Inorganica Chimica Acta, 25 (1977) 113–119
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Spin Density Distribution in Some Paramagnetic Metallocene and Bis-benzene Complexes of the First Transition Series

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Received February 28, 1977

The spin density distribution in bis-cyclopentadienyl $M(C_5H_5)_2$ (M = V, Cr, Ni) and bis-benzene (M = V, V^+, Cr^+) complexes has been calculated by spin unrestricted MO–LCAO–INDO calculations.

The present version of the INDO method, whose results are compared with those obtained with other semiempirical methods, predicts in each case the correct sign of the hyperfine coupling constant for ^1H and ^{13}C nuclei. The spin density distribution is interpreted as due to two mechanisms: the spin delocalisation and the spin polarisation.

Introduction

The electronic structure of the paramagnetic bis-cyclopentadienyl and bis-benzene complexes of the first transition series has been extensively investigated by means of PES, ESR and NMR spectroscopy. The symmetry of the electronic ground state, together with the values of the hyperfine coupling constants for hydrogen and carbon nuclei have been established [1, 2].

The theoretical investigation of the electronic structure of metallocene complexes has been attempted with many different methods of varying degrees of sophistication. Some *ab initio* calculations has been done on ferrocene and on ferrocene anion and cation [3], the symmetry of the ground and excited states has been investigated by means of CNDO–MECI [4] method and INDO type calculations [5] successfully predict the symmetry of the ground state and the sign of spin transfer on hydrogen and carbon atoms for some sandwich complexes [6]. Until now, however, a detailed description of the mechanism of the spin distribution has been attempted only by means of some rather simplified MO–LCAO methods derived from the Extended Hückel theory.

The spin density on each atom must be interpreted as due to two different mechanisms: the direct spin delocalisation and the spin polarisation. The former is directly related to the synergic metal–ligand electron transfer, thus it may be related in a more or less direct way to the covalency of the metal–ligand bond. This may be accounted for by any MO–LCAO approach using a charge dependent hamiltonian, such as for instance the simplest one known as the "iterative Hückel theory" or SCCC (Self Consistent Charge and Configuration). The spin polarisation process, on the contrary, is due to the exchange energy, consequently its description is given by the "spin unrestricted Hartree–Fock" approach (UHF) which takes into account, even in a partial way, the exchange integrals. Obviously, this second contribution is not considered by any approach in which the interelectronic repulsion is neglected, such as SCCC.

The easiest version of the UHF method is the INDO approximation [7] that we have used with the aim of discussing in a semiquantitative way the spin density distribution mechanism.

Computational Method

The computational method adopted here is a simplified version of the original INDO method [7]; the approximation used in constructing the matrix elements of the Hartree–Fock operator have been discussed elsewhere [8]. Two points arise in the use of the UHF method. The first is related to the orbital degeneracy, because the UHF method gives a spin and symmetry unrestricted wave function. This fact means that the spatial wave function spans the full symmetry of a subgroup of the point group to which the nuclear frame belongs (*e.g.* a wave function of D_{4h} instead of O_h symmetry in octahedral complexes). In our complexes of D_{5d} or D_{6h} symmetry, we could not use the symmetry unrestricted wave function (which would give different charges on symmetry equivalent atoms) as we were interested in charge and spin distribution. Consequently for orbitally degenerate cases the true wave function has been obtained as a linear combination of determi-

TABLE I. Charge and Spin Density Distribution in the Cyclopentadienyl Radical.

	$2s_C$	$(2p_x + 2p_y)_C$	$2p_{zC}$	$1s_H$
R	1.0460	1.9600	1.0000	0.9940
$(R^{\alpha})_{BA}$	0.5266	0.9811	0.6000	0.4923
ρ_{BA}	0.0072	0.0021	0.2000	−0.0094
ρ_{SD}	0.0000	0.0003	0.2000	0.0002
ρ_{SP}	0.0072	0.0018	0.0000	−0.0096
$\langle S^2\rangle_{BA}$ =	0.7506	$\langle S^2\rangle_{ASA}$ = 0.7500		

Net charges: q_C = −0.0060; q_H = 0.0060

nants spanning the full symmetry of the true point group but neglecting the Jahn–Teller distortion. The second point is related to the fact that the UHF method does not produce an eigenstate of the S^2 operator but gives a wave function which is a combination of several different spin states. By using the spin annihilation technique [9–11] one can obtain a wave function which is not too far from a pure spin state. As a matter of fact, with the annihilation technique it is possible to separate the spin distribution into two contributions, namely ρ_{SD} and ρ_{SP} [12–14].

The former is the spin delocalisation term and is related to the "restricted" component of the wave function while the second is the spin polarization term which is a special feature of the UHF method. We have calculated for each atomic orbital the following data: R, $(R^{\alpha})_{BA}$, ρ_{BA}, ρ_{SD}, ρ_{SP} which are respectively the values of total electron population ($R = R^{\alpha} + R^{\beta}$), spin α electron population and spin density "before the annihilation" (BA) and the contributions of the spin delocalization and spin polarization respectively. In addition to that, we have calculated $\langle S^2\rangle_{BA}$ and $\langle S^2\rangle_{ASA}$ (After Single Annihilation) in order to prove that our annihilated wave function describes a pure, or a very little contamined, spin state.

The INDO wave functions for the complexes have been constructed with a minimal STO basis set including the valence 4s and 3d orbitals of the metal atom, the 2s and 2p orbitals of the carbon and the 1s orbital of the hydrogen atoms. The Slater exponents are taken from Gouterman [15] or Clementi [16], while the β parameters used in the evaluation of the non diagonal elements of the core matrix are those of Pople [7] and Clack [17].

The parameters for computing the A_{iso} values for ^1H and ^{13}C spectra are taken from Pople [7].

Results

Cyclopentadienyl Radical

In order to prove that our INDO approach gives results as good as those obtained by the original INDO version, we have carried out a calculation of the electronic structure of the C_5H_5 radical with a geometry identical to that of the C_5H_5 anion [18]. When the fivefold axis of D_{5h} symmetry is coincident with the z molecular axis, the sum of the electron population in $2p_x$ and $2p_y$ orbitals of the carbon atoms is invariant under symmetry operations. Consequently, in Table I, only the data reffering to a carbon atom are reported (the same considerations hold for the C_5H_5 and C_6H_6 rings in the metal complexes).

TABLE II. Geometrical Parameters for $M(C_5H_5)_2$ and $M(C_6H_6)_2$ Complexes.

Complex	Inter-ring distance	R_{C-C}	R_{C-H}	Ref.
$V(C_5H_5)_2$	3.79	1.43	1.10	26
$Cr(C_5H_5)_2$	3.60	1.43	1.10	26
$Ni(C_5H_5)_2$	3.58	1.43	1.10	26
$V(C_6H_6)_2$	3.226	1.423	1.090	22
$[Cr(C_6H_6)_2]^+$	3.060	1.423	1.090	22

The majority of the spin density of C_5H_5 radical is associated to the p_z (π type) orbitals of the carbon atoms, while on the $2s_C$ and $1s_H$ orbitals only a spin density of 0.0072 and −0.0094 respectively is localised. An A_{iso} (^{13}C) of 5.90 G and A_{iso} (^1H) of −5.07 have been calculated; they well compare with those obtained with the original INDO [7] method (A_{iso} (^{13}C) = 4.1 G and A_{iso} (^1H) = −4.8 G) and with the experimental value of −5.60 G for A_{iso} (^1H) [19]. The SD and SP data reported in Table I show that the spin density on the p_{π} orbital of the carbon atom is entirely related to the spin delocalization mechanism. By symmetry requirements the SD values on orbitals of σ type ($2s_C$, $2p_{\sigma C}$ and $1s_H$) should be zero; our computed values, on the contrary, are very small and positive (of the order of 10^{-4}) as a result of an accumulation of small numerical errors which in any case do not affect the meaning of our results.

Bis-cyclopentadienyl Complexes

We have carried out INDO calculations on metallocene compounds of vanadium, chromium and nickel (Table II).

If the symmetry is assumed to be D_{5d}, the atomic orbitals of the metal span the irreducible representations as follows:

$$e_{1g}(d_{xz}, d_{yz}), e_{2g}(d_{x^2-y^2}, d_{xy}), a_{1g}(d_{z^2}).$$

All available ESR, NMR and PES data [1, 2] have been interpreted as being consistent with the following ground state symmetry:

$V(C'_5H_5)_2$ e_{2g}^2 a_{1g}^1, $^4A_{2g}$

$Cr(C_5H_5)_2$ e_{2g}^3 a_{1g}^1, $^3A_{2g}$

$Ni(C_5H_5)_2$ e_{2g}^4 $a_{1g}^2e_{1g}^2$, $^3A_{2g}$

TABLE III. Charge and Spin Density Distribution in the Vanadocene Complex.

	$4s_V$	$3d_{z^2}V$	$(3d_{xz}, 3d_{yz})_V$	$(3d_{x^2-y^2}, 3d_x)_V$
R	0.7907	0.9779	0.4331	0.9766
$(R^\alpha)_{BA}$	0.4197	0.9557	0.2413	0.9707
ρ_{BA}	0.0486	0.9335	0.0495	0.9648
ρ_{SD}	0.0416	0.9330	0.0000	0.9643
ρ_{SP}	0.0070	0.0005	0.0495	0.0005
	$2sC$	$(2p_x + 2p_y)_C$	$2p_{zC}$	$1s_H$
R	1.0037	1.9432	1.0998	0.9944
$(R^\alpha)_{BA}$	0.5014	0.9717	0.5478	0.4990
ρ_{BA}	−0.0008	0.0002	−0.0041	0.0036
ρ_{SD}	−0.0003	0.0022	0.0054	0.0021
ρ_{SP}	−0.0005	−0.0020	−0.0095	0.0015
	$\langle S^2\rangle_{BA} = 3.7577$		$\langle S^2\rangle_{ASA} = 3.7500$	

Net charges: $q_V = 0.4117$; $q_C = -0.0468$; $q_H = 0.0056$

TABLE IV. Charge and Spin Density Distribution in the Chromocene Complex.

	$4s_{Cr}$	$3d_{z^2}Cr$	$(3d_{xz}, 3d_{yz})_{Cr}$	$(3d_{x^2-y^2}, 3d_{xy})_{Cr}$
R	0.8573	0.9939	0.4801	1.4370
$(R^\alpha)_{BA}$	0.4426	0.9716	0.2603	0.9601
ρ_{BA}	0.0297	0.9492	0.0404	0.4832
ρ_{SD}	0.0227	0.9492	0.0000	0.4776
ρ_{SP}	0.0552	0.0000	0.0404	0.0056
	$2s_C$	$(2p_x + 2p_y)_C$	$2p_{zC}$	$1s_H$
R	0.9967	1.9429	1.0998	0.9921
$(R^\alpha)_{BA}$	0.4980	0.9714	0.5472	0.4979
ρ_{BA}	−0.0007	−0.0001	−0.0053	0.0037
ρ_{SD}	0.0001	0.0011	0.0027	0.0025
ρ_{SP}	−0.0008	−0.0012	0.0080	0.0012
$\langle S^2\rangle_{BA} = 2.0055$		$\langle S^2\rangle_{ASA} = 2.0000$		

Net charges: $q_{Cr} = 0.3146$; $q_C = -0.0393$; $q_H = 0.0079$

where e_{2g}, a_{1g} and e_{1g} which are pure 3d metal orbitals in ligand field theory have to be interpreted as MO with high 3d contribution in MO–LCAO approach.

In our approach the charge and spin density distributions have been obtained solving the UHF equations with the Roothaan iterative scheme, without *a priori* fixing the symmetry of the α and β occupied MO. In other words, we know the symmetry of the computed state only at self-consistency. Although such a procedure does not produce necessarily the ground state wavefunction, the 3d metal orbital electron and spin density agrees with the above reported experimental ground state symmetry.

Bis-Cyclopentadienyl Vanadium(II)

The largest spin density lies in the 3d orbitals of a_{1g} and e_{2g} symmetry $[(e_{2g})^{1.92}\ (a_{1g})^{0.93}\ (e_{1g})^{0.1}]$. The found $\langle S^2\rangle_{BA}$ value of 3.7577 confirms that the wave function is mainly composed by a quartet (Table III). The sign of the spin density on the coordinated ligand is reversed with respect to the free ligand; moreover on the hydrogen atom both the SD and the SP contributions have the same sign. Spin density values produce an A_{iso} (^1H) value of 0.65 G in agreement with the observed value of 0.832 G [20]. However, the calculated NMR contact shift of the ^{13}C nucleus is +322 ppm, quite far from the observed value of +588 ppm [21].

TABLE V. Change and Spin Density Distribution in the Nickelocene Complex.

	$4s_{Ni}$	$3d_{z^2}\,_{Ni}$	$(3d_{xz}, 3d_{yz})_{Ni}$	$(3d_{x^2-y^2}, 3d_{xy})_{Ni}$
R	0.8783	1.9886	1.3534	1.9807
$(R^\alpha)_{BA}$	0.4382	0.9945	0.9987	0.9908
ρ_{BA}	−0.0018	0.0004	0.6440	0.0009
ρ_{SD}	0.0002	0.0000	0.6436	0.0001
ρ_{SP}	−0.0020	0.0004	0.0004	0.0008
	$2s_C$	$(2p_x + 2p_y)_C$	$2p_{zC}$	$1s_H$
R	0.9991	1.9478	1.1036	0.9961
$(R^\alpha)_{BA}$	0.5014	0.9756	0.5843	0.4976
ρ_{BA}	0.0037	0.0034	0.0650	−0.0009
ρ_{SD}	0.0017	0.0034	0.0650	0.0011
ρ_{SP}	0.0020	0.0000	0.0000	−0.0020

$\langle S^2\rangle_{BA} = 2.0005$ $\langle S^2\rangle_{ASA} = 2.000$

Net charges: $q_{Ni} = 0.4650$; $q_C = -0.0504$; $q_H = 0.0039$

Bis-cyclopentadienyl Chromium(II)

A value of $\langle S^2\rangle_{BA}$ (see Table IV) equal to 2.0055 has been obtained, corresponding to a triplet. Because the e_{2g} orbitals are degenerate, the symmetry restrictions place about one half electron in each of the $d_{x^2-y^2}$ and d_{xy} orbitals: the spin distribution in 3d orbitals is $(e_{2g})^{0.96}$ $(a_{1g})^{0.95}$ $(e_{1g})^{0.08}$ while the total electron distribution is $(e_{2g})^{2.86}$ $(a_{2g})^{0.99}$ $(e_{1g})^{0.96}$.

The signs of the SD and SP contributions on the ligand atoms are the same as in the case of vanadocene complex. The computed A_{iso} (^1H) value is 1.13 G in agreement with the experimental value of 1.23 G [20]. Also the calculated contact shift for the ^{13}C nucleus agrees with the experimental one [21] (291 ppm and 325 ppm respectively).

Bis-cyclopentadienyl Nickel(II)

The total electron population on 3d metal orbitals (see Table V) $[(e_{2g})^{3.96}$ $(a_{2g})^{1.99}$ $(e_{1g})^{2.70}]$ agrees with the ligand field model predictions but shows a large covalent character. The two unpaired electrons in this case are only partially localized on the e_{1g} orbitals of the metal $[(e_{2g})^{0.00}$ $(a_{1g})^{0.00}$ $(e_{1g})^{1.29}]$ and the remaining spin density is delocalized on the ligand. In this respect the nickelocene is markedly different from the vanadocene and chromocene compounds. The SD and SP contributions on hydrogen atoms are also different from the previous cases: the SP contribution has a negative sign and is larger than the SD contribution, producing a net negative spin density on the hydrogen atoms. As a consequence an A_{iso} (^1H) value of −0.25 G has been calculated. Such a value is far from the observed value of −1.24 G [20] but we believe that already the prediction of a correct sign is an important observation. In contrast to the previous compounds a reasonable result is obtained for the NMR contact shift of ^{13}C which has been evaluated as −1240 ppm in agreement with the observed data of −1436 ppm [21].

Bis-benzene Complexes

Similar calculations have been performed on V, V^+ and Cr^+ bis-benzene complexes, assuming a D_{6h} symmetry (Table II). For both complexes $V(C_6H_6)_2$ and $[Cr(C_6H_6)_2]^+$ a doublet ground state $^2A_{1g}$ with one unpaired electron mainly localized on the d_{z^2} orbital of the metal has been reported [1].

Bis-benzene Vanadium(0) and (I)

For the vanadium(O) complex a $\langle S^2\rangle_{BA}$ value of 0.7949 (Table VI) has been calculated, which is not too far from the pure doublet value; moreover the maximum spin density associated to the d_{z^2} orbital of the vanadium atom confirms a $^2A_{1g}$ ground state. A A_{iso} (^1H) value of 3.29 G, which reproduces not too badly the observed value of 3.99 G [22], has also been calculated. Our complete SCF calculation on the $[V(C_6H_6)_2]^+$ ion gives a spin density distribution of the type: $\rho(d_{z^2}) = 0.9484$ and $\rho(d_{x^2-y^2}) = \rho(d_{xy}) = 0.5903$ which should correspond to the state $(e_{2g})^3$ $(a_{1g})^1$ or $^3E_{2g}$. Such a state has been proposed as the ground state for the bis-π-mesitylenevanadium(I) complex on the basis of the He(I) photoelectron spectrum [27].

Drago *et al.* [22] arrived at the same conclusions by a comparison of the computed A_{iso} (^1H) with the experimental data. Indeed for $[V(C_6H_6)_2]^+$ we have obtained a A_{iso} (^1H) value of 1.32 G which is in very good agreement with the experimental value of 1.1 G [22].

TABLE VI. Charge and Spin Density Distribution in the Bis(benzene) Vanadium Complexes.

	$4s_V$	$3d_{z^2}$ V	$(3d_{xz}, 3d_{yz})_V$	$(3d_{x^2-y^2}, 3d_{xy})_V$
R	0.8142	0.9817	0.3363	1.1881
$(R^{\alpha})_{BA}$	0.4165	0.9602	0.1738	0.6660
ρ_{BA}	0.0189	0.9387	0.0113	0.1439
ρ_{SD}	0.0159	0.9384	−0.0001	0.0011
ρ_{SP}	0.0030	0.0003	0.0114	0.1428
	$2s_C$	$(2p_x + 2p_y)_C$	$2p_{zC}$	$1s_H$
R	0.9857	1.9537	1.0785	0.9951
$(R^{\alpha})_{BA}$	0.4923	0.9760	0.5264	0.5006
ρ_{BA}	−0.0011	−0.0016	−0.0258	0.0061
ρ_{SD}	0.0004	0.0002	0.0003	0.0031
ρ_{SP}	−0.0015	−0.0018	−0.0261	0.0030

$\langle S^2\rangle_{BA} = 0.7949$ $\langle S^2\rangle_{ASA} = 0.7493$

Net charges: $q_V = 0.1552; q_C = -0.0179; q_H = 0.0050$

TABLE VII. Charge and Spin Density in the Bis(benzene) Chromium(I) Cation.

	$4s_{Cr}$	$3d_{z^2}$ Cr	$(3d_{xz}, 3d_{yz})_{Cr}$	$(3d_{x^2-y^2}, 3d_{xy})_{Cr}$
R	0.8951	1.0051	0.4391	1.4989
$(R^{\alpha})_{BA}$	0.4516	0.9805	0.2267	0.7806
ρ_{BA}	0.0080	0.9559	0.0143	0.0623
ρ_{SD}	0.0053	0.9556	0.0001	0.0002
ρ_{SP}	0.0027	0.0003	0.0144	0.0621
	$2s_C$	$(2p_x + 2p_y)_C$	$2p_{zC}$	$1s_H$
R	0.9838	1.9708	1.0135	0.9672
$(R^{\alpha})_{BA}$	0.4916	0.9849	0.5006	0.4857
ρ_{BA}	−0.0006	−0.0010	−0.0122	0.0041
ρ_{SD}	0.0003	0.0002	0.0004	0.0023
ρ_{SP}	−0.0009	−0.0012	−0.0126	0.0018

$\langle S^2\rangle_{BA} = 0.7614$ $\langle S^2\rangle_{ASA} = 0.7500$

Net charges: $q_{Cr} = 0.2239; q_C = 0.0319; q_H = 0.0328$

Bis-benzene Chromium(I)

A $\langle S^2\rangle_{ASA}$ value of 0.7614 (Table VIII) has been evaluated corresponding to an unpaired electron mainly localized in the a_{1g} metal orbital. The net spin density of 0.0041 on the $1s_H$ orbital gives a value of 2.21 G for A_{iso} (^1H) while the experimental value is 3.46 G [23]. It is important to point out that in both vanadium and chromium bis-benzene complexes the SD and SP contributions on hydrogen atoms are positive.

Discussion

In the theoretical model of Drago *et al.* [20, 22], which was the only one to attempt a semiquantitative description of the spin density distribution mechanism in the complexes discussed in this paper, it has been proposed that the SP mechanism in a metal complex is similar to that operating in the free ligand. In this way the SP term on the hydrogen atoms may be directly related to the SD term on the $p_{\pi C}$ orbital, by means of the well known Mc-Connell factor type relation. Moreover it has been assumed that the Mc-Connell factor Q can be transferred as such from the organic radicals to the paramagnetic complexes and kept constant through a series of related complexes with different metal atoms. Our spin density description is markedly different from that of the above authors; in some respects it is also rather new. In fact, while in vanadium and chromium complexes the SP and the

TABLE VIII. A_{iso} (^1H) Coupling Constants for Bis-cyclopentadienyl and Bis-benzene Complexes.[a]

	b			c			
	A_{SD}	A_{SP}	A_T	A_{direct}	$A_{indirect}$	A_T	$A_{exp.}$
$V(C_5H_5)_2$	0.38	0.27	0.65	1.18	−0.20	0.97	0.83
$Cr(C_5H_5)_2$	0.76	0.37	1.13	1.84	−0.24	1.60	1.20
$Ni(C_5H_5)_2$	0.30	−0.55	−0.25	1.30	−2.40	−1.10	−1.24
$V(C_6H_6)_2$	1.95	1.34	3.29	4.02	−0.08	3.9	3.99
$V(C_6H_6)_2^+$	0.67	0.65	1.32	1.87	−0.59	1.3	1.10
$Cr(C_6H_6)_2$	1.24	0.97	2.21	3.05	−0.06	3.0	3.46

[a]All coupling constants are in gauss. [b]Present work. [c]From references [20] and [22].

SD terms on the hydrogen atoms are of the same sign (both positive and of comparable magnitude), in the SCCC approach the SP contributions (named indirect contributions) are always negative and much smaller than the corresponding SD contributions. Moreover, our calculations show that in the vanadium and chromium complexes the SD terms on the $p_{\pi C}$ orbitals are always positive, which means that a relation of McConnell's type between the SP term on hydrogen atoms and the SD one on the π-type orbital of the carbon is of little value. In our approach the SP mechanism is important in both the vanadium and chromium complexes but is completely different from that operating in the free ligand. It involves, in principle, all the orbitals of the complex without any restriction of symmetry and it is characterized by a regular alternation of sign: in the vanadium and chromium complexes the alternance of the sign of the SP contributions is metal(+)–carbon(−)–hydrogen(+). In nickelocene, on the contrary, the trend is metal (−)–carbon(+)–hydrogen(−).

In this latter case the spin density on the $2s_C$ orbital is negative; a fact which accounts for the observed downfield NMR contact shift. The SCCC method cannot give negative spin density on the 4s metal orbital or on 2s carbon orbital, as a consequence its prediction of the spin density distribution can be correct only in some special cases.

For instance, the positive SD contribution in the $p_{\pi C}$ orbital of the nickelocene accounts for a σ–π spin polarization mechanism, quite similar to that proposed by Levi–Orgel [24] and in Drago's model [20, 22]. It is only the particular symmetry of the ground state which makes the electron and spin distribution in the coordinated ligand similar to that of the free ligand, thereby satisfying the McConnell type relation. As a matter of fact our INDO approach satisfies the McConnell theory: for instance with the C_5H_5 free ligand, using the computed values of A_{iso} (^1H) and of the SD contribution on the p_π carbon orbital, we obtain $Q = A_{iso}/\rho_{p\pi C} = -25.4$ G, which is not too far from the classical McConnell value of −23.G [7]. In conclusion the INDO method gives acceptable results because it describes the spin polarization mechanism in a quite general manner.

Some interesting points can be raised when examining the values of the A_{iso} (^1H) coupling constants. Our calculated values have been decomposed into the contributions A_{SD} and A_{SP}, whose meaning is obvious, in order to have a comparison with the contributions A_{direct} and $A_{indirect}$ given by other authors [20, 22]. A_{direct} has been obtained as the sum of the electron density related to the MO's containing the unpaired electrons, at the nuclear position of the hydrogen atoms; consequently it is directly related to the A_{SD} terms of our approach. $A_{indirect}$ has been obtained by a McConnell relation with a Q value of −30 G.

Data are compared in Table VIII in which the differences between the two approaches are self-evident. Our A_{SP} contributions may be positive or negative while $A_{indirect}$ are always negative, moreover in vanadium and chromium complexes $A_{indirect}$ is very small while our results show that the A_{SP} contribution always plays an important role.

Compared to SCCC method [20, 22] our agreement with experimental data is sometime less satisfactory but our results relative to $V(C_6H_6)_2$ and $Cr(C_6H_6)_2^+$ are very near to those obtained by other INDO calculations [6]. Lastly, we have found that little variations of the geometrical parameters do not affect significantly the computed values of A_{iso} (^1H). Some calculations have been performed on nickelocene with two geometrical changes with respect to the values of Table II: the inter-ring separation equal to 3.668 Å [20] and the inter-ring separation as in Table II but with the C–H bond forming an angle of 5° with the ring plane (the hydrogen atom pointing toward the metal atom) as was recently observed by electron diffraction on some of our sandwich complexes [25]. The corresponding A_{iso} (^1H) values are −0.33 G and −0.36 G which are only slightly better than that reported in Table VIII.

Conclusions

In this paper we have tested the usefulness of an INDO method in the determination of the spin density distribution on some organometallic compounds of transition metals. Our results are generally quite satisfactory, as they do not describe the spin density distribution by a simple σ–π polarization. At present we cannot safely conclude about the general reliability of the INDO method in predicting the spin distribution. We think, on the contrary, that some caution must be taken as in other semiempirical methods; for instance, the INDO method neglects the two center exchange integrals which may be important in the description of the SP mechanism; probably, the use of a more sophisticated hamiltonian can give results quite different from those presented here. Despite these points, the present version of the INDO method is undoubtedly superior in many respects to the SCCC one; also the computational time is not much greater than that required by an iterative Hückel calculation.

Acknowledgements

Thanks are due to professor R. Ugo for stimulating discussions. The financial support of the Consiglio Nazionale delle Ricerche (Rome) for computational expenses is gratefully acknowledged.

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