Molecular Orbital Calculations on Vanadocene, Ferrocene and Nickelocene

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Semi-empirical molecular orbital calculations were performed for vanadocene, ferrocene and nickelocene. All the valence electrons of the systems were included in the calculations. Diagonal elements of the H-matrix were obtained from valence state ionization potentials and off-diagonal elements were approximated by the Wolfsberg-Helmholz method. An iteration procedure was applied to obtain a consistent charge distribution. The results of the calculations are in agreement with a number of parameters obtained from experiments.

Introduction

Since the discovery of dicyclopentadienyl complexes of transition metals, a large number of experimental data on these complexes have been collected. In consequence, their structure and properties are well-known.

Several theoretical investigations have been carried out for ferrocene in order to gain an insight into the electronic structure of the dicyclopentadienyl complexes. Usually a molecular orbital description is set up for the π-electrons of the cyclopentadienyl rings and the 3d-electrons of the transition metal.[1-4] Several approximate methods have been employed to obtain the matrix elements of the simplified secular determinant. Shustorovich and Dyatkina[1] and also Dahl and Ballhausen[3] used a Pariser-Parr type method, while Fischer[4] followed a simple Wolfsberg-Helmholz approach. The results of all these calculations, which were carried out for ferrocene only, differ considerably, however. To our knowledge, no calculations have been published for the other dicyclopentadienyl complexes.

In order to interpret experimental results for vanadocene and nickelocene[5,6] we performed molecular orbital calculations for these two complexes. For comparison we carried out a similar calculation for ferrocene.

Method of Calculation

Molecular orbital calculations were carried out by a semi-empirical LCAO-MO method.[7] The usual secular equation is of the form

$$|H-S\varepsilon| = 0 .$$

S is the matrix of overlap integrals:

$$S_{ij} = (\chi_i | \chi_j)$$

and H is the Hamiltonian matrix:

$$H_{ij} = (\chi_i | \mathcal{K} | \chi_j) ,$$

where $\mathcal{K}$ is the one-electron Hamiltonian operator. The χ_i are a set of basis functions which for these calculations include the valence atomic orbitals for all atoms (*i.e.* 3d, 4s and 4p functions for the metal, 2s and 2p functions for carbon and a 1s function for hydrogen).

For the metal orbitals we used the functions given by Richardson *et al.*[8] We took the 3d and 4p functions from set II corresponding to M^+ in the d^n and $d^{n-1}p$ configurations, respectively; the 4s function was taken to be the neutral atom function (the only one available). Furthermore we assumed the 2s and 2p functions of carbon to be Slater functions with the orbital exponents given by Clementi and Raimondi[9] and the hydrogen 1s function to be a Slater function with an orbital exponent of 1.00.

Following the usual empirical methods,[10] we approximated the diagonal elements of H as the valence orbital ionization potentials given by

$$H_{ii} = -C - Bq - Aq^2 ,$$

where C, B and A are parameters obtained from spectroscopic data on the free atoms and ions, and q is the net charge on the atom. In these calculations we assumed an initial net charge for each atom, solved the secular equation for eigenvalues and eigenvectors and then computed the charges on each atom with a

(*) Temporarily assigned from Shell Development Co., Emeryville to Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research N.V.).
(1) E. M. Shustorovich and M. E. Dyatkina, *J. Struct. Chem. USSR,* **1**, 98 (1960).
(2) R. E. Robertson and H. M. McConnell, *J. Phys. Chem.,* **64**, 70 (1960).
(3) J. P. Dahl and C. J. Ballhausen, *Dan. Vid. Selsk. Mat.-Fys. Medd.,* **33**, 5 (1961).
(4) R. D. Fischer, *Theor. Chim. Acta,* **1**, 418 (1963).
(5) R. Prins, P. Biloen and J. D. W. van Voorst, *J. Chem. Phys.,* **46**, 1216 (1967).
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(7) M. Wolfsberg and L. Helmholz, *J. Chem. Phys.,* **20**, 837 (1952).
(8) J. W. Richardson, W. C. Nieuwpoort, R. R. Powell and W. F. Edgell, *J. Chem. Phys.,* **36**, 1057 (1962); J. W. Richardson, R. R. Powell and W. C. Nieuwpoort, *J. Chem. Phys.,* **38**, 796 (1963).
(9) E. Clementi and D. L. Raimondi, *J. Chem. Phys.,* **38**, 2686 (1963).
(10) H. Basch, A. Viste and H. B. Gray, *J. Chem. Phys.,* **44**, 10 (1966).

Löwdin[11] charge analysis.* The initial charges were adjusted by an iterative procedure until the assumed and computed charges agreed to 0.002 units.

The values of C, B and A which we used are given in Table I. Values for the metal 3d, 4s and 4p orbitals were selected from Table II of the paper by Basch, Viste and Gray.[10] Values for the 3d functions correspond to the d^n configuration. Since the 4s and 4p orbitals are quite extended and overlap the ligand orbitals considerably, it is difficult to decide which configuration to use for selecting the values of C, B and A for these orbitals. We somewhat arbitrarily chose the values for the $d^{n-1}s$ and $d^{n-1}p$ configurations. No adjustments of C, B and A were made for the computed configuration on each cycle of the iteration on charge. The parameters for carbon and hydrogen were estimated from the VSIP's given by Hinze and Jaffé.[12]

Table I. H_{ii}-parameters (in a.u.)

Orbital	C	B	A
V–3d	0.14315	0.31000	0.06382
V–4s	0.23250	0.24686	0.03898
V–4p	0.12628	0.20720	0.03396
Fe–3d	0.19101	0.39297	0.06291
Fe–4s	0.26122	0.29108	0.03351
Fe–4p	0.13631	0.23160	0.03328
Ni–3d	0.21700	0.43557	0.06474
Ni–4s	0.27718	0.31479	0.03351
Ni–4p	0.14315	0.24093	0.03625
C–2s	0.71738	0.43183	0.04226
C–2p	0.35832	0.39912	0.05696
H–1s	0.48512	0.47225	0.00000

Table II. Distances in $M(C_5H_5)_2$

	r Å
Fe–ring*	1.650
V–ring*	1.895
Ni–ring*	1.790
C–C	1.43
C–H	1.10

* Distance from the metal to the centre of the ring.

We are aware of the fact that in using the free atom and free ion values for C, B and A, the contributions to H_{ii} by other atoms in the molecule are neglected. However, we feel that this is partially corrected by assigning the density in 4s and 4p orbitals to the metal, even though these orbitals have about 90% of their density outside the usual metal radius. This assignment in effect reduces the net charge on the metal and keeps the values of H_{ii} nearer to the neutral atom

(*) According to Löwdin the electron density, d_i, in the ith basis fuction is given by

$$d_i = \sum_k n_k C'_{ik} .$$

where n_k is the occupation number for the kth MO and the C_{ik} are the MO coefficients for Löwdin orthogonalized orbitals. The net charge on an atom is computed by summing the densities in all orbitals assigned to the atom and subtracting the result from the nuclear core charge.

(11) P. O. Löwdin, J. Chem. Phys., 19, 1570 (1951).
(12) J. Hinze and H. W. Jaffé, J. Am. Chem. Soc., 84, 540 (1962).

values. In a more realistic charge distribution at least part of the 4s and 4p density would be assigned to the ligands. The assignment of the density in the 4s and 4p orbitals to the metal corrects the H_{ii} in the same direction as the contributions to H_{ii} by other atoms in the molecule would do.

The off-diagonal elements of H were evaluated by the Wolfsberg-Helmholz approximation[7]

$$H_{ij} = kS_{ij}(H_{ii} + H_{jj})/2$$

with k = 2.00.

Geometric parameters for $Fe(C_5H_5)_2$ were obtained from the structural data of Bohn and Haaland.[13] The M-ring distances for $V(C_5H_5)_2$ and $Ni(C_5H_5)_2$ were estimated from the Fe-ring distance and the unit cell dimensions given by Weiss and Fischer.[14] The geometry of the C_5H_5 ring was assumed to be the same in all compounds. The necessary distances are given in Table II.

Results of Calculations

The results of the calculations on vanadocene, ferrocene and nickelocene are represented in Tables III-V.

Table III. Results of calculations on vanadocene

i	Symmetry	ϵ_i(a.u.)	c_{3d}	Orbital type	Number of electrons
1	a_{2u}	4.2432		$4p_z$	
2	e_{1g}	2.7255	0.104	σ	
3	e_{2u}	2.6993		σ	
4	e_{1g}	1.5161	0.169	σ	
5	e_{1u}	1.4661		σ	
6	a_{1g}	1.0815	0.345	4s	
7	e_{2u}	0.9594		σ	
8	e_{2g}	0.9474	0.005	σ	
9	a_{2u}	0.7531		σ	
10	a_{1g}	0.7440	0.235	4s, σ	
11	e_{1u}	0.6155		σ, 4p	
12	a_{2g}	0.5965		σ	
13	a_{2u}	0.5960		σ	
14	e_{1g}	0.4790	0.140	σ	
15	e_{1u}	0.1792		$4p_{x,y}$	
16	e_{1g}	−0.0965	0.514	π	
17	e_{2u}	−0.1328		π	
18	e_{1g}	−0.1498	1.009	3d	
19	a_{1g}	−0.2382	0.994	3d	1
20	e_{2g}	−0.2685	0.886	3d	2
21	e_{1g}	−0.3810	0.303	π, σ, 3d	4
22	e_{1u}	−0.3878		π	4
23	e_{2g}	−0.4353	0.037	σ	4
24	e_{2u}	−0.4359		σ	4
25	e_{1u}	−0.4585		σ	4
26	e_{1g}	−0.4599		σ	4
27	a_{2u}	−0.4701		π	2
28	a_{1g}	−0.4879	0.010	π	2
29	a_{2u}	−0.5745		σ	2
30	a_{1g}	−0.5799	0.027	σ	2
31	e_{2u}	−0.6577		σ	4
32	e_{2g}	−0.6615	0.024	σ	4
33	e_{1g}	−0.8665	0.003	σ	4
34	e_{1u}	−0.8732		σ	4
35	a_{1g}	−1.0741	0.032	σ	2
36	a_{2u}	−1.1204		σ, $4p_z$	2

(13) R. K. Bohn and A. Haaland, J. Organometal. Chem., 5, 470 (1966).
(14) E. Weiss and E. O. Fischer, Z. Anorg. Allg. Chem., 278, 219 (1955).

Table IV. Results of calculations on ferrocene

i	Symmetry	ε_i (a.u.)	c_{3d}	Orbital type	Number of electrons
1	a_{2u}	6.9638		$4p_z$	
2	e_{2g}	2.7524	0.121	σ	
3	e_{2u}	2.7232		σ	
4	a_{1g}	1.8480	0.252	4s	
5	e_{1u}	1.6354		σ, 4p	
6	e_{1g}	1.5252	0.139	σ	
7	e_{2u}	0.9682		σ	
8	e_{2g}	0.9475	0.004	σ	
9	a_{2u}	0.7329		σ	
10	e_{1u}	0.7194		σ, 4p	
11	a_{1g}	0.7128	0.165	4s, σ	
12	a_{2g}	0.6047		σ	
13	a_{1u}	0.6028		σ	
14	e_{1g}	0.4886	0.150	σ	
15	e_{1u}	0.3091		$4p_{x,y}$	
16	e_{2g}	−0.1071	0.452	π	
17	e_{2u}	−0.1293		π	
18	e_{1g}	−0.1917	0.959	3d	
19	a_{1g}	−0.2720	1.004	3d	2
20	e_{2g}	−0.2968	0.906	3d	4
21	e_{1g}	−0.3834	0.353	π, σ, 3d	4
22	e_{1u}	−0.3936		π	4
23	e_{2g}	−0.4399	0.073	σ	4
24	e_{2u}	−0.4415		σ	4
25	e_{1u}	−0.4643		σ	4
26	e_{1g}	−0.4650		σ	4
27	a_{2u}	−0.4674		π	2
28	a_{1g}	−0.5015	0.010	π	2
29	a_{2u}	−0.5762		σ	2
30	a_{1g}	−0.5861	0.043	σ	4
31	e_{2u}	−0.6581		σ	4
32	e_{2g}	−0.6671	0.033	σ	4
33	e_{1g}	−0.8667	0.018	σ	4
34	e_{1u}	−0.8868		σ	4
35	a_{1g}	−1.0828	0.015	σ	2
36	a_{2u}	−1.1313		σ, $4p_z$	2

Table V. Results of calculations on nickelocene

1	Symmetry	ε_i (a.u.)	c_{3d}	Orbital type	Number of electrons
1	a_{2u}	3.9813		$4p_z$	
2	e_{2g}	2.7321	0.070	σ	
3	e_{2u}	2.7246		σ	
4	e_{1u}	1.5784		σ, 4p	
5	e_{1g}	1.5010	0.081	σ	
6	a_{1g}	1.1512	0.147	4s	
7	e_{2u}	0.9652		σ	
8	e_{2g}	0.9500		σ	
9	a_{2u}	0.7100		σ	
10	a_{1g}	0.6329	0.174	4s, σ	
11	a_{2g}	0.6059		σ	
12	a_{1u}	0.6051		σ	
13	e_{1u}	0.5628		σ, 4p	
14	e_{1g}	0.4773	0.086	σ	
15	e_{1u}	0.2200		$4p_{x,y}$	
16	e_{2g}	−0.1281	0.268	π	
17	e_{2u}	−0.1332		π	
18	e_{1g}	−0.2651	0.904	3d	2
19	a_{1g}	−0.3174	0.996	3d	2
20	e_{2g}	−0.3264	0.967	3d	4
21	e_{1g}	−0.3901	0.433	π, σ, 3d	4
22	e_{1u}	−0.3952		π	4
23	e_{2g}	−0.4412	0.065	σ	4
24	e_{2u}	−0.4420		σ	4
25	e_{1u}	−0.4641		σ	4
26	e_{1g}	−0.4644	0.183	σ	4
27	a_{2u}	−0.4752		π	2
28	a_{1g}	−0.5091	0.009	π	2
29	a_{2u}	−0.5782		σ	2
30	a_{1g}	−0.5849	0.047	σ	2
31	e_{2u}	−0.6599		σ	4
32	e_{2g}	−0.6653	0.027	σ	4
33	e_{1g}	−0.8704	0.019	σ	4
34	e_{1u}	−0.8815		σ	4
35	a_{1g}	−1.0784	0.006	σ	2
36	a_{2u}	−1.1191		σ, $4p_z$	2

In these tables we have listed for each molecular orbital: the symmetry type; the one-electron energy ε_i; the coefficient of the 3d function in this orbital; the orbital type; the number of electrons in that orbital. Under the heading "orbital type" we have listed that orbital which appears with the largest coefficient in the molecular orbital. The orbitals of the σ- and π-systems of the cyclopentadienyl rings are designated as σ and π, respectively. This classification was done with the help of the results of a similar calculation on the $C_5H_5^-$ ion.

Table VI gives the net charges in the complexes, computed by the Löwdin method.[11] These values are only an approximation to the real spacial charge distribution. In our calculations we found a relatively low charge on the metal. However, in order to compute this charge we added the electrons from the 4s and 4p orbitals to the metal charge, which is somewhat unrealistic since, as stated before, the $4p_z$ orbital of the metal, for instance, has most of its density just on the cyclopentadienyl rings. In order to see how the 4s and 4p orbitals affect the results, we performed a calculation on ferrocene in which we used no 4s- or 4p-type basis functions. The results do not differ substantially from those obtained when 4s and 4p functions are included. The ordering of the molecular orbitals, for instance, remains essentially the same. The largest differences are found in the net charges, the charge on the iron atom going up from +0.23 to +0.43.

Table VI. Net charges (4s, 4p included in calculation)

	Vanadocene	Ferrocene	Nickelocene
Metal	0.337	0.230	0.234
Carbon	−0.037	−0.026	−0.023
Hydrogen	0.004	0.003	−0.000

For reasons mentioned in the precious section we shall now only consider the calculations in which 4s and 4p functions were included.

In Table VII we give Mulliken overalp populations for the three systems; these populations are defined by

$$P_{ij} = \sum_{\text{filled orbitals } k} C_{ki} C_{kj} S_{ij} .$$

The overlap population between the central metal atom and a carbon atom involves much the same problem as the net charges: the 4s and $4p_z$ functions do not behave like metal orbitals. As a result, the total overlap population between metal and carbon is slightly negative and cannot be related with a bond order. However, the overlap population between carbon and the metal 3d functions is of the order of 0.04; in the case of the metal 3d functions with a complete cyclopentadienyl ring this works out at approximately 0.2, which is a reasonable number for a metal-to-ligand bond.

Table VII. Mulliken overlap populations

	Vanadocene	Ferrocene	Nickelocene
3d(a_{1g})–C	−0.0046	−0.0057	−0.0019
3d(e_{1g})–C	0.0322	0.0347	0.0048
3d(e_{2g})–C	0.0096	0.0147	0.0056
4s–C	−0.0053	−0.0021	0.0108
4p(a_{2u})–C	−0.0758	−0.0893	−0.0660
4p(e_{1u})–C	0.0102	0.0026	0.0194
C–C (adjacent)	0.5440	0.5460	0.5440
C–H (adjacent)	0.4433	0.4464	0.4389

Finally, Table VIII lists the coefficients of those orbitals which have a predominant 3d character (the numbers 18, 19 and 20 from Tables III-V). The coefficients are given for the molecular orbitals expressed in atomic symmetry orbitals, i.e. for the A_{1g} symmetry $\varphi(3d) = 3d_{z^2}$, $\chi(1S_H) = N(S_{H1} + 1S_{H2} + \cdots + 1S_{H10})$, etc. (In the actual calculation we did not use symmetry orbitals, but diagonalized $(H-\varepsilon S) = 0$ with H and S computed for atomic orbitals).

Most of the existing MO theories assign the highest filled orbitals of ferrocene to the $a_{1g}(3d_0)$ and $e_{2g}(3d_2)$ orbitals.[1,2,4,16,23] Only the calculations of Dahl and Ballhausen are at variance with this assignment.[3] The existing theories, however, do not agree with respect to the assignment of the lowest empty orbital in ferrocene. Dahl and Ballhausen[3] calculated it to be the e_{2u} orbital, whereas Shustorovich and Dyatkina[1] arrived at the $a_{1g}(4s)$ orbital. Only semi-empirical calculations gave the $e_{1g}(3d_1)$ orbital as the lowest empty orbital,[4] which was also predicted by Dunitz and Orgel in their qualitative MO scheme[18] and by Robertson and McConnell in their crystal-field scheme.[2]

Another aspect of the calculated level ordering, the fact that the energy difference between the e_{2g} and a_{1g} orbitals is rather small as compared with that between the a_{1g} and e_{1g} orbitals, is in agreement with the observed spin multiplicities of vanadocene and ferrocene. The experimental fact that the ground state of vanadocene is a quartet spin state and not a doublet spin state means that the gain in exchange energy between the

Table VIII. Coefficients for molecular orbitals with predominant 3d character

Compound	Symmetry	φ (3d)	φ (4s)	χ (2s$_c$)	χ (2p$_x'$)	χ (2p$_y$)	χ (1s$_H$)
Vanadocene	e_{1g}	1.01		0.05	0.31	−0.52	−0.01
	a_{1g}	0.99	−0.22	0.00	−0.13	−0.02	0.08
	e_{2g}	0.88		0.00	−0.11	−0.45	−0.04
Ferrocene	e_{1g}	0.96		0.06	0.30	−0.56	−0.04
	a_{1g}	1.00	−0.13	−0.02	−0.10	−0.05	0.09
	e_{2g}	0.91		0.01	−0.14	−0.39	−0.02
Nickelocene	e_{1g}	0.90		0.05	0.20	−0.57	−0.04
	a_{1g}	1.00	−0.12	−0.01	−0.07	−0.02	0.07
	e_{2g}	0.97		0.00	−0.11	−0.22	−0.01

Comparison with Experiments

The outcome of our calculations is that the level ordering of the highest filled and lowest empty orbitals in vanadocene, ferrocene and nickelocene is the same: $e_{2g} < a_{1g} < e_{1g}$. All the three orbitals have a predominant metal 3d character. This level ordering, which looks like being the result of a splitting of the 3d orbitals in the axial crystal field of the cyclopentadienyl ligands, can be compared with the results of magnetic and optical measurements on the ground states and lowest excited states of these complexes.

ESR measurements on vanadocene,[5,15] Mössbauer experiments on ferrocene[16] and susceptibility measurements on nickelocene[6,15] revealed that the ground state configurations for these molecules are $^4A_{2g}(e_{2g}^2 \cdot a_{1g})$, $^1A_{1g}(e_{2g}^4 \cdot a_{1g}^2)$ and $^3A_{2g}(e_{2g}^4 \cdot a_{1g}^2 \cdot e_{1g}^2)$, respectively. On the other hand, the lowest energetic bands in the electronic absorption spectra of vanadocene, ferrocene and nickelocene are assigned to spin-allowed d–d transitions from the e_{2g} and a_{1g} orbitals to the e_{1g} orbital.[15,17] We conclude that with respect to the highest filled and lowest empty orbitals the results of our calculations are in qualitative agreement with the experimental data.

$e_{2g}^2 \cdot a_{1g}^1$ and e_{2g}^3 configurations is greater than the loss in orbital energy. The requirement that the energy difference btween the e_{2g} and a_{1g} orbitals should not be too large is fulfilled by our calculation. In the same way, the large splitting between the a_{1g} and e_{1g} levels calculated for ferrocene makes it understandable that ferrocene is a low-spin and not a high-spin complex.

Not only qualitatively, but also quantitatively our calculations are in reasonable agreement with the magnetic and optical measurements. The calculated differences in one-electron energies between the 3d levels in vanadocene (2.31, 3.15 eV), ferrocene (2.18, 2.86 eV) and nickelocene (1.42, 1.67 eV) must be compared with the measured absorption bands in the visible region: vanadocene (2.14, 2.43, 3.02 eV),[15,20] ferrocene (2.73, 2.94, 3.82 eV)[15,17,21,22] and nickelocene (1.80, 2.18, 2.82 eV).[15,21] It is assumed that the three bands in the visible region are due to d–d transitions: $A_2 \rightarrow E_1$ ($a_1 \rightarrow e_1$, $e_2 \rightarrow e_1$) and $A \rightarrow E_2$ ($e_2 \rightarrow e_1$). A full discussion on the absorption spectra of these compounds will appear in a separate publication.[15]

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According to Koopmans' theorem the ionization potential is approximated as the opposite of the energy of the highest occupied molecular orbital. The calculated ionization potential of ferrocene is therefore 7.4 eV. This is in good agreement with the value of 7 eV for the appearance potential of the $(C_5H_5)_2Fe^+$ ion in the mass spectrum.[23] The calculated IP for the $C_5H_5^-$ ion was found to be 8.75 eV (experimental value for the C_5H_5 radical is 8,7 eV).[24]

The orbital character of the partly filled orbitals can be inferred from the esr hyperfine data.[5] It is concluded[15] that for the e_{2g} orbital the coefficient of the $3d_2$ metal robital in the molecular orbital is 0.85 ± 0.02 while for the a_{1g} orbital the 4s metal orbital coefficient is equal to 0.27 ± 0.07. These values are in agreement with our calculated values (cf. Table VIII). Dahl and Ballhausen[3] calculated the $3d_2$ metal coefficient in ferrocene to be 0.90, Shustorovich and Dyatkina[1] arrived at 0.85. The 4s metal orbital coefficient indicates that only a small degree of mixing occurs between the $3d_0$ and 4s orbitals. This means that the ideas introduced by Moffit on this point[25] are to be rejected. The theory advanced by Liehr and Ballhausen correctly predicts the vanadocene ground-state configuration to be $^4A_{2g}(a_{1g}e_{2g}^2)$. However, in contrast with the experimental results they identify this a_{1g} orbital with the 4s orbital.[19]

The assignment of the infra-red spectra renders it possible to compare the metal-to-ring bond strength in vanadocene, ferrocene and nickelocene. From the antisymmetric ring-metal stretching vibration (ω_{11}) it is concluded that the force constant of the metal-cyclopentadienyl ring bond amounts to 2.7 mdyn/Å in ferrocene and to 1.5 mdyn/Å in vanadocene and nickelocene,[26] thus indicating that ferrocene has a stronger metal-ring bond than vanadocene and nickelocene. The same conclusion can be drawn from mass-spectral data.[23] Vanadocene and nickelocene show a greater molecule ion instability than ferrocene, with an average bis-cyclopentadienyl-metal positive ion

yield close to 48% of the total ion yield, as compared with 61% for ferrocene. This means that the metal-to-ring bond in vanadocene and nickelocene is weaker than in ferrocene. From heat-of-combustion measurements standard enthalpies of formation of ferrocene and nickelocene were calculated.[27] It was found that nickelocene is less stable than ferrocene by 24 kcal/mole. These results, obtained from IR spectra, mass spectra and combustion measurements, can be compared with the calculated bond orders (cf. Table VII). The overlap populations between a cyclopentadienyl ring and the metal 3d orbitals are calculated to be 0.19, 0.22 and 0.04 for vanadocene, ferrocene and nickelocene, respectively. Although the bond orders calculated for vanadocene and ferrocene have reasonable values for a metal-to-ligand bond, the small bond order calculated for nickelocene is in disagreement with the experimental results mentioned above.

Our calculations indicate that the charge on the vanadium nucleus in vanadocene is higher than that on the iron and the nickel nucleus in their sandwich compounds. Wilkinson gathered some information which seems to indicate that vanadocene in fact has a higher ionicity than ferrocene and nickelocene.[28] Of the three compounds, only vanadocene gives a conducting solution in tetrahydrofuran and liquid ammonia (with which it forms ammoniates). Correspondingly, whereas ferrocene and nickelocene do not react with ferrous chloride, vanadocene forms a faint trace of ferrocene with ferrous chloride. The fact that vanadocene has a dipole moment in a solution of dioxan, while ferrocene and nickelocene have none, has also been explained on the assumption that the metal-ring bond in vanadocene is weakly ionic in character.[29]

In spite of the many objections that can be raised against the semi-empirical method of calculation, the results obtained on transition-metal complexes are fairly well compatible with the experimental data. Therefore, although this method is not very satisfactory from a theoretical point of view, we feel safe in using the results as a guide in experimental work.

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