A Reconsideration of the Role of Slippage in the Activation of Co-ordinated Olefins towards Nucleophilic Attack†

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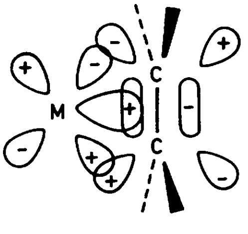
Activation with respect to attack by hydride ion of the co-ordinated olefins in the complexes $[Fe(cp)(CO)_2(olefin)]^+$ (olefin = ethylene or propene; cp = η^5-C_5H_5) has been investigated theoretically utilizing extended-Hückel and INDO methodologies. Extended-Hückel molecular orbital (EHMO) calculations suggest (*a*) that the receptor orbital of the ethylene complex, of predominantly olefin π^* character, is destabilized relative to the corresponding orbital of the free ligand, and (*b*) that nucleophilic attack can only be rationalized by invoking distortion (slippage or tilting) of the co-ordinated olefin during attack. These results are consistent with previous work. In contrast, INDO and (indirectly) *ab initio* calculations suggest that the same receptor orbital is stabilized on co-ordination, in effect resulting in activation of the olefin towards nucleophilic attack without the necessity of invoking distortion, although distortion does result in increased activation. Both the EHMO and INDO calculations suggest that the lowest unoccupied molecular orbital of the ethylene complex is of predominantly CO π^* rather than the olefin π^* character. In addition, both methodologies suggest that there is greater positive charge on the CO than on the ethylene carbon atoms, and thus it would seem that hydride attack should occur at CO rather than at the olefin.

In a previous paper,[1] we presented details of an experimental study of the interactions of cationic complexes of the type $[Fe(cp)(CO)_2(olefin)]^+$ (cp = η^5-C_5H_5) with various hydride donors, mostly tetrahydroborate anions. Although under certain conditions attack occurred initially at a carbonyl carbon atom, apparently yielding $[Fe(cp)(CO)(C_2H_4)(CHO)]$ {which subsequently rearranged to $[Fe(cp)(CO)_2H]$ + C_2H_4}, reactions at room temperature generally yielded the expected alkyl products of hydride addition to the co-ordinated olefins. The latter reactions were shown to proceed *via exo* attack of the hydride on the co-ordinated olefin, without any recognizable pattern of regioselectivity but also without subsequent rearrangements. These hydride addition reactions are of a general class of reactions involving nucleophilic addition to co-ordinated olefins to give new alkyl–metal compounds, *i.e.* equation (1) (Nu = nucleophile). Such reactions are implicated

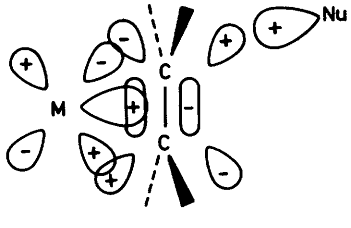
$$\underset{\textbf{(A)}}{M\text{–}CH_2CH(Nu)R} \longleftarrow M(CH_2{=}CHR) + Nu \longrightarrow \underset{\textbf{(B)}}{M\text{–}CHRCH_2(Nu)} \quad (1)$$

in the familiar oxymercuriation of olefins,[2] and have been observed for a wide variety of metal systems, most of them cationic in nature.[3] Often, although not always, the major product is that of Markownikoff (**A**) rather than anti-Markownikoff (**B**) addition.

Theoretical rationalizations of the mode(s) of activation of olefin in equation (1) have been based on the accepted Dewar–Chatt–Duncanson bonding model for olefin–metal complexes,[4] but have been slow in developing. The Dewar–Chatt–Duncanson description involves olefin-to-metal donation (σ-bond formation) from the filled π orbital of the olefin to an appropriate vacant orbital of the metal, complemented by back-donation from a filled metal orbital of appropriate symmetry into the vacant π^* orbital of the olefin (π bond formation) (**C**). For a cationic complex, σ donation is expected to outweigh π back-donation, leading to a build-up of positive charge on the olefin (*via* an essentially inductive effect) and hence to an increased electrophilicity. Any positive charge on the olefin is also expected to lower the energies of the olefinic orbitals and, in particular, the energy of the π^* orbital. As the latter is expected to be the receptor orbital in any nucleophilic addition (**D**), increased susceptibility of the co-ordinated olefin towards nucleophilic attack would result. It is largely on this basis that reactivities of cationic olefin complexes have been interpreted historically.[4a,5]



(C)



(D)

However, other points of view have also been offered. For instance, Eisenstein and Hoffmann[6] have suggested that nucleophilic addition to co-ordinated olefins may be orbitally controlled in a manner not heretofore considered. Qualitative considerations of the interactions of the frontier molecular orbitals of ethylene and a metal fragment, supported by extended-Hückel molecular orbital (EHMO) calculations involving the model olefin complex $[Fe(CO)_5(C_2H_4)]^{2+}$, indicated that that the vacant orbital most closely resembling the ethylene π^* actually lies at higher energy and is less localized than the π^* orbital of free ethylene. Thus interaction of the co-ordinated ethylene with a nucleophile should be decreased relative to interaction of the free olefin with a nucleophile. It was suggested that activation occurs following an η^2- to σ-

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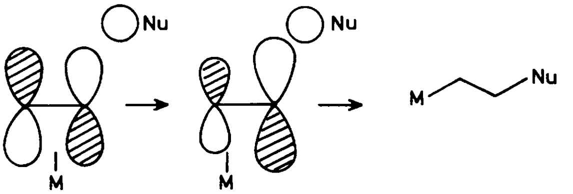
† *Non-S.I. unit employed:* eV ≈ 1.60×10^{-19} J.

deformation of the ethylene–metal linkage (a 'slip' mechanism) of more than 0.6 Å, thus localizing the vacant receptor orbital on the non-bonded carbon atom and increasing the interaction of the receptor orbital with the nucleophile, *i.e.* equation (2).



(2)

These arguments have been criticized by Mingos[4a] on the grounds that they neglect the carbon π^* orbital stabilization anticipated from the development of positive charge on the olefin. Mingos also suggested that a self-consistent field (SCF) approach might be more appropriate for this problem, and indeed, for the silver(I) complex $[Ag(C_2H_4)]^+$, three sets of SCF calculations with various basis sets suggest that the ethylene π^* orbital of the complex *is* stabilized on co-ordination by some 10 eV.[7–9] Thus a favourable stabilizing interaction of the ethylene π^* orbital with a nucleophile should be possible without invoking a slip distortion.

However, the effects calculated for $[Ag(C_2H_4)]^+$ may be largely electrostatic in nature,[8] and it seemed worthwhile to gain a better understanding of the factors involved in activation of an olefin in highly covalent olefin–metal systems. We have therefore carried out theoretical studies [EHMO, intermediate neglect of differential overlap (INDO)] of the addition of a model nucleophile, the hydride ion, to the cationic complexes $[Fe(cp)(CO)_2(olefin)]^+$ (olefin = C_2H_4 or $CH_2{=}CHMe$) which are known to be susceptible to a nucleophilic addition.[10] We have also carried out complementary studies on a model zero-valent complex $[Ni(C_2H_4)(PH_3)_2]$, an electron-rich complex of a type in which the olefin is not activated.*

The cationic system was also of interest because previous ^{13}C n.m.r. data[11] had suggested that, for complexes of the type $[Fe(cp)(CO)_2(CH_2{=}CHR)]^+$ (R = alkyl), the structures are distorted such that the Fe–CHR bonds are longer than the Fe–CH_2 bonds. This suggestion has been verified crystallographically for the propene complex $[Fe(cp)(CO)_2(CH_2{=}CHMe)]^+$.[12] Similar conclusions were reached for 1,1-disubstituted ethylene complexes of the type $[Fe(cp)(CO)_2(CH_2{=}CR_2)]^+$, which were thought to be even more distorted, presumably for steric reasons. The postulated distortions of the olefin moiety will serve the same purpose as the slippage proposed by Eisenstein and Hoffmann[6] in that relaxation of the symmetry leads in both cases to mixing of previously orthogonal orbitals. The greater the distortion, the greater will be the localization of the receptor orbital at the carbon atom further from the metal. The extended-Hückel approximation thus predicts that nucleophilic addition should occur preferentially at the olefinic carbon atom which lies further from the metal atom, and the opportunity was thus presented to search for correlations between degrees of distortion in the ground-state structure and regioselectivity during addition. As the relevant literature is not completely congruous with respect to degrees of regioselectivity obtained,[10] a series of bench experiments was also carried out in order to determine the actual regioselectivities for hydride addition to several complexes. The results of these experiments were reported in a previous paper,[1] which also describes experiments designed both to determine the stereochemistry of hydride addition to the cationic iron–olefin system and to test certain of the calculations described below. A preliminary report of some of this work has been made.[13]

Results and Discussion

The Nature of the Problem.—The impetus for the present study was a questioning of the necessity of any geometric deformation of the metal–olefin linkage to rationalize activation of co-ordinated olefins towards nucleophile addition. Although MNDO calculations, reported as this work was in its final stages, suggest that the ground-state structure of the complex $[Hg(C_2H_4)]^{2+}$ is very strongly slipped,[14] such distortions do not appear to have been demonstrated crystallographically for complexes of simple olefins,[15] even with silver(I),[16] which is isoelectronic with mercury(II). Nor will vibrational motions produce the required distortion, as no normal mode of a metal–olefin moiety corresponds to slippage.[17] Although the asymmetric metal–carbon stretching mode does correspond to a distortion which we shall show can lead to activation, the amplitude is expected to be only *ca.* 0.04 Å,[18] about an order of magnitude too small to be a factor in activating a co-ordinated olefin. Other electronic factors must therefore be considered.

According to frontier molecular orbital theory,[19] there will be a variety of stabilizing and destabilizing interactions possible between the nucleophile and the olefin complex as the reactants approach the transition state. Subject to symmetry considerations, there will be destabilizing interactions between occupied frontier orbitals of the olefin complex and the lone pair of the nucleophile, and stabilizing interactions between low-lying, vacant frontier orbitals of the complex with the same lone pair. The net interaction, whether stabilizing or destabilizing, will depend on the overlap and on the energy difference(s) between pairs of interacting orbitals. The stabilization arising from a two-orbital, two-electron interaction increases as the energy difference between orbitals decreases and/or as the overlap increases. On the other hand, if the energy difference is large and/or if the overlap is small, then reactions may proceed under charge control, a possibility which has been considered in some depth by Brown *et al.*[20] for systems related to those under discussion here.

Although *ab initio* methods have been applied successfully to studies of organometallic reaction mechanisms,[21] we have chosen to begin our studies utilizing EHMO[22] and INDO[23] methodologies in order to explore the applicabilities of these two relatively facile, easily interpreted approaches to the problem at hand. As illustrated by (**D**) above, and consistent with frontier molecular orbital theory,[6,19] nucleophilic addition of hydride ion to a co-ordinated olefin is expected to involve a stabilizing interaction between the filled hydride 1*s* orbital and a vacant orbital of primarily olefin π^* character. The energy of the hydride 1*s* orbital can be readily approximated, and it is therefore necessary to determine the effects of co-ordination to a Lewis acid on the energy of the olefin π^* orbital. We will show below that co-ordination of ethylene to $[Fe(cp)(CO)_2]^+$ does in fact lead to a stabilization of the ethylene π and π^* orbitals and thus, in a perturbational sense, some immediate activation of the ethylene towards addition of hydride may be anticipated.

The Frontier Molecular Orbitals of Symmetrically Protonated Ethylene.—In order quickly to gain an appreciation of how the energies of the olefin frontier orbitals might change on co-ordination, we have carried out a series of calculations (EHMO, INDO, *ab initio*[24]) on a model olefin complex, symmetrically protonated (C_{2v}) ethylene, $C_2H_5^+$. The one-electron energies of the ethylene π and π^* orbitals and those orbitals of the protonated ethylene most closely resembling the π and π^* orbitals are listed in Table 1. Note that the INDO and *ab initio* but not the EHMO calculations suggest that significant

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* For relevant discussion see refs. 5 and 6.

Table 1. Calculated and experimental energies (eV) of the π and π^* orbitals of ethylene[a] and protonated (C_{2v}) ethylene[b]

Orbital	Orbital energies EHMO	INDO	STO-3G	6-31G	Expt.
C_2H_4 π^*	-8.3	3.1	8.5	4.7	1.73[c]
C_2H_4 π	-13.2	-11.9	-8.7	-10.0	-10.51[d]
$C_2H_5^+$ π^*	-8.5	-3.8	-2.0	-4.1	
$C_2H_5^+$ π	-15.7	-23.9	-22.1	-21.8	

[a] For geometry, see W. Palke and W. Lipscomb, *J. Am. Chem. Soc.*, 1966, **88**, 2384. [b] For geometry, see P Hariharan, W. Latham, and J. A. Pople, *Chem. Phys. Lett.*, 1972, **14**, 385. [c] Electron affinity reported by P. D. Burrow, A. Modelli, N. S. Chiu, and K. D. Jordan, *Chem. Phys. Lett.*, 1981, **82**, 270. [d] Ionization potential reported by D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, 'Molecular Photoelectron Spectroscopy,' Wiley-Interscience, New York, 1970, p. 166.

Table 2. Frontier orbital energies (eV) and compositions (%) for $[Fe(cp)(CO)_2(C_2H_4)]^+$

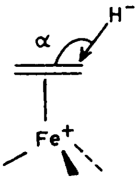
	Orbitals		Energy	Fe	π^*(cp)	π^*(CO)	π^*(CC)	π(cp)
(*a*) EHMO	38	*a″*	-7.1	24		18	47	7
	37	*a′*	-7.6	32		54		6
	36	*a′*	-7.8	22	8	50		5
	35	*a″*	-7.9	4		88	5	
	34	*a′*	-8.1	30	1	44		18
	[a]33	*a″*	-8.5	10	1	69	4	15
	[b]32	*a″*	-12.4	43	4	5	13	28
	31	*a′*	-12.4_4	65	8	14		8
	30	*a′*	-12.7	34	1	13		35
	29	*a′*	-13.1	39	1	12		19
	28	*a″*	-13.2	35		4	2	36
(*b*) INDO	38	*a″*	1.92	15	8	68	7	2
	37	*a″*	1.34	11	10	55	11	13
	36	*a′*	0.95	3		89		2
	35	*a″*	0.08	11	3	49	32	1
	34	*a′*	-0.23	35		52		
	[a]33	*a′*	-0.24	49		35		
	[b]32	*a′*	-12.44	18		1		65
	31	*a″*	-12.88	21		2		63
	30	*a″*	-15.72	77		3	5	1
	29	*a′*	-15.77	57	1	6		1
	28	*a′*	-16.59	50	1	4		

[a] Lowest unoccupied molecular orbital (l.u.m.o.). [b] Highest occupied molecular orbital (h.o.m.o.).

stabilization of the ethylene frontier orbitals occurs with the introduction of the proton.†

While virtual orbital energies obtained from SCF calculations are not well defined and are generally too high,[25] Modelli *et al.*[26] have successfully used *ab initio* methods to calculate electron affinities of substituted ethylenes. The calculated energies of the π^* orbitals of a series of olefins were generally overestimated by only some 2.2 eV, giving us added confidence in the validity of our own *ab initio* and INDO calculations.

Activation of $[Fe(cp)(CO)_2(C_2H_4)]^+$ (**1**) *within the EHMO Approximation*.—We have calculated the frontier orbital energies of the cationic complex $[Fe(cp)(CO)_2(C_2H_4)]^+$ (**1**) in the preferred conformation (C_s symmetry)[11,12] with the ethylene C=C axis essentially parallel to the cp plane [Table 2(*a*)]. As can be seen, the molecular orbital (m.o.) of (**1**) which is predominantly of ethylene π^* character lies at considerably higher energy than does the free ligand π^* orbital. In order to assess the effects of the π^* orbital destabilization on the reactivity of the complex towards nucleophilic attack, we performed EHMO calculations, following Eisenstein and Hoffmann,[6] of a model reaction between the hydride ion and the co-ordinated ethylene of (**1**), computed as a function of approach angle α, at a $C \cdots H^-$ distance of 2.0 Å (**E**).



(**E**)

Consistent with analogous calculations for similar systems,[6] we find that the system is deactivated towards hydride addition (using overlap populations as a guide), and that a slippage, Δ, of *ca.* 0.5 Å is necessary for the co-ordinated ethylene to become activated to a greater extent than is free ethylene, the optimum value for α being *ca.* 110° [Figure 1(*a*)]. Interestingly, tilting the ethylene *ca.* 15° results in a similar activation. Although this deformation corresponds to the asymmetric stretching vibration of the $Fe(C_2H_4)$ moiety,[17] the amplitude of the vibration would appear to be too small to effect activation (within the EHMO approximation).

However, EHMO theory is an approximate method, and the validity of our results to this point should be critically assessed. The EHMO approach is, as mentioned above, electron-density independent,‡ with the result that the energy calculated for the lowest unoccupied molecular orbitals (l.u.m.o.) of a relatively simple system, symmetrically protonated ethylene, does not reflect the expected stabilization relative to the π^* orbital of free ethylene. If the energy of the corresponding orbital of (**1**) is in error in the same direction, then one would have to question our above-mentioned conclusions based on calculated overlap population, as the latter are strongly dependent on the relative energies of the interacting orbitals. In fact, if our INDO calculations on $C_2H_5^+$ are as valid as they appear to be, then it seems likely that similar stabilization of the ethylene π^* orbital also occurs in (**1**).

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† The change in the π^* energy in the EHMO approximation is due entirely to a change in geometry of the ethylene (non-planar, longer C–C bond length), and is not a direct result of interaction with the proton. The failure of the EHMO calculations properly to reflect the change in energy of the π^* orbital on protonation is a result of the electron density independence of the method, as has been noted elsewhere, see G. Blyholder, K-M. Zhao, and M. Lawless, *Organometallics*, 1985, **4**, 1371.

‡ Extended-Hückel and INDO theories are both methods of approximation; however the latter includes bielectronic repulsion (in an average way) and requires an iterative (SCF) solution while the former does not. This difference is most readily observed by the dependence (INDO) *vs.* independence (EHMO) of the molecular orbital energies on the total molecular charge. The density dependence of INDO, for the purposes of our argument, is shown (Figure 2, columns 2 and 4) by the change in fragment orbital energies resulting from complexation of C_2H_4 and $[Fe(cp)(CO)_2]^+$. These energies are the 'environmentally adjusted' orbital energies, and are obtained as the diagonal elements of the SCF Fock matrix in the basis of fragment orbitals. They reflect the change in potential around C_2H_4 due to $[Fe(cp)(CO)_2]^+$, and *vice versa*, occurring on complexation. Note the substantial stabilization of the C_2H_4 π and π^* levels which, according to the frontier molecular orbital theory, should lead to a stronger interaction between an incoming nucleophile and complexed C_2H_4 than between an incoming nucleophile and free ethylene. Note also that because EHMO theory is density independent, the 'environmentally adjusted' orbital energies in the EHMO approximation are the same as the orbital energies of the free fragments. Consequently, any increased interaction between an incoming nucleophile and complexed C_2H_4 due to a stabilization of the C_2H_4 vacant orbitals will not be observed.

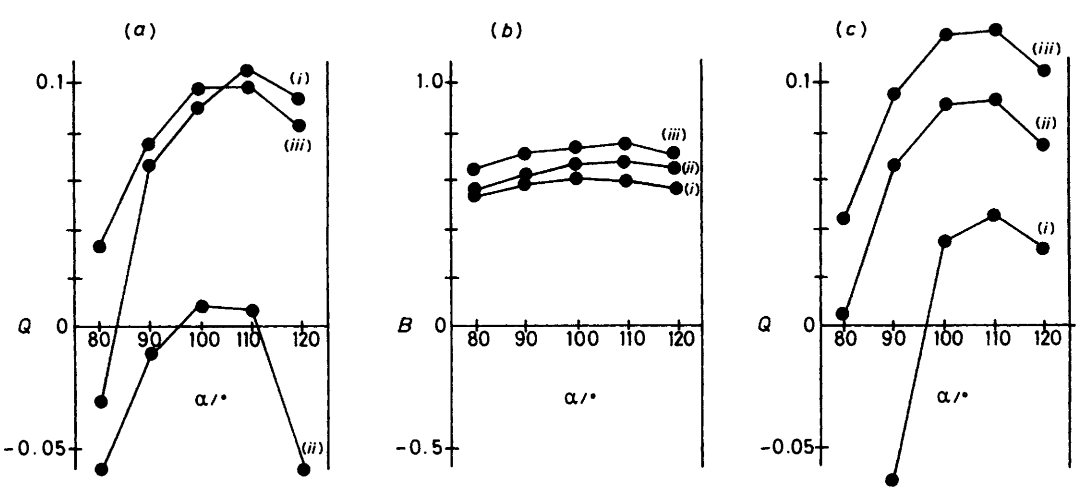

Figure 1. Plots of (*a*) EHMO overlap population (Q), (*b*) INDO bond index (B), and (*c*) INDO overlap population (Q) *vs.* approach angle (α) for the addition of hydride to (*i*) free ethylene, (*ii*) $[Fe(cp)(CO)_2(C_2H_4)]^+$ with $\Delta = 0$, and (*iii*) $[Fe(cp)(CO)_2(C_2H_4)]^+$ with $\Delta = 0.46$ Å

Activation of (**1**) *within the INDO Approximation.*—Figure 2 shows a partial interaction diagram for (**1**) obtained from INDO calculations. The first and fifth columns contain the frontier orbital energies of the isolated fragments, $[Fe(cp)(CO)_2]^+$ and C_2H_4, respectively. The second and fourth columns correspond to the same fragment orbitals, but the energies are the fragment orbital energies of the fragments in the field of the whole molecule (environmentally adjusted orbital energies), defined as the corresponding diagonal elements of the Fock matrix in the fragment orbital basis. The centre column illustrates in the conventional manner the frontier energy levels of the whole molecule; the calculated frontier orbital energies and compositions are listed in Table 2(*b*).†

As can be seen in columns 2 and 4 of Figure 2, the energies of the $[Fe(cp)(CO)_2]^+$ and ethylene fragment frontier orbitals are mutually affected by complex formation, being stabilized or destabilized depending on the nature of the various possible pairwise orbital interactions. The effects are similar to those calculated[8] for the interaction of ethylene with a point positive charge. Note that the ethylene π^* orbital is stabilized by some 3 eV in the presence of the cationic iron fragment, consistent with arguments based on expected inductive effects.[4,5] Note also that the orbital most closely resembling the ethylene π^* orbital in (**1**) is stabilized by *ca.* 7 eV relative to the π^* orbital of the free ethylene. While covalent back-bonding in the complex presumably does drive the orbital to higher energy, it apparently does not, as suggested by the EHMO calculations, overcome the inductive effects. The INDO calculations thus suggest that co-ordination of the ethylene should result in increased susceptibility towards nucleophilic attack.

To determine whether activation has occurred, we performed INDO calculations for the model reaction shown in (E), computed as a function of approach angle α, at a $C \cdots H^-$ distance of 2.0 Å, as carried out above in the EHMO approximation. We have used the bond index[27] and, to facilitate a comparison of INDO and EHMO, Mulliken overlap populations (obtained *via* deorthogonalization of the basis) as criteria of activation. We present in Figure 1(*b*) and (*c*) respectively, the calculated INDO bond indices (B) and overlap populations (Q) as functions of α for (*i*) H^- + free ethylene, (*ii*) H^- + (**1**), and (*iii*) H^- + (**1**) with the olefin slipped by 0.46 Å. In contrast to the EHMO results for the same system, it is clear that symmetric co-ordination of ethylene to the cationic iron fragment does result in activation toward the hydride ion, although slippage results in enhanced activation. The latter conclusion is quite reasonable, as a deformation resembling slippage inevitably occurs along the reaction co-ordinate.

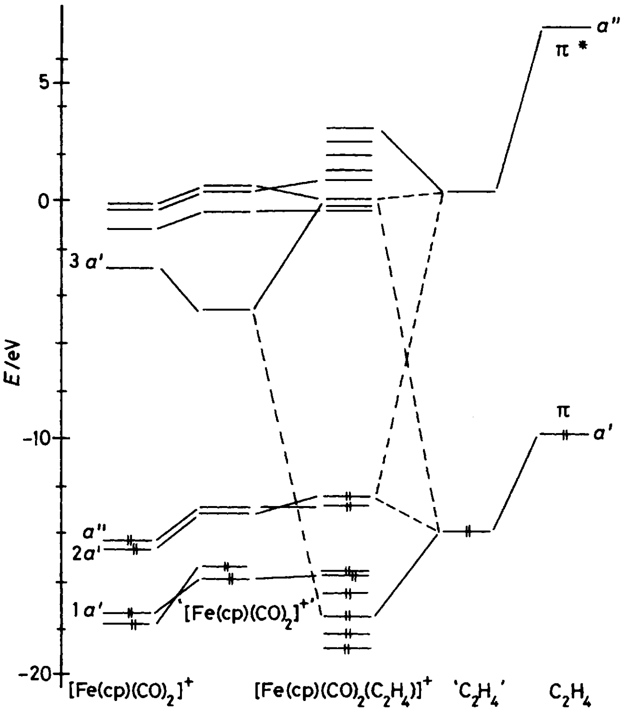

Figure 2. INDO interaction diagram for $[Fe(cp)(CO)_2(C_2H_4)]^+$

It must be kept in mind, of course, that the total ethylene–hydride bond index (or overlap population) results from the interactions of the hydride with all molecular orbitals of the

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† It should be noted that the energy level orderings obtained by the EHMO and INDO calculations are not the same. Nor should either of the orderings of the occupied levels be considered indicative of the relative order of ionization potentials. Significant orbital relaxation and electronic rearrangement on ionization are known to occur in transition metal complexes and, as such, Koopmans' theorem is not expected to hold. See for example, M. C. Bohm, R. Gleiter, G. E. Herberich, and B. Hessner, *J. Phys. Chem.*, 1985, **89**, 2129 and refs. therein; R. F. Fenske, *Prog. Inorg. Chem.*, 1976, **21**, 179.

complex which exhibit ethylene orbital character; as shown in part in Table 2(*b*), significant ethylene π and π* orbital character is found in many of the highly delocalized molecular orbitals of (**1**), both occupied and unoccupied. For this reason one cannot rigorously attribute the olefin activation solely to an increase in stabilizing or a decrease in destabilizing interactions, and we do not claim that the activation is due solely to the computed stabilization of the ethylene fragment orbitals. In a perturbational sense, however, the stabilization of the ethylene orbitals does suggest that activation should occur on symmetrical co-ordination.

It is quite reasonable to expect that the positive charge on the metal centre is going to stabilize both the ethylene orbitals and the donor orbital of the nucleophile (1*s* H), and thus whether or not activation occurs on co-ordination will depend on the difference in the 'environmentally adjusted' energies of the π* and H^- orbitals. From our calculations the average energy differences (over the five α values) between the H^- and π* orbitals are 7.9 and 5.3 eV for H^- addition to free and symmetrically co-ordinated ethylene respectively. Further, the average stabilization energies† are *ca.* 3.5 and 5.2 eV respectively. Therefore, it appears that bond indices, Mulliken overlap populations, and stabilization energies all suggest that symmetric co-ordination is sufficient to provide some activation of ethylene toward nucleophilic attack by hydride ion.

Interestingly, there have been at least three reports in the literature suggesting possible examples of distortions of co-ordinated olefins in the ground state leading to enhanced susceptibility to nucleophilic addition. Thus Chang *et al.*[28] have reported crystal structures for the complexes $[Fe(cp)(CO)_2(CH_2{=}CHX)]^+$ (X = OMe or NMe_2), noting that the iron–olefin linkages of both are tilted, rather than slipped, with the substituted carbon–iron distances being longer by at least 0.12 Å for the vinyl ether complex, and by almost 0.7 Å for the vinylamine complex. The former appears to be more reactive than is (**1**) towards nucleophilic attack by both water and $[Fe(cp)(CO)_2(CH_3CH{=}CH_2)]^+$, but the vinylamine complex is inert to nucleophilic attack. Although the electronic effects of the heteroatom lone pairs could not be assessed, it was concluded that distortion of the metal–olefin linkage may play a role in determining the reactivity of the co-ordinated olefin.

Earlier work with similar iron–olefin complexes is very relevant in this context. As mentioned above, spectroscopic data suggest that complexes of the type $[Fe(cp)(CO)_2(CH_2{=}CHR)]^+$ are distorted,[11] a prediction borne out by a crystal structure of the propene complex which showed that the Fe–CHMe distance is greater than the Fe–CH_2 distance by *ca.* 0.06 Å (see above). Analogous complexes of 1,1-disubstituted olefins are believed to be even more distorted.[11] Although no comparisons of relative reactivities of these types of complexes with that of (**1**) appear to have been reported, it seems likely that complexes of the substituted olefins should exhibit regioselectivity in their reactions with nucleophiles if the observed activation is primarily a result of distortion. Nucleophilic addition should occur preferentially at the substituted carbon atom of the propene complex, and even more preferentially at the substituted carbon atom of a complex of a 1,1-disubstituted olefin. As shown in a previous paper,[1] however, hydride additions under a variety of conditions exhibit no systematic regioselectivity with various olefin complexes. In addition, as nucleophilic attack by hydride does occur *exo* to the iron as in (**D**), the reactions studied do indeed involve the type of addition under consideration here. It is our opinion that both inductive effects and molecular distortions contribute to olefin activation in these systems.

Distortions have been noted in platinum and palladium complexes also. The ethylene of the cationic complex $[PtCl(C_2H_4)(Me_2NCH_2CH_2NMe_2)]^+$ is tilted in the solid state[29] and is said to exhibit enhanced susceptibility to nucleophilic addition. However, no comparative rate data with undistorted complexes were presented and there seems to be no reason to expect distortion in solution. The complex dichloro(η^4-*endo*-3a,4,7,7a-tetrahydro-4,7-methanoindene)palladium(II) is more interesting because, while one of the C=C double bonds is co-ordinated symmetrically, the other is strongly tilted such that the Pd–C bond lengths differ by 0.09 Å.[30] A variety of nucleophiles is known to attack the complex, always at the carbon atom which is tilted away from the palladium atom, and it thus appears that forcing an olefin into a distorted, unsymmetrical mode of co-ordination can result in the directing of nucleophilic attack. However it does not follow, as suggested[30] by these authors, that distortion is necessarily the primary source of the activation.

Activation of $[Ni(C_2H_4)(PH_3)_2]$ (**2**) *within the INDO Approximation.*—The relative effects of σ donation and π back-donation will be very important in determining the energy of the π* acceptor orbital. Significant back-donation, which can be anticipated in zero-valent complexes, is expected to drive the π* orbital to higher energy, thus leading in effect to deactivation of a co-ordinated olefin to nucleophilic addition. In accord with this hypothesis, no authenticated example of nucleophilic addition to an olefin–metal(0) has been reported.[5,6,‡]

It seemed of interest to carry out INDO calculations on a complex such as (**2**) and, as expected, we find that the lowest-lying orbital having significant ethylene π* character is indeed destabilized somewhat relative to the π* orbital of free ethylene.

The Kinetic Product(s) from Hydride Addition to (**1**).—To this point, we have been concerned with the origin of the activation of the olefin in (**1**); we now turn to a fuller description of the frontier orbitals of this cationic complex. Listed in Table 2(*b*) are data concerning all the frontier orbitals (composition and energy) of (**1**), determined from INDO calculations. As can be seen, there are several orbitals, both filled and vacant, of predominantly cp and CO π/π* character. In fact there is a manifold of low-lying, unoccupied orbitals, all of considerable CO π* character and all of energy lower than or comparable with that of the orbital of predominantly ethylene π* character, and one may well wonder why nucleophilic attack does not take place preferentially at CO. Indeed, the question becomes even more pressing when one considers the charge distribution for (**1**), calculated by both EHMO and INDO methods and listed in Table 3. As can be seen, the charge distribution in both approximations suggests that the ethylene should be slightly deactivated and that addition should take place preferentially at CO. These calculations prompted the experiments, described in a previous paper,[1] involving a low-temperature n.m.r. study of the hydride addition to (**1**). It is shown there that addition of hydride to a carbonyl group of (**1**) in acetone at −60 °C is preferred to addition to the olefin, although the resulting formyl compound is unstable with respect to secondary reactions and cannot be detected at higher temperatures. It is gratifying that the INDO calculations could predict tentatively the nature of the kinetic product. We note that attack at CO is a common reaction with similar complexes,[31] although attack at the olefins of complexes such as (**1**) clearly becomes competitive at high temperatures.

[†] The stabilization energy is defined as the decrease in the sum of occupied orbital energies realized when the interaction of a vacant orbital and a doubly occupied orbital is allowed.

[‡] The compound $[Fe(CO)_4(C_2H_4)]$ is reported to undergo nucleophilic addition, but no direct evidence for addenda has apparently been described. See B. W. Roberts and J. Wong, *J. Chem. Soc., Chem. Commun.*, 1977, 20; M. R. Baar and B. W. Roberts, *ibid.*, 1979, 1129; B. W. Roberts, M. Ross, and J. Wong, *ibid.*, 1980, 428.

Table 3. Net atomic charges in $[Fe(cp)(CO)_2(C_2H_4)]^+$

Atom(s)	Net atomic charges EHMO	Net atomic charges INDO
Fe	0.57	−0.46
$C(cp)_{av}$	0.03	0.09
C(CO)	0.79	0.32
$C(C_2H_4)$	−0.05	−0.01

Table 4. Orbital expansion coefficients (π*) and net atomic charges of the olefinic carbon atoms of propene and $[Fe(cp)(CO)_2(CH_2{=}CHMe)]^+$

	Orbital expansion coefficient		Net atomic charges	
	C^1	C^2	C^1	C^2
$C^1H_2{=}C^2HMe$	0.68	−0.70	−0.19	−0.01
$[Fe(cp)(CO)_2(C^1H_2{=}C^2HMe)]^+$	0.31	−0.48	−0.09	0.11

Regioselectivity of Nucleophilic Addition.—Both the EHMO and the INDO methodologies predict that nucleophilic addition to a substituted olefin should occur at the carbon atom further from the metal atom, thus apparently rationalizing the general predominance of Markownikoff products if, as generally appears to be the case, metal–C^2 bonds are longer than metal–C^1 bonds of complexes of 1-olefins.[4a] However, as shown in a previous paper,[1] the complexes $[Fe(cp)(CO)_2(\text{olefin})]^+$ (olefin = propene, 1-hexene, or methylenecyclohexane) exhibit no recognizable pattern of regioselectivity. In an effort to rationalize this apparent inconsistency, we carried out INDO calculations of the net atomic charges and the LCAO–MO† expansion coefficients of the C(2*p*) atomic orbitals (π*) of C^1 and C^2 of free propene and the propene complex; the calculated data are shown in Table 4. As can be seen, addition is expected at C^2 on the basis of both charge and orbital control, although the differences in the parameters for C^1 and C^2 of the complex are not large. It may be that steric factors play a role in determining the site of attack, and we note that the very bulky $[Fe(cp)(CO)(PPh_3)H]$ yields only the products of anti-Markownikoff addition.[1]

Summary.—The model of olefin activation proposed by Eisenstein and Hoffmann[6] is elegant and instructive, and without doubt slippage can be an important component of olefin activation, as evidenced by the numerous examples cited above. It is our opinion, however, that electrostatic effects such as those described in the text could also be an important component of olefin activation, particularly in cationic systems, and that one cannot ascribe the activation of olefins by metal complexes either solely to geometric deformations or solely to electrostatic effects. Indeed, a definitive answer to the origin of olefin activation (beyond the scope of this work) would probably contain both extremes varying in degree of contribution depending upon the particular system being studied.‡

Experimental

Computational Details.—The EHMO calculations utilized the coulomb integrals available in the literature.[22] It was found necessary to use a value for H^- of −10.0 eV[32] in order to duplicate the results of ref. 6, and this value was used here for all EHMO calculations. The off-diagonal matrix elements, H_{ij}, were obtained using the modified Wolfsberg–Helmholtz approximation.[22] The INDO method and the parameterizations used are described elsewhere,[23] as are the methods by which the molecular orbitals of a complex (in an atomic orbital basis) were expanded with respect to a fragment (ligand) orbital basis.[33]

Geometry of (**1**). *r*[CC(cp)] 1.42, *r*[CH(cp)] 1.08 Å; C–C–C(cp) 108, H–C–C(cp) 126°; $r[CC(C_2H_4)]$ 1.37, $r[CH(C_2H_4)]$ 1.09 Å; H–C–$C(C_2H_4)$ 120°; *r*(CO) 1.14, *r*(Fe–CO) 1.75, *r*[Fe–cp(centroid)] 1.74, $r[Fe–C_2H_4(\text{centroid})]$ 2.0 Å; OC–Fe–CO 90.2, cp(centroid)–Fe–CO 120.4, cp(centroid)–Fe–C_2H_4(centroid) 124, OC–Fe–C_2H_4(centroid) 97.2°. The ethylene C=C bond axis lies parallel to the plane of the cp ring (overall symmetry C_s).

Geometry of $[Ni(C_2H_4)(PH_3)_2]$. *r*(NiP) 2.15, *r*(PH) 1.42, *r*(CC) 1.37, *r*(CH) 1.09 Å; P–Ni–P 110.5, H–C–H 120.0, H–C–C 120.0°; C_2H_4 lies in the P_2Ni plane; all angles at P are tetrahedral.

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† LCAO = Linear combination of atomic orbitals.

‡ *Note added in proof:* for very recent complementary studies, see S. Sakaki, K. Muruta, and K. Ohkubo, *J. Chem. Soc., Dalton Trans.*, 1987, 361; *Inorg. Chem.*, 1987, **26**, 2499.

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