Theor Chim Acta (1986) 69: 119-133

Theoretica Chimica Acta

Orientational preference of two ethylene ligands bound to a nickel atom

Per E. M. Siegbahn and Ulf B. Brandemark

Institute of Theoretical Physics, University of Stockholm, Vanadisvägen 9, S-11346 Stockholm, Sweden

(Received August 12/Accepted October 14, 1985)

CASSCF and CCI calculations have been performed to analyze the bonding in $Ni(C_2H_4)_2$. Three different relative orientations of the two olefins have been studied. It is found that a structure with D_{2d} symmetry, where the C—C bonds in the two olefins make a 90 degree angle to each other, gives the lowest energy. A D_{2h} form, with the two C—C bonds and Ni in the same plane, is 10.3 kcal/mol higher in energy. The reason for the preference of the D_{2d} form is analyzed in terms of valence bond theory, and is found to be due to a d^8 structure with two simultaneous d_π bonds. A C_{2v} form, for which the two nickel olefin bonds make a 103 degree angle to each other and the C—C bonds are parallel to each other, is 32 kcal/mol higher in energy than the D_{2d} form. The low binding energy of the C_{2v} form is due to a poor σ interaction with inefficient *sd* hybridization.

Key words; Bis(ethylene)nickel — Ethylene orientation — Dewar-Chatt-Duncanson model - Correlation effects on bonding

1. Introduction

The bonding between transition metals and ligands with unsaturated π systems is classically described by the Dewar-Chatt-Duncanson (DCD) model [1, 2]. In this model there are two different mechanisms in operation. First, there is a motion of electrons from the ligand to the metal in the σ system, σ donation, and second, there is a back donation of electrons from the metal to the ligand in the π system. During the last years a detailed understanding of some of the principles governing this model has been obtained by the application of modern quantum chemical methods on simple model systems. One type of bond which has been particularly well studied is the transition metal-carbonyl bond [3-7]. An interesting conclusion which has been reached in most of these studies [4-7] is that the π bonding is by far more important than the σ bonding. The σ interaction can in many cases even be described as repulsive with essentially unperturbed carbonyl orbitals. A picture of the bonding in terms of σ repulsion and π donation [6-7] is therefore in the case of the metal-carbonyl bond a better description than the original picture of σ donation and π back donation.

The first calculation including electron correlation on the metal olefin bond, was a study of NiC_2H_4, and it gave a surprising and new picture of the bonding [8]. In particular almost no delocalization of the $3d_\pi$ orbital into the ethylene π^* orbital was found, and it was concluded that this feature is in direct contradiction with the standard DCD model. The obtained picture of the bonding was also in contradiction with what was found at the Hartree-Fock level [9] and this was attributed to an overestimation of contributions of ionic character inherent in the *HF* description. A new study of the NiC_2H_4 system was performed recently using MCSCF and CI techniques [10], and it was shown that the calculation in [8] had incorrectly assigned the ground state as a triplet with a calculated binding energy which was almost entirely due to a basis set superposition error. The calculations in [10] showed on the contrary that for the correct singlet ground state the donation - back donation picture is even enhanced when correlation effects are included. A σ donation of 0.42 electrons and a π back donation of 0.61 electrons found at the MCSCF level, makes this system a perfect example of where the DCD model is highly adequate.

The main reason for performing the present calculations on $Ni(C_2H_4)_2$ was to obtain a deeper understanding of the mechanism of the transition metal-olefin bonding. The prime question asked is simply what orientation the second olefin will have relative to the first. Three different geometrical configurations of the complex were studied. In the first structure the second olefin binds in the same plane as the first, thereby making use of the same metal d_π orbital for the π bonding. This structure is shown in Fig. 2 and will be referred to as the D_{2h} structure. A simple argument against the preference for this structure is that it

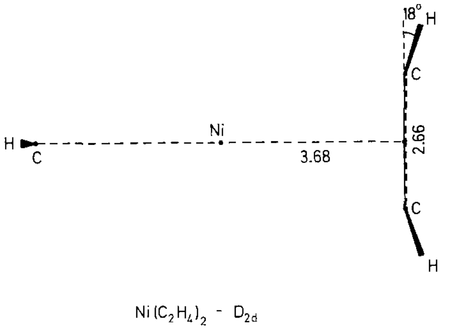

Fig. 1. Optimized geometry for $Ni(C_2H_4)_2-D_{2d}$

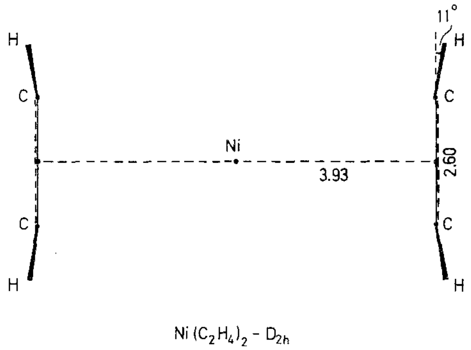

Fig. 2. Optimized geometry for Ni(C$_2$H$_4$)$_2$–D$_{2h}$

seems that it should be more advantageous to make use of two different *d* orbitals for the bonding since more *d* electrons should be available for back donation. In the second structure the second olefin has therefore been twisted 90 degrees to a structure shown in Fig. 1. This structure will be referred to as the D$_{2d}$ structure. A different geometry achieving the same goal is shown in Fig. 3. In this structure, here referred to as the C$_{2v}$ structure, the two olefins are parallel as for the D$_{2h}$ structure but the two bonds to the metal now makes a 90 degree, rather than a 180 degree, angle. By comparing the D$_{2d}$ and the C$_{2v}$ structures, which are equivalent in terms of π bonding, the geometrical preference for the σ system will be illuminated.

In the analysis of the bonding of the three different forms of Ni(C$_2$H$_4$)$_2$ it was found that the standard DCD model either gives the wrong picture, as in the comparison between the D$_{2h}$ and C$_{2v}$ structures, or does not contain enough details, as in the comparison between the D$_{2d}$ and D$_{2h}$ structures. To analyze the results found at the correlated level a valence bond analysis was therefore preferred. Through such an analysis it is possible to understand the origin of the structural preference for the present nickel complex, and also to make predictions about the preferred bonding in M(C$_2$H$_4$)$_2$ where M is another transition metal atom. To understand the energy difference between the C$_{2v}$ form and the other two forms, a detailed analysis of the *sd* hybridization in the first symmetry was necessary.

A second purpose behind the present calculations was to study the importance of correlation effects on the relative energies and geometries of the different

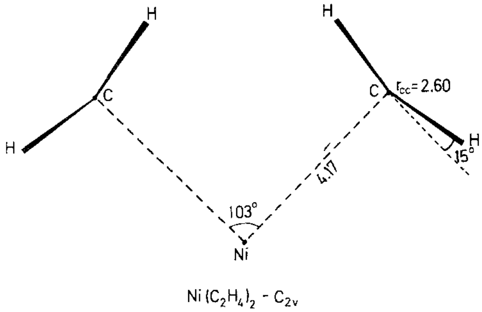

Fig. 3. Optimized geometry for Ni(C$_2$H$_4$)$_2$–C$_{2v}$

structures in Fig. 1-3. Both extended Hückel calculations by Rösch and Hoffmann [11] and large basis set Hartree-Fock calculations by Pitzer and Schaefer [12] have been performed earlier on the D_{2h} and the D_{2d} structures. These two studies agree almost perfectly with each other and place the two structures very close in energy, within 1.5 kcal/mol in [11] and within 0.1 kcal/mol in [12]. In the Hartree-Fock study several states were considered and the lowest calculated energy was obtained for a triplet state. Accounting in a qualitative way for atomic correlation effects, Pitzer and Schaefer argued that the lowest singlet and triplet states should be close in energy, however. A different argument for shifting the relative order between the triplet and the singlet states as obtained at the Hartree-Fock level, is found in the recent studies of NiCO [7] and NiC_2H_4 [10]. It was shown there that it is not atomic correlation effects, but an *sd* hybridization effect, which is responsible for the failure of the Hartree-Fock method to predict the correct ground state. This *sd* hybridization is also essential for the efficiency of the DCD mechanism for the bonding since it leads to an unshielding of the nickel $3d$ shell. In order to compare with the Hartree-Fock results in [12] the lowest singlet and triplet states were therefore reinvestigated here at a correlated level.

A final reason for studying the $Ni(C_2H_4)_2$ system is a recently performed large study of the reaction between two ethylenes to form cyclobutane catalyzed by a nickel(0) atom. The calculation of the potential surface for this reaction has been published elsewhere [13]. Earlier theoretical work considered different reaction pathways for this reaction with emphasis on orbital symmetry arguments [14]. Experimentally, a reaction pathway over a metallacycle has been indicated [15]. Clearly, a knowledge of the preferred geometry in the entrance channel is important for understanding the mechanism of this interesting catalytic reaction.

2. Computational details

The basis sets and methods used in the present study are essentially the same as have been used in our previous studies on similar systems, see for example [7] and [10]. The requirements on the basis sets are that they should qualitatively describe the main correlation effects. Within this framework they are as small as possible. The nickel basis set is the DZC-set of Tatewaki and Huzinaga [16], which has the advantage of having the inner shells described by single contracted functions. With the minimal basis contraction of the inner shells ($1s$-$3p$), these have to be frozen in their atomic shapes, to avoid the most severe superposition errors [17]. To describe the d^8s^2 to d^9s excitation energy reasonably well a diffuse d function (0.1641) was added [18]. The two basis functions describing the $4p$ orbital were obtained in the following way. If the lowest p exponents are extrapolated in an approximately even tempered way, p exponents of 0.355 and 0.1122 are obtained. The function with exponent 0.355 is found to describe only the tail of the $3p$ orbital and is therefore replaced by a function with a 10 times smaller exponent, 0.0355. This last diffuse p exponent is found to be reasonably important in describing an excitation to the atomic $4p$ orbital, but has in all our calculations on molecules been found to be rather unimportant. It is kept here mainly for consistency with our earlier work. For carbon the MIDI-3 basis of Tatewaki and Huzinaga [19] was used with the 1*s* orbital frozen and for hydrogen a 4*s* set contracted to two functions [20] was used. In a recent study on NiO [21] the MIDI-3 basis was found to yield rather large superposition errors for the oxygen 2*p* orbital. This problem is corrected by adding an even tempered 2*p* function to the oxygen basis. To see if the same problem appears for carbon some calculations were repeated with a similar function added on carbon with exponent 0.0866. In these calculations a larger hydrogen basis set of 5*s* contracted to three functions was also used. These additions to the original basis were, however, found to be of negligible importance for the relative energies computed here. For the Mulliken populations they naturally had larger effects, the significance of which can be questioned, however.

The geometries of the three structures of $Ni(C_2H_4)_2$ were optimized at the MCSCF level using the CASSCF method [22]. The demonstration of the importance of near degeneracy effects in transition metal chemistry is probably the most significant contribution from the recent applications of modern quantum chemical methods on organometallic systems. It is usually found that the antibonding orbital for a bond between a transition metal atom *d* orbital and a ligand has a large occupation. To describe this bonding even qualitatively therefore requires an MCSCF treatment. Also the *sd* hybridization in the first symmetry leads to occupation numbers which are significantly different from integer values. The choice of orbitals in the active space is straightforward for the three forms of $NI(C_2H_4)_2$. The two *sd* hybridized orbitals in the first symmetry are always included, likewise the π and π^* orbitals on ethylene. The d_π orbitals are included in case they belong to the same symmetry as an ethylene π^* orbital. For more quantitative accuracy a determination of the dynamical correlation energy is also required. The contracted CI method (CCI) [23] is used here for this purpose. The 10 nickel valence electrons and the 4 ethylene π electrons were correlated and all configurations with coefficients larger than 0.05 in the CASSCF calculation were selected as reference states. We have empirically found that the multireference analogue [24] of Davidson's correction [25] in general improves the relative energies. All of the CCI results discussed here therefore include this correction.

3. Results and discussion

The results from the calculations on the three different geometrical configurations of $Ni(C_2H_4)_2$ are presented and discussed in this section. The geometries and relative energies are given in Table 1 and Figs. 1–3, and the most relevant charges from the Mulliken population analysis are given in Tables 2–3. Each geometrical structure is discussed in a separate subsection below.

The Mulliken populations and the natural orbital occupation numbers shown in Table 2 can be used to study the mechanism of the bonding in detail. It is clear that when diffuse functions are included in the basis set, some of the Mulliken charges will be rather arbitrary. With the present basis set this is particularly true for the nickel 4*p* populations. In an interesting study of $Ni(CO)_4$ Bauschlicher

Table 1. Geometries and energies[a] for different isomers of $Ni(C_2H_4)_2$

Structure	R_{NiC}	R_{CC}	Θ^b	CCI+*Dav.*
$Ni(^1D)+2C_2H_4$	∞	2.56	0°	0.0[c]
$NiC_2H_4+C_2H_4^d$	3.73	2.75	21°	−12.8
$Ni(C_2H_4)_2(D_{2d})$	3.68	2.66	18°	−37.4
$Ni(C_2H_4)_2(D_{2h})$	3.93	2.60	11°	−27.1
$Ni(C_2H_4)_2(C_{2v})$	4.17	2.60	15°	−5.0

[a] Distances in a.u., energies in kcal/mole
[b] CH_2 tilt angle
[c] Total energy = −1656.77153 au
[d] Ref. [10]

Table 2. Active orbitals[a] and charge migration

	σ-system				π-system			
NiC_2H_4								
Orb. symm.	A_1				B_2			
Orb. origin	π	$(sd)_-$	$(sd)_+$		d_π	π^*		
Occupation	1.97	1.81	0.20		1.84	0.19		
donation/backdon.		0.48				0.61		
d increase/decr.		0.44				0.65		
q_{Ni}					+0.18			
$Ni(C_2H_4)_2-D_{2d}$								
Orb. symm.	A_1			B_1	E			
Orb. origin	π	$(sd)_-$	$(sd)_+$	π	d_π	π^*	d_π	π^*
Occupation	1.98	1.95	0.05	1.98	1.84	0.19	1.84	0.19
donation/backdon.		0.80				0.88		
d increase/decr.		0.90				1.00		
q_{Ni}					+0.08			
$Ni(C_2H_4)_2-D_{2h}^b$								
Orb. Symm.	A_{1g}			B_{1u}	B_{3u}	B_{2g}		B_{3g}
Orb. origin	π	$(sd)_-$	$(sd)_+$	π	π^*	d_π	π^*	d_π
Occupation	1.96	1.88	0.13	1.94	0.07	1.88	0.14	2.0
donation/backdon.		0.59 (0.46)				0.41 (0.52)		
d increase/decr.		0.64 (0.60)				0.49 (0.59)		
q_{Ni}					−0.17 (+0.06)			
$Ni(C_2H_4)_2-C_{2v}$								
Orb. symm.	A_1			B_2	B_1		A_2	
Orb. origin	π	$(sd)_-$	$(sd)_+$	π	d_π	π^*	d_π	π^*
Occupation	1.99	1.96	0.04	1.99	1.83	0.19	1.93	0.09
donation/backdon.		0.54				0.69		
d increase/decr.		0.89				0.82		
q_{Ni}					+0.15			

[a] $(sd)_-$, $(sd)_+$ and d_π are asymptotically Ni orbitals. π and π^* are asymptotically ethylene orbitals
[b] Numbers inside parenthesis correspond to a larger basis. (⟨C/3,3⟩, H: $5s \rightarrow 3s$)

Table 3. Mulliken population analysis

	Ni_{3d}	Ni_{4s}	Ni_{4p}	q_{Ni}	q_C	q_H
$Ni(C_2H_4)$	8.74	0.94	0.22	−0.10	−0.39	+0.17
$Ni(C_2H_4)_2$						
$-D_{2d}$	8.89	0.67	0.22	+0.08	−0.38	+0.18
$-D_{2h}$	9.15	0.79	0.22	−0.16	−0.34	+0.19
$-C_{2v}$	9.07	0.42	0.39	+0.12	−0.35	+0.18
		d-orbital populations				
	d_{x^2,y^2,z^2}	d_{xy}	d_{xz}	d_{xz}		
$Ni(C_2H_4)$	3.42	2.00	1.33	2.00		
$Ni(C_2H_4)_2$						
$-D_{2d}$	3.90	2.00	1.50	1.50		
$-D_{2h}$	3.64	2.00	1.51	2.00		
$-C_{2v}$	3.89	1.46	2.00	1.72		

and Bagus [6] have shown that even though they obtained a 4*p* population as large as 0.77, the 4*p* functions could be removed with only a minor loss of energy. In that case it therefore seemed as if the 4*p* populations should rather be counted as ligand populations than nickel populations. For the charges describing the major charge migrations we have decided to give two sets of numbers in Table 2. The first set of numbers are the normal donation/back donation charges. The σ donation is here counted as the increase of electrons on the metal in the A_1/A_{1g} symmetry. The orbitals contributing to this charge are therefore the $3d_\sigma$, the 4*s* and the $4p_\sigma$ oribtals. The π back donation is similarly the decrease of electrons on the metal in the symmetries containing the ethylene π^* orbitals, and includes the charge in the $3d_\pi$ and corresponding $4p_\pi$ orbitals. This definition of donation/back donation is the same as was used on NiC_2H_4 in [10]. The second set of numbers given in Table 2 is labelled d_σ increase/d_π decrease and only concerns the changes in the 3*d* populations. These populations can probably be trusted reasonably well and would certainly have less artefacts than the 4*p* populations. It is our experience that an important balancing factor in the interaction between a nickel atom and a ligand is that the *d* population tends to stay close to nine electrons. Populations concerned with the changes of the *d* shell are therefore expected to be at least as important as the total metal populations in describing the balance between the σ and π interactions.

The orbital names given in Table 2 should not be taken too literally. Clearly these orbitals, as well as any other molecular orbitals, have contributions from many centers. In particular, the π^* orbital has in fact a larger contribution from d_π^* at the equilibrium geometry. π^* is, however, the normal name for this orbital and is also a correct asymptotic name.

3.1. *The twisted* D_{2d} *structure*

The twisted D_{2d} structure of $Ni(C_2H_4)_2$ is found to be the energetically most favorable structure. The energy difference to the next lowest conformer, which is the D_{2h} structure, is 10.3 kcal/mol. The corresponding result found by Pitzer and Schaefer at the Hartree-Fock level was −0.1 kcal/mol [12] and Rösch and Hoffmann obtained a value of +1.5 kcal/mol at the extended Hückel level [11]. The 10.4 kcal/mol error in the Hartree-Fock calculation should be compared to the total binding energy of the second ethylene of 14.3 kcal/mol for the D_{2h} structure and 24.6 kcal/mol for the D_{2d} structure. The relative error obtained in the Hartree-Fock calculation is therefore rather large even though this is a rotation barrier which is normally assumed to be reasonably well predicted at this level of approximation. It should be noted, however, that part of the error (3.2 kcal/mol) on the rotational barrier is due to the nonoptimal geometries used in [11-12] see below.

The binding energy of the second ethylene for the D_{2d} structure, 24.6 kcal/mol, is much larger than the binding energy of the first ethylene, 12.8 kcal/mol, at this level of treatment, which may be found surprising. This is, however, a common trend for transition metal complexes and has been noted in calculations for Ni with H_2O and PH_3 ligands [7] and experimentally for Ni with CO ligands [26].

The explanation for this behavior is that certain hybridizations, which cost energy, are required already with one ligand and can therefore be used without cost for the second ligand. The hybridization of importance in this case is the formation of the orbital $(sd)_-$, which is a minus combination of a Ni 4*s* orbital and a Ni 3*d* orbital, and the corresponding $(sd)_+$ orbital. These two orbitals have single occupation at long distance for the Ni d^9s state, but approach an occupation of two and zero for shorter distances. The effect of the hybridization, which is discussed extensively in [7] and [10] is that charge is moved away from the electron rich region near the ethylene π orbitals out sideways to a region with less electrons, thus reducing the electronic repulsion.

When a single ethylene ligand is bound to nickel, the internal geometry of the ethylene is significantly modified. The CC bond length is increased from 2.56 au to 2.75 au, which is halfway towards a normal single bond distance (2.95 to 3.00 au). At the same time there is a rehybridization of the carbon from sp^2 towards sp^3 leading to a tilt angle (Θ) of the CH_2 group of 21 degrees. The NiC_2H_4 system can consequently in some ways be viewed as a three membered metallacycle. The D_{2d} structure of $Ni(C_2H_4)_2$ has a geometry which is similar to the NiC_2H_4 geometry. The NiC distance is very similar, 3.68 au compared to 3.73 au, and the tilt angle is 18 degrees compared to 21 degrees. The CC distance is, however, somewhat shorter, 2.66 au compared to 2.75 au, which means that the double bond character is dominating. The geometry for the D_{2d} structure is still far away from the assumed geometry in [11-12] of unperturbed ethylenes at a distance of 2 Å from nickel (Ni—C=3.99 au). We find the difference in energy between these two points at the correlated level of treatment to be 8.7 kcal/mol for the D_{2d} structure. The corresponding energy difference for the D_{2h} structure is 5.5 kcal/mol. This means that 3.2 kcal/mol of the total error of 10.4 kcal/mol obtained in [12] is not due to the Hartree-Fock approximation but to the use of nonoptimal geometries.

The similarity between the nickel-olefin bond in NiC_2H_4 and the D_{2d} structure of $Ni(C_2H_4)_2$ is not only apparent in the geometries but also from the occupations and charges shown in Tables 2-3. The main features of the DCD model are clearly seen (for a different analysis see subsection *IIIb*, however). There are large σ donations and π back donations with a dominance of the latter. The d_σ increase per ligand is almost exactly the same, 0.44 with one ethylene and 0.45 with two ethylenes. The d_π decrease per ligand is for some reason slightly larger for one ethylene than for two ethylenes, 0.65 compared to 0.50. The larger π back donation for NiC_2H_4 is seen also on the CC bond length, which as mentioned above is longer than for the D_{2d} form with two ligands, 2.75 au compared to 2.66 au. An extrapolation to three ethylene ligands is finally of some interest since this species has been synthesized [27]. The maximum d_σ increase possible for nickel is one electron since there is only one hole in the d shell. This maximum is nearly achieved with two ethylenes with 0.90 electrons. The σ donation per ligand therefore has to decrease with three ligands, which in turn most probably leads to a decrease also in the π back donation. It can consequently be predicted that the CC bond lengths for $Ni(C_2H_4)_3$ should be shorter than 2.66 au and longer than 2.56 au which is the CC bond length in free ethylene. A value close to 2.60 au is therefore expected. With the smaller π back donation a longer Ni-C distance than the 3.70 au found for one and two ethylene ligands is also expected.

It is also interesting to compare the natural orbital occupations of the D_{2d} structure with those for NiC_2H_4. We first note the striking similarity between the d_π occupations, 1.84 in both cases, and between the π^* occupations, 0.19 in both cases. For the hybrid orbitals $(sd)_-$ and $(sd)_+$ there is on the other hand a slight difference, which is not unexpected. With no perturbation on nickel these orbitals are both singly occupied. The occupations are then expected to approach 2.0 and 0.0 as more ligands are added. This was the trend found for the ligands H_2O and PH_3 studied earlier [7]. It might further be expected that the nickel ligand distance should be shorter when the occupation of $(sd)_+$ is decreased since the repulsion should be decreased. This effect is, however, not seen in the calculations. An explanation for this could be that the smaller π backdonation per ligand with two ethylenes than with one ligand has a compensating effect.

In the extended Hückel study by Rösch and Hoffmann [11] there is an interesting qualitative discussion based on perturbation theory arguments about the preference of the D_{2d} contra the D_{2h} structure of $Ni(C_2H_4)_2$. The question is whether the degenerate or the nondegenerate perturbation theory is applicable for the orbital interactions between d_π and π^*. If the nondegenerate perturbation theory is used the two structures are expected to be energetically equivalent. With the degenerate perturbation theory the D_{2d} structure should be preferred. Since they obtain the same energy for the D_{2d} and the D_{2h} structures they conclude that the d_π and π^* orbitals should not be considered degenerate. The same conclusion must be drawn from the Hartree-Fock study by Pitzer and Schaefer [12] who obtained the same result. Since we obtain a clear preference for the D_{2d} structure we conclude instead that these orbitals are better viewed as degenerate in this model. A further indication of the degeneracy of the d_π and the π^* orbitals is found in the natural orbital occupation numbers in Table 2. The occupation number 0.19 of the π^* orbital is quite high and shows large near degeneracy effects. For a quite different explanation for the preference of the D_{2d} structure, see below.

3.2. The planar D_{2h} *structure*

The primary difference in the electronic structure of the D_{2d} and the D_{2h} structure of $Ni(C_2H_4)_2$ is the number of *d* orbitals involved in the π bonding. In the D_{2d} structure there are two different *d* orbitals which interact with the ethylene π^* orbital, whereas in the D_{2h} structure the same *d* orbital is involved in both interactions. It is clear that the origin of the difference in the binding energies between the D_{2d} form and the D_{2h} form should be found here. As mentioned above, Rösch and Hoffmann analyzed this difference in terms of simple orbital interactions based on the perturbation theory, where they associated an orbital energy with each orbital. This type of analysis is best suited to analyze results obtained at the one configuration level, such as their extended Hückel calculation or a Hartree-Fock calculation such as the one by Pitzer and Schaefer. To analyze results obtained at a correlated level it is often more illustrative to use valence bond theory, which will be adopted here. An advantage with a valence bond analysis is that the conclusions are rather easily transferred over to other transition metal atoms since the respective atomic spectra are accurately known [28].

In the valence bond analysis, we here prefer to include only covalent structures since the nickel atom is essentially neutral, see Table 2. This viewpoint is exactly opposite to the standard DCD model where all interactions are ionic with transfers of electrons between the metal atom and the ligand. The final result from these two models can, of course, still be made to coincide as long as an equal amount of electrons are donated and backdonated in the DCD model. We will focus on the π bonding since there is nothing in the σ interaction that seems to be advantageous for the D_{2d} structure. The 4*s* and 4*p* populations will also be left out in the first stage of the analysis. The two dominating VB configurations for both the D_{2h} and the D_{2d} structure have d^9 occupations on Ni with one π bond to a single ethylene. The π interaction to the second ethylene will be non-bonding. The occupation of one of these configurations are then

$$\pi^1\pi^{*1}(A)+d_\sigma^2 d_{\pi x}^2 d_{\pi y}^1+\pi^2(B), \tag{1,2}$$

where *A* and *B* denote the two ethylenes. $d_{\pi x}$ and $d_{\pi y}$ denote the two π bonding *d* orbitals and d_σ is a *d* orbital in the first symmetry. The remaining *d* orbitals are doubly occupied. The second equivalent configuration is obtained by shifting the occupations of *A* and *B*, and for the D_{2d} structure shifting the occupation of the two d_π oribtals. For these two VB configurations there is no reason why the D_{2d} conformation should be preferred. On the contrary it seems that the non-bonding interaction should be slightly preferred for the D_{2h} structure since the doubly occupied π orbital on ethylene meets a singly rather than doubly occupied d_π orbital. A third VB configuration which probably has a reasonable weight is the nonexcited configuration, which has no π bonding. The occupation of this configuration is

$$\pi^2(A)+d_\sigma^1 d_{\pi x}^2 d_{\pi y}^2+\pi^2(B). \tag{3}$$

In order not to be too repulsive, it is important that this configuration has a singlet coupling between the d_σ orbital and the singly occupied $4s$ orbital, which allows for an efficient *sd* hybridization. Again, there is little reason to expect that this structure should prefer the D_{2d} geometry. A fourth VB configuration, which is often advocated in nickel complex bonding is the d^{10} structure which is also π non-bonding. The occupation of this configuration is

$$\pi^2(A)+d_\sigma^2 d_{\pi x}^2 d_{\pi y}^2+\pi^2(B). \tag{4}$$

This configuration does not have any preference for D_{2d} either. It is clear that to find a configuration which differs between the D_{2d} and the D_{2h} structures one has to go to a d^8 occupation on nickel. An important configuration of this type is,

$$\pi^1\pi^{*1}(A)+d_\sigma^2 d_{\pi d}^1 d_{\pi y}^1+\pi^1\pi^{*1}(B). \tag{5}$$

This type of configuration has a clear preference for the D_{2d} structure since two π bonds are formed compared to the single π bond for the D_{2h} structure. We conclude that configuration (5) is the key for understanding the structural preference in $Ni(C_2H_4)_2$. An indication of the importance of this d^8 configuration for the D_{2d} structure is the lower d population found for D_{2d} compared to D_{2h}.

In a CI expansion of the wave function the configurations with a single π bond should dominate since the energies of the two conformers are so similar, but the coefficient for the structure with two possible π bonds should not be negligible. An important point about the *sp* occupation of structure (5) is that this occupation should not be s^2 as the nickel atom ground state occupation (d^8s^2), since this would lead to a too large σ repulsion. An s^1p^1 occupation of configuration (5) seems most reasonable, but an ionic p^1 occupation should also be possible.

The above VB picture of the bonding is trivially transferred to the other transition metal atoms to the left of nickel. The main contents of the analysis is that configurations with two simultaneous π bonds determine the structural preference for D_{2d}. For the transition metals there are two types of configurations, which are especially suited for bonding. First there is the $d^{n+1}s^1$ configuration which usually dominates in nickel complexes. As discussed above, this configuration should not have a structural preference for D_{2d} for nickel. For the other transition metal atoms, which have more open d orbitals, this configuration should prefer D_{2d} with two π bonds. For atoms like iron and cobalt, where the d^n occupation is preferred energetically, configuration (5) with a $d^ns^1p^1$ occupation is likely to dominate. Since this configuration prefers the D_{2d} structure it seems clear that the D_{2d} structure of $M(C_2H_4)_2$ should be even more preferred for the other transition metal atoms M to the left of nickel.

In terms of the DCD model the π back donation is particularly reduced in the D_{2h} form (0.41) compared to the D_{2d} form (0.88). The occupations of the d_π orbitals are illustrative of the fact that the single bonding d_π orbital in D_{2h} is not able to compensate for the missing other π bond compared to D_{2d}. The occupation of the single π bonding d orbital in D_{2h} is almost exactly the same (1.51) as each one of the occupations of the π bonding orbitals in D_{2d} (1.50). The less efficient π bonding in D_{2h} is clearly seen also on the geometries, with a much longer Ni—C distance (3.93 au compared to 3.68 au), and shorter C—C bonds (2.60 au compared to 2.66 au) than in D_{2d}. The σ donation is also reduced in D_{2h}, 0.59 compared to 0.80.

A basis set extension was tried on the D_{2h} structure to study the sensitivity of the bindng energy and the populations. The populations are given in parenthesis in Table 2. Adding a diffuse p function on carbon and improving the basis set on hydrogen (see Sect. 2 for details) does have a marked effect on the populations, but only a very small effect on the binding energy (2.5 kcal/mol). As expected, the σ donation is decreased and the π back donation is increased by the basis set extension. It is hard to judge if these effects are real or just artefacts of the population analysis, but an indication of the former is that carbon takes electrons from the d shell and not from the $4s, 4p$ shell of nickel.

Since Pitzer and Schaefer [12] obtained the lowest energy for a triplet state of D_{2h}, calculations were also done on this state. The geometry was the same as used in [12]. At the SCF level we obtain almost exactly the same energy splitting between the ^1A_g state and the $^3B_{3u}$ as in [12] with a preference for the latter of 39.8 kcal/mol. At the CASSCF level the energy splitting is reduced to 4.1 kcal/mol still with the triplet lowest. At the CCI level with Davidson's correction the singlet is, however, strongly preferred by 28.7 kcal/mol. The conclusion drawn in [12] that it can be predicted with confidence that the two states lie energetically very close to each other, therefore does not really hold. Just as for the case with one ethylene ligand [10] it seems as if the triplet state is at most very weakly bound. The result for the energy splitting between the singlet and triplet states is another example of the dramatic effects electron correlation can have for relative energies in transition metal complexes.

3.3. *The bent* C_{2v} *structure*

The simultaneous formation of two π bonds in $Ni(C_2H_4)_2$ requires a 90 degree angle between the π orbitals of the two ethylenes. One such structure is the twisted D_{2d} form, which as discussed above is preferred compared to the planar D_{2h} form. Another structure of this type is the bent C_{2v} structure shown in Fig. 3. As seen in Table 1, this structure is, however, much higher in energy compared to both the D_{2d} and the D_{2h} form. Since the π bonding should be quite efficient for the C_{2v} form, the reason for the poor binding energy must be found in the σ system. As discussed at length in previous papers, the key to an efficient σ interaction is the sd hybridization [7, 10]. The goal of the sd hybridization is to form one strongly occupied hybrid orbital $(sd)_-$ shuffling away charge from the Ni—C bond. The other hybrid $(sd)_+$, which is antibonding, is then given a low occupation number. The two hybrids in NiC_2H_4 have the following form,

$$(sd)_- = s - (z^2 - y^2)$$

and

$$(sd)_+ = s + (z^2 - y^2).$$

The z-axis points towards the C—C bond, and the y-axis is out of the NiCC plane. The other d orbital in the first symmetry, which in this case is $2x^2 - y^2 - z^2$, is then doubly occupied. The particular choice of the $z^2 - y^2$ orbital as the hybridizing orbital is explained in [10] as due to $3d$–$3d$ interactions, but this effect is of minor importance in the present context. For the D_{2h} form of $Ni(C_2H_4)_2$ it is obvious that the same hybridization is optimal for both nickel ethylene interactions. For the D_{2d} form the same hybridization is not quite, but almost, optimal for both interactions. In D_{2h} charge will be moved away from the bonding region perpendicular to the NiCC plane. In D_{2d} charge will also be moved out from the bonding region but out along the axis parallel to the C—C bond, which is not quite optimal. For the C_{2v} form, on the other hand, the situation is drastically different. For this form there exists no choice of hybridizing orbital which will not be in conflict with one of the nickel ethylene interactions. Either the hybridization will move charge from one bonding region to the other, or force a double occupation of an orbital which will be strongly repulsive to the ethylene π orbitals.

A closer look at the wavefunction for the C_{2v} structure confirms the picture of a poor σ interaction. The *sd* hybridization, which is a prominent feature of the wavefunction for both the D_{2d} and the D_{2h} forms, is not seen at all in the strongly occupied orbitals of the C_{2v} form. There is some sign of it, however, in the weakly occupied "$(sd)_+$" orbital. Instead, nickel has chosen to reduce the repulsion to the ethylene π orbitals by simply reducing the $4s$ population. The population of the $4s$ orbital, 0.40, is consequently much smaller than for any of the other structures, see Table 3. The poor interaction energy of the C_{2v} form is not seen on the donation/back donation charges given in Table 2. The σ donation is almost as large and the π back donation actually much larger than for the stronger bound D_{2h} form. The DCD model is therefore not very useful in analyzing the energy difference between the C_{2v} and the D_{2h} forms.

The C_{2v} form of $Ni(C_2H_4)_2$ could have been of interest as an intermediate along the reaction pathway for formation of cyclobutane. With the high energy found for the C_{2v} form this reaction pathway does not seem so likely, however. Further calculations along this pathway, closing the C—Ni—C angle and tilting the ethylene groups, confirmed this picture. The in plane reaction pathway, with nickel in the same plane as the two C—C bonds, is therefore much preferable.

4. Conclusions

The twisted D_{2d} geometry is the preferred geometry for $Ni(C_2H_4)_2$. The reason for the preference of this geometry is that two weak covalent π bonds can be formed simultaneously. To understand this it is easier to use simple valence bond theory with covalent structures than to use the DCD model. Whenever there are large donation/back donation charges a conventional covalent picture is more straightforward. A recently performed study of NiN_2 [29] is illustrative of where the DCD model and where a covalent VB model is to be preferred in describing the bonding. For the linear "end on" structure, 0.14 electrons are transferred from d_π over to π^* of N_2, with consequently only a minor perturbation of Ni and N_2. The σ donation is even smaller, 0.07 electrons. Instead of searching for VB structures with very low weights, the DCD model is here preferable for describing the interactions. For the "side on" binding of NiN_2, however, a clear covalent bond is formed in the plane of the molecule between a Ni d_π orbital and an N_2 π^* orbital. Rather than trying to find a reason for the large π transfer of nearly one electron in this case, and even worse, the reason for the large σ donation, it is much easier to describe the bonding with one covalent VB structure.

Calculations have also been performed for a bent C_{2v} structure of $Ni(C_2H_4)_2$, which has not been considered earlier. This conformer also has the possibility of forming two simultaneous π bonds like the D_{2d} conformer. The high energy for the C_{2v} form is illustrative of the importance of an optimal *sd* hybridization in the first symmetry. This hybridization, which is not possible for the C_{2v} structure, is necessary to reduce the direct repulsion with the ethylene π orbitals, as well as to unshield the nickel *d* orbitals, thereby making the d_π bonding more efficient.

Acknowledgments. We are grateful to Margareta Blomberg for many discussions and suggestions. The calculations were performed on the CRAY-1 in Linköping using a grant from the Swedish Natural Science Research Council.

References

1. Dewar MJS (1951) Bull Soc Chim Fr 18:C71
2. Chatt J, Duncanson LA (1953) J Chem Soc 2939
3. Walch SP, Goddard III WA (1976) J Am Chem Soc 98:7908
4. Rives AB, Fenske RF (1981) J Chem Phys 75:1293
5. Bagus PS, Roos BO, (1981) J Chem Phys 75:5961
6. Bauschlicher CW, Bagus PS, (1984) J Chem Phys 81:5889
7. Blomberg MRA, Brandemark U, Siegbahn PEM, Broch-Mathisen K, Karlström G (1985) J Phys Chem 89:2171
8. Ozin GA, Power WJ, Upton TH, Goddard III WA (1978) J Am Chem Soc 100:4750; Upton TH, Goddard III WA (1978) J Am Chem Soc 100:321
9. Åkermark B, Almemark M, Almlöf J, Bäckvall J-E, Roos B, Stögård Å (1977) J Am Chem Soc 99:4617
10. Widmark P-O, Roos BO, Siegbahn PEM (1985) J Phys Chem 89:2180
11. Rösch N, Hoffmann R (1974) Inorg Chem 13:2656
12. Pitzer RM, Schaefer III HF (1979) J Am Chem Soc 101:7176
13. Siegbahn PEM (1985) J Am Chem Soc 107:7408
14. Pearson RG (1976) Symmetry rules for chemical reactions. Wiley, New York
15. Grubbs RH, Miyashita A, Liu M-IM, Burk PL (1977) J Am Chem Soc 99:3863
16. Tatewaki H, Huzinaga S (1979) J Chem Phys 71:4339
17. Pettersson L, Wahlgren U (1982) Chem Phys 69:185
18. Hay PJ (1977) J Chem Phys 66:4337
19. Tatewaki H, Huzinaga S (1980) J Comput Chem 1:205
20. Huzinaga S (1965) J Chem Phys 42:1293
21. Brandemark U, Siegbahn PEM: to be published
22. Roos BO, Taylor PR, Siegbahn PEM (1980) Chem Phys 48:157

23. Siegbahn PEM (1983) Int J Quantum Chem 23:1869
24. Blomberg MRA, Siegbahn PEM (1983) J Chem Phys 78:5682
25. Davidson ER (1974) In: Daudel R, Pullmann B (eds) The world of quantum chemistry. Reidel, Dordrecht
26. Stevens AE, Feigerle CS, Lineberger WC (1982) J Am Chem Soc 104:5026
27. Fischer K, Jonas K, Wilke G (1973) Angew Chem Int Ed Engl 12:565
28. Moore CE (1952) Atomic energy levels. Natl Bur Std, Washington
29. Blomberg MRA, Siegbahn PEM (1984) Chem Phys 87:189