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A Theoretical Treatment of Electron Delocalization and Bonding in Some Paramagnetic Bis-Arene Complexes

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In this article, we report results from an SCC molecular orbital calculation which predict hyperfine coupling constants for a series of bis-benzene complexes which agree well with values obtained from nmr contact shift studies. It is shown that competing σ and π delocalizations are operative, the σ mechanism dominating the observed shifts in the earlier transition metals, while π delocalization dominates shifts toward the later metals. It is shown that Mulliken and Löwdin's population analyses lead to comparable fits of the hyperfine coupling constants, but reasonable bond orders can be obtained only with a Löwdin analysis on these systems. The Löwdin procedure is used both in the final analysis and in the MO iteration to self-consistent charge. The calculations on the bis cyclopentadienyls previously reported were repeated using the Löwdin analysis in order to compare bond orders between the bis-cyclopentadienyl and bis-benzene complexes. An analysis of the Löwdin bond orders establishes (1) an important involvement of σ orbitals on the ring in bonding to the metal in both series, (2) a substantial participation of 4s and 4p orbitals in metal–ring bonding, and (3) an indication that donor–acceptor interaction involving the d_{xz} and d_{yz} orbitals appears important for the metallocenes and bis benzenes, while involvement of the $d_{x^2-y^2}$, d_{xy}, and ring π orbitals gives rise to a more significant bonding interaction in the bis-benzene series.

Introduction

In a previous publication,[2] we discussed the nuclear magnetic resonance contact shifts for a large number of paramagnetic bis-benzene and methyl-substituted bis-benzene complexes of the first transition series. Consistent with earlier work on the metallocenes,[3,4] electron delocalization was rationalized on the basis of competing direct σ and indirect π delocalization mechanisms. The π mechanism becomes dominant only with cobalt and nickel, underlining the importance of the σ in-plane orbitals of the ring in the delocalization process. It should be understood in the subsequent discussion that the σ and π labels are used very loosely to indicate the in-plane (carbon 2s, $2p_x$, and $2p_y$; hydrogen 1s) orbitals and out-of-plane (carbon $2p_z$) orbitals, respectively, of the ring before complexation. To test further the predictive ability of our reported procedures on the metallocenes[5] and to extend our earlier report on $Cr(C_6H_6)_2{}^+$ and $V(C_6H_6)_2$,[6] we decided to carry out SCC, extended Hückel (EH) type molecular orbital calculations of hyperfine coupling constants for the bis-benzene series. Furthermore, we felt that if our wave functions accurately predicted the electron distribution of the unpaired electrons, we could have more confidence in what the calculation says about what is going on in the paired molecular orbitals doing most of the bonding. Research from this laboratory has clearly shown that, contrary to many earlier reports, nmr contact shifts do not provide information about bonding directly. These experiments can provide spin densities which have the potential of being employed to test the ground-state wave function from a semiempirical molecular orbital calculation on a large molecule. Should this potential develop, this would constitute one of the most significant uses to which contact shift measurements can be put. Indeed, it appears that obtaining sufficiently accurate ground-state wave functions will provide one of the few ways of gaining insight into the nature of the metal–ligand bond. The interpretation of results from most physical measurements is ambiguous to say the least.

Molecular orbital calculations on the bis-benzene series were pioneered in the work of Shustorovitch and Dyatkina,[7,8] who employed Roothaan's SCF method. Unfortunately, this work included only the $2p_z$ orbitals on the ring in the basis sets employed, which neglects the possibility of any important role for the ring σ orbitals. Fisher[9] carried out Wolfsberg–Helmholz type calculations for $V(C_6H_6)_2$; again only $2p_z$ ring orbitals were explicitly considered in metal–ring bonding. In a preliminary note, Prins and Reinders have reported an extended Hückel calculation on $Cr(C_6H_6)_2{}^+$, employing a complete basis set for the ring carbons[10] which they utilized in an analysis of the epr spectrum, but they made no attempt to calculate proton hyperfine coupling constants or carry out a detailed population analysis of bonding. A later publication by Prins[4] on this cation confirmed our analysis of the hyperfine coupling constant, indicating the importance of σ orbitals in delocalization. Finally, Hillier and Canadine[11] have recently reported calculations for $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$ using their SCCEI scheme (self-consistent charge with electron interaction) which includes σ and π ring orbitals but neglects 4s and 4p metal orbitals. The latter omission was dictated by their use of the Mulliken population analysis.[12] Negligible participation of σ orbitals to bonding was indicated by an overlap population analysis of the metal–carbon bond.

Negative orbital populations are by no means a new observation in MO calculations involving metals.[13-15]

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This phenomenon often results in a Mulliken charge analysis due to the rather arbitrary partitioning of the overlap charge density *equally* between two atoms which are bonded together. This procedure is hardly realistic, especially if the valence-state ionization potentials of these atoms differ greatly. The only recourse by these various workers has been to assume that bonding contributions from orbitals which show negative occupations (4s and 4p) are negligible and that they may justifiably be omitted from the basis set used in the final calculations. In light of recent work by Cusachs and Politzer,[16,17] a Löwdin population analysis[18] appears more realistic than the Mulliken method, predicting charge distributions, orbital energies, and dipole moments in better accord with experiment, particularly when used with iterative self-consistent charge and configuration methods. The advantage of using the Löwdin method in addition to realism is that one can use *all* metal valence orbitals (3d, 4s, and 4p) and ascertain whether or not the 4s and 4p bonding contributions are in fact negligible.

In spite of the well-known dangers of overextending EH methods, the good correlation obtained with experiment, particularly in the case of hyperfine coupling constants for a *series* of complexes, leads us to believe that, contrary to a published claim,[19] a molecular orbital picture[5,6] gives a satisfactory description of bonding in all sandwich molecules.

Experimental Section

All molecular orbital calculations were carried out using the IBM 360/75 at the University of Illinois and the CDC 6400 facility at the College of Wooster. The extended Hückel program employed has been described previously,[5] the major changes being a conversion to FORTRAN IV, consolidation to an all-core program, and use of GIVENS[20] and ONE-ELECTRON IV[21] to effect matrix diagonalization and overlap evaluation, respectively.

All calculations were carried out with basically the same parameters as used previously,[5] except that the off-diagnonal matrix elements were calculated employing Cusach's approximation[22]

$$H_{ij} = {}^1/_2(2 - |S_{ij}|)S_{ij}(H_{ii} + H_{jj}) \qquad (1)$$

rather than the Wolfsberg–Helmholz expression which required an arbitrary $K = 1.75$, where S_{ij} is the overlap integral calculated in the local coordinate system and the H_{ii}'s are the appropriate VOIP's. In all of our calculations, Basch, Viste, and Gray[23] VOIP data were used to charge correct the diagonal elements. The data for carbon were taken as an average of the configurations tabulated. When the calculation included a metal, the charges were iterated to self-consistency within a test value of 0.01, although, strictly speaking, there is no simple relationship between atomic charges from population analysis and the diagonal matrix elements. It was our observation that iteration to within a test of 0.01 gave eigenvector coefficients within 0.0004, orbital populations within 0.01, and molecular orbital energies within 0.02 eV. The increase in computer time required for lower test values of self-consistency was not judged to be worth the very slightly improved results.

The Löwdin population analysis[18] was used for charge iteration in contrast to previous calculations[5] using the Mulliken method.[12] As will be seen, the hyperfine coupling constants were similar for the two procedures. In the Löwdin method, the secular equation is solved using the Löwdin symmetric orthogonalization procedure. The matrix elements of the Löwdin density matrix are given by

$$d_{ij} = \sum_{k}^{\substack{\text{all} \\ \text{MO's}}} n_k c_{ik} c_{jk} \qquad (2)$$

where n_k is the occupation number of the kth MO and the c_{ij}'s are the eigenvector matrix elements in the Löwdin basis. The diagonal elements d_{ii} give the orbital charges for the ith basis function; the off-diagonal elements are the bond orders. The former obviously will always be positive.

Metal orbitals used were the multiexponential orbitals of Richardson[24] or Clementi.[25] Clementi's "double-ζ" functions were used for carbon. An orbital exponent of 1.2 was used for hydrogen in all calculations. Atom coordinates and details are discussed below for the different calculations.

1. **Bis(benzene)chromium(I) Cation.**—Coordinates for $Cr(C_6H_6)_2^+$ were calculated using the inter-ring distance observed in the crystal structure of $Cr(C_6H_5CH_3)_2I$ by Starovskii and Struchkov.[26] The ring coordinates were calculated from the electron diffraction work of Haaland for neutral bis(benzene)-chromium(0).[27] The following distances were used: C–C, 1.423 Å; C–H, 1.090 Å; inter-ring distance, 3.060 Å. The molecular geometry and atomic numbering for this species are shown in Figure 1a. D_{6h} symmetry was assumed, giving an eclipsed conformation of the rings.

To ascertain the effect of various metal basis orbitals, different calculations using Richardson's Cr(I) and Cr(II) 3d and 4p functions and Clementi's[25b] 3d and 4s orbitals for the configuration $^5D(3d^44s^2)$ were tested. Richardson's 4s function for an atom is the same for all spectral states. The total calculation involved a complete valence basis set of 69 atomic orbitals.

2. **Bis(benzene)chromium(0).**—The calculation was identical with that described above, except the inter-ring separation of 3.226 Å was taken from Haaland's[27] electron diffraction structure. Richardson's neutral metal 3d, 4s, and 4p functions were employed.

3. **Bis(benzene)vanadium(0).**—Since the detailed structure of $V(C_6H_6)_2$ has not been studied, we estimated a V–C bond distance of 2.24 Å from the work of Engebretson and Rundle on $(C_5H_5)(C_7H_7)V$,[28] who found equivalent V–C bond distances in spite of differing ring size. An alternate series of calculations employed Haaland's distances taken for the neutral $Cr(C_6H_6)_2$ molecule. Richardson's neutral metal 3d, 4s, and 4p functions were used in both calculations. V(II) functions were also tested.

4. **Bis(benzene)vanadium(I) Cation.**—The V–C bond distance was estimated from the observed decrease in going from $Cr(C_6H_6)_2$ to $Cr(C_6H_6)_2^+$, which reduces the inter-ring separation by 0.20 Å. Using the above V–C distance of 2.24 Å for the neutral species, a value of 2.16 Å was calculated for $V(C_6H_6)_2^+$. Richard-

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[20] F. Prosser and H. H. Michels, Program No. 62.3, Quantum Chemistry Program Exchange, Bloomington, Ind.

[21] P. O'D. Offenhartz, Program No. 118, Quantum Chemistry Program Exchange, Bloomington, Ind.

[22] (a) L. C. Cusachs and B. B. Cusachs, *J. Phys. Chem.*, **71**, 1060 (1967). (b) Cusachs' expression is not rotationally invariant [see M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **88**, 2353 (1966)]. While we recognize this possible theoretical objection to the use of this relationship in calculating the off-diagonal elements of the EH Hamiltonian matrix, the object of this work is to compare trends for a series of molecules, introducing as few arbitrary parameters as possible into the EH approximation. The z axis was chosen as the principal axis for all calculations to eliminate a comparison of orientation-dependent wave functions. In the light of a referee's concern about this problem, we tested the effect of rotation of the molecule in the coordinate system on our wave functions by repeating the vanadocene calculation using the x axis as the principal axis. Compared to the z-axis result, the MO energies were identical (within 0.01 eV), as were the hyperfine coupling constants. Slight mixing of the eigenvectors (involving 3d and 4p metal orbitals) did occur, however, demonstrating the invariance.

[23] H. Basch, A. Viste, and H. B. Gray, *Theor. Chim. Acta*, **3**, 458 (1965).

[24] (a) J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962); (b) J. W. Richardson, R. R. Powell, and W. C. Nieuwpoort, *ibid.*, **38**, 796 (1963).

[25] (a) E. Clementi, "Tables of Atomic Functions," IBM Corp., San Jose, Calif., 1965; (b) E. Clementi, R. Matcha, and A. Veillard, "Simple Basis Set for Molecular Wave Functions Containing Third Row Atoms," IBM Research Note, IBM Corp., San Jose, Calif., 1968.

[26] O. V. Starovskii and Y. T. Struchkov, *Dokl. Akad. Nauk SSSR*, **135**, 620 (1961).

[27] A. Haaland, *Acta Chem. Scand.*, **19**, 41 (1965).

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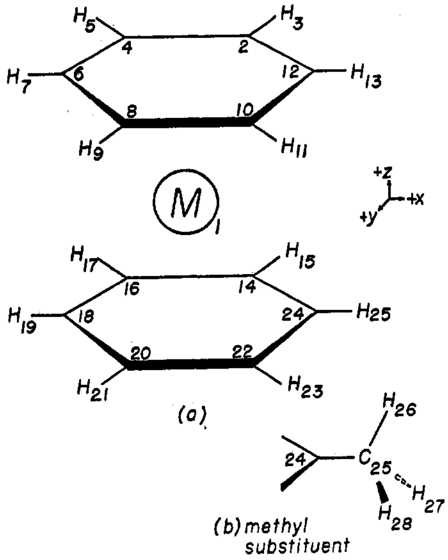

Figure 1.—Atom numbering and coordinate system for the bis-benzene complex molecular orbital calculations for (a) unsubstituted and (b) methyl-substituted complexes.

son's V(II) 3d, 4s, and 4p orbitals were used. Since it was found that $V(C_6H_6)_2^+$ has three electrons in a doubly degenerate orbital, initial calculations would not converge. The input population of each degenerate orbital was divided equally, allocating 1.5 electrons to these two highest filled orbitals. Convergence was readily achieved by this process.

5. **Bis(benzene)cobalt(I) Cation.**—The same coordinates were employed as for $Cr(C_6H_6)_2^+$ since no structural determination is available for $Co(C_6H_6)_2^+$. This gives a Co–C distance very close to that for cobaltocene. Co(II) Richardson functions were used for the 3d, 4s, and 4p orbitals. A comparative calculation was also done with Co(III) orbitals derived by Richardson.

6. **Bis(toluene)chromium(I) Cation.**—The bis(toluene)chromium(I) cation was simulated by monomethylbis(benzene)-chromium(I) cation as was done in 1,1′-dimethylmetallocenes[5] by a calculation of the monomethylmetallocene. This is a good approximation because the rings are relatively independent of one another, and allows considerable saving in computer time. The complete valence orbital basis set required 75 atomic orbitals. The overlap matrix from the bis(benzene)chromium(I) cation calculation (Cr(II) orbitals used) was employed as input and only the *new* overlap integrals involving the methyl group orbitals were calculated, replacing those involving a ring proton. A distance of 1.490 Å was used for the $C–CH_3$ bond length as determined by Starovskii;[26] the C–H distance was taken as 1.095 Å in the methyl group. The methyl group was placed on the lower ring so that the $C–CH_3$ bond was in the plane of the ring. Only one conformation was calculated as shown in Figure 1b.

7. **Bis-Cyclopentadienyl Complexes. a. Vanadocene, Cobaltocene, and Nickelocene.**—Earlier[5] calculations were repeated, as mentioned previously, using instead the Löwdin population analysis as well as Cusach's off-diagonal approximation. In addition, all of the metal valence basis orbitals (3d, 4s, and 4p) were employed in this work.

b. Ferrocene.—Coordinates for this calculation were taken from the electron diffraction work of Bohn and Haaland.[29]

c. Chromocene.—The full calculation was carried out in the usual manner using the coordinates for the ring again taken from the ferrocene structure of Bohn and Haaland. An inter-ring distance of 3.74 Å was calculated using a Cr–C distance of 2.23 Å interpolated by Weiss and Fischer.[30]

Because of space limitations complete eigenvectors, eigenvalues, and detailed population analyses are not presented in this paper but are available from ASIS–NAPS.[31]

Results and Discussion

Our main goal in carrying out the extensive experimental study of spin delocalization in the metallocenes and the bis-benzene complexes was to gain further information about the bonding which occurs in these systems. Our strategy in this regard was to test the theoretical wave functions determined in our calculations by using a molecular property more closely related to the ground-state electron distribution than the electronic absorption spectra or ionization potential. Both a satisfactory prediction of the proton hyperfine coupling constants and prediction of the correct ground state as established by magnetic susceptibility measurements resulted. Our reasonable success in this then led us to attempt a detailed study of the Löwdin population analyses of metal–ring bonding for a complete series of bis-arene complexes, a feat which has not been attempted previously. An extension of this study to the metallocenes[5] was then made to elucidate a consistent picture of the bonding using the molecular orbital model.

Hyperfine coupling constants for ring, A_H, and methyl, A_{CH_3}, protons were calculated from our wave functions using expressions derived previously[5] (eq 6 and 7 from ref 5) which are based on the McConnell relationship[32] for indirect π delocalization (all other spin polarization mechanisms are foreign to the calculation) and on the Fermi relationship for direct σ delocalization.[5,33] Only molecular orbitals containing unpaired electrons are included in the summations.

The values of Q_H and Q_{CH_3} appropriate for the bis-arene complexes are difficult to assess, although they are reasonably invariant for a wide range of organic radicals and methyl-substituted radicals. Arguments were presented[5] to show that these constants should be transferable to the metallocenes, and we will assume this to be the case for the analogous bis-arene complexes. We have chosen $Q_H = -30$ G and $Q_{CH_3} = +30$ G as typical values encountered in organic radicals.

The basis of the McConnell mechanism is, of course, configuration interaction which we discussed in our paper on the experimental contact shifts.[2] The effect is inversely proportional to the energy separation between the ground state and the low-lying excited states. The constancy of the Q's in organic systems has been attributed to a relatively constant energy separation between these levels; *a priori* there is no reason to expect that this energy separation will remain constant throughout the series of metal complexes to be studied, especially as the metal is changed. This will be discussed further for various calculations we have attempted. The strict nonseparability of "σ" and "π" orbitals in these molecules is a further limitation to this approach.

Calculation of Hyperfine Coupling Constants.—The various bis-arene calculations will now be discussed in turn and generalizations will be made concerning trends in energy level ordering. Comparisons will then be made with the metallocenes and trends in

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(30) E. Weiss and E. O. Fischer, *Z. Anorg. Allg. Chem.*, **284**, 69 (1956).

(31) Tabulations of the molecular orbital results have been deposited as Document No. NAPS-01785 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting $12.00 for microfiche or $37.80 forphotocopies. Advance payment is required. Make checks or money orders payable to: CCMIC–NAPS.

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TABLE I

COUPLING CONSTANT CALCULATIONS FOR BIS(ARENE)CHROMIUM CATIONS

Basis set	Population analysis[e]	Charge on Cr[d]	ψ^2 at hydrogen ($\times 10^3$)	A_H (calcd)[c] "direct"	A_H (calcd) "indirect"	A_H (total)	A_H (exptl)
				A. $Cr(C_6H_6)_2{}^+$			
I	L	+0.328	1.91	3.05	−0.06	3.00	
II	M	+0.779[a]	3.38	5.39	−0.15	5.2	3.46[g]
III	M	+0.677[b]	0.95	1.52	−0.02	1.5	
				B. $Cr(C_6H_6)(C_6H_5CH_3)^+$			
I	L	+0.325	1.78[f] (H)	2.94 (H)	−0.06 (H)	2.9 (H)	4.0[h] (H)
			0.11[f] (CH_3)	0.18 (CH_3)	+0.07 (CH_3)	0.25(CH_3)	−0.75 (CH_3)

[a] 4s population is −0.324. Corrected metal charge is +0.454. [b] 4s population is −0.366. Corrected metal charge is +0.311. [c] All *A*'s are in gauss. [d] E. M. Shustorovich and M. E. Dyatkina, *Zh. Strukt. Khim*, **2,** 49 (1961). These workers calculated a charge of +1.4 on the chromium. [e] L = Löwdin; M = Mulliken. [f] Average value of ψ^2. [g] Reference 10. [h] Yu. S. Karimov, Y. M. Chibrikin, and I. F. Shchegolev, *J. Phys. Chem. Solids*, **24,** 1683 (1963).

bonding will be discussed for both series of compounds. (See Figure 1 for the atom numbering and coordinate system for the bis-benzene complex MO calculations.)

A. $Cr(C_6H_6)_2{}^+$ and Monomethylbis(benzene)chromium(I) Cation.—The following basis sets were used for the central metal to ascertain the effect of the metal orbitals themselves on the magnitude of the calculated coupling constants: I, Cr(II) 3d, 4s, 4p Richardson functions; II, Cr(I) 3d Richardson functions, 4p overlaps set to 0.0; III, Cr(^{5}D) Clementi 3d, 4s functions, 4p overlaps set to 0.0. The various aspects of the calculation for $Cr(C_6H_6)_2{}^+$ using these basis sets are summarized in Table I, including the "direct" and "indirect" contributions to the coupling constant. As previously reported,[6] basis set I gives the best reproduction of the experimental coupling constant. Furthermore, there is no basis for the claim[19b] that the positive coupling constant arises through "direct overlap" of the hydrogen with Cr d orbitals since the contribution to ψ^2 from the d orbitals is negligible.[6] We shall see that σ delocalization and possibly exchange polarization[34] are the predominant mechanisms of spin delocalization.

Our results agree with the EH calculation of Prins and Reinders and are consistent with their MO analysis based upon epr.[10] The hydrogen 1s coefficient is not in good agreement (0.057 in this work, compared to 0.13), however, and we have already shown that this coefficient dominates ψ^2 evaluated at the proton.[6] The latter value would lead to a calculated coupling constant of ~6 G which is in very poor agreement with the experimental value of 3.46 G. For all three basis sets, the main contribution to A_H is the "direct" Fermi contact mechanism, the "indirect" McConnell mechanism being negligibly small. While the Mulliken[12] and Löwdin[13] population analyses give much different charges on the metal at first glance, if the Mulliken charge is corrected for the negative 4s population which arises using the Mulliken population analysis, the charges determined by the two methods are almost identical (~0.3). The 4p overlaps were set to zero for basis sets II and III because preliminary calculations gave a total 4p population of −0.70 illustrating the inappropriateness of the Mulliken analysis on these systems.

The calculation for monomethylbis(benzene)chromium(I) cation was carried out using basis set I. The final charge on the Cr atom was found to be +0.325, almost identical with the calculation for $Cr(C_6H_6)_2{}^+$. The unpaired electron has almost exclusively d_{z^2} character. The calculated coupling constant of 2.9 G is somewhat less than the experimental value of 4.0 G for ring protons; the calculated methyl coupling constant is +0.25 G which is in poor agreement with the −0.75-G experimental value as expected. As discussed previously,[2] this large negative coupling constant most probably arises from metal-centered polarization of e_{2g} electrons to leave net β spin in this orbital which is then directly delocalized onto the methyl hydrogens to give the *negative* observed A_{CH_3}. It may be significant then that we have *underestimated* the value of A_H (2.9 *vs.* 4.0 G) in our calculation because, as pointed out, this e_{2g} polarization will also make a *positive* (~1.2 G[6]) contribution to the observed A_H (*i.e.*, α spin from this secondary polarization effect augments σ delocalization of α spin at the ring protons). Recent experimental work on the metallocenes[34a] and 1,1′-dimethylmetallocenes[34b] involving ^{13}C isotropic nmr shifts seems to indicate that this exchange polarization mechanism is indeed operating in the V and Cr species as witnessed by *upfield* ^{13}C shifts. At any rate, the formalism of the extended Hückel calculation is incapable of reproducing these second-order contributions of negative spin density. This, of course, would require an unrestricted calculation.

It is significant that only slight splitting of the ring protons is predicted in this calculation of the methyl-substituted species. The values of the ψ^2 calculation for the two sets of ortho and meta ring protons are 1.51×10^{-3} and 1.61×10^{-3}, respectively. The para proton has the value 2.10×10^{-3}. The unsubstituted ring has a ψ^2 value in this range. Calculating A_H for the range of ψ^2 values predicted for ortho and para protons (considering direct mechanism only) gives a range of 2.4–3.4 G. A splitting of ~1.0 G would not be resolved, for the typical wide-line nmr line width is ~2.5 G for a partially substituted bis-arene species.

B. Bis(benzene)vanadium(0).—The following basis sets were considered in our calculations: I, V(I) 3d, 4s, 4p Richardson functions; II, V(I) Richardson 3d, 4s functions, 4p overlaps set to 0.0; III, V(II) Richardson 3d, 4s functions; 4p overlaps set to 0.0.

The coupling constant calculations for $V(C_6H_6)_2$ are summarized in Table II and show good agreement with the experimental coupling constant of +3.99 G. As

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TABLE II

COUPLING CONSTANT CALCULATIONS FOR $V(C_6H_6)_2$

Basis set	Charge on V^c	ψ^2 at hydrogen ($\times 10^3$)	A_H (calcd)^b "direct"	A_H (calcd) "indirect"	A_H (total)	A_H (exptl)^a
I^c	+0.339	2.52	4.02	−0.08	3.9	
I^{c,g}	+0.317	2.17	3.46	−0.06	3.4	
II^d	+0.648^e	2.85	4.55	−0.05	4.5	3.99
III^d	+0.648^f	1.86	2.97	−0.11	2.9	

[a] Measured in this work (see ref 2). [b] All A's are in gauss. [c] Löwdin population analysis. [d] Mulliken population analysis. [e] 4s population −0.313. [f] 4s population −0.337. [g] V–C bond distance of 2.24 Å employed.

in the calculation for $Cr(C_6H_6)_2^+$, the direct σ delocalization dominates the observed shift with a very small indirect mechanism competing with this dominant mechanism. The V(I) Richardson functions give the best value of the coupling constant as expected since these orbitals correspond to the neutral metal. If the total vanadium charges determined for basis sets II and III are "corrected" for the negative 4s population, charges of +0.33 and +0.31 are obtained, in agreement with the charge of 0.34 determined using basis set I and the Löwdin population analysis. Setting the 4p overlaps to zero (basis set II) does not affect the eigenvector coefficients substantially. The charge of the metal alone is substantially affected by this change. All three basis sets yield similar orbital energies for the a_{1g} molecular orbital; −6.77 for basis set I and ~7.6 for basis sets II and III were calculated. The mass spectral ionization potential is 6.26 eV. The calculations also reproduce the experimentally required $^2A_{1g}$ ground state, the unpaired electron being almost exclusively in the metal d_{z^2} orbital (d_{z^2} coefficient ~1.00 in all cases).[6]

C. Bis(benzene)vanadium(I) Cation.—Final charges were calculated to be as follows: V, +0.350; C, +0.049; H, +0.005. The coupling constant results are summarized in Table III; A_H was calculated to be +1.3 G as compared with our experimental nmr coupling constant of +1.1 G. The agreement is quite good. Looking more closely at the contributions to the delocalization, we see that both the a_{1g} and e_{2g} orbitals give quite large, positive, direct contributions to the calculated coupling constant. As we observed earlier for $Cr(C_6H_6)_2^+$ and $V(C_6H_6)_2$, a very small, indirect, negative contribution arises in the a_{1g} molecular orbital by virtue of a small $2p_z$ coefficient for the ring carbons (~0.05). However, in $V(C_6H_6)_2^+$ where an unpaired electron is now delocalized in the predominantly π e_{2g} orbitals, we have a fairly large *negative* π contribution ($2p_z$ coefficient ~0.17) which opposes the σ delocalization. This results in a net coupling constant less than half that observed for $V(C_6H_6)_2$ where one *less* unpaired electron is present, the *distribution* of total spin being determinative.

TABLE III

COUPLING CONSTANT CALCULATION FOR $V(C_6H_6)_2^+$ CATION

Charge on V^c	ψ^2 ($\times 10^3$)	σ contribution		π contribution		A_H (total)^b	A_H (exptl)
		a_{1g}	e_{2g}	a_{1g}	e_{2g}		
+0.350	1.86 (a_{1g}) 0.48^a (e_{2g})	2.98	−0.04	0.76	−1.14	1.3	1.1

[a] Average at ring protons including *both* e_{2g} molecular orbitals. [b] A_H(calcd) is obtained by summing over σ and π contributions and dividing by $2S$, where $S = 1$. A's are in gauss. [c] Löwdin population analysis.

TABLE IV

COUPLING CONSTANT CALCULATION FOR $Co(C_6H_6)_2^+$ CATION

Charge on Co^c	ψ^2 ($\times 10^3$)	Contributions in e_{1g}^* to A_H				A_H^b	
		σ		π			
		e_{1g}^*(a)	e_{1g}^*(b)	e_{1g}^*(a)	e_{1g}^*(b)	Total	Exptl
+0.211	0.92^a	1.47	1.47	−1.03	−1.03	0.44	−0.276

[a] ψ^2 is equal for e_{1g}^*(a) and e_{1g}^*(b). [b] In gauss. [c] Löwdin population analysis.

The excellent agreement of calculated and observed coupling constants supports an orbital configuration . . . $(e_{2g})^3(a_{1g})^1$ for the $V(C_6H_6)_2^+$. The qualitative interpretation of the shifts[2] did not permit us really to distinguish between the above configuration and an alternative $(a_{1g})^2(e_{2g})^2$ configuration which would give a $^3A_{1g}$ ground state. If the latter configuration is assumed in calculating the coupling constant, a value of −0.14 G results which is in complete disagreement with experiment. Of course, the $^3E_{2g}$ ground state is predicted from the molecular orbital energies themselves, but this agreement of calculated and observed coupling constants lends confidence in the *physical* reality of this assignment.

D. Bis(benzene)cobalt(I) Cation.—The Löwdin population analysis gave charges of +0.211 on the Co atom, +0.058 on the C atoms, and +0.076 on the H atoms. The charge on the metal in all these complexes is considerably below the charge (+1.1 to +1.5) predicted by Barinskii's X-ray absorption edge studies.[35] The results of the coupling constant calculation are summarized in Table IV. A value for A_H of +0.44 G was calculated as compared to the experimental value of −0.276 G from the nmr contact shift studies. The magnitude of the π delocalization has been underestimated (Table IV). The sign disagreement can be attributed to a small difference between two large numbers. Errors of the order of magnitude observed in the previous systems could cause the observed sign discrepancy here. At any rate, since the actual metal–ring distance is unknown, the important thing established by the calculation is that a large π contribution to the coupling constant is predicted which cancels a σ contribution of almost equal magnitude, accounting for the low A_H. The same trend is observed in the calculations for cobaltocene and nickelocene.[5]

The very large carbon $2p_z$ coefficients in the antibonding e_{1g}^* molecular orbitals are consistent with considerable mixing in the bonding counterpart. A larger π delocalization of electron spin is certainly to be expected in this complex on this basis alone.

(35) R. L. Barinskii, *Zh. Strukt. Khim.*, **3**, 458 (1962).

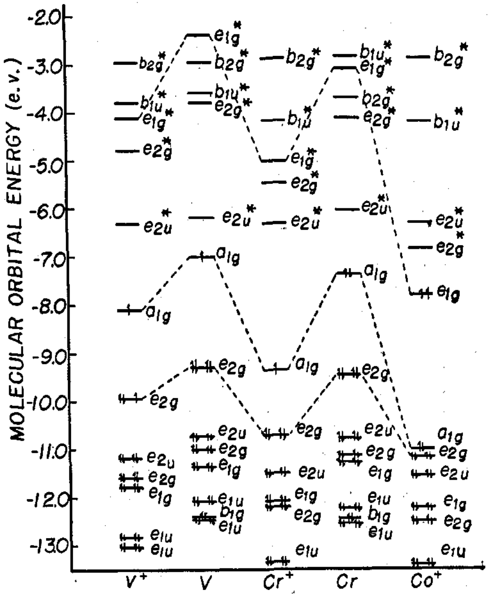

Figure 2.—Molecular orbital symmetries and relative energies in the bis-arene complexes. Only the highest bonding and lowest antibonding MO's from the extended Hückel output are shown.

An orbital configuration of . . .$(a_{1g})^2(e_{1g}^*)^2$ was predicted, giving an $^3A_{1g}$ ground state. This gratifying result is consistent with theoretical and experimental work on the isoelectronic nickelocene and is consistent with our qualitative nmr conclusion[2] on the $Co(C_6H_6)_2^+$ species.

Molecular Orbital Energies.—Figure 2 summarizes the results of the MO calculations for the bis-benzene species discussed above and in addition that of $Cr(C_6H_6)_2$ which has been included for comparison purposes. Several observations can be made: (1) the relative orbital energies of the neutral complexes are higher than those of the charged species as is expected; (2) the e_{2u}^* antibonding orbitals which are comprised totally of ligand atomic orbitals are relatively high in energy and are not occupied for the entire series; (3) the relative ordering of the occupied MO's is not invariant, but shows slight changes as we traverse the series of complexes. [One of the referees was bothered by the fact that e_{1g}^*(metal) was of higher energy than many ligand antibonding orbitals which implied to him that charge-transfer transitions would be of lower energy than the first d–d transition. We wish to emphasize that electronic transitions cannot be predicted from energies of empty orbitals of the ground-state wave function. Indeed, the parametrization of the MO calculation to fit these data by early workers leads to incorrect ground-state wave functions. We are suggesting the nmr criterion as a better test of the ground-state wave function.]

While extended Hückel calculations cannot be expected to give accurate orbital energies or even reliable ordering of orbitals for any *single* system, the success in predicting ground states and hyperfine coupling constants for both the metallocenes and bis-benzene species lends confidence that the *trends* in wave functions for the series of molecules are reliable indications of both bonding trends and electron delocalization. This should be particularly true in the region of the highest filled orbitals. The ground states are in accord, furthermore, with all magnetic properties.

Comparison with Metallocene Calculations.—As described in the Experimental Section, calculations performed earlier on the metallocenes[5] were repeated in this work so that comparisons could be made on a consistent basis of the same off-diagonal approximation, similar basis sets, and the Löwdin charge analysis. Furthermore, our goal of a model able to account for both the bis-benzene and metallocene complexes required this.

A. Correlation with Experimental Data.—Table V compares our calculations with results obtained earlier.[5,36] The difference in the two calculations is so small as to be trivial, and we can conclude that the differences in basis set and population analysis, as well as off-diagonal approximation, do not affect our conclusions regarding the mechanisms of spin delocalization. The difference in the charges can be rationalized as being due to different population analyses, both of which depend upon rather arbitrary definitions of the charge on an atom, as mentioned earlier.

TABLE V

A COMPARISON OF CALCULATIONS ON THE METALLOCENES

	$V(C_5H_5)_2$	$Cr(C_5H_5)_2$	$Co(C_5H_5)_2$	$Ni(C_5H_5)_2$
Coupling constants, G				
Calcd				
a	0.97	1.6[h]	−0.86	−1.1
b	1.1	1.8	−1.1	−1.2
Exptl[i]	0.83	1.2	−1.0	−1.2
Ionization potential,[j] eV				
Calcd				
a	9.10		7.27	8.70
b	8.00	8.54	6.42	7.76
Exptl	7.56[c]	6.91[c]	6.21[e]	7.06[c]
	7.33[e]	6.26[e]	5.95[d]	7.16[e]
Metal charge				
Calcd				
a	+0.61		+0.43	+0.49
b	+0.32	+0.30	+0.27	+0.26
Exptl	(+0.4)[f]	(+0.4)[f]	+0.4[f]	+0.65[g]

[a] Reference 5 employed the Wolfsberg–Helmholz expression for off-diagonal Hamiltonian matrix elements and Mulliken population analysis. 4p orbitals were omitted. [b] This work. All calculations used Cusach's off-diagonal expression and Löwdin's population analysis. 4p orbitals were included. [c] L. Friedman, A. P. Irsa, and G. Wilkinson, *J. Amer. Chem. Soc.*, **77**, 3689 (1955). [d] S. Pignataro and F. P. Lössing, *J. Organometal. Chem.*, **10**, 531 (1967). [e] J. Müller and L. D'Or, *ibid.*, **10**, 313 (1967). [f] R. L. Barinskii, *Zh. Strukt. Khim.*, **1**, 200 (1960). Values in parentheses are values for ferrocene. [g] E. E. Vainshtein and Yu. F. Kopelev, *ibid.*, **3**, 448 (1962). Barinskii has severely criticized this work. [h] Estimated from eigenvectors calculated for $V(C_5H_5)_2$. [i] Reference 3. [j] Ionization potentials obtained from Koopman's theorem suffer some of the same disadvantages as electronic transitions as criteria for ground-state wave functions.

Table VI compares calculations for isoelectronic metallocene and bis-benzene species where identical electronic configurations are predicted. The most important eigenvector coefficients are included for the sake of comparison. It is interesting to note that the carbon $2p_z$ coefficient is much larger for $Ni(C_5H_5)_2$ compared to that for $Co(C_6H_6)_2^+$ which explains the much larger π contribution to spin delocalization which we discussed earlier.[2]

In several cases, we were able to compare calculations for neutral and oxidized species, *e.g.*, $Cr(C_6H_6)_2$ with $Cr(C_6H_6)_2^+$ and $V(C_6H_6)_2$ with $V(C_6H_6)_2^+$. While few

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(36) M. F. Rettig, Ph.D. Thesis, University of Illinois, 1967.

TABLE VI

A COMPARISON OF ISOELECTRONIC METALLOCENE AND BIS-BENZENE COMPLEXES

	...$(e_{2g})^3(a_{1g})^1$ confign				...$(a_{1g})^2(e_{1g}^*)^2$ confign	
	$V(C_6H_6)_2^+$		$Cr(C_5H_5)_2$		$Co(C_6H_6)_2^+$	$Ni(C_5H_5)_2$
	a_{1g}	e_{2g}	a_{1g}	e_{2g}	e_{1g}^*	e_{1g}^*
	MO coeff[a]					
Carbon						
2s	−0.021	0.004	−0.016	0.007	0.060	0.043
$2p_z$	0.039	0.276	0.022	0.192	0.258	0.372
$2p_x$		0.048		0.000	0.093	0.073
	0.033		0.056			
$2p_y$		0.156		0.130	0.125	0.124
Hydrogen						
1s	0.057	0.038	0.060	0.032	0.051	0.041
Metal						
$3d_{z^2}$	1.008		0.984			
$3d_{x^2-y^2}$, $_{xy}$		0.641		0.865		
$3d_{xz}$, $_{yz}$					0.846	0.686
4s	−0.127		−0.226			
	Coupling const					
Calcd	1.3		1.8		0.44[b]	−1.2
Exptl	1.13		1.23		−0.276	−1.24

[a] Coefficients for degenerate orbitals are expressed as the geometric mean; *e.g.*, for e_{2g}, $C_{e_{2g}} = \sqrt{C_{e_{2g(1)}}{}^2 + C_{e_{2g(2)}}{}^2}$. This mean is also used in the a_{1g} orbitals to express the $2p_{x,y}$ coefficients. [b] Calculations using more contracted Clementi orbitals give this coupling constant to be 0.19 G, a trend toward the negative observed value.

generalizations can be made from a comparison of eigenvector coefficients (since all of the MO's change slightly), a more meaningful conclusion is possible from an analysis of the final output charges from these respective calculations. Comparison of the results for the neutral species and the ions illustrates the folly, in some cases, of the often asked question, "What got oxidized, the metal or the ligand?" The electron came out of what is an essentially metal molecular orbital. The Löwdin charges show that the metal charge changes very little (∼+0.01 to +0.05) on going from neutral to oxidized species. The ring atoms are each affected about the same (*e.g.*, carbon, ∼+0.06; hydrogen, ∼+0.02). The result is that the whole molecule got oxidized with the ring acquiring most of the delocalized *positive* charge. Comparing calculations for $Fe(C_5H_5)_2$ and ferricenium ion, $Fe(C_5H_5)_2^+$, the same conclusion holds for the metallocenes.

In Table VII, we have summarized the contributions which various metal atomic orbitals make to the final molecular orbitals of the d^6 $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$ species.

TABLE VII

METAL ORBITAL MOLECULAR ORBITAL COEFFICIENTS FOR $Fe(C_5H_5)_2$ AND $Cr(C_6H_6)_2$

Metal AO (MO)	Fe-$(C_5H_5)_2$	Cr-$(C_6H_6)_2$	Metal AO (MO)	Fe-$(C_5H_5)_2$	Cr-$(C_6H_6)_2$
d_{xz}, d_{yz} (e_{1g}^*)	0.88	1.02	4s (a_{1g})	−0.15	−0.15
$d_{x^2-y^2}$, d_{xy} (e_{2g}^*)	0.48	0.79	$d_{x^2-y^2}$, d_{xy} (e_{2g})	0.84[a]	0.62
d_{z^2} (a_{1g})	0.99	1.01	d_{xz}, d_{yz} (e_{1g})	0.28[a]	0.25

[a] See C. B. Harris, *Inorg. Chem.*, **7**, 1517 (1968). Harris estimated, from an MO interpretation of experimental field gradients for ferrocene, $C_{e_{2g}} = 0.78$ and $C_{e_{1g}} = 0.34$. This is in excellent agreement with our calculated values.

B. Molecular Orbital Energies.—The molecular orbital ordering for the series of metallocenes in the region of the highest filled molecular orbital is shown in Figure 3 and may be compared with the analogous results for the bis-benzene complexes in Figure 2.

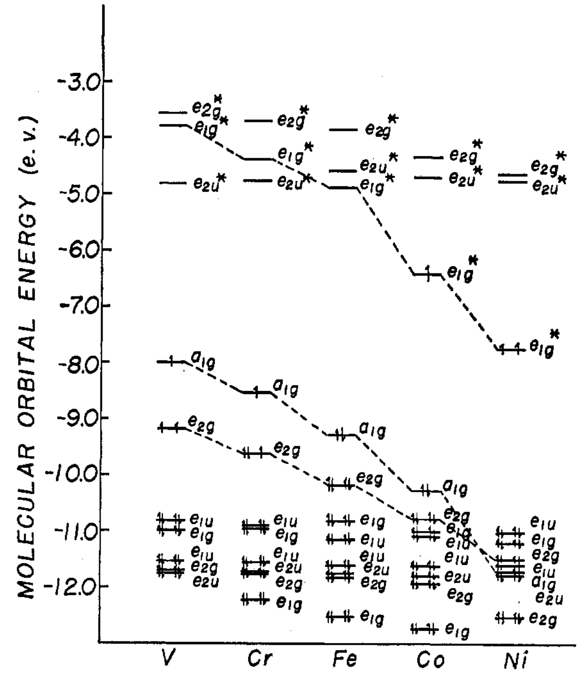

Figure 3.—Molecular orbital diagram for the metallocene series. Only the highest bonding and lowest antibonding MO's from the extended Hückel output are shown.

The effect of increasing nuclear charge is more pronounced in the former series of neutral molecules, the orbitals involved in bonding becoming progressively more stable as shown by the dotted lines.

A contrast can be seen regarding the energy of separation between the predominantly metal molecular orbitals of these two series of complexes. The e_{2g}–a_{1g} separation is always greater in the bis-benzene series than in the metallocenes as has been noted previously for specific examples.[10,37] The same generalization emerges in our consideration of the metal–ring bond orders as will be seen shortly.

Finally, Figure 3 indicates that the a_{1g} level actually falls below the e_{2g} level with $Ni(C_5H_5)_2$ which is opposed to crystal field predictions. However, it may be noted in general that the occupied MO's become closer in energy the heavier the central metal atom.

C. Population Analysis.—A goal of this work has been to arrive at a consistent picture of bonding in the bis-benzene and metallocene complexes using the molecular orbital model. By employing the Löwdin population analysis, we were able to include 4s and 4p metal orbitals in the calculations reported. As we have shown earlier in the evaluation of hyperfine coupling constants, omission of 4s and 4p makes little difference in the values obtained. However, to ascertain the effect of these orbitals on bonding, they must be included in the basis set as we have done. Some earlier work on the metallocenes by Schactschneider, Prins, and Ros[38] included 4s and 4p orbitals by virtue of the Löwdin analysis, but no analysis of bond orders was attempted in detail. The results of our analysis are tabulated in Table VIII. The relative bond orders for each metal orbital of the basis set with the "σ" and "π" orbitals of a ring carbon atom (lo-

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(37) D. R. Scott and R. S. Becker, *J. Phys. Chem.*, **69**, 3207 (1965).

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

TABLE VIII

BOND ORDERS[a] FOR THE BIS-BENZENE AND METALLOCENE COMPLEXES

	A					B				
	$V(C_6H_6)_2^+$	$V(C_6H_6)_2$	$Cr(C_6H_6)_2^+$	$Cr(C_6H_6)_2$	$Co(C_6H_6)_2^+$	$V(C_5H_5)_2$	$Cr(C_5H_5)_2$	$Fe(C_5H_5)_2$	$Co(C_5H_5)_2$	$Ni(C_5H_5)_2$
$3d_{z^2}$ σ	0.07	0.08	0.07	0.03	0.02	0.10	0.11	0.04	0.03	0.03
π	0.02	0.01	0.03	−0.02[b]	−0.01[b]	0.03	0.02	−0.02[b]	0.03	0.03
$3d_{xz}$ σ	0.31	0.31	0.33	0.32	0.17	0.29	0.30	0.31	0.21	0.13
$3d_{yz}$ π	0.29	0.28	0.31	0.28	0.17	0.37	0.38	0.38	0.30	0.20
$3d_{x^2-y^2}$ σ	0.16	0.12	0.07	0.12	0.08	0.17	0.13	0.07	0.05	0.03
$3d_{xy}$ π	0.30	0.39	0.38	0.39	0.31	0.17	0.24	0.31	0.24	0.18
4s σ	0.13	0.13	0.14	0.14	0.16	0.11	0.12	0.13	0.15	0.15
π	0.10	0.11	0.09	0.10	0.12	0.14	0.15	0.14	0.16	0.18
$4p_z$ σ	0.11	0.02	0.12	0.01	0.14	0.01	0.01	0.01	0.02	0.03
π	−0.04[b]	0.04	−0.04[b]	0.05	0.07	0.02	0.03	0.05	0.03	0.01
$4p_x$ σ	0.14	0.13	0.15	0.13	0.15	0.15	0.15	0.16	0.15	0.15
$4p_y$ π	0.19	0.08	0.18	0.07	0.20	0.13	0.12	0.10	0.13	0.17

[a] The σ bond order is actually a hybrid (sp^2) and is defined here as the expression $\sqrt{(2s)^2 + (2p_x)^2 + (2p_y)^2}$, where the quantities in parentheses are the respective carbon 2s, $2p_x$, and $2p_y$ bond orders. The π bond order is defined between the metal orbital and the carbon $2p_z$ orbital only. [b] Negative bond orders imply that the net interaction is antibonding.

cated along the $+x$ axis in all cases) are listed for each complex studied. Note that the σ-bond order is for a hybrid (effectively sp^2) given as a geometric mean of the 2s, $2p_x$, and $2p_y$ bond orders, these orbitals lying, of course, in the plane of the ring. The "π"-bond order includes only the $2p_z$ out-of-plane orbital. It must be noted that we have defined these bond orders unconventionally for the sake of easier comparison.

Looking first at the bond orders for the bis-benzene series in Table VIII (section A), it is apparent from the trend across the transition series that bond orders involving the d_{z^2} orbital with both the σ and π orbitals of the rings decrease. It is significant that the σ-bond orders in this series are about 2–4 times larger than the π-bond orders. This observation is consistent with the very large contribution (>75%) which the d_{z^2} orbital makes to direct σ delocalization when occupied by an unpaired electron. Direct σ delocalization, of course, must involve the in-plane orbitals of the ring. The fact that the bond orders involving the d_{z^2} orbital are much *smaller* than those involving the $e_{1g}(d_{xz}, d_{yz})$ or $e_{2g}(d_{x^2-y^2}, d_{xy})$ metal orbitals shows that the extent of delocalization is not necessarily related to the bond order. This can be seen quite clearly in $Co(C_6H_6)_2^+$ where the direct contribution to the coupling constant is much smaller (unpaired electrons are in the e_{1g}^* orbitals) than in $V(C_6H_6)_2$ or $Cr(C_6H_6)_2^+$ which has one unpaired electron in the a_{1g} orbital (~99% d_{z^2}). Shulman and Sugano have shown that the extent of electron delocalization in σ or π orbitals has no necessary correlation with contributing bond energies from these respective orbitals in $KNiF_3$.[39]

Another surprising observation is the nearly equal σ- and π- bond orders involving the $e_{1g}(d_{xz}, d_{yz})$ orbital set in the bis-benzene series. The σ-bond orders are slightly larger than the π. It is interesting that donor–acceptor bonding involving the e_{1g} set with the ring π orbitals is almost as large as back-bonding due to the interaction of the ring π orbitals with the e_{2g} set. The bonding to the ring σ orbitals is considerably smaller with the e_{2g} set compared to e_{1g}. A similar conclusion is reached by noting the trends in the AO coefficients in the e_{2g} MO's. This will be discussed below in our comparison of metallocene and bis-benzene bonding. Considering the trend across the series, both the σ- and π-bond orders attain their maximum value with $Cr(C_6H_6)_2^+$, which parallels the relative thermodynamic stability of this species compared to the instability of the others.

The role of the $e_{2g}(d_{x^2-y^2}, d_{xy})$ orbitals is very interesting. To the extent that mixing the "d orbitals" into the former ligand empty π* in effect empties the d orbitals, this can be considered a back-bonding interaction when the metal e_{2g} set is filled. The bond orders are relatively large. The effect furthermore is seen to be larger with the ring π orbitals with a smaller σ contribution. Across the series, e_{2g}–σ bond orders are from one-half to one-fifth the magnitude of the e_{2g}–π bond orders. A similar conclusion can be reached by noting the trends in AO coefficients in the e_{2g} MO's themselves.

The Löwdin population analysis predicts small 4s and 4p orbital occupations (~0.07) in contrast to the fairly large negative occupations predicted by the Mulliken charge analysis. These small occupations are entirely reasonable. Several generalizations are possible from an analysis of the bis-benzene data in Table VIII: (1) the 4s σ-bond orders are quite large—much larger (by a factor of 2) than the d_{z^2} σ-bond orders and about the same order of magnitude (~0.1) as those involving the $e_{2g}(\sigma)$ set; (2) the σ-bond orders associated with the $4p_z$ orbital are as large as the analogous 4s bond orders; (3) both the σ- and π-bond orders associated with $4p_x$ and $4p_y$ are larger than either those of 4s or $4p_z$. A conclusion we may draw, therefore, is that these orbitals are more important to actual bonding than has been previously thought, their effect being greater than that of the d_{z^2} orbital, and increasing markedly in importance with the cobalt species. This series of observations should not be surprising at all since recent SCF–MO calculations have shown the importance of 4s and 4p orbitals in various metal complexes, specifically $Ni(allyl)_2$[40] and anions such as CrO_4^- and MnO_4^-.[41] It should be noted that 4p bond orders become more important in the charged bis-arene species.

The conclusions for the metallocenes (see Table VIII, section B) are essentially identical with those for the bis-benzene series. The trends are somewhat easier to observe, since the series is more uniform. These data have been presented in graphical form in Figure 4,

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[39] S. Sugano and R. C. Shulman, *Phys. Rev.*, **130**, 517 (1963).

[40] A. Veillard, *J. Chem. Soc. D*, 1022, 1427 (1969).

[41] I. H. Hillier and V. R. Saunders, *ibid.*, 1275 (1969).

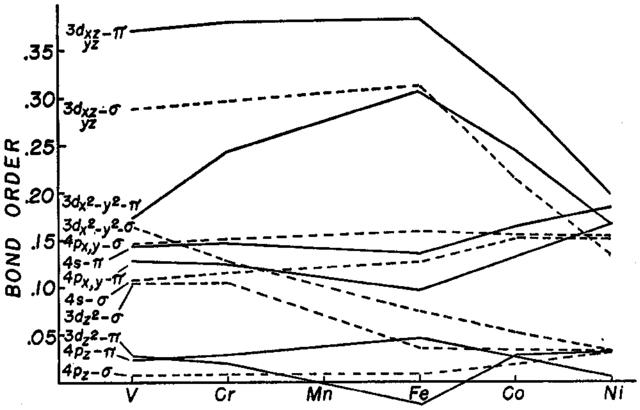

Figure 4.—Metal–ring σ- and π-bond orders as a function of metal for the metallocene series. Bond orders: σ, ---; π, —.

the bond order of various metal orbital–ring orbital combinations being plotted as a function of the respective metals. The diagram clearly illustrates the importance of the d_{xz} and d_{yz} orbitals in both σ and π bonding followed closely by π bonding involving the $d_{x^2-y^2}$ and d_{xy} set. A significant trend is the maximization of these bond orders, parallelling maximum stability at $Fe(C_5H_5)_2$. Some additional trends which are clearly shown are as follows: (1) σ bonding is important compared to π bonding; (2) with increasing atomic number, σ-bonding effects fall off much faster than π-bonding effects; (3) the σ- and π-bonding contributions involving the 4s orbital are increasingly important.

Figure 5 shows the value of the metallocene overlap

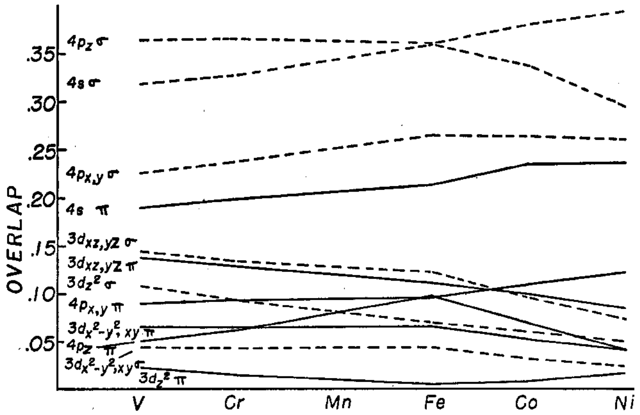

Figure 5.—Metal–ring 2s(σ) and 2p$_z$(π) overlaps as a function of the metal for the metallocene series. Overlaps: σ, ---, π, —.

integrals of the metal orbitals with the carbon 2p$_z$(π) and 2s (the latter as representative of the σ system) as a function of metal. It is immediately apparent that there is little correlation between the magnitudes of the overlaps and the bond orders we have discussed for the metallocenes. The trend in the overlaps furthermore does not necessarily reflect the trends in the bond orders. This is particularly true for the d_{xz}, d_{yz}, $d_{x^2-y^2}$, and d_{xy} orbitals which have quite small overlaps compared to the 4s and 4p orbitals and yet actually dominate the bonding effects. While this observation may reflect the well-known diffuseness of the 4s and 4p orbitals, this glaring inconsistency is used to point out the fallacy of using overlap integrals indiscriminately as substitutes for an analysis of bond orders to ascertain important contributions to bonding in these complexes. This has been done in several studies on both the bis-benzene and metallocene series to underline the importance of back-donation involving the e_{2g} orbitals,[7,8] as well as to show the importance of the in-plane orbitals of the ring.[14] The classification of the compounds as "π complexes" was perpetuated on the basis of this misleading criterion, which, while qualitatively correct in many cases, can very well often be quite wrong.

Perhaps the most significant result of this study is the comparison between the bis-benzene and metallocene series of complexes which formally differ in the size of the rings bonded to the central metal and therefore the net charge density per orbital since these ligands are both formally six-electron "π systems." The comparison between the molecular orbitals and their energies (and related properties) has already been made. The bond orders indicate substantially greater bonding between the ring π orbitals and the metal d_{xz} and d_{yz} orbitals for the cyclopentadienyl complexes of V, Cr, and Fe compared to analogous bis-benzene complexes. They also support a much greater contribution to the bonding from metal e_{2g} orbitals in the bis-benzene complexes. The lower ionization potential of $Cr(C_6H_6)_2$ compared to that of $Fe(C_5H_5)_2$ correlates with the higher (less stable) energy of the a_{1g} MO (see Figure 2). A comparison of the d_{z^2} bond orders in general substantiates a greater role in the metallocenes compared to the bis-benzene series giving rise to a somewhat greater stability of the a_{1g} MO for the five-membered ring species.

The bond orders suggest that bonding involving $d_{x^2-y^2}$ and d_{xy} metal orbitals with e_{2g} ligand orbitals as well as the e_{1g} orbitals bonding to metal d_{xz} and d_{yz} orbitals is important for *both* series. The following comparisons can be made: (1) The conventional interaction involving d_{xz} and d_{yz} metal orbitals and filled ligand orbitals is substantially larger for the metallocene series. (2) Interactions involving the "σ" ring orbitals are important in both series. (3) Bonding involving the filled $d_{x^2-y^2}$ and d_{xy} orbitals occurs in both series but is significantly larger in the bis-benzene series. (4) Significant bond order contributions result from the metal 4s and 4p orbitals. Contrary to the results of Hillier and Canadine,[11] our results do not find π bonding predominating the bonding (80–90%), nor do we find the interaction with the in-plane ring orbitals to be antibonding.

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