

A Theoretical Study of the Interaction of Ethylene with Transition Metal Complexes

E. J. Baerends, D. E. Ellis*, and P. Ros

Scheikundig Laboratorium, Vrije Universiteit, Amsterdam, The Netherlands

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In order to be able to describe the ethylene molecule bonded to an active site of a Titanium- or Nickel fluoride crystal, we have used the Hartree-Fock-Slater model, implemented by a Discrete Variational Method, as introduced by Ellis and Painter. The study of the ethylene molecule at a crystal surface then gives a clear, easily interpreted picture of the electronic structure. The π -back donation from metal to olefin is found to be extremely important, both in the Ti- and in the Ni-complex. This back donation is caused by a strong interaction of a d orbital of the central ion with a σ^* as well as the π^* molecular orbital of ethylene. As a result of these interactions, the C-C bond of ethylene is weakened considerably.

A comparison is made between the Ti-ethylene and the Ni-ethylene systems.

Die Elektronenstruktur von Äthylen, das an ein aktives Zentrum eines Titan- bzw. Nickel-fluoridkristalls gebunden ist, ist mittels der Hartree-Fock-Slater-Theorie kombiniert mit der sog. Discrete Variational Method theoretisch behandelt worden. Es zeigt sich, daß die π -Backdonation sowohl im Nickel- als auch im Titankomplex außerordentlich wichtig ist; sie entsteht durch eine starke Wechselwirkung eines Metall- d -Orbitals sowohl mit einem σ^* - als auch einem π^* -Orbital des Äthylens. Dies führt zu einer erheblichen Schwächung der Doppelbindung.

Außerdem werden die beiden Systeme (Titan und Nickel) miteinander verglichen.

1. Introduction

The metal olefin bond in transition-metal π -complexes is very interesting, both because of its wide occurrence in organometallic chemistry and because of the special character of this type of chemical bond. The bonding in these π -complexes can be explained in terms of a σ -bond, which is formed through electron donation from the olefin to the metal, and a π -bond which is formed through back donation of electrons from the metal to the olefin. Although this model, due originally to Dewar [1] and Chatt *et al.* [2], has been generally accepted, there is still quite some uncertainty as to the extent to which each of these bonding mechanisms, σ -donation and π -back donation, is operative. Recently, this problem has been extensively discussed in the literature [3-6].

Not only can quantum chemical calculations shed some light on the intricacies of the metal olefin bond, they should also aim at a better understanding of the extremely important role of transition metals in olefin chemistry. In particular, catalysis of many reactions of olefins by transition metals is very intriguing.

* Alfred P. Sloan Research Fellow, permanent address: Department of Physics, Northwestern University, Illinois, USA.

In order to study the catalytic activity of transition metals in reactions of olefins, the participants in these reactions, viz. the catalytic site and the reacting molecules, have to be known in detail. Such a detailed description can only be given for a limited number of catalytic reactions. The heterogeneous catalysis of the polymerization of α -olefins at the surface of an α -TiCl₃ crystal (Ziegler-Natta) forms an example of this category. Here the reaction can be described in some detail due to the fact that a well-crystallized compound can be employed as a catalyst, and due to the high stereoregularity of the product [7].

The main obstacle to the use of quantum chemical calculations as an aid in clarifying the problems indicated above, is the complexity of the systems involved. Thus, only a few calculations on transition-metal olefin π -complexes have been reported, most of them taking Pt for the transition metal. Two calculations on Zeise's salt, K⁺[PtCl₃(C₂H₄)], have been published, the first using the iterative Extended Hückel method [8], the other a CNDO-type method [9]. Although the absolute accuracy of these calculations is rather poor, both of them indicate σ -bonding as well as π -back bonding to be important. Recently an *ab initio* calculation on the Ag⁺ - C₂H₄ complex, employing a limited basis set of Gaussian orbitals has appeared [10]. For this complex the σ -donation was found to be significantly larger than the π -back donation. We should also mention here the extension of the Dewar-Chatto scheme to acetylene, which has been based on non-iterative Extended Hückel calculations [11]. To obtain some insight in the Ziegler-Natta catalysis mentioned above, Extended Hückel calculations have been used [12].

In order to study both the bonding model and the role of transition metal ions in catalytic reactions, we have performed a number of quantum chemical calculations on two model systems. These model systems consisted of a TiF₅ or NiF₅ cluster and an ethylene molecule at various distances. We have used a method which we believe to be more reliable than the semi-empirical schemes, being at the same time practicable even for large systems. The method used essentially is based on the Hartree-Fock-Slater model, which has been widely applied in solid state calculations. The method, which contains a number of new features, is described in Section 2. Section 3 contains a detailed description of the model systems we have used. The results are discussed in Section 4 and the conclusions are summarized in Section 5.

2. The Quantum Chemical Method

The quantum chemical approach used in this work can be described in three steps:

- a) Replacement of the conventional Hartree-Fock equations for the one-electron spinorbitals by those of the simpler Hartree-Fock-Slater (HFS) model.
- b) Solution of the HFS equations by efficient numerical discrete variational methods (DVM).
- c) Definition of a minimal effort self-consistent iterative scheme based on the main quantities of interest, viz., the molecular charge matrix.

We discuss each of these steps and their implications in the following section.

A. One Electron Model

We begin by reviewing the familiar Hartree-Fock equations for the one-electron spinorbital which for a closed shell system can be written as

$$f(1)\varphi_i(1) = \varepsilon_i\varphi_i(1), \quad (1)$$

or

$$\{V_k(1) + V_N(1) + V_c(1) + V_x(1)\} \varphi_i(1) = \varepsilon_i\varphi_i(1),$$

where $V_k(1) = -\frac{1}{2}\nabla^2(1)$, (kinetic energy)

$$V_N(1) = -\sum_{\alpha} \frac{Z_{\alpha}}{r_{1\alpha}} \quad (\text{electron-nucleus interaction})$$

$$V_c(1) = \int \frac{\sum_k n_k \varphi_k^*(2) \varphi_k(2)}{r_{12}} d\tau_2 = \int \frac{\rho(2)}{r_{12}} d\tau_2 \quad (\text{coulomb repulsion})$$

$$V_x(1) = -\int \frac{\sum_k n_k \varphi_k^*(2) P_{12} \varphi_k(2)}{r_{12}} d\tau_2 \quad (\text{exchange interaction})$$

(n_k is the occupation number of spin-orbital φ_k). Usually these equations are solved in the expansion scheme (LCAO-MO), formulated by Roothaan [13]. For large systems however, solving these equations straightforwardly, that is, using a non-empirical all-electron all integral scheme, becomes intractable.

Moreover, uncertainties in a calculation due to limitations in the basis set can be quite large, [14], and the necessity of using limited basis sets in calculations of this type on large systems (if possible at all), remains a serious drawback of these methods. The semi-empirical methods one has to resort to, then, (iterative [8, 12], or even non-iterative Extended Hückel [11] or CNDO-type [9]) are known to be somewhat unreliable as far as quantitative results are concerned.

In an attempt to overcome the difficulties presented both by the non-empirical and semi-empirical methods mentioned, we have used a method which leans heavily on techniques from solid-state calculations (as suggested by the crystal-line part of our systems). In solving the HF-equations (1), the largest difficulties are due to the HF exchange potential V_x because of its non-local character. Slater suggested replacing the non-local exchange terms in the original equations by an averaged local exchange potential. He approximated this average by the exchange potential of a free electron gas with the same local density [23]:

$$V_{xs}(1) = -3 \left(\frac{3}{8\pi} \rho(1) \right)^{1/3}. \quad (2)$$

This exchange approximation has been used extensively in energy-band calculations and in calculations on heavy atoms. We refer to [24] for a recent discussion and a comprehensive bibliography. We have adopted the Slater exchange approximation throughout. Then, we only need the density in each sample point, which is determined as mentioned under C, to generate the Hamiltonian. We have, in the present calculations, not yet treated the spin-up and spin-down densities

separately, which is necessary if we want to carry through our calculations in an Unrestricted Hartree-Fock formalism (different orbitals for different spins). In fact, in our calculations we neglect the spin polarization due to the presence of one unpaired spin in the Ti-complexes. It is not expected that this will lead to serious errors, since only the gross features of the charge distribution and bonding in these complexes are being studied.

B. Numerical Integration and the Discrete Variational Method

The Discrete Variational Method (DVM) and some of its previous applications have been described elsewhere [15–19]. We give a brief survey of the method here, treating successively the most important features.

Using the atomic orbital χ_i , we have to calculate the matrix elements $\langle \chi_i | f | \chi_j \rangle$. We evaluate these integrals directly by numerical integration, i.e. we approximate the integral $\langle \chi_i | f | \chi_j \rangle$ with the sum:

$$\sum_{k=1}^N \chi_i^*(\mathbf{r}_k) (f \chi_j(\mathbf{r}_k)) w(\mathbf{r}_k).$$

For the generation of the integration points \mathbf{r}_k we have used the Diophantine procedure. This is a method for the numerical evaluation of multidimensional integrals, developed by Haselgrove [20], and applied to the molecular integral problem by Conroy [21] and Ellis [15]. A number of integration points is distributed around each nucleus of the system, the distribution in the periodic ϑ - and φ -domains following immediately from the Diophantine procedure. In the r -domain a fermi-distribution appears to be most useful [15]. Convergence is rather rapid: an accuracy of roughly 1% in energy can be obtained with two to three hundred points for first row elements, while six to eight hundred points may suffice for third row transition elements. It should be stressed that, even if the absolute accuracy in the matrix elements may not be high, due to the necessarily limited number of sample points, it is an over-all accuracy we are dealing with. The error is *not*, as in most methods, propagated in an uncontrollable way through some n^4 operations (where n is the number of basis functions). This means that we need not fear an imbalance caused by the fact that some matrix elements deviate much more from their exact value than others. The latter situation is quite common in semi-empirical calculations, where some integrals are calculated exactly, others approximated more or less severely, and many neglected completely.

The evaluation of the one-electron matrix elements for the kinetic energy and potential energy with respect to the nuclei doesn't present any special difficulty. Further approximations which have been made to simplify the electron potentials (Coulomb and exchange) are considered next.

C. Approximations in Coulomb Potential

In the numerical evaluation of $\langle \chi_i | V_c | \chi_j \rangle$ we need to know the value of the Coulomb potential $\int \rho(\mathbf{r}_2) / |\mathbf{r}_k - \mathbf{r}_2| d\mathbf{r}_2$ at each sample point \mathbf{r}_k . In principle we can again determine this integral numerically, which, however, raises the total

computational effort considerably. So we have approximated the density $\rho(\mathbf{r})$ with a sum over spherically symmetric densities around each center, $\rho(\mathbf{r}) \approx \sum_A \rho_A(\mathbf{r})$.

This reduces the determination of the Coulomb potential at each sample point to the calculation of a number of one-center integrals, which can be done analytically. A Mulliken population analysis is used to decide in which way the total density must be broken up into atomic parts. We simply use the total gross orbital populations of the atomic sub-shells to calculate the spherically symmetric densities around each nucleus. It should be noted that we do not further approximate the densities around the atoms in the molecule by their "muffin tin" average, as is often done in energyband calculations (APW and KKR methods) and sometimes in molecular calculations (cf. the scattered wave method [22]). This point is of some importance when considering the origins of molecular bond formation.

D. Iterative Procedure

As a self-consistency criterion we have used the requirement that the gross orbital populations of the $1s$ -, $2s$ -, $2p$ -, etc. subshells of the atoms, which follow from a Mulliken population analysis, should be the same as those which are used in calculating the spherically symmetric atomic densities. This procedure can be criticized as well as the Mulliken population analysis on which it is based. Since, however, in our calculations the majority of the overlap populations are very small (ionic bonds), the conventional equipartitioning of the overlap charges hardly affects the results. The resulting SCF procedure is easier to implement, and converges more rapidly than the conventional scheme. This form of self-consistent constraints on the input potentials is admittedly an ad hoc construction; nevertheless, it seems well suited to the problem at hand.

E. Possible Extensions of the Method

We may make a few remarks concerning the advantages offered by this combination of approximations. In the first place, we can handle arbitrary basis functions, STO's taking no more time, for instance, than GTO's. Secondly, the number of matrix elements to be calculated increases only as the square of the number of orbitals (not as the fourth power!). Furthermore, we have gained so much in speed of computation and in storage requirements, that large systems can be dealt with in an all-electron treatment. An additional advantage lies in the nature of the approximations involved, which makes it possible to get a very direct physical picture of the interactions, and what may be sources of errors.

As is immediately apparent, the relative position of metal d orbital and hydrocarbon π -orbital energies is crucial to any discussion of d - π interactions in the systems studied here. In addition to depending upon the molecular environment, we must expect these level spacings to be somewhat model dependent. This model dependence can be anticipated because of the relatively different response of (somewhat tightly bound) d orbitals and (rather diffuse) hydrocarbon π orbitals under *exchange scaling*. Very briefly, one can put forward arguments for choosing slightly different numerical parameters in Eq. (2); the so-called X_z

method is one prescription for choosing the exchange scaling parameter, which has been widely exploited [24]. For the present we have only used the unscaled full Slater exchange, as in Eq. (2), but recognize that in future calculations it may be important to consider modified potentials.

To obtain a more detailed understanding of reaction mechanisms, one would like to study variations of *total energy* of the molecular systems for various geometries. Several obstacles have to be overcome before the present methods can be extended in this direction. First, "tighter", more rigorous self-consistency conditions must be imposed, since we are then interested in small changes in total energy which are rather sensitive to molecular charge re-arrangement. Good progress is being made in this direction; however, the computational load is greatly increased. Second, we must consider whether approximate total energy expressions (derived in the spirit of the HFS model) are sufficiently accurate for our purpose, and devise more effective ways of obtaining numerical values to the required accuracy. We consider that, at present, the values for the total energy obtained by our methods are not accurate enough to perform a meaningful geometry optimization.

F. Ethylene, A Comparison with Other Methods

That the present method can be used to obtain an adequate description for the crystalline part of our systems, may be inferred from experience with applications to crystals [15–18]. To test the validity of this method in molecular calculations, we performed calculations on some small molecules. The results for ethylene, which are most interesting in the context of this paper, will be discussed briefly. In Table 1 we present the orbital energies calculated by the present (DVM)-method in a double ζ basis of STO's (exponents from Clementi [25]). For comparison purposes we also give the orbital energies from an all-integral Hartree-Fock calculation in a Gaussian basis [26]. The latter basis consists of 10s, and 5p functions on C and 5s functions on H, contracted to a (4,21) basis. We may consider this basis to have double ζ quality. The geometry is the same in both calculations. We see that the agreement between the orbital energies calculated by the two methods is satisfying. The largest deviations occur for the highest orbitals, but always they remain less than 0.1 a.u.

A more sensitive test for the quality of a wavefunction is a population analysis. It is rather difficult to compare population analyses which have been performed in different bases. Therefore we compared a Hartree-Fock calculation by Palke and Lipscomb [27] on ethylene, in a minimal Slater basis, with a DVM calculation using exactly the same geometry and basis set. The agreement for the orbital energies was even better than in the previous Gaussian case. The population analyses for the two calculations are given in Table 2. The agreement in overlap populations is striking. The gross orbital populations also compare favourably, although for the 2s and 2p_y orbitals we observe slight deviations. These deviations, being all of the same sign, add up to significant differences in atom charges. We may conclude from these test calculations that the method employed gives a rather correct picture (i.e., agrees with HF) of one electron energies and charge densities, not only for crystals but also for covalent molecules.

Table 1. Comparison between orbital energies of C_2H_4 from the present approximate Hartree-Fock-Slater method, and from an *ab initio* all-electron, all-integral calculation [26]

Symm.	HFS	<i>Ab initio</i>
A_g	- 11.2136	- 11.2358
	- 0.9904	- 1.0344
	- 0.6553	- 0.5863
B_{2u}	- 11.2133	- 11.2343
	- 0.8278	- 0.8002
B_{3u}	- 0.6956	- 0.6481
B_{1g}	- 0.5890	- 0.5085
$B_{1u}(\pi)$	- 0.4560	- 0.3691

Table 2. Comparison between population analyses from the present approximate Hartree-Fock-Slater method, and from an *ab initio*, all-electron, all-integral calculation [27]. Exactly the same, minimal Slater, basis has been used in both calculations

	HFS	<i>Ab initio</i>
Atom-atom		
Overlap populations		
C-C	0.58	0.61
$(C-C)_\pi$	0.21	0.21
$(C-C)_\sigma$	0.37	0.40
C-H	0.39	0.41
Orbital populations		
C 1s	2.00	2.00
2s	1.31	1.20
2p _x	1.04	1.01
2p _y	1.14	1.07
2p _z	1.00	1.00
H 1s	0.76	0.86
Atom charges		
C	-0.49	-0.28
H	+0.24	+0.14

When we compare the results of the present method with those of semi-empirical methods, it appears that our method is certainly in better agreement with all-integral all-electron Hartree-Fock calculations. It is our own experience that the *orbital energies* calculated with a CNDO or INDO scheme deviate considerably from the *ab initio* values. This fact has already been noted by Pople *et al.* [28], and must be considered a most unfortunate feature of the semi-empirical schemes if we want to study the interaction between such different systems as a hydrocarbon like C_2H_4 and a transition metal ion in a crystal environment. It is an additional advantage of the present method that the electronic bonding structure, as determined from a population analysis, is much closer to the all-integral Hartree-Fock results than the bond structure calculated by a semi-empirical method.

3. Model Systems

As model systems we have chosen the $[(C_2H_4) TiF_5]^{2-}$ and $[(C_2H_4) NiF_5]^{3-}$ complexes (see Fig. 1), with Ti formally trivalent and Ni divalent. The metal-fluorine distances have been taken from the respective crystals; the ethylene geometry has been kept constant in all calculations. The metal-ethylene distance has been varied to get an idea of the changes which occur when an ethylene molecule approaches the vacant coordination position. Details of the geometry are given in Fig. 1. The Ti-complex bears a close resemblance to the Ziegler-Natta catalyst; however, we have replaced the Cl^- ligands by F^- , because of the smaller number of basis functions required. It is plausible to assume that substituting F^- for Cl^- has little effect on the Ti-ethylene interaction. This is substantiated by our results which indicate that the purely electrostatic effect of the negative charges on these ligands is by far the dominating factor.

We have neglected in all our calculations the influence of the rest of the crystal, and confined ourselves to the first coordination sphere of Ti (or Ni). The Madelung part of the potential energy, due to the second and following coordination spheres, can be considered to be constant over a sphere with a radius of approximately 7 a.u., centered at the position of the metal. Only our calculations with ethylene at a distance of 10 a.u. from the metal fall outside this range, and we have merely used these calculations as a reference, since there is virtually no interaction between ethylene and the crystal at this distance. Thus the only effect of the Madelung potential would be an equal shift of all one-electron energies. We have neglected the influence of the non-spherical terms occurring in the lattice sum, which makes up the potential due to the rest of the crystal. Their contribution is difficult to calculate for all the points of interest and, anyhow, small. For comparison purposes we have performed analogous calculations on the interaction between an ethylene molecule and a Ni^{2+} ion in a nickel fluoride crystal, where one finds a d^8 system instead of the d^1 system of Ti^{3+} .

The metal-orbitals which are important with respect to the σ -donation from ethylene to the metal are the $3d_{z^2}$ and perhaps the $4s$ orbital. These orbitals belong

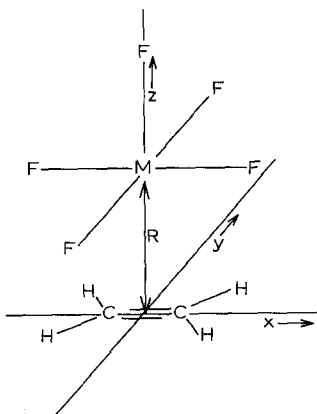


Fig. 1. Geometry of the model system. M is Ti^{3+} or Ni^{2+} . The $M-C_2H_4$ distance, R , has been varied (10, 6, 4 and 3 a.u.). The following distances have been used (in a.u.): C-C, 2.534; C-H, 2.003; Ti-F, 3.61; Ni-F, 3.79. The HCH angle was 120°

to the A_1 representation of the C_{2v} symmetry group of our complexes. The orbital with the proper symmetry for π -back donation is the $3d_{xz}$ orbital, having B_1 symmetry. The ethylene orbitals which play a dominant role in σ -donation and π -back donation are supposed to be the π and π^* MO's respectively. We continue to use the conventional symbols π and π^* for the ethylene MO's, although these MO's have, with respect to the metal ethylene bond, σ and π type symmetry respectively. It is to be noted, moreover, that it is no longer forbidden by symmetry for the carbon $2s$ AO's, to mix with the carbon $2p\pi$ AO's. We have used, in all calculations reported, a complete double- ζ basis of Slater-type orbitals. The exponents have been taken from Clementi [25], and Clementi *et al.* [29]. Although we did not optimize the basis set, we believe this basis to be sufficiently flexible to describe bonding and hybridization effects adequately.

It is satisfying, indeed, that our method allows the use of such an extensive basis for systems which are quite large.

4. Results

We will now consider the results of the calculations in detail.

A. Atom Charges

The atom charges, resulting from a Mulliken population analysis, have been collected in Table 3. We should not attach too much significance to the absolute quantities, but they are useful for a comparison between the different metal-ethylene distances. Looking first at the trends in the Ti complex, we see a sharp increase in the negative charge on ethylene if we go from 6–4 a.u., which is followed by a decrease if we go further to 3 a.u. The positive charge on Ti exhibits the same trend. As the π -back donation and σ -donation have an opposite effect upon the charges, it is clear that we have to be careful in interpreting these changes in the charges. However, from the net negative charge on C_2H_4 we can safely conclude that the π -back donation is stronger than the σ -donation at all distances, although in going from 4–3 a.u. the σ -donation must become relatively more important. We furthermore see that the F^- ions act as a buffer: the building up of a large positive charge on Ti is opposed by an electron shift from the negative ligands towards the central metal ion.

Table 3. Charges resulting from a Mulliken population analysis for the systems $TiF_5-C_2H_4$ and $NiF_5C_2H_4$. R is the distance from the metal atom to center of the CC bond

R (a.u.)	3	4	6	10
Ti	+2.30	+2.32	+2.21	+2.16
F_5	-4.16	-4.115	-4.18	-4.16
C_2H_4	-0.13	-0.20	-0.02	0.00
Ni	+1.72	+1.685	+1.66	+1.60
F_5	-4.48	-4.52	-4.55	-4.59
C_2H_4	-0.24	-0.16	-0.11	-0.005

The situation in the Ni-complexes is slightly different. The positive charge on Ni and the negative charge on C_2H_4 now increase monotonically. We shall see in a following paragraph, that the large negative charge found on ethylene even when this molecule is still at a distance of 6 a.u. from Ni, is caused by the fact that at this distance only π -back donation is operative; σ -donation, which could lower the charge, becomes important only at smaller distances.

B. Orbital Energies

In Fig. 2 we show the orbital energies in the Ti-complex at different values of R , the Ti-C=C bond distance.

The shifts in orbital energies of the ethylene MO's can (apart from binding effects, which influence mainly the π and π^* orbitals), be explained in detail as

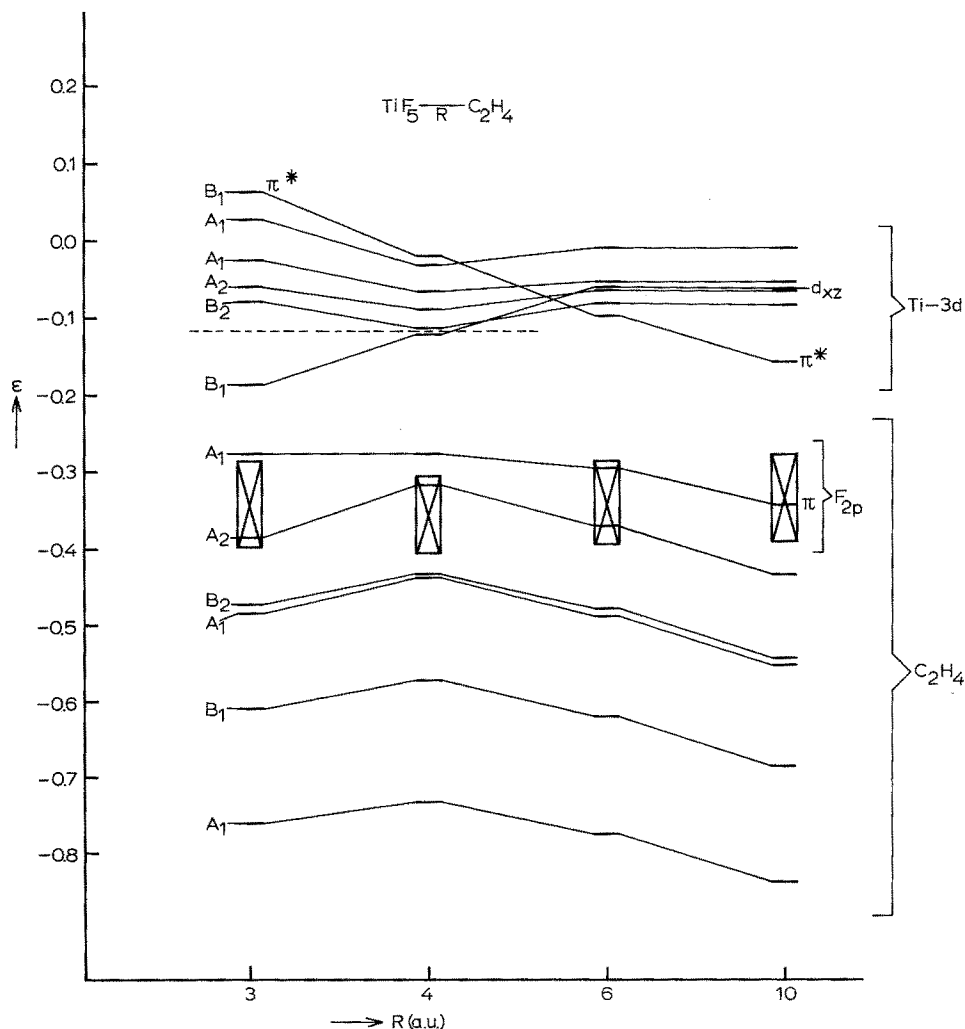


Fig. 2. Orbital energy diagram for the $TiF_5-C_2H_4$ complex. R and ϵ in a.u.

arising from two effects: a) the purely electrostatic potential due to the ions of the cluster; b) the negative charge on ethylene. The relatively high orbital energies at 4 a.u. reflect, for instance, the high negative charge on ethylene at that distance, whereas the low orbital energies of the Ti-3*d* orbitals arise from the high positive charge on Ti. The most striking feature of this energy diagram is the strong interaction between the Ti-3*d*_{xx} and the ethylene π^* MO. There is one *d*-electron in Ti³⁺. If we use an Aufbau principle we should place it in the π^* MO of ethylene, at *R* = 6 or 10 a.u. However, if we occupy the π^* MO, we deal with a negative ethylene ion, and a Ti⁴⁺ ion. Of course, the π^* MO then rises, the Ti-3*d* orbitals descend and become much lower than the ethylene π^* MO. The situation that we have a negative ethylene molecule at these large distances, is totally unrealistic, so we avoided this oscillation by simply putting the *d*-electron in one of the Ti-3*d* orbitals, the π^* MO thus being empty, as it should be. In fact, at these distances there is not yet any binding between ethylene and the cluster, and we merely use the calculations at these distances as a reference point for comparison with the shorter distances. For this reason, we took the Ti-3*d*_{xx} orbital as the one to be filled, providing a continuous transition to the situation which occurs also at *R* = 3 and 4 a.u. We are able, then, to follow the mixing of the Ti-3*d*_{xx} and ethylene π^* MO's through the decrease of the Ti-3*d*_{xx} population and increase of the π^* population. The latter effect is exactly what is commonly denoted as π -back bonding.

The orbital energy diagram for the Ni-complex is quite analogous to that given for the Ti-complex, so we do not show it here. The most remarkable feature is again the interaction between the Ni-3*d*_{xx} and ethylene π^* orbitals.

The σ -donation doesn't show up as clearly as the π -back donation in the orbital energy diagrams. Only the very slight deviation of the shift in the ethylene π MO as compared with the general pattern of the other ethylene MO's indicates this orbital to be involved in bonding.

C. Orbital Populations

To obtain a more quantitative description of the σ -donation, we may use the gross orbital population of the 3*d*_{z²} orbital, which appears, together with 3*d*_{x²-y²} in the A₁ symmetry. The σ -donation effect will result in an increase of this orbital population. We have collected in the Tables 4 and 5 the total *s* and total *p* gross orbital populations, and the *d* populations for each symmetry separately (3*d*_{xx} has B₁-symmetry, 3*d*_{xy} A₂- and 3*d*_{yz} B₂-symmetry). The total *s* and *p* populations remain constant, so we may conclude that these orbitals are not involved in σ -donation or π -back donation. The only significant changes in orbital populations occur in the 3*d*_{xx} and 3*d*(A₁) orbitals. This very simple picture allows the following scheme to be set up: we assume the π -back donation to be equal to the decrease in 3*d*_{xx} population, and infer from the charge on C₂H₄ how large the σ -donation must be. Internal consistency of this very simple scheme follows from the increase in 3*d*(A₁) population, which should be roughly equal to the σ -donation as determined in this way. The agreement is rather good indeed. The deviations find a natural explanation in two effects, first the influence of the F⁻ ions, secondly slight redistributions of the electrons in the metal ion. As far as the

Table 4. Gross orbital populations of Ti-orbitals in $\text{TiF}_5\text{-C}_2\text{H}_4$, charges on C_2H_4 and amounts of π -back donation and σ -donation derived from these quantities

$R(\text{a.u.})$	10	6	4	3
Ti $3d(xz)$	1.04	1.02	0.74	0.58
$3d(xy)$	0.09	0.09	0.10	0.11
$3d(yz)$	0.09	0.08	0.10	0.13
$3d(A_1)$	0.50	0.49	0.63	0.77
s	6.11	6.10	6.11	6.10
p	12.01	12.01	12.01	12.01
$Q(\text{C}_2\text{H}_4)$	0.00	- 0.02	- 0.20	- 0.13
π -back donation	0.00	0.02	0.30	0.46
σ -donation	0.00	0.00	0.10	0.33

Table 5. Gross orbital populations of Ni-orbitals in $\text{NiF}_5\text{-C}_2\text{H}_4$, charges on C_2H_4 and amounts of π -back donation and σ -donation derived from these quantities

$R(\text{a.u.})$	10	6	4	3
Ni $3d(xz)$	2.00	1.90	1.82	1.52
$3d(xy)$	2.00	2.00	2.00	2.00
$3d(yz)$	2.00	2.00	2.00	1.99
$3d(A_1)$	2.24	2.28	2.34	2.60
s	6.16	6.16	6.16	6.16
p	12.00	12.00	12.00	12.00
$Q(\text{C}_2\text{H}_4)$	- 0.01	- 0.11	- 0.16	- 0.24
π -back donation	0.00	0.10	0.18	0.47
σ -donation	0.00	0.00	0.03	0.24

first point is concerned, we have already seen from the atom charges that the electron flow from the negative ligands towards the central metal ion is always small. Moreover, these electrons go mainly into $3d_{x^2-y^2}$ (and $3d_{z^2}$), and do not enhance the $3d_{yz}$ and $3d_{xy}$ populations, a result which also gives us good grounds to neglect their influence on the $3d_{xz}$ population. By way of illustration we take the Ni complex, at $R=3$ a.u., where the increase of the $3d(A_1)$ population exceeds the σ -donation by 0.12 electrons. This is due almost entirely to electrons from the F^- ions (0.11 e).

Turning now to the second point, we find an example of internal rearrangement in the metal in the Ti-complex at $R=3$ a.u. The 0.33 electrons, donated by C_2H_4 , through the σ -donation, go largely (0.27 e) into $3d(A_1)$, but also contribute noticeably to the $3d_{xy}$ and $3d_{yz}$ populations (0.02 and 0.04 e respectively).

The estimates for the π -back donation and σ -donation obtained in this way, show some remarkable features. The π -back donation is larger than the σ -donation at all distances, but the latter effect becomes relatively more important at shorter distances. It should be pointed out however, that the calculation at $R=3$ a.u. describes a rather unrealistic situation. From Van der Waals radii

one can infer [12] that a distance of approximately 4 a.u. between the center of the ethylene double bond and the central metal ion is to be expected. So our results indicate that σ -donation will be quite small in the Ni case, which is not unexpected since Ni^{2+} is a much more electron-rich ion than Ti^{3+} . For the same reason it is not surprising that we find a considerable π -back donation in the Ni-complex, which is, at $R = 6$ a.u., even larger than in the Ti-complex.

When $R = 4$ a.u. however, which is probably closest to the actual bond distance, we see a much larger interaction with ethylene in the Ti complex, both with respect to π -back donation and to σ -donation.

Although one should be careful not to attach too much significance to these quantities, this might be considered to reflect the experimentally found strong interaction in the Ti-complex. That we have found throughout a larger π -back donation than σ -donation is rather unexpected, because of the high formal charge of the central metal ions. It has been generally assumed that σ -donation will prevail in these cases, while π -back donation might be important in complexes with electron-rich metals, like zero valent group VIII elements. Direct information about the balance between the two effects is of course difficult to obtain, but calculations on the $\text{Ag}^+-\text{C}_2\text{H}_4$ complex [10] showed σ -donation to be already dominant in that case. The crucial point here is probably the relative position of the metal d orbitals, with respect to the π and π^* orbitals of ethylene. Metals with d orbitals close to or below the ethylene π orbital will be predominantly acceptors; metals with valence-shell electrons in the energy range of the π^* orbital will form strong π -bonds [3, 30]. It is precisely here that the role of the crystal environment of the central metal ions becomes manifest. Due to this crystal environment the position of the metal d orbitals is favourable for π -back donation to occur. The π -back donation heavily influences the electronic structure of the ethylene molecule, as we shall see next.

D. The Ethylene Double Bond

It is clear that both σ -donation and π -back donation tend to weaken the ethylene double bond. The strength of this bond can be related to the C-C overlap population. We give, in Table 6, these overlap populations. The $(\text{C}-\text{C})_\pi$ overlap population is that part of the total which is due to the p - π orbitals of the

Table 6. C-C Overlap populations in $\text{TiF}_5-\text{C}_2\text{H}_4$ and $\text{NiF}_5-\text{C}_2\text{H}_4$

$R(\text{a.u.})$	10	6	4	3
	$\text{F}_5\text{Ti}-\text{C}_2\text{H}_4$			
$(\text{C}-\text{C})_\sigma$	0.29	0.29	0.16	-0.17
$(\text{C}-\text{C})_\pi$	0.21	0.20	0.14	0.10
$(\text{C}-\text{C})_{\text{total}}$	0.49	0.50	0.31	-0.07
	$\text{F}_5\text{Ni}-\text{C}_2\text{H}_4$			
$(\text{C}-\text{C})_\sigma$	0.29	0.27	0.16	-0.18
$(\text{C}-\text{C})_\pi$	0.20	0.19	0.17	0.09
$(\text{C}-\text{C})_{\text{total}}$	0.49	0.46	0.33	-0.09

carbon atoms (the p orbitals perpendicular to the plane of the C_2H_4 molecule), whereas $(C-C)_\sigma$ is due to the σ -frame. We see comparable trends in the Ni- and Ti-complexes, viz., a large decrease in the total overlap population, which is mainly due to the $(C-C)_\sigma$ part, particularly at short distances. These overlap populations reveal the unrealistic character of the situation where we have pushed the ethylene molecule as close as 3 a.u. to the central metal ion. There is virtually no bonding between the C-atoms any more. If we compare the situation at larger distance, with $R = 6$ and 4 a.u., we see that at $R = 6$ a.u. the overlap population in the Ni-complex is lower than in the Ti-complex. The reason for this is the π -back donation, which is already considerable in the former complex at this distance. At $R = 4$ a.u. however, we see that the overlap population in the Ti-complex has become the smaller of the two, as we expect because of the stronger interaction already noted in this complex.

A detailed analysis of the factors which cause the large decrease in the $(C-C)_\sigma$ term, reveals that this must be ascribed to the mixing of carbon $2s$ orbitals into the π^* MO. As a consequence of the larger overlap between the $2s$ AO's than between the $2p$ - π AO's, there is a pronounced effect upon the overlap population. Although it is evident that the σ - π separation in the ethylene molecule cannot be carried through in these complexes, one still might be inclined to do so in qualitative considerations of this type of bond. Our calculations indicate this to be a simplification that is not allowed.

E. The Geometry of the Ethylene Molecule

In the π -complexes studied here, (and similar examples) the protons of C_2H_4 are known to be bent away from the central metal ion in a symmetrical way [11c, and references therein]. Also, the C-C distance is often longer than in free ethylene. Although we were not able to perform a geometry optimization, we may conclude from the lowering of the C-C overlap population, that we should expect a lengthening of the C-C bond in our complexes. The *cis*-bending of the protons away from the central metal ion has been explained by Blizzard and Santry [31] as a purely electronic effect for the analogous case of acetylene bonded to a transition metal. They were able to relate this bending to the populations of the π^* and π MO's. Although they could only perform simplified model calculations, without explicitly including the central metal ion, we may point out an interesting parallelism between their calculations and ours, as far as the bonding in these π -complexes of olefins is concerned. From their model calculations and symmetry considerations, Blizzard and Santry concluded that *cis*-bending indicates that π -back bonding is very important, a result which is confirmed by our calculations on the complete complexes. Moreover, they found the contribution of the σ^* MO ($2s_{C1}-2s_{C2}$) to the π -bond to be nearly as important as that of the π^* MO, a result which is also confirmed by our calculations. In view of this correspondence, we may, arguing along the same lines as they did, expect that a proper geometry variation would lead to a *cis*-bent structure. Of course we cannot give a definite answer about the magnitude of the angle of deviation from planarity of the ethylene molecule.

5. Conclusions

We may conclude that the method presented here lends itself very well to the description of a system which consists of such diverse subsystems as a hydrocarbon and a transition-metal crystal. We recall that this is achieved without any need for reparametrization or special adaptations in the theoretical model.

Although we must classify the central metal ions, in particular Ti^{3+} , as electron acceptors ("hard"), we find the π -back donation to be extremely important in both the Ti- and the Ni-complex. This is probably due to the crystal environment of the ions. Especially important is the back bonding because of its great influence upon the electronic structure of the ethylene molecule. The large decrease in C-C overlap population (from 0.50–0.31 at 4 a.u.), which is due mainly to the π -back bonding, reflects the weakening of the C-C double bond. This weakening will lead to a considerable lengthening of this bond. It appears that the decrease of the C-C overlap population must be attributed to the strong interaction of the central metal ion with a σ^* as well as the π^* MO of ethylene. These findings are contrary to habitual thinking in chemistry, although the considerations of Blizzard and Santry, based on simple model calculations and symmetry arguments, already pointed in the same direction. Comparing the Ni^{2+} and Ti^{3+} complexes, we find at $R = 4$ a.u., a considerably stronger interaction between ethylene and the central metal ion for Titanium than for Nickel. This can be related to the experimentally found catalytic activity of the Ziegler-Natta catalyst but we should not lose sight of the model character of our systems. We mention in this respect, not only the replacement of a chloride by a fluoride crystal, but also the fact that the influence of steric factors fell outside the scope of this investigation. The latter, however, may play an important role in the actual catalytic reaction [7].

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Prof. Dr. P. Ros
Scheikundig Laboratorium
Vrije Universiteit
Amsterdam
Holland