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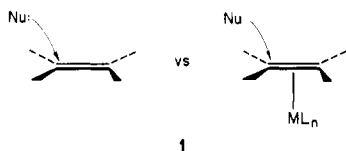
Transition-Metal Complexed Olefins: How Their Reactivity toward a Nucleophile Relates to Their Electronic Structure

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Abstract: On theoretical grounds a symmetrically η^2 coordinated olefin is deactivated toward attack by an external nucleophile. A detailed molecular orbital analysis points to the crucial role of olefin slipping, a deformation to η^1 coordination, in activating the olefin. The similarities and differences of the activation process in d^2 Cp_2WR^+ , d^6 $\text{Fe}(\text{CO})_5^{2+}$ and $\text{CpFe}(\text{CO})_2^+$, d^8 PtL_3 and $\text{Fe}(\text{CO})_4$, and d^{10} $\text{Ni}(\text{PR}_3)_2$ olefin complexes are the subject of this study.

While a nucleophile does not add with ease to an unactivated double bond, it may react readily with an olefin coordinated to a transition metal (see 1). Many organometallic complexes have



been found to react in this way.¹ They differ widely in their charge, electron count, and number of ligands. For instance one finds some dicationic examples [e.g., $\text{Cp Rh}(\text{PMe}_3)_2(\text{C}_2\text{H}_4)^{2+}$, d^6] and monocationic²⁻⁶ ones as well [e.g., $\text{CpFe}(\text{CO})_2(\text{C}_2\text{H}_4)^+$, d^6 ,^{3a,b} $\text{C}_6\text{H}_5\text{Ru}(\text{PMe}_3)(\text{C}_2\text{H}_4)^+$, d^6 ,⁴ $\text{Cp}_2\text{WMe}(\text{C}_2\text{H}_4)^+$, $d^{2,5}$ $\text{Cp}(\text{CO})_3\text{M}(\text{C}_2\text{H}_4)^+$, d^4 , $\text{M} = \text{Mo}$ and W ,^{3c,6} a stable monoolefin $\text{Pd}(\text{II})$ compound, $\text{CpPdPPH}_3(\text{C}_2\text{H}_4)^+$, d^8 , was reacted with a nucleophile⁷]. One also finds neutral systems. Nucleophilic addition has been observed in olefinic compounds of $\text{Fe}(\text{CO})_4$,⁸ d^8 , and of PtXY_2 .⁹ The reactivity of $\text{Pd}(\text{II})$ ¹⁰ has been thoroughly examined

because it is involved in the important industrial oxidation of ethylene to acetaldehyde, the Wacker process. Unfortunately the olefinic complex in this reaction has never been isolated and most of the steps are postulated. The analogy with PtXY_2 chemistry supports the formation of an olefinic complex. Bisolefinic complexes of $\text{Pt}(\text{II})$ ¹¹ and $\text{Pd}(\text{II})$ ¹² such as metal-1,5-cyclooctadiene complexes have been attacked by nucleophiles. As they are more

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stable than monoolefinic systems they were used to probe the mechanism of the reaction. Addition to $\text{CpNi}(\text{diene})^+$ (diene = norbornadiene or 1,5-cyclooctadiene) has also been observed.¹³

Since these substrates interact with a wide variety of neutral and anionic nucleophiles, it seems that the electrostatic attraction between the organometallic complex and the nucleophile, while certainly helpful, cannot be the only driving force for the reaction.

The detailed mechanism of nucleophilic addition to a coordinated double bond has been the subject of much controversy. This is due to the fact that interest focused strongly and naturally on the mechanism of the Wacker process, in which unfortunately the metal complexes are not stable observable intermediates.

A kinetic study of the Wacker process^{10c} was in agreement with a prior addition of the nucleophile to the metal followed by a rearrangement, the migration of the nucleophile to the olefin. Such a mechanism implies cis addition to the olefin. Subsequent stereochemical studies were at variance with this hypothesis. Addition to Pd- and Pt-coordinated nonconjugated dienes (such as 1,5-cyclooctadiene) has been shown to be trans.^{11b,12b} It was argued that the addition to diene and monoolefin may occur by a different mechanism.^{12a} In the diene, a double bond cannot rotate by 90° in order to be coplanar with the metal-nucleophile bond. But such a coplanar structure would induce substantial steric difficulties between the cis ligands and the olefin, even in the monoolefin case.^{14b} Afterward it was proved that the addition was trans on a stable monoolefin Pt compound.^{9f} It appears to be the same for Pd,^{7,10d} Fe,^{3e} and Ni.^{13b} Exceptions to this behavior are scarce and are due to a prior addition to the metal.^{10e-g,11c} For most reactions studied a direct addition to the coordinated double bond is thus a secure starting hypothesis.

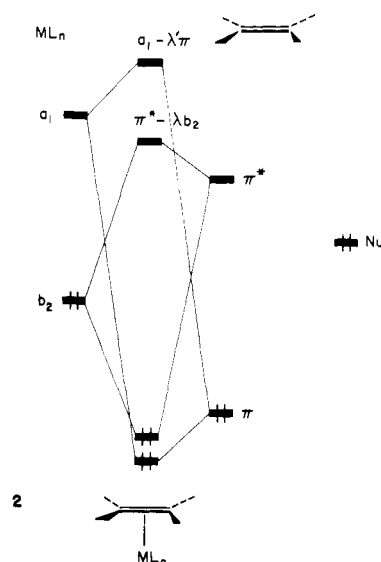
Therefore, the obvious problem is the origin of the electrophilic property of the double bond. One can relate the activation to the electroattractive property of the metal fragment. The metal with its ligands, acting as a sink of electrons, deprives the olefin of a part of its electronic density.¹⁵ This effect certainly exists (acidic metals such as Fe(II) strongly activate the double bond). But some difficulties arise from this presumption of electronic depletion.

The direction and extent of net charge transfer in metal-olefin bonding is difficult to estimate. As we have known since the development of the Dewar-Chatt-Duncanson model¹⁶ the electronic transfer from the olefin to the metal is accompanied by a reverse charge transfer from the metal to the olefin. Detailed calculations justify this bonding model¹⁷ but disagree on the amount of charge shift involved.^{15c,17} This seems to be strongly dependent on the method of calculation. The theoretical problem is complicated further by the fact that there is no unique definition of charge residing in a piece of composite molecule. Thus Hay^{17e} has shown that the olefin in the Zeise salt would be strongly positively charged were a Mulliken population analysis used. A modified definition makes the back-donation nearly equivalent to the donation. Hay obtains a similar result for $\text{PdCl}_3(\text{C}_2\text{H}_4)^-$. If the reader despairs of these theoretical problems let him ponder the difficulties of determining experimentally such intramolecular charge reorganizations.

One could also imagine that the weakening of the C-C bond upon coordination to the metal might be of some help in the addition reaction. This does not seem to be a very good indicator of reactivity. For instance the $\text{Ni}(\text{PH}_3)_2$ olefin complexes, which have relatively elongated C-C bonds,¹⁸ have never been found to react with a nucleophile.

Charge is not the only driving force for a nucleophilic addition. From a perturbation theoretic viewpoint^{19,20} the electrophilic reactivity of a given substrate resides fundamentally in the energy and localization of its low-lying vacant orbitals.

With this frontier picture in mind, a first look at the reaction in fact reveals more factors pointing to olefin deactivation on coordination than activation.²¹ A fragment analysis of the bonding in olefin complexes has been previously carried out.^{17b,22,23} For any ML_n metal fragment coordinated the essentials of the Dewar-Chatt-Duncanson¹⁶ model of olefin bonding apply: as indicated schematically in **2** the ML_n fragment has a high-lying filled



orbital of b_2 symmetry to interact with ethylene π^* and a more or less low-lying vacant a_1 orbital to mix with π . The b_2 interaction, back-donation, cannot be neglected. It often accounts for the strong conformational preferences of coordinated olefins.^{17b,22,23} The b_2 interaction must lead to a decrease in the reactivity of the nucleophile toward the double bond. The vacant orbital most localized on the ethylene ligand, $\pi^* - \lambda b_2$, both is at higher energy and is less localized on the ethylene in the complex, compared to a free ethylene.

Some compensation might be provided by a new unfilled orbital in the complex, the $a_1 - \lambda' \pi$ combination. But this orbital is mainly a_1 of the metal fragment, slightly delocalized to the ethylene. It is thus unlikely that this extra interaction will make up for the decreased reacting "power" of $\pi^* - \lambda b_2$.

So where does the activation come from? We began with the establishment of a reliable index of nucleophilic activity by analysis of a reaction which has been well studied experimentally and theoretically. This is the addition of a nucleophile to a carbonyl.²⁴

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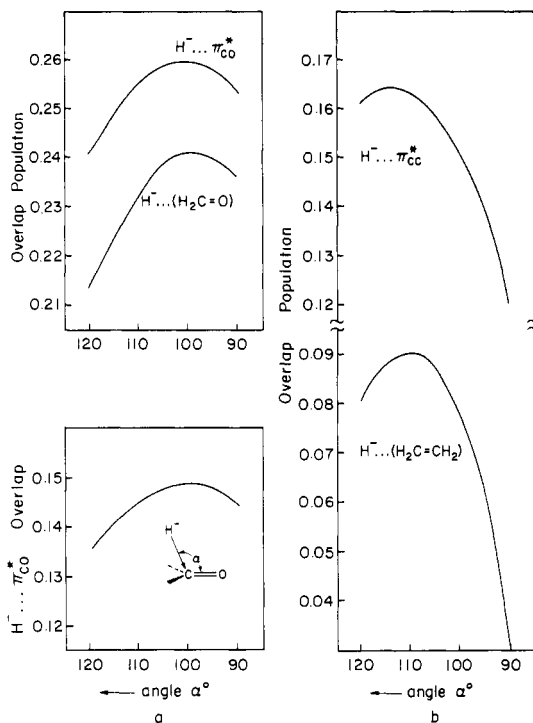
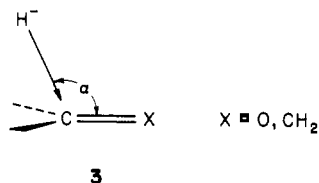


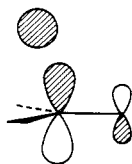
Figure 1. (a) Overlap population $H^-\cdots\pi^*_{CO}$ and between H^- and the entire formaldehyde molecule, $H^-\cdots(H_2C=O)$, as function of the angle α (top). Overlap $H^-\cdots\pi^*_{CO}$ as a function of the same α (bottom). (b) $H^-\cdots\pi^*_{CC}$ and $H^-\cdots(H_2C=CH_2)$ overlap population as a function of the angle α .

Extended Hückel calculations of H^- attack to a planar $H_2C=O$ and $H_2C=CH_2$ were carried out as a function of approach angle α , at a $C-H^-$ distance corresponding to moderate interaction, 2.0 Å (see 3). The overlap population between the entire carbonyl



3

moiety and the nucleophile nicely follows the known aspects of the reaction. It is known that the nucleophile does not add strictly perpendicular to the carbonyl plane but at an average α angle of $\sim 107^\circ$.²⁴ Indeed the overlap population is maximal around 100° (Figure 1a, top). The main contribution to the total overlap population comes from the interaction between H^- and π^*_{CO} . The repulsive action of π_{CO} is negligible due to its very deep energy and its primary localization on the oxygen atom. Therefore the maximum bonding interaction is obtained when the overlap between H^- and π^*_{CO} (see 4), is maximal, which occurs around $\alpha = 100^\circ$ (Figure 1a, bottom). More elaborate calculations have provided the same qualitative analysis.²⁵



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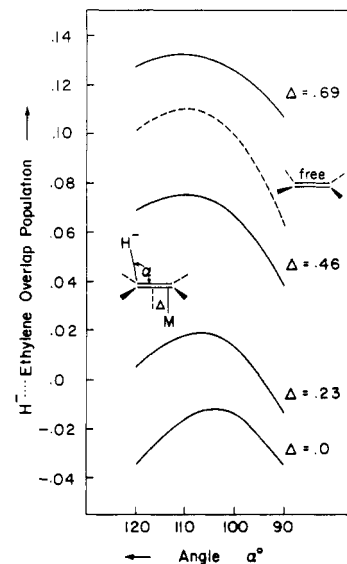


Figure 2. The H^- -ethylene overlap population in the model complex $(CO)_5Fe(ethylene)^{2+}\cdots H^-$, as a function of the approach angle, α , and the slipping of the ethylene, Δ . $\Delta = 0.0$ represents the η^2 -bonded olefin system.

The energy criterion predicts the same optimal approach angle, but the total energy surface possesses only a shallow minimum around 100° . The HOMO of the supersystem ($H^-\cdots H_2C=O$), composed mainly of the bonding combination of H^- and π^*_{CO} , varies in a still gentler way with α .

A similar analysis can be made for the nucleophilic addition to $H_2C=CH_2$.^{25a} A clearly diminished reactivity for the ethylene substrate appears when it is compared to $H_2C=O$.

The total overlap population between H^- and $H_2C=CH_2$ is less than half of the one calculated for formaldehyde (Figure 1b). The total energy shows a corresponding trend. At the optimum approach angle there was 1.80 eV of stabilization energy with respect to the separated reactants in the formaldehyde case. It is only 0.08 eV in the case of the ethylene. Similarly the HOMO of the composite system ($H^-\cdots H_2C=X$) was about 0.9 eV lower than the energy of the isolated nucleophile in the formaldehyde case, for ethylene the composite system HOMO was slightly higher in energy than the isolated nucleophile.

The origin of the decreased reactivity of the olefin is manifold. First, the π^*_{CC} is higher in energy and is less localized on the attacked carbon than π^*_{CO} . Second the π_{CC} is higher in energy and is more localized on the attacked carbon than π_{CO} . These factors, unfavorable to the ethylene case, are revealed in an examination of $H^-\cdots\pi^*_{CO}$ and $H^-\cdots\pi^*_{CC}$ overlap population. At the optimal approach angles, the $H^-\cdots\pi^*_{CC}$ overlap population is 0.16 (0.26 for $H^-\cdots\pi^*_{CO}$) and the $H^-\cdots\pi_{CC}$ overlap population is -0.024 (-0.002 for $H^-\cdots\pi_{CO}$).

Although both the overlap and the energetical criteria give the same answer in the comparison of formaldehyde and ethylene, we prefer to emphasize the overlap guide. The interfragment overlap seems to be more sensitive to structural changes and can be more easily analyzed in terms of separate contribution of π_{CC} and π^*_{CC} .

Now that we have established a reactivity index we can apply it to the coordinated ethylene. First consider a d^6 model compound, $Fe(CO)_5(C_2H_4)^{2+}$ which according to the isolobal analogy corresponds to $CpFe(CO)_2(C_2H_4)^+$,²⁶ which in turn is known to

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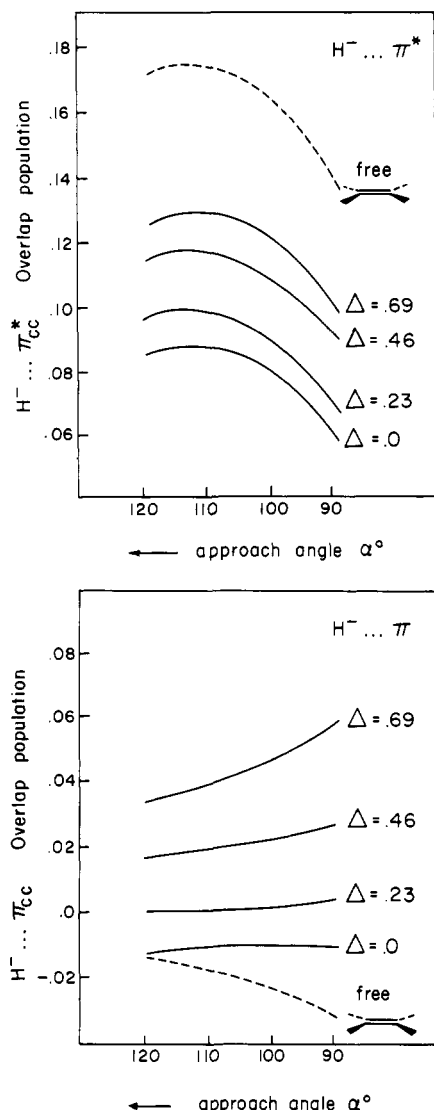
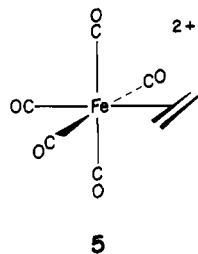


Figure 3. $H^- \cdots \pi^*$ (top) and $H^- \cdots \pi$ (bottom) overlap populations as a function of approach angle α and the slipping Δ . In each case the dashed line is the free ethylene value.

activate a double bond toward nucleophilic attack.³ A calculation of the complex in its equilibrium η^2 geometry (5), ethylene kept



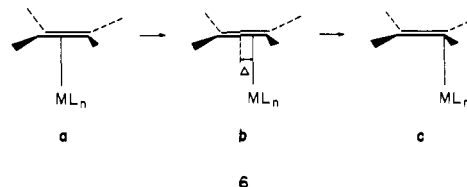
planar, shows that the olefin has lost a net of 0.20 electron resulting from a larger loss of π density (0.47) than a gain by back-donation (0.32). Despite this loss in electron density, which decreases the repulsion between the occupied orbitals of the olefin ligand and those of the nucleophile, the olefin is found to be deactivated toward the nucleophile on coordination to $Fe(CO)_5^{2+}$. The amount of deactivation is impressive. Compare the free olefin and $\Delta = 0$ curves in Figure 2. The H^- complexed olefin overlap population is even negative.

In the composite $H^- \cdots \text{ethylene} \cdots ML_n$ overlap population we can isolate out contributions due to $H^- \cdots \pi_{CC}^*$ and $H^- \cdots \pi_{CC}$. These are shown as the $\Delta = 0$ curves in Figure 3. As implied by our earlier qualitative analysis, the $H^- \cdots \pi_{CC}^*$ overlap population has decreased substantially. By examining the overlap matrix between the

fragments, we conclude that both perturbation theoretic factors—the rise in energy and the greater dispersion of the olefin π^* in the complex—are behind this. The additional contribution of the other vacant component, $a_1 - \lambda' \pi$, is not important because one does not see any noticeable $H^- \cdots \pi_{CC}$ overlap population built up.

Thus it appears that in the transition state for the nucleophilic addition the organometallic olefinic complex cannot be near its equilibrium η^2 structure.

A certain deformation of the complexed olefin, one which has no equivalent in the free molecule, supplies the anticipated but missed activation. This is a slipping of the ML_n fragment along the ethylene, idealized by a simple displacement from the center, Δ in 6b. $\Delta = 0$ is the symmetrically bonded $\eta^2 \pi$ complex, while



$\Delta = 0.69$ is in our geometry a model for an $\eta^1 \sigma$ complex. The dramatic effect of this motion on the H^- -olefin overlap population is shown in Figure 2 for the model d^6 complex $(CO)_5Fe(\text{ethylene})^{2+} \cdots H^-$.

The activation could arise in principle from two factors. It can be due to an increase of interaction of H^- with π_{CC}^* or to a decrease of the repulsion between the nucleophile and π_{CC} .

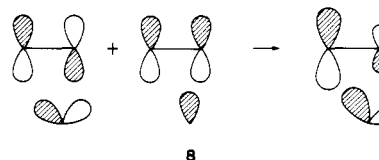
In Figure 3 we show the evolution of the two individual overlap populations as Δ increases. The $H^- \cdots \pi_{CC}^*$ overlap population increases to a certain extent but never surpasses the value it has in the free olefin (Figure 3). Indeed the interaction with the metal b_2 orbital still tends to destabilize π_{CC}^* . The coupling overlap has diminished (see 7), and as a consequence the energy of $\pi^* - \lambda b_2$



is lowered as Δ increases. But the level always lies higher than it does in the free olefin. This coupled with the dispersion of $\pi^* - \lambda b_2$ is sufficient to keep the reacting power of π_{CC}^* down.

The most spectacular change is in the $H^- \cdots \pi_{CC}$ overlap population. It is repulsive in the free olefin and in the symmetrically bonded system, but it does become positive as Δ increases (Figure 3). This positive $H^- \cdots \pi_{CC}$ overlap population derives from a localization of the LUMO of the slipped, complexed olefin on the far carbon, as illustrated in Figure 4.

There are two different ways to understand this localization of the LUMO in the slipped olefin structure. Olefin slipping results in a lowering of symmetry, which allows orbitals to mix which could not mix in the most symmetrical complex geometry. The LUMO of the slipped system can be thought of as a mixture of the unfilled orbitals $a_1 - \lambda' \pi$ and $\pi^* - \lambda b_2$ of the symmetrical system. The signs of the admixture are given in 8. As the



nucleophile approaches the ethylene above the left-hand carbon, mixing π_{CC}^* in-phase, it will also mix in π_{CC} in-phase, leading to a positive $H^- \cdots \pi_{CC}$ overlap population.

Alternatively, in order to visualize more directly the independent roles of the two fragments ML_n and olefin, it is useful to depict

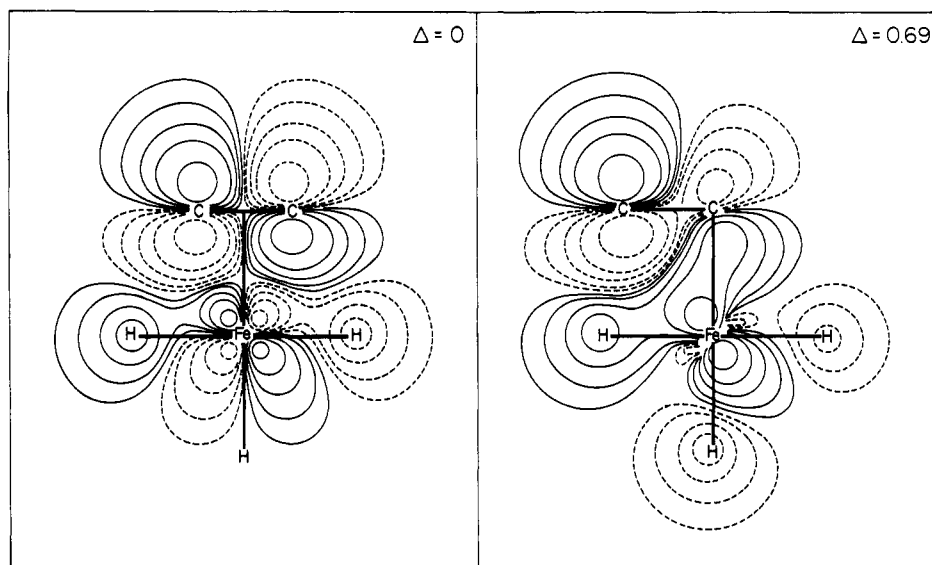
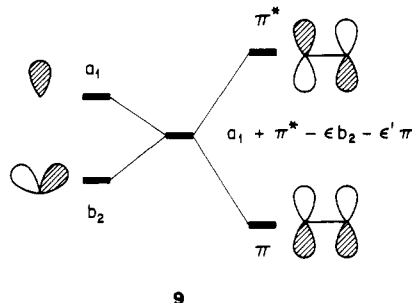
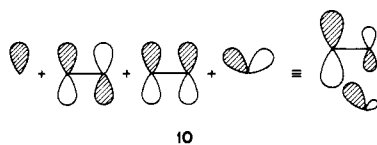


Figure 4. A plot of the $(\pi^*-\lambda b_2)$ MO in the $\eta^2\text{-H}_3\text{Fe(ethylene)}^{3-}$ ($\Delta = 0$) and of the LUMO of the $\eta^1\text{-H}_3\text{Fe(ethylene)}^{3-}$ ($\Delta = 0.69$). The contour values of Ψ are $\pm 0.2, 0.1, 0.055, 0.025$, and 0.01 .

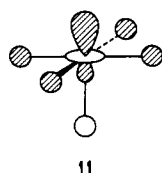
the same orbital as a direct mixture of the four fragment orbitals a_1 , b_2 , π , and π^* (see 9). Four orbitals mix. Normally this is



a complicated matter. But in this case it is easy to break down the interaction into a simple first-order mixing once one notices that, due to their proximity in energy and strong overlap in the slipped structure, the only orbitals which mix strongly are a_1 and π^* . The π and b_2 enter only as a slight perturbation. So the LUMO is the bonding combination of a_1 and π^* into which π mixes slightly in an antibonding way with respect to a_1 and b_2 enters in an antibonding way with respect to π^* . The sign of the mixing is given by 10.



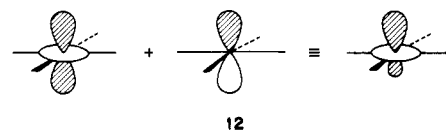
The introduction of π into the LUMO is primarily due to the a_1 orbital, which overlaps simultaneously with π^* and π . The admixture of π increases if the a_1 comes closer in energy to π . For a given coordination the energy of the vacant a_1 orbital depends mostly on the σ -donating capability of the ligands. As the a_1 orbital is antibonding between the metal and the ligands (as shown in 11 for an ML_5 fragment) strong electron donor ligands



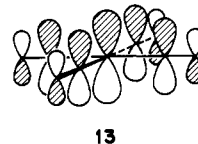
will push the a_1 orbital up more than weak electron donor or σ -acceptor ones. In the case of weak electron donors the a_1 orbital

is also more localized on the metal than in the case of strong electron donor ligands. Both factors make the interaction between the a_1 orbital and the π_{CC} larger for σ acceptors than for σ donors and therefore activate more efficiently the olefin. To test this analysis, we varied the electronegativity of the L ligand (Table I). The expected trend is found. Strong donors push up the a_1 orbital. The orbital is less localized on the metal. The amount of π admixture in the LUMO of the slipped complex is small. The orbital is mostly π^* . The reverse is obtained for an acceptor ligand. The a_1 is lower in energy, more localized on the metal. The amount of π admixture is larger.

The introduction of a π -acceptor ligand also has favorable influence in lowering the energy of a_1 . The a_1 orbital is a hybrid of d_{z^2} and p_z (see 12). The π -acceptor ligands create a vacant



orbital, bonding between p_z and π^*_{CO} (13), which due to its low energy mixes strongly with d_{z^2} .

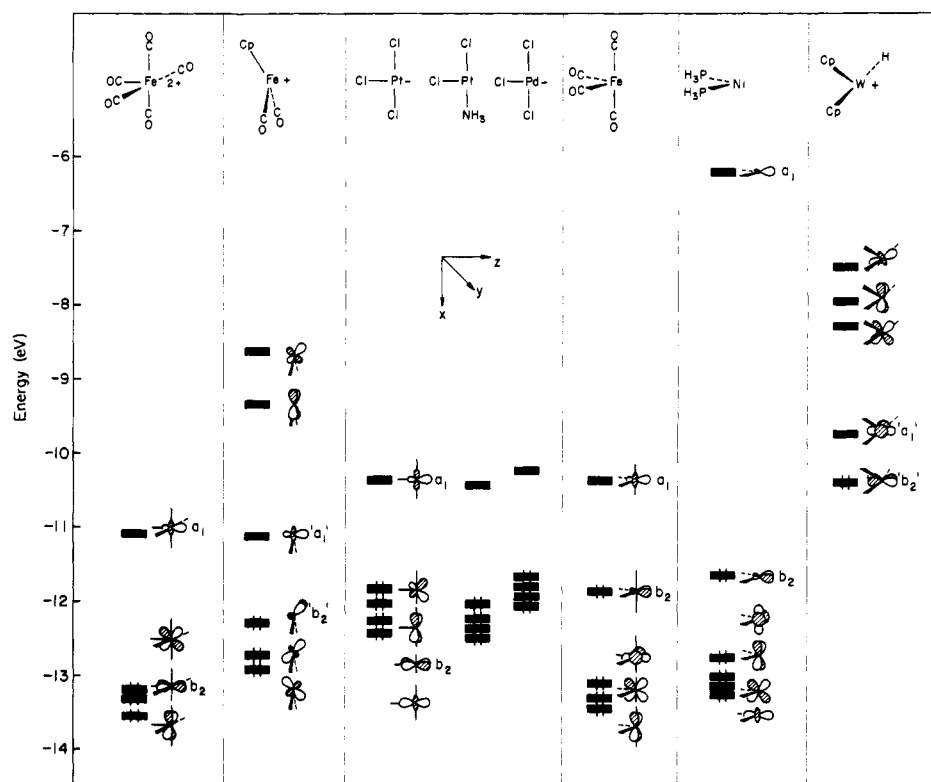


It appears that electron-withdrawing substituents on the metal activate nucleophilic addition to the olefin. Of course such an influence is already present in the η^2 -olefin complex, where the a_1 orbital is used to deprive the ethylene of a part of its electron density. But in the η^2 complex the a_1 orbital is not exercising fully its power for interaction—in the slipped olefin the efficiency of a_1 is maximized.

Up to now we have considered only a model olefin complex. We have seen the role of a_1 - and b_2 -type orbitals on the reactivity of the olefin. But the shape, the energy of these orbitals depend on the number and spatial arrangement of the ligands. Some additional orbitals may also be important. Therefore it is time now to turn to the various ML_n olefin compounds. We will first study the bonding characteristics of these molecules in their equilibrium geometries, which may presage their reactivities. Then we will study explicitly the reactivity of η^2 compounds, where all the potential reactivity is already present. Indeed it will turn out that the less deactivated is the olefin in the symmetrical η^2 complex, the more activated it is as an η^1 slipped olefin.

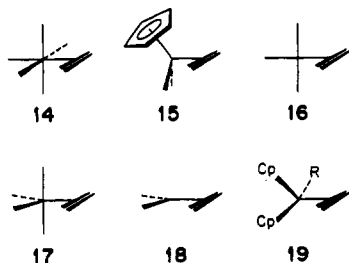
Table I. Influence of Substituent Electronegativity on Various Aspects of the η^1 L_5 Fe-Ethylene LUMO

ligand character of ML_5	$E(a_1$ in ML_5), eV	% Fe in a_1	% π in LUMO of $\eta^1 L_5 Fe-C_2H_4$	% π^* in LUMO of $\eta^1 L_5 Fe-C_2H_4$	E LUMO of $\eta^1 L_5 Fe-C_2H_4$, eV
$L = \sigma$ donor	-9.39	60	7	58	-8.05
$L = H^-$	-10.09	73	10	54	-8.31
$L = \sigma$ acceptor	-10.48	83	12	51	-8.45

**Figure 5.** Valence molecular orbitals of ML_n fragments. a_1 and b_2 orbitals are singled out and marked as such. The notation " a_1 " " b_2 " is used in those cases where the true symmetry is lower than C_{2v} .

Bonding Characteristics of ML_n -Olefin Complexes. The way an ethylene binds to a metal fragment has been examined previously,^{17b,22,23} stressing the consequences of such bonding on the barriers to internal rotation about the metal-olefin axis. Here we reexamine the metal-ethylene bond, focusing on the balance of donation and back-donation and its relevance to the reactivity of the complexed unsaturated ligand.

There is an infinity of real and potential olefin complexes. Our concentration on the known aspects of olefinic reactivity or unreactivity leads us to select a subset of these myriad complexes. The set, 14-19, contains most common olefin complexes and spans



a range from three- to eight-coordination, from d^2 to d^{10} electron counts.

To emphasize similarities in the bonding patterns, we orient the ethylene fragment in an identical way in each molecule. In some cases this leads to an unfamiliar (16) or uncomfortable (19) perspective, but the advantages of the uniform orientation are substantial.

For each olefin- ML_n complex we can get at the essentials of metal-olefin bonding by constructing an interaction diagram between the ML_n fragment and an ethylene. The relevant ML_n

fragment orbitals are assembled in Figure 5, all drawn on the same energy scale. As was already indicated in the introduction, the Dewar-Chart-Duncanson model serves as a convenient starting point in a discussion of complexed olefin reactivity. For this reason we single out the crucial a_1 (unfilled, acceptor) and b_2 (filled, donor) levels on the metal by labeling them specifically on the figure. Note that in some cases there are other frontier orbitals of a_1 and b_2 symmetry in these fragments. They complicate the scheme yet sometimes cannot be neglected.

The reader should be warned that since we are using the extended Hückel methodology that some of the bonding aspects may not be well represented. In those complexes which carry a net positive or negative charge a self-consistent procedure would give orbital contractions or dilations, with corresponding level shifts down or up in energy, which a non-self-consistent field procedure cannot reproduce. Those level shifts in turn might influence forward- and back-donation to a coordinated ligand, just the effect we want to study. In reality we think the situation is not so bad. The fully charged complexes are hypothetical gas-phase molecules, and in solution the net charging is small. Most of the charge resides on the ligands anyway, the electroneutrality principle is at work. Finally we think that our experience with extended Hückel methodology for inorganic complexes indicates that the level schemes and relative electron distributions obtained with this most approximate molecular orbital method are reasonably reliable. A further cautionary note is that we have in each case kept the complexed olefin planar, not allowed its hydrogens to bend back. This was done to allow a fair intercomparison of different complexes and the free ethylene.

With the fragment orbitals before us in Figure 5 and with our previous experience in the analysis of metal-olefin bonding in mind,^{17b,22,23} we can proceed to a discussion of the similarities and

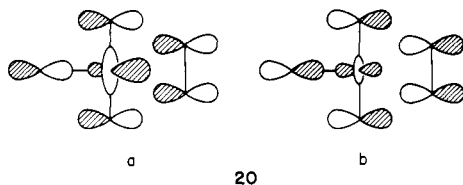
Table II. Electron Densities in the Ethylene Fragment π and π^* Orbitals of Some Complexed Olefins and the Total Charge on the Complexed Ethylene.

ML_n	π electron density	π^* electron density	total charge on the olefin
$Fe(CO)_5^{2+}$	1.53	0.32	0.20
$CpFe(CO)_2^+$	1.54	0.32	0.19
$PtCl_3^-$	1.63	0.24	0.11
$PtCl_2NH_3$ (trans)	1.63	0.24	0.15
$PtCl_2NH_3$ (cis)	1.64	0.24	0.10
$PdCl_3^-$	1.71	0.21	0.02
Cp_2WH^+	1.74	0.60	-0.36
$Fe(CO)_4$	1.66	0.48	-0.15
$Ni(PH_3)_2$	1.81	0.44	-0.28

individualities in these molecules.

The isolobal analogy between $(CO)_5Fe^{2+}$ and $CpFe(CO)_2^+$ indicates some equivalence between the two systems. In the equilibrium geometry **15**, the HOMO of $CpFe(CO)_2^+$ is an a'' orbital which efficiently overlaps with π_{CC}^* and the LUMO is an a' orbital able to overlap with π_{CC} (Figure 5).²¹ We identify a'' as " b_2 " and a' as " a_1 " in our previous general discussion of olefin bonding. As in $(CO)_5Fe^{2+}$, the a_1 interaction dominates and the olefin is positively charged (Table II). The local electron distribution in the two isolobal systems is essentially similar.

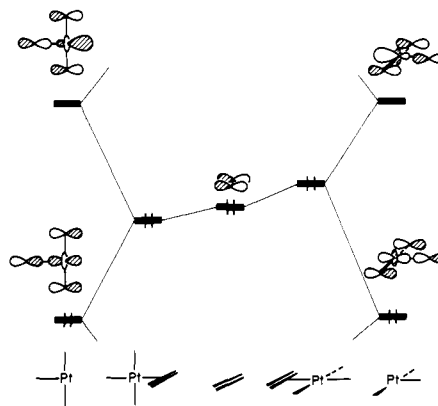
The analysis of metal-olefin bonding in Zeise's salt was given by us elsewhere and will not be repeated here. It is well-balanced case of forward- and back-donation. As the corresponding entry in Table II shows the olefin is also positively charged overall, although slightly less so than in the six-coordinate d^6 $Fe(II)$ complexes. There are reasons, which will become clear below, for thinking about both the predominant "upright" orientation of the ethylene, shown in **16**, and a "planar" configuration, 90° twist from there, both ethylene carbons in the coordination plane. Going from the upright to the planar geometry increases the positive charge on the ethylene. The charge is due to greater donation from π_{CC} into the vacant a_1 orbital. This effect is not a consequence of a larger overlap between π_{CC} and a_1 in the in-plane geometry. In fact this overlap is smaller, as indicated in **20a**, because of the negative overlap contribution produced by the Cl p orbitals mixing into the metal d function.



It comes from the repulsive influence of an occupied orbital concentrated on the chlorines. In the planar geometry the repulsion is large due to the substantial overlap (see **20b**). Therefore the π orbital destabilized gets closer to the vacant a_1 and consequently loses more electrons (see **21**). Following an electrostatic argument, the olefin should be more reactive toward a nucleophile in an anti-Zeise's salt geometry. We will see later on that a frontier orbital analysis contradicts this conclusion.

We can compare our results with more elaborate calculations.^{17c-e} Ab initio computations on the Zeise salt^{17e} also favor a weak positive charge on the olefin. The author says that this weak positive charge may be exaggerated and is an artifact of the Mulliken overlap population when very diffuse orbitals are present. A modified Mulliken overlap population restores the electroneutrality of the olefin. X- α calculations^{17d} imply weak back-donation and suggest that most of the bonding is accomplished by the π orbital.

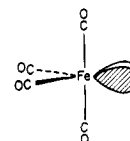
Table II and Figure 5 also contain entries for two molecular fragments related to $PtCl_3^-$, namely, $PtCl_2NH_3$ and $PdCl_3^-$. The former was included because it is a neutral fragment of the same coordination geometry and electron count as the anionic Zeise's salt. It is also representative of four-coordinate d^8 complexes which

**21**

have been studied in addition reactions. As would have been expected from our non-self-consistent-field computational method, there is no essential change in the level pattern of the fragment (Figure 5) or consequent electron reorganization on olefin complexation (Table II) when an amine is substituted for a chloride.

The comparison between Zeise's salt and its equivalent with a palladium is interesting, although uncertain with our method. One may nevertheless expect a weaker interaction (less forward- and back-donation) with Pd than with Pt since the orbitals of the palladium are more contracted than those of the platinum. Ab initio calculations yield a similar result.^{17e}

An ethylene coordinated to $Fe(CO)_4$ (**17**) becomes negatively charged (Table II). The large back-donation into π_{CC}^* , 0.48 electron, is due to the strong hybridization of b_2 (see **22**) away

**22**

from the equatorial CO groups. This causes a large overlap of 0.24 between b_2 and π^* . The electronic structure of this complex and the next one has been analyzed in detail earlier.^{17b}

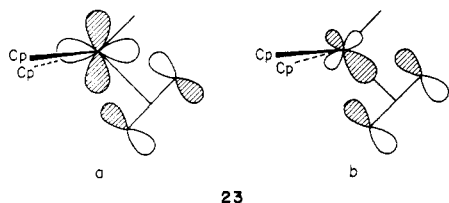
$Ni(PH_3)_2(C_2H_4)$ (**18**) also gives a negative ethylene ligand, in agreement with ab initio results.^{15b} Two factors conspire to cause this large negative charge: (a) a donation into the π^* which is large (0.44) but not exceptional; (b) the absence of any efficient electron-attracting orbitals. Since **18** is a d^{10} complex, the only vacant orbital which can interact with π_{CC} and so remove electrons from it, is a very high lying and therefore inefficient hybrid, mainly of p character.

The structure of $Cp_2WR(C_2H_4)^+$ is unknown, but that of an isoelectronic molecule $Cp_2NbC_2H_5(C_2H_4)$ has been determined.²⁷ One can analyze the electronic structure of the molecule in two ways: (a) as a bent Cp_2M in interaction with two ligands;²³ (b) since we want to focus only on the olefin, the complex can be viewed as Cp_2MR in interaction with an olefin. The Cp_2MR fragment has two low-lying orbitals which are symmetric with respect to the unique plane of symmetry of the molecule. (An exact symmetry only exists if the cyclopentadienyls are in an eclipsed conformation. In a staggered conformation it would be a good approximation.) The lower of these two orbitals avoids the equatorial ligands (**23a**) and is perfectly oriented to overlap with π_{CC}^* (if the ethylene lies in the equatorial plane).

In $Cp_2WR(C_2H_4)^+$, this orbital is occupied and produces the required back-bonding into π_{CC}^* . The interaction is strong because the orbitals of W are high in energy and diffuse. Therefore the back-donation is large. The electron density in π_{CC}^* is 0.60. This is typical of early transition metals of the third period.²⁸ It

(27) Guggenberger, L. J.; Meakin, P.; Tebbe, F. N. *J. Am. Chem. Soc.* **1974**, *96*, 5420-5427.

(28) Goddard, R.; Hoffmann, R.; Jemmis, E. D. *J. Am. Chem. Soc.* **1980**, *102*, 7667-7676.



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originates from a good match in overlap and energy among the d orbitals and the vacant orbitals of the ligands. The LUMO of Cp_2WR^+ is an orbital which points nicely toward the vacant site as it tries to avoid overlap with R (23b). It is perfectly suited to interact with π_{CC} . The interaction stays quite weak due to the larger difference in energy between π_{CC} and the LUMO in question. The larger overlap does not compensate. Consequently the olefin is strongly negatively charged, -0.36 . Such a large negative density does not surprise us. It is for instance well documented for electron-deficient tantalum-carbene complexes, in which the carbene behaves as a nucleophile.²⁸

It is possible to relate the amount of donation and back-donation to any experimental observable? This is a difficult question. The correspondence between the electronic density on the carbon and the ^{13}C NMR shift is not straightforward, although it is widely used. There is a general trend to an upfield shift of the coordinated carbon.²⁹ The CC bond length, as determined by crystallographic or other structural methods, is an attractive possibility for correlation. There is a limitation on the utilization of this geometrical criterion because one cannot separate forward- and back-donation. Transfer of electrons from π_{CC} or their acceptance into π^*_{CC} both lead to a C-C stretching.

We feel that the back-donation influences the stretching more than the reverse effect. According to our results, and focusing on the back-donation, one can distinguish two classes of compounds. In the set formed by $(\text{CO})_5\text{M}(\text{olefin})$, $\text{CpFe}(\text{CO})_2(\text{C}_2\text{H}_4)^+$, Pd, or $\text{PtXY}_2(\text{C}_2\text{H}_4)$ back-donation is weak; in the other set, $\text{Cp}_2\text{WH}(\text{C}_2\text{H}_4)^+$, $\text{FeCO}_4(\text{C}_2\text{H}_4)$, and $\text{Ni}(\text{PH}_3)_2(\text{C}_2\text{H}_4)$, the back-donation is large. For the Pd and Pt olefin compounds the weak back-donation is even accompanied by a weak transfer of electrons in the opposite direction (Table II). Indeed an accurate structure of Zeise's salt gives 1.374 \AA for the CC bond length,³⁰ a small elongation. For the Pd analogue we can only compare with calculations. The optimized CC bond length is found to be shorter with Pd, which follows the less efficient charge transfer. In the six-coordinate Fe(II) complex the electron-attracting power of the metal has increased, but the back-donation has essentially the same value. One observes experimentally a large range of CC distances, $1.38\text{--}1.42 \text{ \AA}$.³¹

In the second set of complexes more electrons occupy the π^*_{CC} , and the stretching is somewhat larger. CC bond lengths of 1.42 \AA for $\text{Fe}(\text{CO})_4(\text{olefin})$ ³² and 1.43 \AA for $\text{Ni}(\text{PR}_3)_2(\text{olefin})$ ¹⁸ have been reported. There is no experimental value for $\text{Cp}_2\text{WR}(\text{olefin})^+$. In the niobium analogue the authors report the value of 1.406 \AA .²⁷ A calculation of the Nb compound gives an electron occupancy of π^*_{CC} equal to 0.41 and π_{CC} equal to 1.64 and a total charge on the ethylene equal to -0.04 .

It is interesting to add here a tantalum-olefin-carbene complex, $\text{CpTa}(\text{PMe}_3)(\text{C}_2\text{H}_4)(\text{CHCMe}_3)$, where the CC bond length reaches the amazing value of 1.477 \AA .³³ Preliminary calculations on this species indeed yield a very large electron transfer into π^*_{CC} .

Reactivity of ML_n Olefinic Complexes. For which of these molecules will the nucleophile add to the coordinated olefin? By considering only the net charge on the ethylene one would conclude that only $\text{CpFe}(\text{CO})_2(\text{C}_2\text{H}_4)^+$ is likely to be a good reactant and

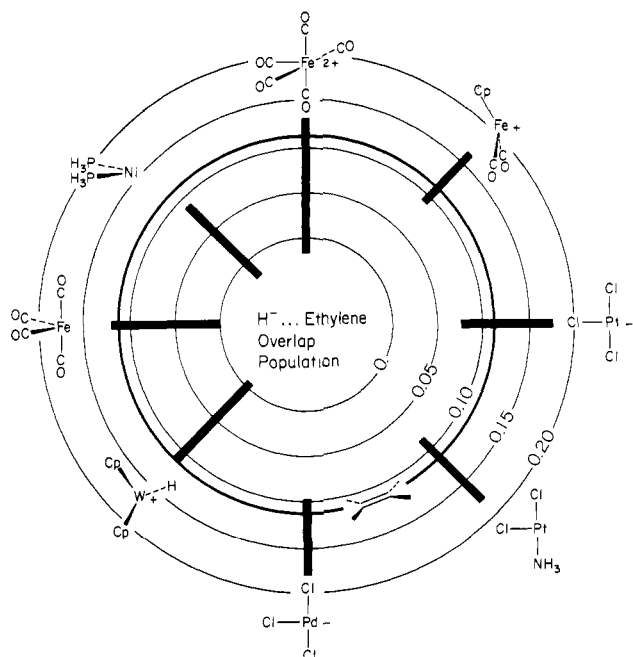


Figure 6. $\text{H}^+\cdots\text{C}_2\text{H}_4$ overlap population for ethylene coordinated to ML_n . The lower limit of the bar corresponds to η^2 -bonding mode $\Delta = 0$. The upper limit corresponds to the slipped olefin, $\Delta = 0.69$. The approach α angle is 110° . The darker circle gives the overlap population for the free olefin.

that the $\text{Ni}(\text{PH}_3)_2(\text{C}_2\text{H}_4)$ or the $\text{Cp}_2\text{WH}(\text{C}_2\text{H}_4)^+$ complexes look like very bad candidates. These immediate conclusions are experimentally supported. $\text{CpFe}(\text{CO})_2(\text{C}_2\text{H}_4)^+$ is indeed a very good reactant, and no nucleophilic addition to $\text{Ni}^0\text{L}_2(\text{C}_2\text{H}_4)$ has been observed.

However, in the study of our model reaction we have seen that the symmetrically bonded olefin of $(\text{CO})_6\text{Fe}(\text{C}_2\text{H}_4)^{2+}$ is less reactive than the isolated olefin, despite the positive charge on the olefin. $\text{Cp}_2\text{WR}(\text{C}_2\text{H}_4)^+$ also reacts, even though it contains a negatively charged olefin. We think that one cannot rely on the electronic density in the olefin as a reliable indicator of the olefin's electrophilic behavior. A more thorough examination is in order.

For all the important fragments we carried out the same calculations which were described above for $\text{Fe}(\text{CO})_5(\text{C}_2\text{H}_4)^{2+}$. The optimum angle of approach remains around 110° . Therefore we will not present the full study of the dependence of the overlap population on α . Only the values obtained for $\alpha = 110^\circ$ will be reported. It should be noted that we have kept the ethylene planar throughout, and if it were puckered, as it is to a varying extent in the complexes, the optimum α might change somewhat.

The circular graph of Figure 6 plots a bar for each molecule. The lower limit of the bar is the $\text{H}^+\cdots\text{C}_2\text{H}_4$ overlap population in the η^2 -bonding mode, $\Delta = 0$. The upper limit corresponds to the slipped olefin, $\Delta = 0.69$. The darker circle is the comparison value of the overlap population for a free olefin.

Deactivation of the ethylene upon η^2 coordination is a general phenomenon, whatever the ML_n fragment. The amount of deactivation is nevertheless highly variable. It is quite mild with $\text{CpFe}(\text{CO})_2^+$ and Pt or Pd XY_2 fragments. It is impressive with the other metallic fragments, especially with $\text{Ni}(\text{PH}_3)_2(\text{C}_2\text{H}_4)$. On going from η^2 to η^1 coordination, using the slipping motion we described before, reactivation occurs. The reactivity as measured by the $\text{H}^+\cdots\text{C}_2\text{H}_4$ overlap population in the η^1 -coordination, is also highly variable. $\text{CpFe}(\text{CO})_2(\text{C}_2\text{H}_4)^+$ and Pt or Pd $\text{XY}_2(\text{C}_2\text{H}_4)$ appear especially activated. $\text{Ni}(\text{PH}_3)_2(\text{C}_2\text{H}_4)$ remains less reactive than the free olefin. The other complexes give intermediate values. Thus, those complexes which are characterized by weak deactivation in the η^2 bonding may become very reactive in the η^1 -slipped geometry. On the other hand, great deactivation in the η^2 complex leads to an absence of reactivity even in the η^1 structure. In other words, one has to start as well as possible in the η^2 complex if one wants to arrive high in the

(29) Chisholm, M. H.; Godleski, S. *Prog. Inorg. Chem.* **1976**, *20*, 299-436.

(30) Love, R. A.; Koetzle, T. F.; Williams, G. J. B.; Andrews, L. C.; Bau, R. *Inorg. Chem.* **1975**, *14*, 2653-2656. DeRenzi, A.; Ganis, P.; Panunzi, A.; Vitagliano, A.; Valle, G. *J. Am. Chem. Soc.* **1980**, *102*, 1772-1723. Other ML_3 olefin structures can be found in ref 17b.

(31) (a) Reference 18 of ref 22. (b) Brown, L. D.; Barnard, C. F. J.; Daniels, J. A.; Mawby, R. J.; Ibers, J. A. *Inorg. Chem.* **1978**, *17*, 2932-2935.

(32) Cotton, F. A.; Lahuerta, P. *Inorg. Chem.* **1975**, *14*, 116-119.

(33) Schultz, A. J.; Brown, R. K.; Williams, J. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 169-176.

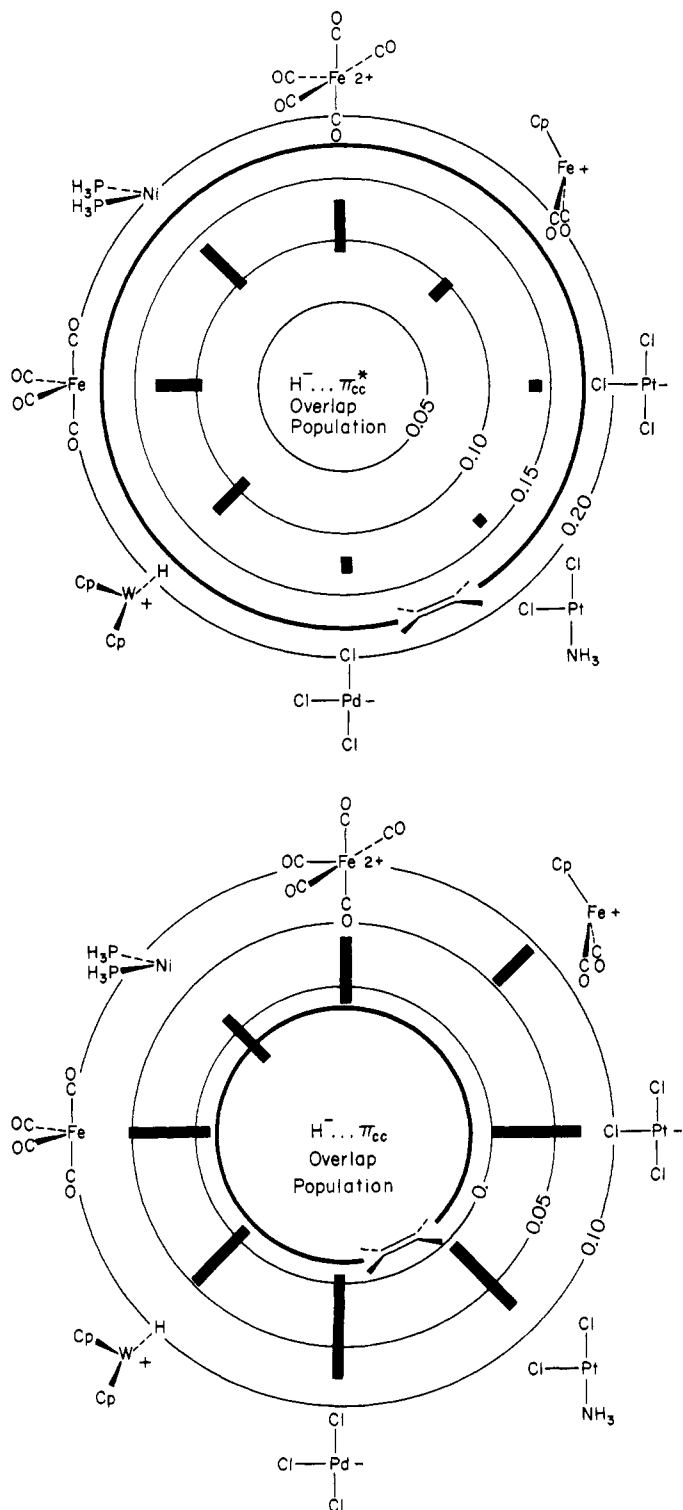


Figure 7. Top: $H \cdots \pi^*_{CC}$ overlap population. Bottom: $H \cdots \pi_{CC}$ overlap population. The convention is similar to that in Figure 6.

η^1 complex. Every favorable factor which activates the olefin is already preexistent in the η^2 complex. It is for this reason that somewhat later in our discussion we will focus on the symmetric η^2 complex.

To analyze the reactivity of each complex, we have also examined the major contributions to the $H \cdots C_2H_4$ overlap population. They are the $H \cdots \pi^*_{CC}$ and $H \cdots \pi_{CC}$ overlap populations shown in Figure 7.

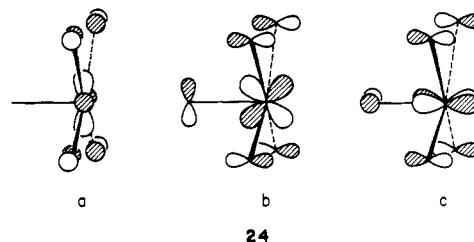
We now proceed to analyze each compound in turn.

The comparison between $CpFe(CO)_2(C_2H_4)^+$ and $Fe(CO)_5(C_2H_4)^{2+}$ is especially instructive. These two complexes are isolobal and therefore must be in some way analogous. Indeed

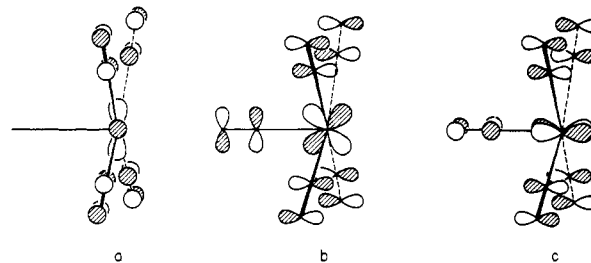
we saw earlier (Table II) that the charge on the olefin, and its breakdown into π and π^* electron drifts, was nearly identical in these two compounds. Nevertheless the reactivity of these two complexes toward the nucleophile is quite different (Figures 6 and 7). The presence of the Cp ring seems to have prevented the deactivation of the olefin. This is a counterintuitive result because the Cp ring is an electron donor, relative to the three carbonyls it replaces. The Cp ring would have been expected to decrease the electrophilic properties of the $CpFe(CO)_2$ fragment, but it does not do so. The difference in reactivity does not derive from a different reactivity of the π^* of the olefin because the $H \cdots \pi^*_{CC}$ overlap population is nearly identical for both compounds. The activation comes from an entirely different value of the $H \cdots \pi_{CC}$ overlap population. While this population is negative (-0.012) repulsive, for $Fe(CO)_5^{2+}$, it becomes positive for $CpFe(CO)_2^+$ (0.056) (Figure 7). The difference may be traced to the behavior of the vacant orbital, schematically represented as $a_1 - \lambda'\pi$ in 2. Since this level is mostly centered on the a_1 orbital, its strength to activate the olefin is small, if it is also high in energy. Lowering $a_1 - \lambda'\pi$ activates the double bond and creates a positive $H \cdots \pi_{CC}$ overlap population. In $CpFe(CO)_2(C_2H_4)^+$ and $(CO)_5Fe(C_2H_4)^+$ it lies respectively at -9 and -7.7 eV.

Why is there such a difference between two isolobal molecules? Because the differential is so striking let us digress here to try to understand it. Two factors are involved: the presence of a ring and the removal of the plane of the olefin system as a plane of symmetry.

What is the consequence of replacing three ligands by a ring in an octahedral complex? First consider the ML_5 unit. The three orbitals coming from the t_{2g} set of the octahedron are found almost unchanged. They interact strongly with the p orbitals of the ligands. If L is a π donor, the three orbitals are destabilized by L and in a d^6 complex the antibonding combination of the d's and the ligands is occupied (see 24). If L is a π acceptor, the antibonding combination of the d's and the vacant orbitals of the ligands is vacant (see 25).

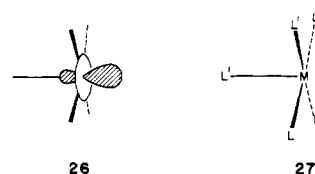


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In C_{4v} symmetry these orbitals cannot mix with the cylindrically symmetric orbital 26 which is the one involved with π_{CC} and which

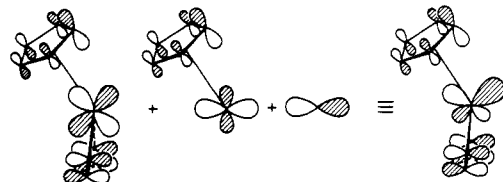


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we call a_1 in a general way. Replace three cis ligands by three different ligands L' (27). The symmetry is lowered and mixing of 24a, 24b, 25a, and 25b with 26 becomes possible. 24a and 24b are lower in energy than 26 and destabilize the antibonding

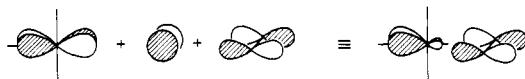
combination of **26** and π (the one we call $a_1-\lambda'\pi$). Since **25a** and **25b** are higher in energy, they stabilize the combination in question. The lower **25a** and **25b** are, the stronger is the stabilization. It is here that the Cp ring finds its utility. The calculation shows the **25b** stabilizes strongly the $a_1-\lambda'\pi$ combination. There are several reasons why the **25b** lies low in energy when a Cp ring is present. The Cp orbitals do not overlap as efficiently with metal orbitals as the p orbitals of the $3L'$ do. Therefore between the occupied orbitals, as shown in **24b**, is quite weak. Second, there are high vacant orbitals on the Cp which can directly stabilize the orbital in question. In case of the $\text{CpFe}(\text{CO})_2^+$ fragment the orbital which is created is at -8.7 eV and has a large overlap with π . It is represented schematically in **28**. One notes its

**28**

substantial extension toward the vacant site. Both this orbital and **26** interact with π of ethylene. The middle orbital of the resulting three-orbital pattern, the one we call $a_1-\lambda'\pi$, does not rise high in energy. This in turn is responsible for its augmenting the $\text{H}^-\cdots\pi$ bonding interaction.

One sees that there is an advantage to replacing ligands by a Cp ring. Analogous activation can be expected with an η^6 -phenyl ring. It is thus understandable that a phosphine prefers to replace a carbonyl in $(\text{CO})_5\text{Mn}(\text{C}_2\text{H}_4)^+$,^{2b} while it adds to the double bond in $\text{CpFe}(\text{CO})_2(\text{C}_2\text{H}_4)^+$ ^{3b,j} and $\eta^6-(\text{C}_6\text{H}_6)\text{RuPMe}_3(\text{CH}_3)(\text{C}_2\text{H}_4)^+$.⁴ This last example is especially interesting as all the ligands are π donors (or at least not acceptors) and therefore would have been expected to deactivate the double bond.

The olefin complexes of PtXY_2 and PdXY_2 also are quite reactive toward a nucleophile. From a theoretical perspective this is apparent in the weak deactivation of the olefin when it is π bonded to the metal which, as the reader will recall, is connected to strong activation in the slipped olefin. Unlike $\text{CpFe}(\text{CO})_2-(\text{C}_2\text{H}_4)^+$, the activation does not originate from an unusual $\text{H}^-\cdots\pi_{\text{CC}}$ overlap population but from a substantial $\text{H}^-\cdots\pi^*_{\text{CC}}$ overlap population which is nearly comparable to the one in the free olefin (Figure 7). This means that the π^*_{CC} has not been strongly deactivated by the b_2 orbital of the metal (see 2). Indeed $\pi^*-\lambda b_2$ has nearly the same energy as in the free olefin. This arises from the additional stabilization of the p orbital on the metal. As there is no ligand perpendicular to the primary metal-ligands coordination plane, the p orbital of b_2 symmetry is relatively low in energy and adds in phase into $\pi^*-\lambda b_2$, as shown in **29**. A contour plot of this orbital is illustrated in Figure 8.

**29**

Activation toward nucleophilic attack in four-coordinate d^8 complexes is a function of the geometry of the molecule. A calculation of the less stable conformation, the one in which the olefin lies in the coordination plane, shows a large decrease in reactivity in the η^2 geometry. This is because the important p orbital is not available for stabilization in the in-plane geometry. Slipping does not provide sufficient activation with respect to the isolated olefin in this geometry. To test this hypothesis it would be interesting to study the reactivity of the dichloro(5-methylenecycloheptene)platinum(II) (**30**), whose structure has

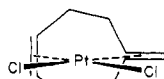
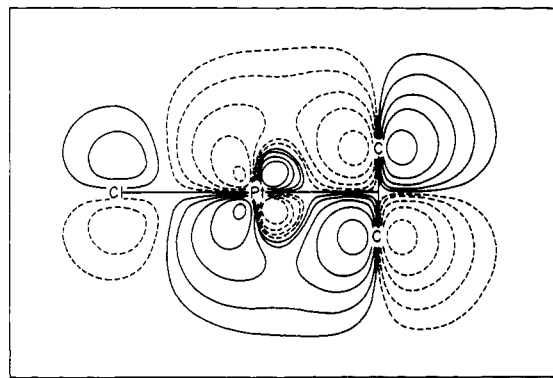
**30**

Figure 8. Plot of the $\pi^*-\lambda b_2$ orbital in the plane of the olefin of the Zeise salt in its equilibrium geometry. The contour values of Ψ are $\pm 0.2, 0.1, 0.055, 0.025$, and 0.01 .

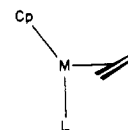
been determined recently.³⁴ In this molecule one of the double bonds is perpendicular to the PtCl_2 plane, the other is coplanar. The perpendicular double bond should be reduced more easily by a nucleophile. Were the charge of the olefin to control the reactivity the in-plane double bond should be the one attacked preferentially. This we would conclude from our earlier analysis of coordinated olefin charges. Coming back to the perpendicular complex, our line of reasoning implies that the olefin should be less reactive if the two vacant sites on the metal were occupied by extra ligands. One goes back to the octahedral system, which is indeed much less reactive. Only the presence of π -acceptor carbonyls activated the complex. If one adds only one ligand to go to $d^8 \text{ML}_4$ (olefin), one should also deactivate the addition. This is because the vacant p orbital of the metal is involved with the equatorial ligands of the trigonal-bipyramid **31**.

**31**

This deactivation of an $\text{ML}_3(\text{olefin})$, d^8 , compound upon addition of another ligand to give an $\text{ML}_4(\text{olefin})$, d^8 , is also apparent in the weak reactivity of $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$. Again what prevents complete deactivation is the presence of the CO's, strong π acceptors. In the η^2 geometry the olefin is largely deactivated and the reactivity is not very high in the η^1 olefin either. The individual analysis of the $\text{H}^-\cdots\pi^*_{\text{CC}}$ and $\text{H}^-\cdots\pi_{\text{CC}}$ overlap populations (Figure 7) shows no favorable factor, apart from the slipping off the metal. As the a_1 orbital is low in energy, it is strong enough to activate the distorted complex.

Is it possible to activate an $\text{ML}_4(\text{olefin})$ d^8 complex? One can, of course, replace the carbonyls by better acceptors such as NO^+ . Apart from the introduction of a net charge on the complex our calculations on a model compound do not show any real change in the reactivity.

A much greater enhancement of reactivity may be obtained by introducing a ring in the place of three carbonyls (see **32**). An

**32**

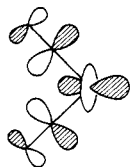
analysis paralleling that for the $\text{CpFe}(\text{CO})_2(\text{olefin})^+$ complex

(34) Wright, L. L.; Wing, R. M.; Rettig, M. F.; Wiger, G. R. *J. Am. Chem. Soc.* **1980**, *102*, 5950-5952.

(35) Bäckvall, J.-E.; Åkermark, B. *J. Organomet. Chem.* **1974**, *78*.

points to a large reactivity. One can note that a relatively stable $\text{CpPd}(\text{PPh}_3)(\text{C}_2\text{H}_4)^+$ reacts with a nucleophile.⁷ A similar reactivity is observed for $\text{CpNi}(1,5\text{-cyclooctadiene})^+$.^{13b} Making use of the charge argument, Åkermark and co-workers have mentioned the high reactivity of the $\text{Ni}(\text{II})$ complex.^{15b}

Every favorable factor we have seen up to now disappears in the $\text{d}^{10} \text{Ni}(\text{PH}_3)_2(\text{C}_2\text{H}_4)$ compound. The metal b_2 occupied orbital pushes up the π^*_{CC} very high in energy, and no additional vacant orbital can prevent its rise. The ML_2 fragment acceptor a_1 orbital is high in energy, made up primarily of metal p . From its weak mixing with π_{CC} no low-lying $a_1-\lambda'\pi$ combination emerges. There is little net electrophilic character in the $\text{Ni}(\text{PH}_3)_2(\text{C}_2\text{H}_4)$ complex, and the system is not going to be very active, even in the η^1 distorted geometry. Indeed one notes the nearly total absence of localization on the far carbon in the LUMO of the distorted complex. To activate a $\text{d}^{10} \text{ML}_2$ complex, one might in principle replace the donor group by some acceptor as CO. Upon carrying out such a replacement, one finds indeed a small activation. This is due to the appearance of a low-lying a_1 orbital, mainly centered on π^*_{CO} , mixing in an antibonding way with z^2 (see 33). In the



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distorted system, the $\text{H}^--\text{C}_2\text{H}_4$ overlap population reaches the value of the free olefin. However, the kinetic instability of the $\text{Ni}-\text{C}$ bond makes the use of such a complex extremely unlikely.

Thus, a $\text{d}^{10} \text{ML}_2$ fragment is not a good candidate for activation of an olefin. A $\text{d}^8 \text{ML}_2(\text{olefin})$, on the other hand, is going to be extremely reactive, as mentioned by Åkermark.^{15b} This coordinatively unsaturated molecule will have a very low-lying unfilled orbital. The interaction diagram that is behind this conclusion is similar to one given by us earlier.^{17b}

$\text{Cp}_2\text{WH}(\text{C}_2\text{H}_4)^+$ presents a picture of very weak reactivity. It is strongly deactivated in the η^2 geometry, and it hardly passes the reactivity of the olefin in the η^1 mode. Indeed the orbitals of the metal are high in energy and consequently are close to the vacant orbitals of the ligands and far from the occupied orbitals. In particular the LUMO of Cp_2WH^+ which plays the part of the a_1 -type orbital of the other fragments, interacts only weakly with π , and does not introduce enough polarization in the LUMO of the η^1 complex. One may wonder if the positive charge does provide the required additional reactivity. It would be interesting to study the reaction of $\text{Cp}_2\text{NbR}(\text{C}_2\text{H}_4)$, with good nucleophiles. As the Nb orbitals are lower in energy, this should be a more reactive species. Up to now no addition to the olefin has been reported. Activation might also be achieved through introducing asymmetry while keeping a Cp ring, e.g., in $\text{CpM}(\text{CO})_3\text{R}(\text{olefin})$ complexes, $\text{M} = \text{Zr}$ and Ti .

$\text{CpM}(\text{CO})_3(\text{olefin})^+$ with $\text{M} = \text{W}$ and Mo reacts with a nucleophile, with addition to the olefin. This reaction has been utilized to obtain dinuclear species by using $\text{CpM}(\text{CO})_3^-$ as a nucleophile.^{6c} It is difficult to estimate the structure of such olefin complexes, but one may reasonably expect that the simultaneous presence of the Cp ring and the CO's make them as good reactants as is $\text{CpFe}(\text{CO})_2(\text{olefin})^+$.

Conclusions and Extensions

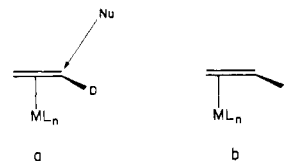
We have now analyzed the influence of an ML_n fragment on the reactivity of an olefin. In the η^2 geometry the olefin is deactivated. A distortion toward a η^1 geometry reactivates the double bond. We cannot commit ourselves on the amount of slipping needed. According to our calculations, the passage to activation occurs when the slipping is substantially nearer to a fully formed σ complex. But other geometrical changes in the olefin, not studied by us, certainly take place as the reaction proceeds. Thus activation may in fact occur earlier.

Furthermore, the nature of the transition state depends also on the nature of the nucleophile. Some nucleophiles may favor a reactant-like transition state, some a more product-like. Comparing the rate of reaction of a *cis*- and *trans*-butene in aminopalladation, Åkermark and co-workers have proposed that the reaction was more product-like,^{10c} whereas it seems that the oxypalladation is more reactant-like.^{10f}

Trans addition to olefins and oxymercuration^{10a,35} also proceed by complexation of the electrophile to the olefin. The orbital pattern of the intermediate in these reactions is similar to the one discussed in our work. Thus one can expect the same sort of behavior. Some calculations on nucleophilic addition to a triple bond in presence of a cation show a slight displacement of the cation.^{25c}

To what extent can our hypothesis be supported by experimental facts? The general pattern of reactivity, as one moves across a range of geometries and d electron counts, is certainly in accord with our analysis. Detailed proof of the importance of the slipping mode will not be easy to come by. Without eventual slipping the reaction cannot be completed. It is our contention that the η^2 to η^1 deformation is an essential and early component of any nucleophilic addition, but it will be difficult to get information on the reaction path detailed enough to probe this conclusion.

The general pattern of regioselectivity is in agreement with our hypothesis. If the olefin is substituted unsymmetrically with a donor group, the addition occurs preferentially to the substituted carbon^{3h-k} (see 34), if steric constraints are not of overriding



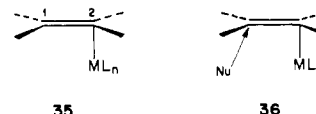
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importance. This is in accord with unsymmetrical olefin bonding. Structural data available show a shorter bond length between the metal and the unsubstituted carbon, **34b**.^{3j-k,18}

A striking example is provided by the work of Rosenblum and co-workers. Nucleophilic addition to $\text{CpFe}(\text{CO})_2(\text{vinyl ether})$ occurs easily and with high regioselectivity.^{3j} Only addition to the substituted carbon is observed. An X-ray crystallographic study of $\text{CpFe}(\text{CO})_2(\text{CH}_2\text{CHNMe}_2)^+$, very similar to the vinyl ether complex, shows that the iron to vinyl carbon distances differ by almost 0.7 Å, the shorter distance being the one to the unsubstituted carbon.^{3k}

Acceptor-substituted structures often also show a slipping of the olefin, again so that the shorter bond is to the unsubstituted carbon. So again the substituted carbon should be activated by the slipping mechanism, and yet it bears an acceptor substituent. Two effects are operating in opposite directions. The case needs further theoretical and experimental study. Perhaps the addition is still at that substituted site but less regioselective. This problem has been pointed out to us by T. A. Albright.

This unsymmetrically bonded olefin complex raises anew the problem of the stereochemistry of the addition. As long as the olefin is symmetrically coordinated, an addition of the nucleophile *cis* to the metal appears geometrically unlikely and *trans* addition is favored. The situation is quite different in the unsymmetrical structure. The interaction between the metal and the far carbon is rather weak. In other words the $\text{M}-\text{C}_1$ bond is activated (see 35), and a direct addition to C_1 , *cis* to the metal (see 36), could become more favorable.



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Despite the $\text{M}-\text{C}_1$ weakening we do not think that such a direct *cis* addition can happen. For an ML_5 and ML_4 complex the *cis* approach is highly hindered by the presence of the ligands on the

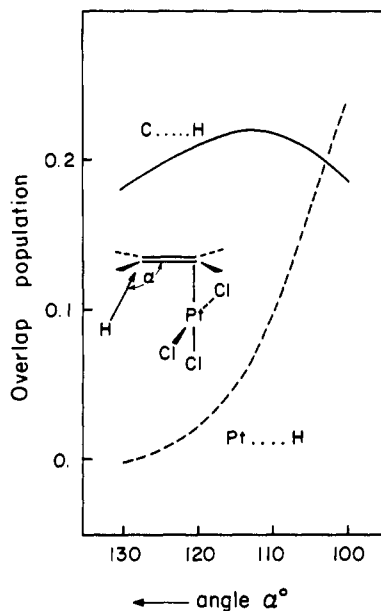


Figure 9. Overlap population with the nucleophile for a syn addition to a distorted Zeise salt (see 35) as a function of the approach angle α . The solid line corresponds to the carbon-nucleophile overlap population and the dashed line to that between the metal and the nucleophile.

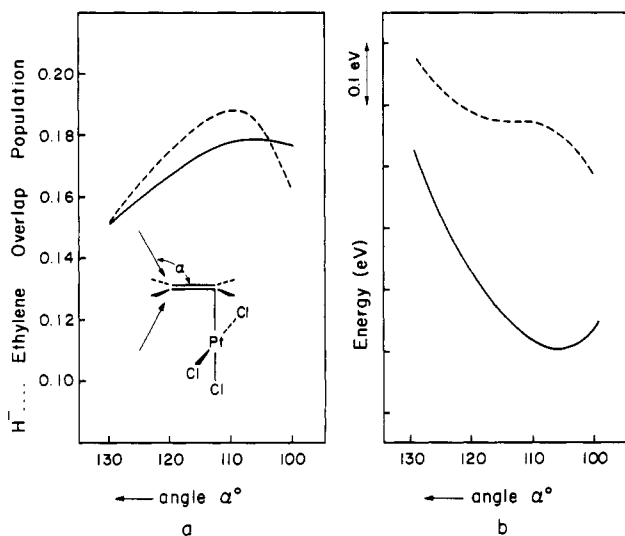
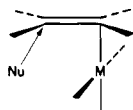


Figure 10. (a) $H \cdots C_2H_4$ overlap population for syn and trans addition to a distorted Zeise salt, as a function of the approach angle α . The solid line corresponds to trans addition and the dashed lines, to syn addition. (b) Energy for syn and trans addition.

metal. The steric hindrance is less severe for an ML_3 system if the transition-state geometry is based on a distorted upright complex, 37. This possibility was investigated.



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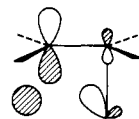
We do not wish to compare the factors favoring direct addition to the metal relative to addition to the carbon, primarily because we are uncertain of the reliability of the extended Hückel method for such bond-forming processes. So we limited ourselves to locations of the hydride where the interaction with the metal is negligible. Furthermore, for the sake of comparison with the trans attack we are compelled to keep the nucleophile-carbon separation at 2 Å. The model calculations were done with $PtCl_3^-$, varying the nucleophile-C-C angle, as was done for the trans addition.

Table III. Parameters Used in Extended Hückel Calculations

orbital	H_{ii}	exponents	
		ξ_1	ξ_2
Fe 4s	-9.17	1.9	
4p	-5.37	1.9	
3d	-12.7	5.35 (0.5366)	1.80 (0.6678)
Ni 4s	-6.86	2.10	
4p	-4.90	2.10	
3d	-12.99	5.49 (0.5663)	2.00 (0.6242)
Pd 5s	-7.32	2.19	
5p	-3.45	2.152	
4d	-12.02	5.983 (0.5535)	2.613 (0.6701)
Pt 6s	-9.08	2.55	
6p	-5.48	2.55	
5d	-12.59	6.01 (0.6334)	2.7 (0.5513)
W 6s	-8.26	2.341	
6p	-5.17	2.309	
5d	-10.37	4.982 (0.6940)	2.068 (0.5631)
Nb 5s	-10.1	1.90	
5p	-6.85	1.85	
4d	-12.1	4.08 (0.6401)	1.64 (0.5516)
C 2s	-21.4	1.625	
2p	-11.4	1.625	
O 2s	-32.3	2.275	
2p	-14.8	2.275	
P 3s	-18.6	1.60	
3p	-14.0	1.60	
Cl 3s	-30.0	2.033	
3p	-15.0	2.033	
H 1s	-13.6	1.3	

The $H \cdots Pt$ overlap population remains negligible compared to the $Pt \cdots$ carbon one, except for the region where the $H \cdots Pt$ becomes too short.

It is likely that the direct addition to the metal would follow another pathway comparing cis and trans addition. We see that the overlap populations $H \cdots$ olefin are comparable (Figure 10a) but that the trans addition is energetically favored (Figure 10b). Unfavorable interactions with the metal appear. Remember that the nucleophile interacts mostly with the LUMO of the substrate (see 38). The LUMO is antibonding between the far carbon



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and the metal. The nucleophile interacts in bonding fashion with the carbon, and consequently it must interact in an antibonding way with the metal. To put it another way, it is not favorable to approach close to a node of an orbital. So cis direct attack on the carbon is not favored and cis addition likely originates from addition to the metal followed by insertion of the olefin into the metal-nucleophile bond. This process has been already examined.^{25a} However a complete study of cis vs. trans addition, evaluating Nu-M vs. Nu-C bonding, must await better theoretical tools.

Acknowledgment. Our work was generously supported by the National Science Foundation through research Grant CHE 7828048. The permanent affiliation of O.E. is with the Laboratoire de Chimie Théorique, Orsay, France, and her stay at Cornell was made possible by grants from CNRS and NATO. We thank T. A. Albright for his comments on the paper, J. Jorgensen for the drawings, E. Stolz for the typing.

Appendix

All calculations were performed by using the extended Hückel method.³⁶ The values for the H_{ii} 's and orbital exponents are listed

(36) Hoffmann, R. J. *Chem. Phys.* **1963**, *39*, 1397-1412. Hoffmann, R.; Lipscomb, W. N. *Ibid* **1962**, *36*, 2179-2195; **1962**, *37*, 177-184, 2872-2883.

in Table III. The modified Wolfsberg-Helmholz formula was employed.³⁷ The following bond lengths were used: C-C (olefin), 1.38 Å (for the comparison of free carbonyl and free ethylene, the C-O bond length was 1.22 Å and the C-C bond length was 1.34 Å); C-H, 1.08 Å; N-H, 1.01 Å; P-H, 1.42 Å; FeC(CO) = 1.78 Å (Fe(CO)₅, Fe(CO)₄); FeC(CO), 1.75 Å (CpFe(CO)₂); FeH, 1.7 Å; CO, 1.14 Å; PtCl, 2.2 Å; PtN, 2.14 Å; Fe to center of C₂H₄,

(37) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* 1978, 100, 3686.

1.88 Å (Fe(CO)₅(C₂H₄), Fe(CO)₄(C₂H₄), Fe to center of C₂H₄, 2 Å (CpFe(CO)₂(C₂H₄); Pt to center of C₂H₄, 2 Å; Ni to center of C₂H₄, 1.88 Å; Pd to center of C₂H₄, 2 Å; Fe to center of Cp, 2.09 Å; Ni to center of Cp, 2.09 Å; C-C (Cp), 1.43 Å; FeP, 2.36 Å; NiP, 2.15 Å; NiC(CO), 1.82 Å. The angles in ML₅ and ML₃ were set to 90°. C(O)FeCO (equatorial) is 115° (Fe(CO)₄), PNiP is 110.5°, and HPH is 109.47°. The geometry of Cp₂WH(C₂H₄)⁺ was adapted from Cp₂NbC₂H₅(C₂H₄),²⁷ CpML = 125° (CpML₂, CpML). A pseudooctahedral geometry was assumed for CpML₂(C₂H₄). In Cp₂WH(C₂H₄)⁺ the angle CpWCp is 136°.

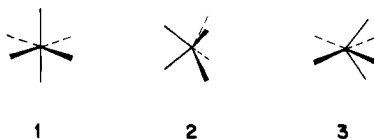
Deformations from Octahedral Geometry in d⁴ Transition-Metal Complexes

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Abstract: There are observed substantial deformations from octahedral symmetry in several diamagnetic d⁴ complexes of Mo(II) and W(II). Two of the compounds are of the stoichiometric type Mo(CO)₂L₂L'₂, and while both deform roughly along a C_{2v} mode, in one the carbonyls move together, while in the other they move apart. A detailed theoretical analysis of molecular distortions in ML₂L'₂L'' and ML₆ complexes is presented. It utilizes the additivity of effects of each ML₂, ML'₂, ML'' subunit and, within each unit, the angularly dependent σ- and π-donating or -accepting capability of the ligands. An M(CO)₂ subunit generates a double minimum in the total energy. In one of the minima the carbonyls move together and in the other they move apart. One of these minima is then deepened by the composite effect of the other ligands in the molecule.

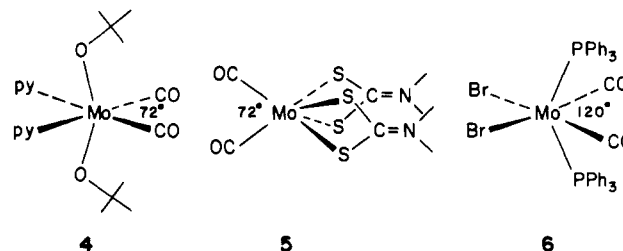
The preeminence of the octahedral geometry (1) in transition-metal six-coordination is assured by both steric and electronic factors.¹⁻³ Nevertheless, substantial departures from this poly-



hedral paradigm are well established. There is a reasonably well-populated class of trigonal prismatic complexes (2) as well as molecules intermediate in local symmetry between the octahedron and the trigonal prism.⁴ Still smaller is the group of complexes distorted toward a bicapped tetrahedron (3).⁵

Within the past year we noticed three crystal structures in which d⁴ six-coordinate complexes departed substantially from octahedral symmetry—Mo(O-*i*-Bu)₂(CO)₂(py)₂ (4),⁶ Mo(CO)₂[S₂CN(*i*-Pr)]₂ (5),⁷ and an older MoBr₂(CO)₂(PPh₃)₂ structure (6),⁸ the last

brought to our attention by J. L. Templeton.^{9,10} The schematic structures 4-6 do not do justice to, but only indicate approximately, the deformations of these molecules. Compounds 4 and 6 are



distorted toward a bicapped tetrahedron,¹¹ and 5 is a trigonal prism.

In fact most d⁴ complexes are octahedral or close to octahedral in the solid state.^{12,13} A Jahn-Teller deformation, albeit weak,

(1) Kepert, D. L. *Prog. Inorg. Chem.* 1977, 23, 1-65 and references therein.

(2) Pearson, R. G. "Symmetry Rules for Chemical Reactions"; Wiley: New York, 1976.

(3) Hoffman, R.; Howell, J. M.; Rossi, A. R. *J. Am. Chem. Soc.* 1976, 98, 2484-2492 and references therein.

(4) For a leading review, see: Wentworth, R. A. D. *Coord. Chem. Rev.* 1972, 9, 171-187.

(5) (a) Guggenberger, L. J.; Titus, D. D.; Flood, M. T.; Marsh, R. E.; Orio, A. A.; Gray, H. B. *J. Am. Chem. Soc.* 1972, 94, 1135-1143. (b) E. A. McNeill, Ph.D. Dissertation, Cornell University, 1975. (c) McNeill, E. A.; Scholer, F. R. *J. Am. Chem. Soc.* 1977, 99, 6243-6249. (d) Vancea, L.; Bennett, M. J.; Jones, C. E.; Smith, R. A.; Graham, W. A. *G. Inorg. Chem.* 1977, 16, 897-902.

(6) Chisholm, M. H.; Huffman, J. C.; Kelly, R. L. *J. Am. Chem. Soc.* 1979, 101, 7615-7617.

(7) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* 1980, 6568-6569.

(8) Drew, M. G. B.; Tomkins, I. B.; Colton, R. *Aust. J. Chem.* 1970, 23, 2517-2570.

(9) We are grateful to J. L. Templeton, University of North Carolina, for informing us of his work in this area.

(10) Another distorted d⁴ structure of W(CH₃)₂(PMe₃)₄ (Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* 1979, 926-927) is in fact a carbyne. (CH₃)W(CH₃)(PMe₃)₄: M. B. Hursthouse, private communication.

(11) The crystal structure of 6 is of limited accuracy. There appears to be an additional distortion from the idealized C_{2v} symmetry, a slight twist of the P-Mo-P unit around the axis which bisects C-Mo-C.

(12) (a) Ti(CO)₆ and Ti(N₂)₆, matrix-isolated species, are distorted to an unknown degree from O_h symmetry: Busby, R.; Klotzbücher, W.; Ozin, G. A. *Inorg. Chem.* 1977, 16, 822-828. (b) For references to the structures and chemistry of some d⁴ hexacyanides, see: Sharpe, A. G. "The Chemistry of Cyano Complexes of the Transition Metals"; Academic Press: New York, 1976; pp 44, 84-85. (c) For references to the structures and chemistry of some d⁴ hexahalides, see: Colton, R.; Canterford, J. H. "Halides of the First Row Transition Metals"; Wiley-Interscience: New York, 1969; pp 237, 238. Cotton, S. A.; Hart, F. A. "The Heavier Transition Elements"; Wiley-Halstead: New York, 1975; pp 60, 110. Griffith, W. P. "The Chemistry of the Rarer Platinum Metals: Os, Ru, Ir, and Rh"; Wiley-Interscience: New York, 1967; pp 53-57, 132-133, 231, 316.