Their values were found to be 3.67 and 0.041, respectively, their ratio providing the equilibrium constant of

$$B^{-}\cdot,Na^{+} + Trph \rightleftarrows B + Trph^{-}\cdot,Na^{+}$$

viz., 89. Thus, the difference of the redox potentials of these hydrocarbons (in a process yielding ion pairs in THF) determined from the results of our kinetic study is 115 mV. The potentiometric titration[8] leads to a difference of 113 mV in agreement with the kinetic findings. The redox potential of 1,1-diphenylethylene appears to be higher than that of biphenyl but lower than that of triphenylene. Accepting Bergman's[9] value for the redox potential of triphenylene, namely −2.49 V (vs. SCE), we find the redox potential of D (vs. SCE) to be −2.52 V. Recent unpublished polarographic determination by Bard[10] gives a value of −2.59 V in DMF with 0.1 M TBAP as supporting electrolyte.

An apparent discrepancy noted in the earlier stage of this research is now accounted for by the magnitude of K_{Trph} and K_B. The transient spectrum recorded 100 μs after flashing a $Na^{+},^{-}DD^{-},Na^{+}$ solution containing about 20-fold excess of biphenyl showed unmistakably the characteristic features of the $B^{-}\cdot,Na^{+}$ absorption, an intense peak at 400 nm and a weaker, broad band peaking at 630 nm. However, the absorbance at 400 nm was by ~35% weaker than would be calculated from the 470-nm bleaching and the assumed 2:1 stoichiometry, this being in contrast with the results obtained in the presence of triphenylene when the observed and calculated intensities agreed well. The value of K_B shows that for $[B]/[D] \approx 30$ the ratio $[B^{-}\cdot,Na^{+}]/[D^{-}\cdot,Na^{+}]$ should be about 1.2. Since the absorbance of $D^{-}\cdot,Na^{+}$ at 400 nm is about five times lower than that of $B^{-}\cdot Na^{+}$, the above "discrepancy" is now explained.

Comparison of Present Findings with Those Reported by Matsuda et al.[11]

Dimerization of $D^{-}\cdot,Na^{+}$ radical anions was previously investigated in this laboratory by stop-flow technique. A solution of $Trph^{-}\cdot,Na^{+}$, containing a large excess of Trph, was mixed with a small excess of D. This led to a relatively slow dimerization of $D^{-}\cdot,Na^{+}$, since its concentration was kept low. Monitoring the reaction at 470 nm allowed the calculation of an apparent rate constant k' related to k_3 (dimerization constant of $D^{-}\cdot,Na^{+}$) by the relation

$$(1 + K_{Trph}[Trph]/[Trph^{-}\cdot,Na^{+}])^2 k' = k_3$$

The only method available at that time for calculating K_{Trph} was very susceptible to experimental errors and this difficulty, coupled with the technical problems of experimentation, resulted in a greatly erroneous value of $K_{Trph} = 6.2 \times 10^{-2}$ instead of the presently found 3.67. However, using the reported values of k' and of $[Trph]/[Trph^{-}\cdot,Na^{+}]$ together with the presently derived value of K_{Trph}, we find values of k_3 varying from 3 to $6 \times 10^8\ M^{-1}\ s^{-1}$, whereas the value of k_3 now directly determined is $5 \times 10^8\ M^{-1}\ s^{-1}$. The previously claimed[11] value $k_3 = 1.5 \times 10^6\ M^{-1}\ s^{-1}$ should be discarded.

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Chemical Bonding and Reactivity in Nickel–Ethene Complexes. An ab Initio MO–SCF Study

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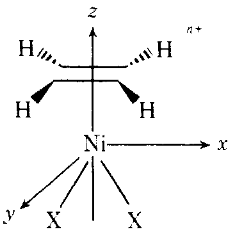
Abstract: A number of nickel-ethene complexes with various additional ligands have been studied using *ab initio* MO-SCF calculations. Nickel(0)-olefin complexes are found to have C-C bond distances much longer than normal double bonds. Special interest has been focused on parameters relevant to the Dewar-Chatt-Duncanson model for the olefin-metal interaction. Attempts have also been made to estimate the reactivity of the ethene molecule in different nickel complexes. Reactions such as nucleophilic addition and cycloaddition are discussed. Cationic nickel(II) complexes are the main candidates for promotors of nucleophilic addition and the cyclic insertion reaction. By contrast, cyclobutane formation and other related, cyclic product forming reactions probably require nickel(0) complexes as promotors.

Organometallic reactions are frequently complex and theoretical models which could serve as a guide for experimental work are highly desirable. We have been particularly interested in the factors that promote cycloaddition and nucleophilic addition to complexed olefins.[2,3] The major factors are likely to be the charge on the complexed olefin relative to the free olefin and the metal, as well as the general weakening of the double bond due to the interaction with the metal. These properties may be determined by an evaluation of σ donation from the olefin to the metal and π-back-donation from the metal. The Dewar-Chatt Duncanson[4] model qualitatively describes these properties, but a quantitative evaluation is obviously required in order to make chemical conclusions feasible. Semiempirical calculations have recently been done for this purpose, but the predictive value of these studies is doubtful. For instance, a recent CNDO calculation strongly suggests that palladium promoted hydroxylation should be a cis process,[5] contrary to the experimental evidence,[6] which suggests a trans process. Furthermore, the results from semiempirical calculations on bis-π-allylnickel[7] and Zeise's salt[8] do not agree with those obtained by more accurate methods.[9,10]

Since the nickel triad elements (Ni, Pd, Pt) catalyze both nucleophilic type of additions and oligomerization reactions, it seemed of value to determine electron distribution and charge for a series of model complexes **1** and **2** by ab initio methods and attempt to use the result for rationalizing experiments in the triad. Many of the complexes **1** and **2** are not known as stable complexes but may be expected as intermediates in chemical reactions. The results would therefore be useful for elucidating trends in the properties of the complexes, as the ligands and the metal oxidation state are changed. Although the calculations are done on nickel complexes, these trends could perhaps be used to understand reactions of olefin complexes of Pd and Pt merely by taking the differences in ionization potentials into account.



1a, $n = 0$; X = F^-, Cl^-, CH_3^-, CN^-, NH_2^-
b, $n = 2$; X = H_2O, NH_3, PH_3
2, $n = 0$, X = H_2O, NH_3, PH_3

In the present work, the electron distribution and charge, as calculated by ab initio methods, are compared with experimental data.

Details of the Calculations

All the calculations were performed in the MO-LCAO-SCF framework, using contracted Gaussian functions for the expansion of the molecular orbitals. In addition to complexes of the type $Ni(C_2H_4)X_2$ the smaller systems $Ni(C_2H_4)$ and NiX_2 were also investigated.

For all systems containing ethene, the C-C double-bond distance was optimized. In addition to total energies and bond distances, orbital energies and atomic populations were computed.

When extensive calculations are performed for a series of complexes, the choice of basis functions deserves some consideration. The basis set must be flexible enough to give a satisfactory description of the specific physical properties connected to the problem. At the same time the number of functions must be kept as low as possible to avoid excessive computation. In the work presented here, atom-optimized basis sets, obtained from the literature, were used with certain modifications in order to fit our particular demands.

For nickel, an atomic (12, 6, 4) basis set optimized[11] for Ni(0) was taken as the starting set. Diffuse functions of the p and d types with exponents of 0.3 and 0.2 were then added, giving a (12, 7, 5) basis set. For each of the functions the totally symmetric combination of the 3s type was automatically included in the basis set. Of these functions the two outermost ones have radical density maxima at 1.56 and 2.74 au, corresponding to 1s exponents of 0.203 and 0.067, respectively. On the other hand, the two most diffuse s orbitals in the original basis have exponents 0.0464 and 0.1258. The basis set thus overemphasizes the 4s region of the nickel atom. In order to obtain a more balanced basis, these two latter functions were deleted yielding a final basis set of the type (10 (15), 7, 5) for nickel. This was then contracted to a (3 (5), 4, 2) basis set. The fact that the 3s basis functions are slightly more contracted than the original diffuse 1s functions is likely to improve the quality of the wave function, since the 4s orbital of the nickel atom can be expected to be more contracted in the complex than in the free atom. For hydrogen, basis sets given by Huzinaga[12] were used, with a scaling factor of 1.3 applied to the exponents. The hydrogen atoms in ethene were described by four s-type functions contracted to two, whereas for all the hydrogen-containing ligands three s functions were contracted to a single hydrogen basis function.

All the first- and second-row atoms were described using the basis sets suggested by Roos and Siegbahn,[13] i.e., 7s 3p for C, N, O, F and 10s 6p for P and S. These were contracted to minimal basis sets except for the carbon atoms of the ethene molecule for which a double-ζ type contraction was chosen, in order to give some additional flexibility to the regions of particular interest.

The choice of basis used in this investigation, with a less flexible contraction on the ligands than on ethylene, deserves some further discussion.

It would be easy to construct examples where the use of such an unbalanced basis would lead to an artificial flow of electron density from the regions described by the poorer basis. Here, one might perhaps anticipate such an effect would be minor, the interaction between the ligands and ethylene being comparatively weak and indirect. In order to check this assumption, the calculations for the complex $F_2Ni(C_2H_4)$ were repeated, using a double-ζ contraction also for the fluorine basis set.

The differences between these results and those obtained in the minimal-basis calculations were quite small. The charges on fluorine and ethene changed from -0.45 and $+0.01$ to -0.48 and $+0.02$, and the equilibrium C-C distance increased by 0.001 Å. These shifts were considered insignificant for the purpose of the present study, and the minimal-basis results are therefore used in all discussions throughout this paper for the sake of consistency.

In the largest of the systems studied, $Ni(C_2H_4)(PH_3)_2$, the number of primitive Gaussians amounted to 183. These were then contracted to a final number of 79 basis functions. All calculations were performed on the Univac 1110 Computer at the University of Bergen using the program package MOLECULE.[14] The largest system studied (183 basis functions) required 90 min central processing time for the integral evaluation and the SCF iterations. In the few $Ni(C_2H_4)X_2$ complexes for which the structure has been determined so far,[29] nickel usually has a square-planar coordination geometry, i.e., the metal is approximately quadratically coordinated by the central atoms of the ligands and the carbon atoms of ethylene.

This geometry was therefore used in the calculations, but recent studies indicate that even pentacoordination has a relatively small effect on properties like atom charges and the ethene C=C bond length.[15] The metal-ligand distances and the coordination angles were deduced from experimental data when available.[16] The values used for these parameters are summarized in Table I. For the internal geometries of the ligands standard values[16a] were used.

The spin state of a metal atom in a complex of this type is often difficult to assess on the basis of quantum-mechanical calculations. However, available experimental information indicated that a quadratically coordinated Ni complex has a

Table I. Metal-Ligand Distances in Ångströms[a]

Ni-F	Ni-Cl	Ni-C(cyanide)	Ni-C(methyl)	Ni-N	Ni-P	Ni-O
1.986[b]	2.38[b]	1.86[b]	1.87[c]	2.15[b]	2.18[d]	2.10[b]

[a] The angle X-Ni-X was set to 112° in all cases and the distance Ni-C(ethylene) was teken to be 2.01 Å.[27a] [b] Reference 16a; the Ni-Cl distance was taken from $NiCl_2$(pyridine). [c] Reference 16b. [d] Reference 27a.

Table II. Calculated Ethene C-C Distances and Total Populations of the π and π^* Orbitals of Ethene in the Complexes $Ni(C_2H_4)X_2$

Ligand X	$P(\pi)$	$P(\pi^*)$	R_{C-C}, Å[a]	Q(Ni)
Ni(II)-	1.37	0.02	1.360	+1.39
$-F^-$	1.79	0.19	1.352	+0.89
$-Cl^-$	1.74	0.19	1.360	+0.93
$-NH_2^-$	1.76	0.21	1.352	+0.83
$-CN^-$	1.78	0.21	1.391	+1.20
$-CH_3^-$	1.77	0.26	1.346	+1.05
$-H_2O$	1.54	0.07	1.347	+1.15
$-NH_3$	1.53	0.09	1.349	+1.12
$-PH_3$	1.49	0.13	1.356	+0.93
Ni(0)-	1.81	0.52	1.390	+0.33
$-H_2O$	1.83	0.98	1.452	+0.56
$-NH_3$	1.85	0.93	1.455	+0.58
$-PH_3$	1.87	0.61	1.410	+0.35

[a] The C-C distance was computed to be 1.320 Å (experimental value 1.338 Å).

Table III. Binding Energies between the Ethene Molecule and the Fragments NiX_2[a]

	$-E$, au		
Ligand	$Ni(C_2H_4)X_2$	NiX_2	ΔE, kcal/mol
Ni(II)-	1581.0423	1502.9697	80.53
$-F^-$	1780.0851	1702.1501	−5.84
$-Cl^-$	2498.9482	2421.0016	1.44
$-NH_2^-$	1692.4847	1614.5187	13.62
$-CN^-$	1765.7676	1687.8235	−0.13
$-CH_3^-$	1660.7128	1582.7591	5.90
$-H_2O$	1732.8010	1654.7869	43.80
$-NH_3$	1693.2729	1615.2738	34.39
$-PH_3$	2264.7133	2186.7207	30.31
Ni(0)-	1581.7355	1503.7479	27.18
$-H_2O$	1733.3337	1655.2956	58.86
$-NH_3$	1693.8073	1615.7770	53.97
$-PH_3$	2265.3082	2187.3070	35.70

[a] $E_{C_2H_4} = -77.9443$ au.

low-spin ground state.[17] The calculations were therefore only performed on low-spin complexes. In all cases the calculations were repeated for a number of different C–C bond distances of ethene, keeping all the other bond lengths constant. By this process the energy minima were obtained by interpolation using a parabolic fit.

Results

The calculations show several interesting features. The charge on the central metal atom varies relatively moderately from the formally zero-valent to the two-valent complexes (Table II). For instance, the charge on nickel in the zero-valent complex **2** (X = NH_3) is 0.58 and in the two-valent complex **1** (X = NH_2^-) +0.83. However, the charge of the olefin, which is the most interesting property in the present context, varies strongly, from about −0.8 for the formally nickel(0) complexes to +0.4 for the charged nickel(II) complexes. It is further of interest that the cyano complex **1a** (X = CN) which has the highest positive nickel charge of all the investigated complexes, cannot induce a positive charge on the olefin.

The calculated equilibrium C–C bond distances of ethene in the complexes are in all cases longer than in the free ethene molecule (cf. Table II). This increase in bond length is explained by the model adopted for the nickel–ethene interaction. Both the charge transfer from the bonding π system of ethene and the back-donation to the antibonding π^* orbital decrease the double-bond character and consequently increase the length of the C–C bond. The results in Table II also show that the Ni(0) complexes have longer C–C bond distances than the Ni(II) complexes. This difference becomes more pronounced when the various ligands are added. In the case of Ni(0), an addition of neutral ligands causes a further increase in the C–C bond distance of up to 0.06 Å. The values for the H_2O and NH_3 complexes of 1.452 and 1.455 Å indicate that the olefin has lost about half of its double-bond character. The trend in the C–C bond distances is not quite so clear for the Ni(II) compounds. With the exception of the CN^- complex, the ethene molecule in these systems has approximately the same C–C bond length as in the $Ni(ethene)^{2+}$ complex.

The binding energies between the ethene molecule and nickel are given in Table III for the different complexes. In the Ni(II) systems, binding energies are very much lower when ligands are added to the $Ni(ethene)^{2+}$ complex. On the other hand, in neutral Ni(0) complexes with H_2O, NH_3, and PH_3 the binding energies increase relative to the binding energy of Ni(0)(ethene).

Since the nickel–ethene distance has not been optimized, the absolute values of these binding energies should not be taken too literally but the trends shown by the relative values are most probably relevant (cf. also ref 15).

The validity of the concepts of σ symmetry donation to the metal and π back-bonding to the olefin can be checked by an inspection of the gross populations of the basis functions of π and π^* symmetry of ethene. However, a perfect σ–π separation of the ethene orbitals is not possible due to the presence of the metal atom and the nonplanar ethene geometry, as shown by experimental evidence.[18] Therefore, the gross populations of ethene, for the entire set of irreducible representations in question, were computed instead. The population of the π and π^* orbitals derived from these values are presented in Table II.

In Table IV, the energies of the highest occupied (b symmetry) and the lowest unoccupied (a symmetry) Ni orbitals for the free NiX_2 molecules are given. These can be used to predict the mode of interaction with an olefin when a complex is formed.

Finally, the total charges on nickel and on ethene were calculated for the complexes (Table V). These values are of particular interest for a discussion of the influence of various ligands on the reactivity of the complexed olefin.

Discussion

The calculated bond energies of the nickel–ethene bond for the species $Ni(C_2H_4)$ and $Ni(C_2H_4)^{2+}$ were 27.2 and 80.5 kcal mol^{-1} (Table III). These values are of the same magnitude as those obtained by Basch for $Ag(C_2H_4)^+$ (27.6 kcal mol^{-1}), using a basis set similar to the one used in this work but

Table IV. Energy (eV) of the Highest Occupied and Lowest Unoccupied Orbital of the Fragment NiX_2

	Ni(II), X =									Ni(0), X =			
	None	F^-	Cl^-	NH_2^-	CN^-	CH_3^-	H_2O	NH_3	PH_3	None	H_2O	NH_3	PH_3
a orb	−16.35	1.25	−0.20	2.05	−0.23	2.34	−11.42	−10.98	−10.91	4.45	8.72	9.10	7.17
b orb	−39.89	−22.04	−23.09	−20.65	−21.43	−20.50	−33.90	−33.36	−30.53	−6.44	−4.65	−4.72	−6.02

Table V. Gross Charges on Ni, Ethene, and the Ligands X in the Complexes $Ni(C_2H_4)X_2$

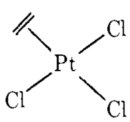
	Ni(II), X =									Ni(0), X =			
	None	F^-	Cl^-	NH_2^-	CN^-	CH_3^-	H_2O	NH_3	PH_3	None	H_2O	NH_3	PH_3
Q(Ni)	+1.39	+0.89	+0.93	+0.83	+1.20	+1.05	+1.15	+1.12	+0.93	+0.33	+0.56	+0.58	+0.35
$Q(C_2H_4)$	+0.61	+0.01	+0.07	+0.02	−0.01	−0.02	+0.38	+0.38	+0.39	−0.33	−0.80	−0.78	−0.48
Q(X)		−0.45	−0.50	−0.43	−0.59	−0.51	+0.23	+0.25	+0.34		+0.12	+0.11	+0.07

somewhat less flexible.[19] The fact that the bond strength computed for the charged nickel(II) complexes is considerably higher than for the nickel(0) complexes is most probably due to the electrostatic interactions between the positively charged metal and the readily polarizable π-electron system of the olefin. It is therefore not unexpected that the addition of ligands to the charged nickel(II) complex decreases the binding energy of the olefin. This is especially true for X_2Ni(ethene) complexes where X is a negatively charged ligand like halogen or methyl. In these complexes the binding energies for the Ni(0)ethene complexes are increased on the addition of ligand. This cannot be explained by simple electrostatic considerations since the ligands serve as electron donors to the metal in this case (cf. Table V). The higher binding energy in these cases is the result of a more pronounced charge transfer to the π^* orbitals of the olefin. This is also nicely reflected in the gross charges of the olefin and in the equilibrium C-C bond distances (Tables II and IV).

The calculated low binding energies in the nickel(II) series derive indirect experimental support from the fact that no neutral nickel(II) complexes $X_2Ni(C_2H_4)$ have been isolated. By contrast, several complexes of zero-valent nickel have been isolated. The metal-ethene binding energy for one such complex $(R_3P)_2Ni(C_2H_4)$, R = *O-o*-tolyl, has been estimated at 33 kcal/mol,[20] which is in good agreement with the value of 36 kcal/mol calculated for $(H_3P)_2Ni(C_2H_4)$, Table III.

Acceptor properties of the metal seem to be important for the stabilities of the divalent nickel-olefin complexes (cf. Table III). As evidenced by their second ionization potentials (Ni (18.15 eV), Pt (18.56 eV), Pd (19.9 eV)) palladium(II) and platinum(II) should be better electron acceptors than nickel(II) and thus give more stable complexes. Several olefin complexes of palladium(II) and platinum(II) have been characterized in accordance with this prediction. Assuming that entropy effects are essentially constant, bond strengths in these olefin complexes may be estimated from the equilibrium data for the reactions $MCl_4^{2-} \rightleftarrows MCl_3^- + Cl^-$ and $MCl_4^{2-} + C_2H_4 \rightleftarrows MCl_3^-(C_2H_4) + Cl^-$ [21] (M = Pd, Pt(II)). Estimates of 6-10 kcal/mol for the palladium(II) and platinum(II) metal-olefin bond energies are obtained in this way. This is in fair agreement with the values obtained for nickel(II) olefin complexes (Table III and ref 15). Although more data are necessary to assess the calculated influence of ligands on the metal-olefin bond energies, the gross features of the bonding and the relative bond energies of nickel(II) and nickel(0) complexes are probably adequately described by the present calculations.

No simple nickel(II) olefin complexes have been investigated by x-ray crystallography. However, in the palladium and platinum series much experimental evidence is available and although the bond strengths are probably somewhat greater than in the nickel complexes, the differences are probably small enough to allow a comparison between the experimental results for palladium and platinum complexes and the calculations on the nickel complexes. A minor difficulty is introduced by the fact that all structure determinations are not equally accurate. For instance, the bond lengths determined for Zeise's salt **3** range from 1.35 to 1.48 Å[22] but a recent neutron diffraction study gives 1.354 Å,[23] which is probably the most reliable result and in agreement with the value of 1.360 Å obtained from the calculation on the nickel chloride-ethene complex (Table II). Similarly, the C-C bond length in the complex **4** was initially found to be 1.46 Å; this abnormal bond length was, however, shown to be an artifact introduced by thermal disorder in the crystal. The bond length, remeasured at liquid nitrogen temperature, was 1.366 Å,[24] again in agreement with the value obtained from the present calculations. Other recent studies exist[25,26] which give C-C bond lengths for palladium and platinum compounds in the range of 1.30-1.40 Å, with a predominance around 1.35 Å.



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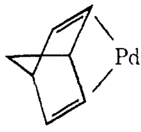

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For the metal(0) complexes, distinctly longer C-C bond lengths have been determined, ranging from 1.40 to 1.48 Å, with predominance around 1.43 Å.[27-29] Most of these complexes of the type X_2M(olefin) contain phosphine as ligand X. The experimental results thus agree with the computed value of 1.41 Å for the nickel-phosphine-olefin complex (Table II).

A model very similar to the Dewar-Chatt-Duncanson model for the metal-olefin bond has recently been discussed for the binding mechanism in three-membered heterocyclic ring systems of the type XC_2H_4.[30] Ab initio MO-SCF calculations were performed in the cases where X = S, SO, and SO_2,[30b] including variations of the C-C and C-S bonds. From these results it was possible to relate the C-C bond weakening to the donor-acceptor strength of the group X in an appropriate valence state, the orbital interacting with the π orbital of ethene being doubly occupied and the orbital interacting with the π orbital being empty. The model was also found to work well for a number of other groups containing first- and second-row atoms.

In order to investigate whether such a quantitative correlation also exists for the nickel-olefin complexes, a number of calculations have been performed on the NiX_2 moieties. The geometries were taken to be the same as in the corresponding olefin complex and the electron configurations were chosen so that the Ni donor orbital (of b symmetry) was doubly occupied while the acceptor orbital (of a symmetry) was empty. The results of these calculations are shown in Table IV. Some insight into the bonding mechanism can be obtained from an analysis of the orbital energies given in this table. For Ni(0) complexes the 3d shell is filled and the acceptor orbital must therefore belong to the next shell (4s-4p hybrid). The orbital energy is accordingly very high and therefore the donation of electrons to Ni is unimportant in these complexes. Instead, the strength of the bond is almost entirely determined by the donor strength of the b orbital which increases with increasing orbital energy. For the Ni(0) complexes there exists a close correlation between the orbital energy of the b orbital in NiX_2 and the donated charge (cf. Tables II-IV), the bond energy, and the length of the ethene double bond. The model also explains the effects of the extra ligands. The donor orbital is antibonding with respect to the ligands X. Its energy is therefore raised, making the charge transfer to ethene more effective. As a result, the Ni-ethene bond is strengthened. The effect is more pronounced for H_2o and NH_3 than for PH_3.

The opposite situation occurs in the charged $Ni(II)C_2H_4$ complexes. In this case the donor orbital has too low an energy to be effective. The bond strength is therefore determined by the energy of the acceptor orbital which in this case is a Ni 3d orbital of a symmetry ($3d_{z^2}$). Interaction with the ligands raises the energy of this orbital too. This weakens the acceptor strength and consequently also weakens the Ni-ethene bond strength. This is borne out by the results given in Tables III and IV. Again, H_2O and NH_3 have been found to have a stronger effect than PH_3.

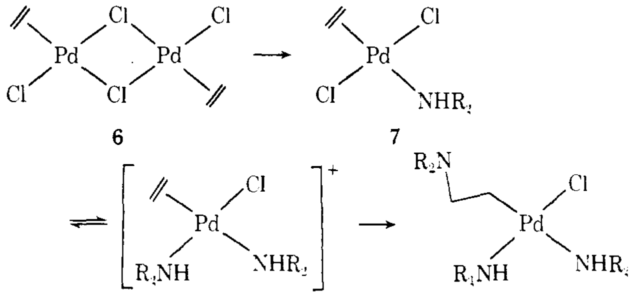
Chemical Reactivity

Nucleophilic Addition. In the palladium and platinum(II) series there are numerous examples of nucleophilic addition to olefins[3] while the reaction is rare for nickel(II). Furthermore, nucleophilic addition, e.g., amination, is more rapid with palladium(II) than with platinum(II).[31,l] Since this reactivity order correlates well with the acceptor properties of the metals in the two-valent state, it appears that the induction of positive charge on the olefin is more important than the weakening of the double bond by the combination of σ donation and π back-donation. A direct comparison between these effects for nickel and palladium(II) will have to wait for calculations on palladium, which are in progress. However, for platinum(II) a reasonably accurate calculation on Zeise's salt (**3**) is available.[10] This calculation shows that σ donation is about three times as large as π back-donation, leaving the olefin with a considerable positive charge. This may be compared with the present results, which show that even in the neutral nickel(II) complexes **1a** ($X = Cl^-, F^-$), only a small positive charge (+0.1) is induced since σ donation and π back-donation are essentially equal (Tables II and V). Additional halide ligands can only be expected to decrease further the positive charge on the olefin, as illustrated by a calculation on the complex **5**.[15]

$$\|\text{—}NiF_3^-$$

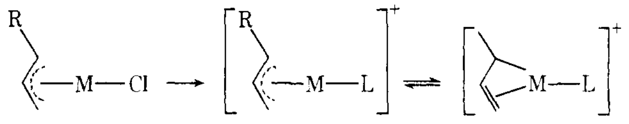
5

The superior acceptor properties of platinum(II) compared with nickel(II) are thus clearly demonstrated. The present calculations indicate that the relatively poor acceptor properties of nickel may to some extent be compensated by the auxiliary ligands. Replacement of the anionic ligands in **1a** by two neutral ligands like H_2O, NH_3, or PH_3 sharply increases σ donation (0.47-0.51) and decreases π back-donation (0.07-0.13). A charge of the order of +0.4 is thus induced on the olefin which is also activated by the considerable electron withdrawal from its bonding π orbital. Nucleophilic attack should therefore be possible on complexes of the general structure **1b** ($X = H_2O$, etc.). Another important conclusion may also be drawn from the present calculation. In the neutral complexes **1a**, the positive charge on the metal (ca. +0.9) is high relative to that on the olefin (+0.1). A nucleophile would therefore be expected to attack predominantly on the metal. In the complexes of the type **1b** the unfavorable metal-to-olefin charge ratio is decreased due to the increase of the positive charge on the olefin. The relative probability for nucleophilic attack on the olefin is thus markedly increased. Although a direct theoretical comparison between nickel and palladium is not yet possible, these trends are illustrated by experimental results on the palladium promoted amination of simple olefins.[31] When an amine R_2NH is added to the complex **6**, the first mole per mole of Pd appears to attack exclusively at palladium to yield the monomeric complex **7**. The olefin-to-metal charge ratio of this complex would be expected to be more favorable for attack on the olefin than that of the corresponding nickel complex **1a** ($X = Cl^-$). In spite of this the second mole of amine appears also to attack preferentially at the metal (presumably with the formation of a charged complex **8**). Only the third mole of amine attacks at the olefin to give a σ complex **9**. The intermediacy of a charged complex would explain these results.



6 **7** **8** **9**

The accuracy of these ideas and their relevance to nickel complexes is illustrated by the reactions of π-allyl nickel and palladium complexes (**10, 11**).[31,32] Both nickel and palladium complexes react with nucleophiles but only after conversion to the charged species **11**. The palladium complex is much more reactive than the nickel complex, in accordance with the qualitative considerations based on acceptor properties.

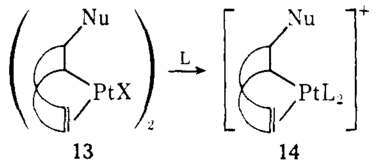


10a, M = Ni
b, M = Pd

11a, M = Ni
b, M = Pd

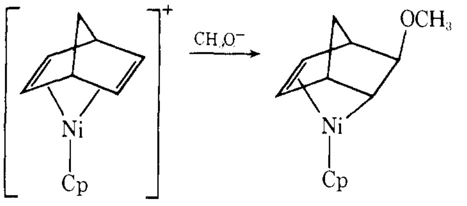
12a, M = Ni
b, M = Pd

A parenthetic observation is that the complexes **11**, which can also be described by **12**, may be regarded as alkyl-olefin complexes. According to the present calculations, an alkyl group would be expected to be a slightly better electron donor than halide. The simple π-olefin complexes, e.g., **8**, would thus be expected to react more rapidly than the corresponding π-allyl complexes, e.g., **12b**. This is shown to be the case by experimental data. Further support for these ideas may also be derived from the complex **13**, which is stable toward nucleophiles but may react after ionization to the positively charge complex[33] **14**.



13 **14**

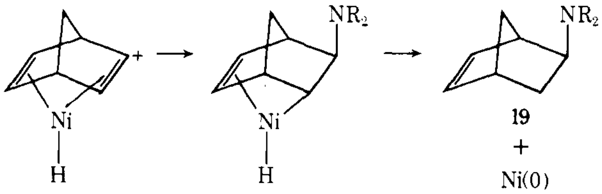
These experimental and theoretical results indicate that nucleophilic reactions in the nickel series should be possible, provided charged intermediates analogous to **1b** could be formed. Only one well-characterized reaction of this type is known, namely **15** → **16**.[34] Although the cyclopentadienyl anion is a rather different ligand than halide and alkyl, the example still illustrates the necessity for the formation of a charged complex.



15 **16**

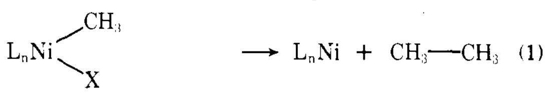
Cp = cyclopentadienyl

The results of the calculations also suggest a novel interpretation of the nickel(0)-catalyzed amination of norbornadiene, which requires the presence of trifluoroacetic acid.[35] The reaction has been postulated to involve the addition of nickel hydride to the double bond, followed by the attack of a nucleophile on saturated carbon, with displacement of nickel(0). An alternative explanation is now that the protonation of nickel(0) complexed to norbornadiene gives a charged nickel(II) complex **17.** Nucleophilic addition to give **18** followed by reductive elimination then yields the observed product **19** and nickel(0).



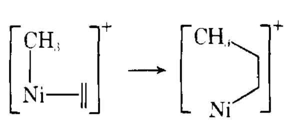
17 **18** **19**

Cyclic Reactions. There are formally three different types of cyclic reactions of particular interest to organometallic chemistry: $(2\sigma + 2\sigma)$, $(2\sigma + 2\pi)$, and $(2\pi + 2\pi)$. The question whether these reactions are concerted or proceed by a stepwise mechanism has attracted considerable interest.[2,36] The first type, eq 1, which does not involve olefins is discussed elsewhere.[37] Here, some aspects of the second and third types, eq 2-4, will be considered. Important examples of the $(2\sigma + 2\pi)$ addition are the insertion of the olefin of an alkyl-metal-olefin complex into the alkyl-metal bond (eq 2) and the related reaction for hydride metal-olefin complexes. Our calculations on the dimethylnickel complex **1a** ($X = CH_3$) indicate that the methyl groups are likely to react as nucleophiles, since they carry a substantial negative charge (−0.51). This is also probably true for the methyl group of the mixed methyl halide complex **20b,** since the electron distribution within the complex is expected to be essentially unaffected by the exchange of one methyl for halide (cf. Table V). If the alkyl group of alkyl metal-olefin complexes acts as a nucleophile, in the insertion reaction, a close parallel between insertion and nucleophilic addition is anticipated. Neutral complexes should thus be relatively inert whereas charged complexes like **21** should readily undergo insertion. These predictions are supported by experimental evidence, which shows that neutral alkyl metal-olefin complexes of nickel, palladium, and platinum are unreactive[33,38,39] while at least the charged complexes of palladium and platinum readily undergo insertion.[33,40] It has not yet been possible to experimentally verify these ideas for charged alkyl nickel-olefin complexes since they undergo competing decomposition reactions.[38b]



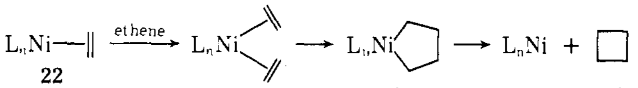
$$\mathrm{L_nNi}\begin{smallmatrix}\diagup \mathrm{CH_3}\\ \diagdown \mathrm{X}\end{smallmatrix} \longrightarrow \mathrm{L_nNi} + \mathrm{CH_3{-}CH_3} \qquad (1)$$

20, $X = CH_3$
20a, L_n = ethene; $X = CH_3$
20b, L_n = ethene; X = Cl

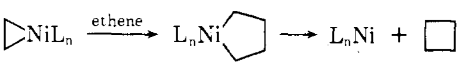


(2)

21



22 **23** (3)



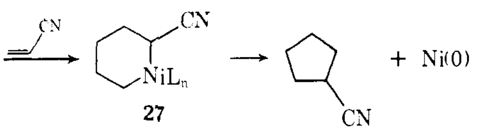
24 **23** (4)

Like the first two reaction types, $(2\pi + 2\pi)$ additions should be symmetry forbidden and thus nonconcerted.[41] However, it has been suggested that the combined effects of σ donation to and π back-donation from the metal will make this reaction symmetry allowed and concerted.[2d,e,g,h,42] According to the present calculations these effects are perhaps sufficiently large for nickel(0) and charged nickel(II) complexes, **2** and **1b,** but not for neutral nickel(II) complexes, **1a.** Experimental evidence seems to support these ideas since only nickel(0)[43] and possibly charged nickel(II) complexes[44] seem to promote cycloaddition.

However, the reactivity of nickel(0) complexes may also be explained by entirely different models. The calculations show that the electron configuration of the nickel(0)-olefin complexes ($\sim\pi^2\pi^{*1}$, Table II) is similar to that of an n-π^* excited carbonyl or an α,β-unsaturated carbonyl compound. Such compounds frequently undergo stepwise radical addition to olefins to give four-membered rings (cf. ref 42c). Although the analogy must be used with caution, similar stepwise reactions might be anticipated for nickel(0)-olefin complexes. The addition could proceed directly to give cyclobutane but could also yield an intermediate metallocycle, e.g., **23.** Recent experiments show that such metallocycles may in fact appear as intermediates.[36]

This result, combined with the result of our calculations, indicates still another possible reaction path for the nickel(0)-catalyzed $(2\pi + 2\pi)$ addition. Since the olefinic carbons of a complex **2** carry a considerable negative charge (ca. −0.5), they should be capable of adding as nucleophiles to an approaching olefin, especially if the olefin is electron deficient. An insertion type of reaction (eq 4) would then lead to an intermediate metallocycle. This would in fact be very similar to the reaction between strained cyclopropanes and electron-deficient olefins, which may be depicted as proceeding via the metallocycles **26** and **27.**

25 **26**



27

Conclusions

The present ab initio calculations on the complexes $X_2Ni(C_2H_4)$, **1a, 1b,** and **2,** give a quantitative estimate of the variation of the electron density within these complexes as the ligands X and the oxidation state of the metal are changed. In particular, the effects of these changes on the complexed olefin can be determined. These results, which show that the polarizable olefin is more strongly affected than the central metal, can be used to predict the reactivity pattern of complexed olefins. This is difficult or impossible when more qualitative models are used, e.g., the Dewar–Chatt–Duncanson model.

The present calculations show that nucleophilic addition should be promoted by cationic nickel(II) complexes with structures related to **1b.** They also show that the two types of cyclic reactions that are discussed here, $(2\sigma + 2\pi)$ and $(2\pi + 2\pi)$, are likely to have very different electronic requirements. The $(2\sigma + 2\pi)$ reaction, e.g., the insertion of ethene in a nickel–carbon bond, seems to have similar requirements as a nucleophilic addition. This reaction should therefore be favored by cationic complexes, e.g., **21.** By contrast, the $(2\pi + 2\pi)$ addition should be favored by negative charge on the olefin. Thus, electron-rich nickel(0) complexes like **2** should catalyze this reaction. All these theoretical predictions are supported by experimental evidence.

Since even the theoretical model used here is relatively crude, extensions of the work are desirable. In addition to extension to other metals than nickel, more sophisticated calculations which take into account correlation effects are planned and also a calculation of the potential surface for a model reaction. However, despite their shortcomings, e.g., the limited basis set, the restricted geometrical optimization and the simplified theoretical model, the present calculations describe both structural features and chemical properties remarkably well. We therefore feel that this type of calculation is of great aid in rationalizing and predicting reactivity patterns in organometallic chemistry.

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(15) The calculations reported here have recently been extended to include an optimization of the Ni–C_2H_4 distance for some of the complexes (Å. Stögård, to be published). The Ni–C distance was not changed significantly for the Ni(0) complexes (less than 0.05 Å), whereas for Ni(II) the distance increased by 0.3–0.4 Å. Except for the binding energies, for which more realistic values were obtained, no parameters pertinent to this investigation were significantly changed by the optimization. The $F_2Ni(C_2H_4)$ complex, for example, was found to have a binding energy of 12 kcal/mol with a Ni–C distance of 2.41 Å. This change was accompanied by a charge migration of 0.05 electron from the ethylene molecule to the fluorine atoms, leaving the charge on the Ni atom unchanged. Calculations have also been performed on complexes like $F_3Ni(C_2H_4)^-$ and $F_2(H_2O)_2NiC_2H_4$. Essentially the same C–C distances and atomic charges as in the simpler complex $F_2NiC_2H_4$ were obtained. The conclusions drawn in the present paper are thus supported by this extended investigation.

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Ab Initio SCF Study of the $C_2H_4 + Cl_2$ Reaction

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Abstract: An ab initio SCF study of the $C_2H_4 + Cl_2$ reaction has been carried out, assuming an intermediate state. When only two molecules are involved in the reaction, the energy of this ionic state (bridged or open) is much too high for a chemically acceptable intermediate state. The stabilization of this intermediate state by a solvent can make the reaction possible through such a path. The nature of the transition state involved in the first step of the reaction is discussed. Our calculations confirm the possibility of a $C_2H_4\cdots Cl_2$ complex, due to a charge transfer from the π orbital of C_2H_4 toward the Cl_2 molecule.

1. Introduction

Since the early work of Roberts and Kimball,[1] an intermediate cyclic ion is often used to explain the trans addition of halogen molecules to olefins.[2-4] Several mechanisms have been discussed, involving, for instance, a nonsymmetric intermediate,[3] an open ion intermediate,[5,6] a radical path,[7] or a termolecular reaction.[4,5,8] However, the hypothesis of a cyclic halogenium intermediate ion is the most widely accepted one for an interpretation of experimental data. It is generally assumed that the first (slow) step of the reaction corresponds to the formation of the halogenium and halide ions, while the second (fast) step leads to the final product.[4] In fact, the first step might involve the formation of a complex olefin···halogen molecule. Analogously to the stable charge-transfer complexes (CTC) described by Mulliken,[9] Dubois et al.[10b-d] called such complexes "CTCE" (evolutive charge-transfer complexes[11]), meaning that they have a short lifetime and dissociate into the ions. Other authors[12,13] describe them as "Dewar's π complexes",[14] assuming a three-center covalent bond; the theoretical status of these complexes will be discussed below. The nature of the σ halogenium ion is not well defined and may have varying degree of carbonium character.[10d] It has also been suggested that the gas-phase reaction could proceed through not fully dissociated ions, while in solutions the separation can arise due to solvation.[15] This solvent effect and, related to it, the nature of the transition state of highest energy in the first step of the reaction are perhaps the most puzzling aspect of this problem. Olah et al.[13] studying the bromination of alkenes in low polar solvents suggest that, in this case, the transition states of highest energy should be early transition states,[13] while in polar solvents[10] they would occur later along the reaction coordinate.

With the hope that quantum chemical calculation can help to elucidate the mechanism of this reaction, we have undertaken an ab initio SCF study of the $C_2H_4 + Cl_2$ reaction.

2. Details of the Calculations

SCF-LCGO-MO calculations have been performed.[16] Thus the molecular orbitals are expanded over a set of Gaussian functions. A double ζ basis set, called basis I, is used in most cases. The exponents are taken from ref 17 for C and H, and from ref 18 for Cl. In the (9,5) [4,2] set used for C the s functions are contracted according to the scheme[19] 5-2-1-1 and the p functions according to 4-1. For H, the (4) [2] set is contracted to 3-1. In the (11,7) [6,4] set used for Cl, the s functions are contracted to 5-2-1-1-1-1 and the p functions to 4-1-1-1. As shown in ref 20 and 21, small basis sets can give misleading results. The basis set used in this work is a double ζ basis set. Thus the results obtained with such a basis are expected to be qualitatively correct. However, when a great accuracy is needed (for instance in the calculation of the long-range complex) a d function is added on each chlorine, optimized on Cl_2 or on the bridged ion. We shall discuss in detail the special problem of the determination of the π complex.

The geometries used are discussed in the text. In all cases we fixed the distance CH = 2.05 bohrs (1.086 Å) and the angle ∠HCH = 115.6° to the values given in ref 22, while the parameters a, b, c, and α (see Figure 1) are varied.

3. Energy Data for the Initial, Intermediate, and the Final States

Initial States. Table I collects the computed energies. With basis I, the energy of the chlorine molecule is −918.8253 hartrees for an optimized distance b = 4.140 bohrs (2.190 Å). The addition of a d function with exponent 0.518142 gives −918.8664 hartrees for b = 3.834 bohrs (2.029 Å). The experimental distance is 1.988 Å.[23]

The energy of C_2H_4 is −78.0047 hartrees (basis I) for an optimized parameter $c = R_{CC}$ = 2.523 bohrs (1.335 Å) (as mentioned above R_{CH} and ∠HCH have not been varied). This distance is within the range of the experimental values ranging from 1.332 to 1.339.[22,23] Our energy is very close to that obtained by Basch et al. (−78.0054 hartrees[22]) and by Whitten et al. (−78.0048 hartrees[24]). Other results may be found in ref 25.

Thus the energy of the whole system at infinite separation is −996.8300 hartrees with basis I and −996.8711 hartrees when a d function is added on each chlorine (Table I).

The $C_2H_4\cdots Cl_2$ Complex (π Complex or CTCE). As stated above, the first step of the reaction probably involves a formation of a $C_2H_4\cdots Cl_2$ complex, described as a π complex (three-center covalent bond[12-14]) or as a CTCE,[10] the nature of this complex being somewhat ambiguous. In the present work, only the perpendicular and central approach of Cl_2 is