, 26 (1967).

(13) M. Zerner, M. Gouterman, and H. Kobayashi, *ibid.*, **6**, 363 (1966).

(14) M. Zerner and M. Gouterman, *Inorg. Chem.*, **5** 1699 (1966).

(15) M. Zerner and M. Gouterman, *ibid.*, **5**, 1707 (1966).

(16) M. Zerner and M. Gouterman, *Theoret. Chim. Acta*, **4**, 44 (1966).

(17) (a) R. S. Drago and H. Petersen, Jr., *J. Am. Chem. Soc.*, **89**, 3978, 5744 (1967); (b) R. E. Cramer and R. S. Drago, *ibid.*, **90**, 4790 (1968).

(18) J. H. Schachtschneider, R. Prins, and P. Ros, *Inorg. Chim. Acta*, **1**, 462 (1967).

(19) We are indebted to Dr. Steven Zumdahl, who wrote the multiexponential overlap program.

(20) (a) E. Clementi, "Tables of Atomic Functions," IBM Corp., 1965; (b) J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962); (c) J. W. Richardson, R. R. Powell, and W. C. Nieuwpoort, *ibid.*, **38**, 796 (1963).

(21) H. Basch, A. Viste, and H. B. Gray, *Theoret. Chim. Acta*, **3**, 32 (1965).

(22) H. Basch, A. Viste, and H. Gray, *J. Chem. Phys.*, **44**, 10 (1965).

(23) R. S. Mulliken, *ibid.*, **23**, 1833 (1955).

(24) M. Wolfsberg and L. Helmholz, *ibid.*, **20**, 837 (1952).

(25) L. C. Cusachs and B. B. Cusachs, *J. Phys. Chem.*, **71**, 1061 (1967).

(26) R. K. Bohn and A. Haaland, *J. Organometal. Chem.*, **5**, 470 (1966).

atoms in the unsubstituted and methyl-substituted metallocenes. Limitations on computer storage forced us to carry out calculations on the monomethylmetallocenes as model compounds for the 1,1′-dimethylmetallocenes. The metal-to-ring distances were estimated from the interpolated results of Weiss and Fischer.[27] These distances are (metal–ring): vanadocene, 1.957 Å; cobaltocene, 1.75 Å; nickelocene, 1.834 Å. Substitution of a methyl group was assumed to have no effect on the metal–ring distance.

5. **Molecular Orbital Program and Calculations.** (a) The molecular orbital calculations were done using an extensively modified version of the original Hoffmann molecular orbital program.[28] In general, the overlap matrix was computed separately and was read into the MO program as data. After each iteration, the computed atom charges and orbital populations were weighted with the input charges and populations, and the Basch, Viste, Gray expressions were used to compute the new H_{ii}'s, using the weighted parameters. This procedure was repeated until the input and output charge of each atom agreed to within less than 0.03 unit.

(b) **Vanadocene.** The vanadium atomic orbitals were the multiexponential V^0 functions of Richardson, *et al.*[20b,c] The carbon AO's were Clementi's "double-ζ" functions.[20a] Calculations including and not including vanadium 4p orbitals were carried out.

(c) **Vanadocene (Single Exponentials).** In an attempt to find a more efficient method of carrying out the MO calculations, single exponential Slater-type functions were sought which accurately reproduced the overlap integrals obtained from the multiexponential functions of (b). Vanadium 4p orbitals were not included in this calculation. The exponents were derived first for a C═C—H fragment with the C═C—H distances the same as in vanadocene. Overlap matrices for the C═C—H fragment were generated for a range of carbon 2s and 2p exponents, keeping the hydrogen 1s exponent fixed at 1.20. The "best-fit" exponents were determined by comparison of the derived overlap matrix elements with those obtained from the multiexponential functions, element by element. Once carbon exponents had been derived, a V–C fragment was investigated. Here the derived carbon exponents were held fixed while the vanadium 3d and 4s exponents were varied. Thus was derived a set of single exponential functions which "best-fit" the overlap matrix elements from the multiexponential functions. In general, corresponding overlap matrix elements agreed within ±5%. The derived exponents are: C, 2s (1.65); C, 2p (1.44); V, 3d (1.70); V, 4s (1.35). These single exponentials were used both for MO calculations and for the evaluation of $\Psi(0)^2$, to be described below.

(d) **Monomethylvanadocene.** Calculations were carried out for two methyl conformations of monomethylvanadocene, as shown in Figures 2a and 2b. Using the overlap program and the same multiexponential functions used in the vanadocene calculation, an overlap matrix for the V–C(20)–CH$_3$ fragment was generated. Two methyl group conformations were considered, as indicated in Figures 2a and 2b. Two types of overlap matrices were then available, the first for vanadocene, and the second for the V–C(20)–CH$_3$ fragment. A computer program was written which effected the replacement of one vanadium C(20)–H unit in the vanadocene overlap matrix by a C(20)–CH$_3$ unit from the V–C(20)–CH$_3$ fragment. In this way an approximate methylvanadocene overlap matrix was obtained with a minimum of computer time. This procedure was used for each of the two CH$_3$ conformations. The monomethylvanadocene calculation was done neglecting vanadium 4p orbitals entirely.

(e) **Monomethylcobaltocene and Cobaltocene.** In the same manner as described under (c), single exponential functions were derived for Co^0. Cobalt 4p orbitals were not included. The MO calculations were then carried out using the derived single exponentials for Co^0: 3d, 2.25; 4s, 1.40.

(f) **Nickelocene and Monomethylnickelocene.** These calculations were carried out using Richardson's 3d and 4s functions for Ni^0, with neglect of the 4p orbitals. Clementi's double-ζ functions were used for carbon, with a single exponent of 1.20 for hydrogen. The methylnickelocene calculation was done by calculating the entire overlap matrix at once, not by fragments as described for monomethylvanadocene. Only one methyl orientation was used—that corresponding to Figure 2a.

Results and Discussion

1. **Conversion of Calculated Spin Densities to Hyperfine Coupling Constants.** The Fermi contact Hamiltonian[29] for the unpaired electron nuclear coupling is given by

$$\mathcal{H} = \left(\frac{8\pi g_e\beta_e g_N\beta_N}{3a_0^3}\right)\left\{\sum_i S_{iz}\delta(r_i)\right\}I_z \tag{2}$$

where g_e and g_N are electron and nuclear g values, respectively, β_e and β_N are the Bohr and nuclear magnetons, respectively, a_0 is the Bohr radius, and $\delta(r_i)$ is the Dirac δ function for the ith electron. According to eq 2, only half-filled molecular orbitals with nonzero hydrogen 1s coefficients will contribute to the direct electron–proton coupling. The hyperfine coupling constant for the ith nucleus, A, is given by

$$A_i = \left(\frac{8\pi g_N\beta_N}{6Sa_0^3}\right)|\Psi(0)|^2 \text{ (gauss)} \tag{3}$$

where S is the total spin and $\Psi(0)$ is the molecular wave function (a Slater determinant in the MO's) evaluated at the coordinates of the ith nucleus. In (3), the coupling constant A has units of gauss. The collection of constants in (3) has the value $1.5957 \times 10^3/2S$ for electron–proton coupling.

In some cases it will be necessary to make use of expressions 4 and 5 in the calculation of hyperfine coupling constants, where ρ_c is the spin density in the aromatic carbon p$_z$ orbital, which is taken to be equal to the square of the carbon p$_z$ coefficient and Q_H and Q_{CH_3} are proportionality constants (see text for discussion). These expressions have been shown to be appropriate in the analysis of esr spectra of aromatic

$$A_H = Q_H\rho_c \tag{4}$$

$$A_{CH_3} = Q_{CH_3}\rho_c \tag{5}$$

radicals, but it is not clear that they are appropriate when the aromatic system is interacting with a metal ion, as in the present case. We can, however, bring to bear experimental evidence relating to this problem. Nishiguchi and coworkers[30a] examined the esr spectrum of the potassium salt of biphenyl in a number of solvents. In some cases, potassium hyperfine splittings are observed, indicating that the ion pairing occurs, with potassium both covalently and electrostatically interacting with the radical ion. The proton hyperfine splittings are, however, independent of the degree or strength of ion pairing, as can be seen from Table I.

Table I. Esr of K$^+$(biphenylide) in Various Solvents[a,b]

Solvent	A_{ortho}	A_{meta}	A_{para}	$A_{potassium}$
Tetrahydropyran	2.65	0.43	5.30	0.083
2,3-Dihydropyran	2.70	0.43	5.40	0.061
Tetrahydrofuran	2.65	0.43	5.29	0.043
Dimethoxyethane	2.66	0.41	5.31	0

[a] Data from ref 30a. [b] Coupling constants in gauss.

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(27) E. Weiss and E. O. Fischer, *Z. Anorg. Allgem. Chem.*, **278**, 219 (1955).

(28) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179 (1962).

(29) E. Fermi, *Z. Physik*, **60**, 320 (1930).

(30) (a) H. Nishiguchi, Y. Nakai, K. Nakamura, K. Ishizu, Y. Deguchi, and H. Takaki, *J. Chem. Phys.*, **40**, 241 (1964); (b) N. Atherton and S. I. Weissman, *J. Am. Chem. Soc.*, **83**, 1330 (1961).

Atherton and Weissman[30b] observed similar behavior with the sodium naphthalenide ion pair. While the sodium hyperfine splittings varied from 0 to 1.27 G, the ring proton coupling constants are constant within ±3%. These results are consistent with the theoretical expectation[31a,b] that Q_H should be a constant for a wide range of planar aromatic radicals, since the exchange integrals and energy differences in the perturbation calculation of Q_H have no explicit dependence on the details of the π-electron system. The only energy term in the perturbation calculation of Q_H[31b] involves $^1\sigma \rightarrow {}^3\sigma^*$ excitation in the C–H σ bond, which should be quite constant for most olefinic C–H bonds including the metallocenes. These considerations support our use of Q_H for free cyclopentadiene as an approximation for the metallocenes. We therefore take $Q_H = -29.9$ G.[32]

The value of Q_{CH_3} appropriate to the substituted metallocenes is more difficult to assess. The methyl group electron coupling arises mainly by virtue of covalent interaction between the aromatic carbon $2p_z$ atomic orbitals and the methyl C–H σ bond orbitals. From the molecular orbital viewpoint, the strength of this interaction will be dependent upon the overlap integrals and the energy differences between the C–H bonds and C_{2p_z} orbitals. In cyclopentadiene, the unpaired electron resides in a bonding π molecular orbital. The energy of this bonding π MO is undoubtedly less negative than the energy of the hydrogen 1s orbital, or the C–H σ-bonding orbital. Hence perturbations stabilizing the MO would thus lead to an increase in Q_{CH_3}' according to the energy-matching criterion. Destabilization of the π MO would thus lead to a decrease in Q_{CH_3}. These considerations seem to have been borne out experimentally by the results of Colpa and de Boer,[33] where it was found that the aliphatic proton splittings in pyracene cation and pyracene anion are quite different. A similar result was obtained for acenaphthene cation and anion. In each case larger splittings were observed for the cation. This is expected on the basis of energy matching arguments, as the positive charge would stabilize the π orbitals relative to the H_{1s}. As will be seen, the calculated charges on the coordinated cyclopentadienyl ring carbon atoms are very small, so the charge dependence of the energy should not enter directly. In the complexes, however, the unpaired electrons are found in antibonding molecular orbitals which are largely localized on the metal atom. One might expect that the energies of these molecular orbitals would be significantly different from the energy of the e_1 orbital of cyclopentadiene. The e_1 energy for cyclopentadiene is approximately -10.7 eV according to our own calculations, which is to be compared with the calculated π orbital energies in vanadocene and cobaltocene, approximately -10.5 (e_{2g}) and -7.5 eV (e_{1g}), respectively (*vide infra*). The usual range of Q_{CH_3} for organic systems is 20–35 G. If we consider the e_1 energy in cyclopentadiene to be typical of the MO energies in organic systems, it would seem that the $Q_{CH_3} \approx 20$–35 G is also appropriate for vanadocene since the e_{2g} energy is not much different than the e_1 energy of cyclopentadiene. On the basis of this argument, Q_{CH_3} for cobaltocene (and nickelocene) should be somewhat smaller than for vanadocene. The conclusions based on Q_{CH_3} will not depend greatly on the precise magnitude chosen. Hence the value $Q_{CH_3} = 25$ G is chosen for convenience in calculation, and it is recognized that a modest error may be incurred.

The hyperfine coupling constants for the ring hydrogens were calculated by means of eq 6. In (6) the

$$A_H = (1.5975 \times 10^3/2S) \sum_{\substack{i=\text{half-}\\ \text{filled}\\ \text{MO's}}} \left\{ \frac{1}{n} \left(\sum_{\substack{j=1\\ \text{equiv-}\\ \text{alent}\\ \text{H atoms}}}^{n} |\phi_i^j(0)|^2 \right) \right\} + \frac{1}{2S} \sum_{\substack{k=1\\ \text{equiv-}\\ \text{alent}\\ \text{C atoms}}}^{n} Q_H \rho_i^k \quad (6)$$

$\phi_i^j(0)$'s are extended Hückel MO's evaluated at the nuclear coordinates, as described by Drago and Petersen.[34,35] For this part of the calculation the overlap-fitted single exponential carbon and metal functions were used in conjunction with the eigenvector coefficients. The ρ_i^k's in (6) are squared $2p_z$ carbon coefficients, as in eq 4. Thus, each A_H is a sum of a "direct" or σ-bond contribution, and an "indirect" or π-bonding contribution. In an analogous fashion, the hyperfine coupling constants for methyl hydrogens are given by eq 7, in which we have averaged the methyl hydrogen spin

$$A_{CH_3} = (1.5957 \times 10^3) \sum_{\substack{i=\text{half-}\\ \text{filled}\\ \text{MO's}}} \left\{ \frac{1}{3} \left(\sum_{\substack{j=1\\ \text{CH}_3\text{ H's}}}^{3} |\phi_i^j(0)|^2 \right) \right\} + \sum_i Q_{CH_3} \rho_i \quad (7)$$

densities $|\phi_i^j(0)|^2$, in order to take into account in a crude way the free rotation of the methyl group. The quantity ρ_i in (7) is the $2p_z$ coefficient squared for the carbon to which the methyl is attached, as in eq 5. Thus we again recognize a "direct" or σ coupling, and an "indirect" or π interaction, the latter given by the $Q_{CH_3}\rho_i$ term.

2. Molecular Orbital Calculations. Tables of eigenvectors, eigenvalues, and population analysis are not presented here because of space limitations.[36] Figure 3 summarizes the results for the highest filled levels of vanadocene, cobaltocene, and nickelocene. The levels for the methyl-substituted compounds are nearly identical. The results for the various metallocenes will now be discussed in turn.

Vanadocene. The extended Hückel calculations were done both with and without vanadium 4p orbitals. The details have been discussed in the Experimental Section and will not be repeated here. It was found that the results are virtually the same whether or not one includes the vanadium 4p orbitals. Hence, all results reported here are for calculations not including 4p orbitals.

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(31) (a) H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, **28**, 107 (1958); (b) A. D. McLachlan, H. H. Dearman, and R. Lefebvre, *ibid.*, **33**, 65 (1960).

(32) P. J. Zandstra, *ibid.*, **40**, 612 (1964).

(33) J. P. Colpa and E. de Boer, *Mol. Phys.*, **7**, 333 (1963–1964).

(34) R. S. Drago and H. Petersen, Jr., *J. Am. Chem. Soc.*, **89**, 3978 (1967).

(35) We are indebted to Mr. Roger Cramer for the $|\Psi(0)|^2$ program.

(36) Tabulations of the molecular orbital results have been deposited as Document No. NAPS-0038-3 with the ASIS National Auxiliary Publication Service % CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. A copy may be obtained by citing the document number and remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to ASIS–NAPS.

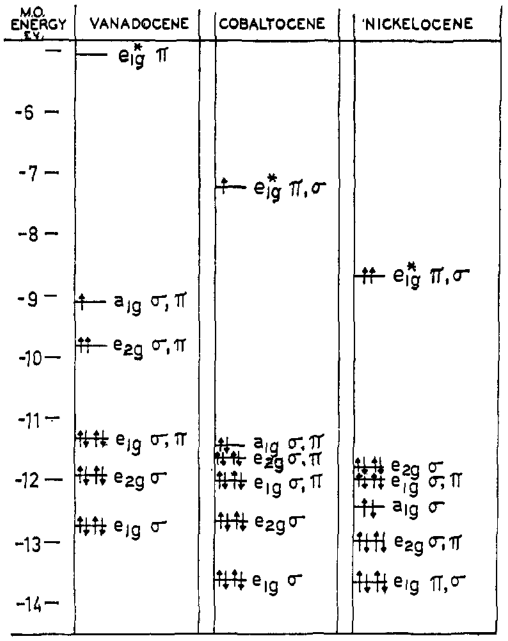

Figure 3. Molecular orbital energies in the metallocenes.

(a) Predicted Vanadocene Ground States. The calculated results indicate that the ground state is $^4A_{2g}$. The three unpaired electrons are found in molecular orbitals which are chiefly d_{z^2}, d_{xy}, and $d_{x^2-y^2}$ (see Figure 3). Hence, the ground electron configuration is $(e_{2g})^2(a_{1g})^1$, which is consistent with our earlier discussion of the ground state of vanadocene.[3] The energy separation $e_{2g} - a_{1g}$ is about 0.7 eV, with a_{1g} lying higher. This result agrees with the partial calculation of vanadocene done by Shustorovich and Dyatkina.[6] The calculated near-degeneracy of e_{2g} and a_{1g} is also consistent with the deductions of Scott and Becker.[37] The large vanadium coefficients and small ring coefficients in the e_{2g} and a_{1g} eigenvectors indicate that the metal-ring interactions are weak in these MO's. It will be noted that both a_{1g} and e_{2g} MO's have both σ and π character. Hence, the ring π as well as σ orbitals are mixed with each of the metal d orbitals, a consequence of the symmetry of the molecule.

(b) Ionization Potential. The highest field MO is a_{1g} at −9.10 eV. According to Koopman's theorem,[38] the predicted ionization potential is therefore equal to 9.1 eV. This result is in fair agreement with the mass spectral result of 7.56 eV.[39] In connection with other work we have found that the calculated ionization potential is fairly sensitive to the choice of H_{ii}, while the eigenvectors are not so sensitive. Hence, we were able to approach the experimental ionization potential more closely on correcting H_{ii} for charges on the other atoms.

(c) Final Atom Charges. The final calculated charges are: vanadium, +0.609; carbon− 0.0284; hydrogen, −0.0324. Shustorovich and Dyatkina[6] estimated the vanadium charge to be about +1.0, on the basis of their incomplete calculation. Our result is in fair agreement with the estimate of +0.4 for iron in ferrocene, based on X-ray absorption edge studies.[40]

The very small charges on the ligand atoms lead to small corrections of the ligand H_{ii}'s for charge, while the metal ion energy correction for charge is significant. This accidental feature of the calculation makes the procedure nearly the same as the Basch, Viste, Gray SCCC-MO method.[22]

(d) Isotropic and Anisotropic Vanadium Hyperfine Splitting. The electron spin resonance spectrum of vanadocene has been interpreted by Prins and coworkers[41] to give $A_{\text{isotropic}} = -27 \times 10^{-4}\ \text{cm}^{-1} = -80$ Mcps; $A_{\text{anisotropic}} = -37 \times 10^{-4}\ \text{cm}^{-1} = -111$ Mcps; $B = -21.5 \times 10^{-4}\ \text{cm}^{-1} = -64.5$ Mcps. According to Robertson and McConnell, an unpaired electron in a vanadium 4s orbital should give rise to an isotropic contact hyperfine splitting of about 4600 Mcps.[42] Another contribution to the isotropic splitting has been discussed by Heine.[43] This mechanism involves the exchange polarization of inner-shell electrons by the unpaired 3d electrons of the transition metal. Positive spin density builds up near the periphery of the atom, while negative spin density is favored near the nucleus. The experimental coupling constant for ionic V^{2+} is −264 Mcps from the exchange polarization process.[44] Hence we can approximate the isotropic coupling constant for V^{2+} in a molecule as the sum of −264 Mcps from the three unpaired d electrons and s(4600 Mcps) from the 4s electron, where s is the total fractional 4s character in half-filled MO's. The −80-Mcps isotropic splitting for vanadocene[41] implies that there is about $[(264 - 80)/4600] \times 100$, or 4% 4s character in the highest filled a_{1g} molecular orbital of vanadocene. The Mulliken population analysis for our calculation indicates that about 6% of the charge in the a_{1g} MO is in the 4s orbital. This is in excellent agreement with the 4% deduced from the esr spectrum.

The anisotropic hyperfine interaction arises from dipolar electron-nuclear coupling. In the present case, the anisotropic splitting arises from unpaired spins in d_{z^2}, $d_{x^2-y^2}$, and d_{xy}. Prins[41] deduced from the anisotropic hyperfine splitting in vanadocene that the coefficients of d_{xy} and $d_{x^2-y^2}$ in the e_{2g} MO's are approximately 0.86, assuming a coefficient of 1.0 for d_{z^2} in the a_{1g} MO. These results are in excellent agreement with our calculated coefficients of −0.986 for d_{z^2} in a_{1g} and 0.908 for d_{xy} or $d_{x^2-y^2}$ in the e_{2g} orbitals. The fact that slightly *less* covalency in e_{2g} is predicted by the MO calculation than is experimentally indicated is contrary to the claims made that molecular orbital calculations of this type greatly overestimate covalency.[11,45]

(e) Comparison of the Vanadocene MO Coefficients to SCF Results for Chromocene. Shustorovich and Dyatkina carried out an approximate SCF calculation for the metal orbitals and ring π orbitals of chromocene.[5] The results of the SCF calculation indicate a d_{xy} coefficient of 0.83 in the bonding e_{2g} orbital, and a d_{xz} coefficient of 0.39 in the bonding e_{1g} orbital. The

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(37) D. R. Scott and R. S. Becker, *J. Organometal. Chem.*, **4**, 409 (1965).

(38) T. Koopman, *Physica*, 1, 104 (1933).

(39) L. Friedman, A. P. Irsa, and G. Wilkinson, *J. Am. Chem. Soc.*, 77, 3689 (1955).

(40) R. L. Barinskii, *Zh. Strukt. Khim.*, 1, 200 (1960).

(41) R. Prins, P. Biloen, and J. D. W. van Voorst, *J. Chem., Phys.*, 46, 1216 (1967).

(42) R. E. Robertson and H. M. McConnell, *J. Phys. Chem.*, **64**, 70 (1960).

(43) V. Heine, *Phys. Rev.*, 107, 1002 (1957).

(44) A. Abragam, J. Horowitz, and M. H. L. Pryce, *Proc. Roy. Soc.* (London), **A230**, 169 (1955).

(45) R. F. Fenske, K. G. Caulton, D. D. Radtke, and C. C. Sweeney, *Inorg. Chem.*, **5**, 960 (1966).

Table II. Contributions to the Hyperfine Coupling in Vanadocene and Methylvanadocene

	"σ"			"π"			Total calcd A, G	Exptl A, G[a]
	a_{1g}	e_{2g}[a]	e_{2g}[b]	a_{1g}	e_{2g}[a]	e_{2g}[b]		
Vanadocene, ring H	1.15	0.017	0.017	−0.003	−0.10	−0.10	0.97[b]	0.832
Methylvanadocene, H-13	1.27	0.06	0.03	−0.0007	−0.10	−0.08	1.17	0.908[c]
Methylvanadocene, H-15	1.13	0.03	0.04	−0.01	−0.01	−0.18	1.00	
Methylvanadocene, methyl H	0.16	0.013	0.013	~0	0.17	~0	0.36	0.32

[a] Experimental results for vanadocene and dimethylvanadocene.[3] [b] To obtain total calculated A, add across the row. [c] Different protons not resolved.

d_{z^2} coefficient was assumed to be one, *i.e.*, d_{z^2} is nonbonding. The d_{xy} coefficient obtained here is 0.907; the d_{xz} is 0.38; and the d_{z^2} coefficient is 0.98. Although the SCF results are for chromocene, it is expected that an SCF calculation for vanadocene would give similar results. The excellent agreement of our d orbital coefficients with the SCF results and with the coefficients deduced from experimental data (esr, above) suggests that the method of calculation will lead to an accurate description of nmr contact shift results.

(f) Calculation of Electron–Proton Hyperfine Coupling. This calculation was carried out by means of eq 6. The quantities $|\phi_i^j(0)|^2$ in (6) were evaluated using each eigenvector coefficient together with an overlap-fitted single exponent, as described above. The results are given in Table II, in which the "σ" contribution to the coupling constant arises from the $|\phi_i^j(0)|^2$ terms in (6), while the "π" contributions are evaluated from carbon $2p_z$ coefficients (the $Q_{\mathrm{H}}\rho_i^k$ in (6)). The calculated coupling constant of 0.97 G is in excellent agreement with the experimental value of 0.83 G from ref 3. Further, the coupling constant is strongly dominated by the hydrogen 1s coefficient in the a_{1g} MO (−0.0544), with very small contributions from any other orbital. In particular there is a vanishingly small contribution to the $|\phi_i^j(0)|^2$ from any vanadium orbital, which means that there is no direct overlap of vanadium AO's with the hydrogen nucleus. The MO most important in the hyperfine coupling is thus found to be the a_{1g} MO, made up primarily of $3d_{z^2}$, 4s, carbon 2s, $2p_x$, $2p_y$, and hydrogen 1s orbitals. Conversely, the much smaller e_{2g} contribution is nearly completely determined by the indirect p_z hydrogen 1s exchange polarization term. Thus we can crudely separate the σ and π contributions to the hyperfine interaction, concluding that the a_{1g} (σ) contribution is most important. We therefore find that the extended Hückel calculations support the earlier experimental deduction of σ delocalization in vanadocene. Further support is given by the methylvanadocene results (below).

Two alternative hyperfine coupling mechanisms will now be examined: (1) the "direct overlap" mechanism; (2) the "bent hydrogens" mechanism. It might be supposed that the metal d orbitals extend out far enough to directly place positive spin density at the proton nucleus. The importance of this type of interaction is indicated by the $|\phi_i^j(0)|^2$ calculation. The total contribution of the vanadium d orbitals is about 1.3×10^{-6} for $|\phi_i^j(0)|^2$, which leads to a coupling constant of about 0.7 mG. A more careful calculation of $|\phi_i^j(0)|^2$ using Clementi's[20a] vanadium(0) and nickel(0) functions indicates that a direct overlap of the SCF orbital with the hydrogens in vanadocene or nickelocene still leads to a predicted coupling constant only of the order 10^{-3}–10^{-4} G in each case. Clearly the "direct overlap" mechanism cannot contribute significantly to the observed shifts.

The second alternative mechanism involves bending the ring hydrogens out of the plane of the cyclopentadienyl rings, either toward or away from the metal. There is some experimental evidence which suggests that this type of distortion occurs. The electron diffraction study of Bohn and Haaland[26] indicates that the ring hydrogens are bent approximately 5° toward iron in ferrocene. Also Cotton and Reynolds[46] suggest that the infrared intensity of the A_1 C–H stretching vibration in ferrocene implies a distortion toward nonplanarity. If in fact the hydrogens were bent out of the plane of the ring, the 1s orbitals would no longer be orthogonal to the $2p_z$ orbitals in carbon. Unpaired electron density in the $2p_z$ orbitals could then be *directly* delocalized onto the hydrogen atoms. One also needs to know what to expect of the *indirect* atomic exchange polarization mechanism ($A_{\mathrm{H}} = Q_{\mathrm{H}}\rho$) when the hydrogen is no longer orthogonal to the p_z orbital. Karplus[47a] and Schrader and Karplus[47b] have shown that the relation $A_{\mathrm{H}} = Q_{\mathrm{H}}\rho$ remains valid for distortions as small as 5°, with only a slight variation in Q_{H}. We assume, therefore, that the indirect mechanism can be computed as before. An extended Hückel calculation was carried out for vanadocene with the ring hydrogens bent 5° toward the metal. No significant changes in eigenvector coefficients, energies, or atom charges were found. The value of $|\phi_i^j(0)|^2$ for the a_{1g} orbital was found to be 2.35×10^{-3}, compared to 2.14×10^{-3} for the undistorted case. Because of the near-identity of the results, a complete $|\phi_i^j(0)|^2$ analysis was not carried out. It is of interest that the direct p_z contribution to the coupling constant is of the order 1×10^{-6} G due to the nonorthogonality. We therefore conclude that the direct delocalization of p_z electron density is negligible for a 5° distortion. No significant interaction with metal d orbitals is observed even when the hydrogens are bent toward the metal, further emphasizing the insignificance of this effect. This result directly contradicts recent claims[48] that the vanadocene and

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(46) F. A. Cotton and L. T. Reynolds, *J. Am. Chem. Soc.*, **80**, 269 (1958).

(47) (a) M. Karplus, *J. Chem. Phys.*, 30, 15 (1959); (b) D. M. Schrader and M. Karplus, *ibid.*, 40, 1593 (1964).

(48) H. P. Fritz, H. J. Keller, and K. E. Schwarzhans, *Z. Naturforsch.*, 23b, 298 (1968).

chromocene low-field shifts result from direct overlap of metal orbitals with the ring hydrogens.

Methylvanadocene. Extended Hückel calculations were carried out for monomethylvanadocene rather than dimethylvanadocene in order to conserve computer time. In the subsequent discussion, the calculated results for the substituted ring in monomethylvanadocene will be compared with the experimental results for 1,1′-dimethylvanadocene. It is expected that this is a reasonable approach, since the methyl group only slightly affects the other coefficients. Similar remarks apply to the other unsubstituted and substituted metallocenes.

The methyl group overlaps were "attached" to the vanadocene Clementi basis overlap matrix in the manner described in the Experimental Section. Calculations were done for two conformations, as indicated in Figures 2a and 2b. The two conformers give practically identical results in all respects, so the discussion will be limited to results for the conformation of Figure 2b. In this discussion, the eigenvectors will still be referred to as a_{1g} and e_{2g} even though the symmetry is no longer D_{5d}. This is justifiable for clarity's sake, and because the coefficients are not greatly perturbed by the presence of the methyl group. A detailed discussion of results other than hyperfine coupling constants will not be given, since only slight differences from the vanadocene calculation were noted. The eigenvector energies are essentially identical, except that now all electronic degeneracy is lifted. Hence formerly doubly degenerate levels now differ in energy by 0.05–0.10 eV. The final atom charges are nearly the same as for vanadocene (charge on V in methylvanadocene is + 0.616). It is clear therefore that the methyl group makes only a small perturbation. The three singly occupied eigenvectors are a_{1g}, $e_{2g}{}^{a}$, and $e_{2g}{}^{b}$, as before. The metal coefficients in these eigenvectors are nearly identical with the vanadocene calculation.

(a) Calculation of the Hyperfine Coupling Constant for the Ring Hydrogens. The method used is the same as that already described for vanadocene. It is now observed that hydrogens 13 and 15 (*ortho* and *meta* to the methyl group) are no longer equivalent. This is due primarily to the different hydrogen "σ" coefficients in the a_{1g} MO, with the e_{2g} contributions being minor. The predicted splitting of ring hydrogens is about 0.17 G, or ~3800 cps (Table II). The experimental spectrum has a line width of 2680 cps (ref 3); hence splitting as large as ~2000 cps would not be resolved. Careful examination of the spectrum suggests that it possibly is a superposition of two very broad peaks. It appears that the MO calculation somewhat overemphasizes the nonequivalence of the hydrogens, a not surprising result at this level of approximation. The calculations also predict a somewhat greater delocalization to ring hydrogens in methylvanadocene, which is observed experimentally.

(b) Calculation of the Hyperfine Coupling Constant for the Methyl Hydrogens. The calculations for the methyl group are subject to certain approximations made necessary by the conformational dependence of the coefficients. It was indicated earlier that two conformations were calculated (Figures 2a and 2b). It happens, however, that these two conformations are very nearly equivalent insofar as interaction with the ring π system is concerned. This occurs since each conformation has one hydrogen eclipsed with the ring carbon p_z orbital. Further, the particular conformations chosen are in position for maximum overlap and therefore maximum interaction with the π system. We would not therefore be justified in taking the coefficients of the methyl hydrogen as a measure of the coupling with the π system, since a full rotational average of the coefficients would be required. Since such a rotational average is out of the question in a molecule of this size, it was decided to compute the methyl-p_z interaction with the relation $A_{CH_3} = 25\rho_c$, which was arrived at earlier. Next we introduce two approximations (1) that the coefficients of the methyl hydrogens in a a_{1g} orbital represent σ-type interactions only, and (2) that the coefficients of the methyl hydrogens in the $e_{2g}{}^{b}$ orbital represent the contribution due to σ interaction in $e_{2g}{}^{a}$ and $e_{2g}{}^{b}$. The first approximation is justified on the basis of the very strong σ dominance of the a_{1g} orbital, and in view of the small p_z coefficient in a_{1g} at carbon 20. The second seems reasonable since there is, in fact, a node in the $e_{2g}{}^{b}$ π orbital at the point of attachment of the methyl group. With these approximations the calculated methyl coupling constant is 0.36 G, in excellent agreement with the experimental value of 0.32 G (Table II). Further, the ratio of calculated ring/metal coupling constants (~3) is also in good agreement with experiment.

The strong σ attenuation in the a_{1g} orbital gives rise to a very small σ contribution to the methyl group coupling constant. Indeed, the indirect π delocalization contributes as much as the σ delocalization at the methyl group (Table II). Were it not for the appearance of a node in $e_{2g}{}^{b}$ at the point of attachment of the methyl group, a somewhat larger positive coupling constant would have been predicted. The appearance of a π node at the methyl group is consistent with the "electron-repelling" character of that group. This point will be considered in more detail in connection with dimethylcobaltocene.

It is felt that the eigenvectors obtained from the extended Hückel calculation of vanadocene and monomethylvanadocene are quite good, based on comparison of calculated results with experiment. Hence, we had success with both vanadium isotropic and anisotropic hyperfine interactions, and with the isotropic proton hyperfine splittings. Unfortunately, good experimental work relating to the electronic absorption spectrum of vanadocene is lacking. This, coupled with a belief on our part that the electronic spectra should not be fit by this type calculation led us to omit a detailed analysis of the MO energies.[49]

Chromocene. No molecular orbital calculations were carried out for chromocene. However, we are probably quite justified in using vanadocene eigenvectors to predict hyperfine coupling constants for chromocene, since the metal–ligand interaction is undoubtedly very similar. The difference in a_{1g} and e_{2g} MO energies (a_{1g} lies 0.7 eV above e_{2g}) in vanadocene suggests the ground electronic configuration $(e_{2g})^3(a_{1g})^1$ for chromocene, or ${}^3E_{2g}$. This is the ground state which was shown earlier to be most reasonable for chro-

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(49) R. Prins and J. D. van Voorst[18] indicate that a discussion of electronic spectra on the basis of extended Hückel results will be published.

mocene. In order to calculate the hyperfine coupling constant for chromocene, we make use of eq 6 with the vanadocene eigenvectors, noting that now one e_{2g} orbital is filled and the total spin $S = 1$. The results are found in Table III. The calculated result for chromocene is again in excellent agreement with the experimental value and tends to justify the use of vanadocene eigenvectors for the calculation. It is worthwhile noting that the alternate choice of ground state for chromocene, $(a_{1g})^2(e_{2g})^2$, would lead to a calculated coupling constant of −0.26 G, in complete disagreement with experiment, both in magnitude and sign. It is concluded that the ground state of chromocene is $(e_{2g})^3(a_{1g})^1$, and that the a_{1g} MO dominates the contact shift in chromocene just as it dominates in vanadocene.

Methylchromocene. The results for methylchromocene obtained using methylvanadocene eigenvectors are summarized in Table III. The calculated and experimental results are again in very good agreement. The ring hydrogen splitting is not predicted to be as large as is observed for dimethylchromocene, but the agreement is still highly acceptable. A methyl group coupling constant three times larger than experimental is predicted, however.

Table III. Contributions to the Hyperfine Coupling in Chromocene and Methylchromocene

	"σ"		"π"		Total calcd	Exptl
	a_{1g}	e_{2g}[a]	a_{1g}	e_{2g}[a]	A, G	A,[a] G
Chromocene, ring H	1.21	0.02	−0.005	−0.16	1.58	1.23
Methylchromocene, H-13	1.90	0.09	−0.001	−0.16	1.84	1.43
Methylchromocene, H-15	1.70	0.04	−0.015	−0.015	1.71	1.21
Methylchromocene, methyl H's	0.25	0.02	∼0	0.25	0.52	0.14

[a] Experimental results for chromocene and dimethylchromocene.[3]

The earlier discussion of pseudocontact shifts[3] leads to the conclusion that the only large pseudocontact contribution is expected at the methyl group of dimethylchromocene, where the geometric factor can be of significant magnitude. For $g_{\parallel} > g_{\perp}$, a large positive pseudocontact shift is indicated. The magnitude was earlier estimated at several thousand cycles per second for reasonable values of the anisotropy. The difference in the calculated and observed methyl group coupling constants is 0.38 G, which is equivalent to an upfield shift of about 4000 cps. We therefore conclude that a large pseudocontact shift is contributing to the observed methyl proton shifts, giving rise to a much less negative shift than is expected on the basis of the contact contribution. The corresponding pseudocontact shift for the ring hydrogens is expected to be smaller by a factor of about 4 and negative, owing to the peculiarities of the geometric factors. A pseudocontact shift of ∼1000 cps would make the agreement between calculated and experimental ring coupling constants somewhat poorer but still quite acceptable.

Discussion of the Molecular Orbital Results for the Vanadium and Chromium Metallocenes. The major difficulties with the Levy–Orgel model for electron delocalization in the metallocenes occur with vanadocene and chromocene and their dimethyl derivatives. It was with these four compounds where the predictions of the Levy–Orgel theory were found to be inadequate.[3] We have now shown that the too often ignored σ orbitals in the metallocenes are mainly responsible for the nmr contact shifts in vanadocene and chromocene. The importance of π delocalization is rather minor, except perhaps for the methyl contact shifts, and even here π delocalization is not dominant. Both the magnitudes and the sign of the nmr coupling constants are predicted accurately by the molecular orbital model, while at the same time a reasonable account is given of other experimental facts. Outstanding in this latter regard is the good agreement with the V^{51} hyperfine splittings, which implies that the correct degree of mixing of metal and ligand orbitals does result from the molecular orbital calculation. We therefore feel that the description given here is nearly correct.

The Levy–Orgel model for cobalt and nickel metallocenes favors the dominance of π-delocalization effects, and the experimental nickel results tend to support this idea. It was decided to carry out MO calculations for cobalt and nickel metallocenes in order to further assess the relative importance of σ- and π-type delocalization in the e_{1g}* orbitals. The results of these calculations follow.

Cobaltocene. (a) Predicted Ground State. The highest filled MO is derived from d_{xz} and d_{yz}; hence the predicted ground state is $(e_{1g}^*)^1$ or $^2E_{1g}$ (see Figure 3). This ground state was considered earlier to be the most likely on the basis of the available experimental evidence. It might be remarked in connection with this result that the 4p orbitals, if considered nonbonding, would lie 2–3 eV above the half-filled e_{1g}*. Our results for vanadocene indicate that interaction of the 4p orbitals with the ligand e_{1u} makes them considerably higher in energy. Essentially this implies that, regardless of the degree of interaction of the 4p orbitals, it is unlikely that they will ever fall low enough in energy to be part of the ground-state configuration in either cobaltocene or nickelocene. This result strongly implies that the ground-state configuration of nickelocene is $(e_{1g}^*)^2$, since only $(e_{1g}^*)^2$ and $(e_{1u}^*)^2$ (from $4p_x$ and $4p_y$) are consistent with the large zero-field splitting.[50]

(b) Ionization Potential. The energy of the highest filled, singly occupied MO, e_{1g}*, is calculated to be −7.27 eV, in reasonable agreement with the observed ionization potential of 6.2 eV.[39]

(c) Atom Charges. The final charge on cobalt was found to be 0.43, with the charges on the other atoms being small in absolute magnitude (less than 0.1). There is an irregular variation in the C, H charges as a result of the unsymmetrical interaction of the metal e_{1g}* electron with the ring. The charge of 0.43 on cobalt is close to that observed experimentally by Barinskii[40] for cobaltocene: +0.4. The lower calculated positive charge on Co than on V reflects the increasing "electronegativity" of the transition metals as one passes from Ti to Cu across the transition series.

(d) Calculation of Hyperfine Coupling Constants. This calculation was done straightforwardly using eq 6. The results are summarized in Table IV. The agreement of calculated and observed coupling constants is

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(50) R. Prins and J. D. W. van Voorst, *Chem. Phys. Letters*, 1, 54 (1967).

quite remarkable, especially since the calculated result is a difference of two large numbers. The results indicate a significant "σ" contribution to the delocalization even in cobaltocene. Thus, the +1.19 G (Table IV) arises by virtue of the interaction of d_{xz} and d_{yz} with the in-plane σ system of the rings, including the hydrogen 1s orbitals. The net result (−0.86 G) reflects the somewhat larger "π" interaction with the ring $2p_z$ orbitals. It should be noted that the use of eq 6 implies that the unpaired electron undergoes frequent $e_{1g}{}^{a*} \leftrightarrow e_{1g}{}^{b*}$ transitions on the nmr time scale. This leads to an average spin density at the hydrogen, giving only a single nmr resonance as is experimentally observed.

Table IV. Contributions to the Hyperfine Coupling in Cobaltocene and Methylcobaltocene[a]

	"σ" $e_{1g}{}^{a*}$	"π" $e_{1g}{}^{a*}$	Total calcd A, G	Exptl A, G
Cobaltocene, ring H	1.19	−2.05	−0.86	−1.00
Methylcobaltocene, H-13	2.10	−3.70	−1.60	−1.33
Methylcobaltocene, H-15	0.80	−1.46	−0.66	−0.901
Methylcobaltocene, methyl H's	0.16	~0	0.16	0.213

[a] Experimental results for cobaltocene and dimethylcobaltocene.[3]

Methylcobaltocene. (a) Molecular Orbital Calculation. The details of the calculation have been given in the Experimental Section. The eigenvector energies and final atom charges are little affected by the presence of the methyl group. The final calculated charge on cobalt is +0.430, which is the same as the result for cobaltocene.

(b) Calculation of Hyperfine Coupling Constants. The calculation proceeds as before, only we now treat the ring hydrogens separately. It is found that one of the $e_{1g}{}^{*}$ orbitals lies 0.1 eV below the other, owing to the presence of the methyl group. The lower lying $e_{1g}{}^{*}$ has a node at carbon 20, the point of attachment of the methyl, as was observed in the methylvanadocene calculation. The coupling constants are calculated using only the lower energy half-filled $e_{1g}{}^{a*}$ orbital. Since there is a node in $e_{1g}{}^{a*}$ at carbon 20, we assume as before that no unpaired π spin density is delocalized onto the methyl group. The small coefficients of the methyl hydrogens are assumed to arise from σ (in-plane) interactions in the $e_{1g}{}^{a*}$ orbital. The results of the calculations are summarized in Table IV. The results for the ring hydrogens in methylcobaltocene indicate that the coupling constants are once again made up of large σ and π contributions of opposite sign. The predicted ring hydrogen splitting is 0.94 G (3600 cps) compared to the observed splitting of 0.43 G (1600 cps). The ratio of calculated coupling constants for hydrogens 13 and 15 is 2.43. This ratio should be exactly 2.61 in an e_{1g} orbital with a node at carbon in D_{5d}, by symmetry. The experimental fact is that the ratio of ring hydrogen coupling constants is 1.47, while a very small spin density is found on the methyl hydrogens. This small methyl coupling constant, taken alone, suggests that the molecular orbital calculation is correct; *i.e.*, the lower energy $e_{1g}{}^{*}$ orbital has a node at the methyl carbon. However, the calculated ring hydrogen splitting is incorrect by nearly a factor of 2, even though the absolute values of calculated coupling constants are in reasonable agreement with experiment.

It is felt that there are two possible explanations for the observed dimethylcobaltocene results, both of which involve the participation of the second $e_{1g}{}^{*}$ molecular orbital. These alternatives will now be discussed.

(i) Thermal Population of the Higher $e_{1g}{}^{b*}$ Orbital in Dimethylcobaltocene. The molecular orbital calculation indicates that there is a very small energy difference between the $e_{1g}{}^{a*}$ and $e_{1g}{}^{b*}$ MO's of approximately 10^{-2} eV, or about 0.2 kcal/mole. If both $e_{1g}{}^{a*}$ and $e_{1g}{}^{b*}$ are populated at room temperature, then we might expect an anomalously low ratio of ring coupling constants. However, we showed earlier[3] that the ring coupling constants are temperature independent, which is inconsistent with a low-lying thermally populated state.

(ii) Configurational Mixing of $^2E_{1g}$ States. In dimethylcobaltocene, the two nearly degenerate $e_{1g}{}^{*}$ orbitals ($e_{1g}{}^{a*}$ and $e_{1g}{}^{b*}$) give rise to the ground $^2E_{1g}{}^{a}$ term and a very low-lying $^2E_{1g}{}^{b}$ excited state. Configurational mixing of these states is possible and would lead to a ground-state wave function of the form $\Psi = E_{1g}{}^{a} + \lambda E_{1g}{}^{b}$. In the present case of near degeneracy, λ may be large, and a value of λ can be found which correctly reproduces the ring hydrogen splitting. This hypothesis is consistent with the independence of the ring coupling constants with temperature. A disadvantage is that a methyl coupling constant of about 0.8 G and independent of temperature is predicted, contrary to the experimental result.

It is believed, however, that the behavior of the methyl group can be rationalized in a manner consistent with the present hypothesis. The behavior of the methyl group at low temperature is reminiscent of the negative spin density which appears at the central carbon in allyl radical. The methyl group in dimethylcobaltocene is attached to a carbon atom where a relatively small positive spin density is expected. If the ground state is in fact close to $^2E_{1g}{}^{a}$, we would expect exchange interactions to favor net positive spin density to appear in the filled cyclopentadiene orbitals at the carbons other than the carbon to which the methyl is attached. The result could well be (and is in allyl and many other cases) the appearance of negative spin density on the methyl hydrogens. This could account for the unexpectedly small positive methyl coupling constant at room temperature, and for the negative coupling constants at low temperatures (the methyl coupling constant at −100° is about −0.2 G). The extreme *variation* of the methyl coupling constant is not easily accounted for, however. It is felt that the great sensitivity of the methyl shift to temperature and the discontinuity in the temperature dependence of the type-A ring protons are both part of the same process. The type-A protons, according to our calculations, are probably to be assigned as hydrogens 13 and 19, since these hydrogens are predicted to have the larger coupling constants (see Table IV). It is interesting that both the methyl hydrogens and the type-A hydrogens (which are adjacent to methyl) show anomalous shifts

Table V. Contribution to the Hyperfine Coupling in Nickelocene and Methylnickelocene[a]

	"σ" e_{1g}^{a*}	"π" e_{1g}^{a*}	"σ" e_{1g}^{b*}	"π" e_{1g}^{b*}	Total calcd *A*, G	Exptl *A*, G
Nickelocene, ring H	0.65	−1.20	0.65	−1.20	−1.10	−1.29
Methylnickelocene,[b] H-13	0.57	−2.18	0.06	−0.32	−1.87	−1.28
Methylnickelocene, H-15	0.22	−0.84	0.47	−1.71	−1.86	−1.28
Methylnickelocene, methyl H	0.06	0	0.06	2.02	2.14	1.00

[a] Experimental results for dimethylnickelocene (ref 3). [b] See Figure 2a for atom numbering.

in the same temperature range.[3] In fact, it is estimated from Figure 5 of ref 3 that the break in the plot of type-A proton contact shift *vs.* *T* represents a change in the coupling constant of −0.17 G between −40 and −101° (at −101°, the observed shift is 640 cps more positive than extrapolation of the high-temperature line would predict; this is equivalent to −0.17 G). Between −40 and −101°, the methyl shift is about +1200 cps, and the change in coupling constant is ~+0.32 G (see Figure 6, ref 3). The combined type-A coupling constants (−0.34 G) represent an accumulation of net *positive* spin density, while the +0.32 G for methyl implies a nearly equal accumulation of net *negative* spin density in the p_z orbital of carbon 20. These facts strongly suggest that the spin density distribution is rearranged by a temperature-dependent process and that the main interaction involves positions of high positive spin density (carbons 12 and 18) and nearly a π node at carbon 20. A reasonable temperature-dependent process could involve some geometric distortion in the complex, but we will not speculate further.

In summary, a fairly accurate account of the cobaltocene and dimethylcobaltocene coupling constants can be given on the basis of the extended Hückel calculation. However, it does appear that in methylcobaltocene higher order calculations would be required to reproduce the experimental results more closely. It is believed that more complex calculations will not be likely to change the general conclusions concerning the delocalization mechanisms. It is particularly interesting that the σ contributions to the hyperfine coupling constants are nearly as large as the π contributions.

Nickelocene. (a) Predicted Ground State. The two highest filled orbitals in nickelocene were calculated to be the antibonding e_{1g}^{a*} and e_{1g}^{b*}, which are degenerate and are derived from d_{xz} and d_{yz}. This result is consistent with the large zero-field splitting in nickelocene.[50] The energies of e_{1g}^{a*} and e_{1g}^{b*} are found to be −8.70 eV, which predicts an ionization potential of 8.70 eV, in reasonable agreement with the mass spectral result of 7.06 eV.[39] The final atom charges for the nickelocene calculation are: Ni, +0.489; C, −0.020; H, −0.029.

(b) Calculation of Hyperfine Coupling Constants. The coupling constants were calculated by means of eq 6 and 7. The results are given in Table V. As in the case of cobaltocene, the coupling constant has significant contributions from both σ and π interactions of d_{xz} and d_{yz} with the rings. Here again the σ contribution is roughly half as large as the π contribution. The agreement with the experimental value of −1.26 G is very good.

Methylnickelocene. The MO calculation for methylnickelocene proceeded exactly as for nickelocene. The same ground state was found: $(e_{1g}^{*})^2$. The splitting of e_{1g}^{a*} and e_{1g}^{b*} is 0.05 eV, and the predicted ionization potential is 8.64 eV. The final charge on nickel in methylnickelocene is 0.477. Clearly, the methyl group makes only a small perturbation.

The coupling constant results are given in Table V. The agreement with experiment for the ring hydrogens in less satisfactory than with nickelocene. It is observed, however, that the extent of calculated π delocalization is virtually the same for nickelocene and methylnickelocene (the sum of π coupling constants for a given hydrogen on either compound is 2.48 ± 0.08 G). The discrepancy in the calculated coupling constants arises from the σ contribution in methylnickelocene, which, for a given hydrogen, is considerably smaller than for nickelocene. This reflects the sensitivity of the calculation to small changes in the already small σ coefficients.

The methyl coupling constant for methylnickelocene was calculated by eq 7, using $Q_{CH_3} = 25$ G. The σ contribution was taken from the lower energy e_{1g}^{a*} MO, which has a π node at carbon 20. The fact that the calculated methyl coupling constant is too large by a factor of 2 probably results from an incorrect choice of Q_{CH_3}. This point was discussed above, where it was observed that the presence of unpaired electrons in relatively high-energy antibonding orbitals should probably lead to a lower than usual value of Q_{CH_3}. It does seem clear, however, that the methyl coupling constant is strongly dominated by π (or hyperconjugative) interaction with the cyclopentadienyl π system. σ effects at methyl are quite small.

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