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Ethylene Complexes. Bonding, Rotational Barriers, and Conformational Preferences

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Received September 19, 1978

Abstract: Rotational barriers and conformational preferences are a primary probe of bonding in olefin complexes. Such barriers in ethylene–ML_{2-5} are analyzed in terms of differential interactions between the frontier orbitals of the ML_n fragment and the ethylene π and π^*. It is found that the large barrier to internal rotation about the M-ethylene axis in ethylene–ML_2 complexes, favoring the in-plane orientation, is due to loss of overlap between ethylene π^* and an ML_2 b_2 orbital—the dominant interaction in these compounds. An analogous situation exists for rigid rotation in ethylene–ML_4 within the trigonal-bipyramidal geometry. A much lower energy pathway for this complex is found if rotation is accompanied by pseudorotation. The barrier in square-planar ethylene–ML_3 compounds of the Zeise's salt type, on the other hand, is largely set by steric factors which favor the upright geometry. Various strategies are devised to lower the barrier or reverse the conformational preference in these complexes. This may be accomplished by changing the electronic or steric properties of the ligands on the metal or the ethylene. Finally unsymmetrically substituted olefin complexes are examined. In the ML_3 case the metal–carbon bond to the carbon bearing the weaker donor or weaker acceptor should be the stronger or shorter one. In the ML_2 and ML_4 complexes of ethylene the acceptor effect is accentuated, that of the donor less important.

Few qualitative pictures have served the chemist as beautifully as the Dewar–Chatt–Duncanson model of metal–olefin bonding.[1] In the flowering of organometallic chemistry this model has proven a stimulus to much synthetic, structural, and mechanistic work. Not surprisingly, considerable theoretical effort has also been devoted to obtaining a detailed description of the electronic structure of transition metal–ethylene complexes.[2] One aspect of the chemistry of these complexes where the experimental information is relatively new, and yet provides the most direct evidence on the nature of the bonding, is the barrier to internal rotation about the metal–olefin axis. This is the primary focus of the present study,[3] which forms part of a general analysis of polyene–ML_n rotational barriers.[4]

The problem then that we will attack is the origin of the barrier to internal rotation in the molecules i–iv. The interre-

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lationship between the various coordination geometries will prove to be illuminating. We will rationalize the observed equilibrium geometries and the magnitude of the rotational barriers in these complexes. The understanding obtained in the process will be used to explore ways in which these barriers may be modified by varying substituents on the ethylene or the metal, or by sterically imposed geometrical deformations. A specific problem of asymmetry in metal–olefin bonding will be studied at the end. The discussion presented in this paper will serve as an introduction and guide to a general analysis of polyene and cyclopolyene ML_2, ML_4, and ML_5 complexes.

ML_{2-5} Fragments

A natural framework for the analysis of rotational barriers is found in the conceptual construction of the complex from ML_n and olefin fragments. The MOs of the ML_n fragments are first developed and then interacted with the levels of the ethylene in several extreme geometries which correspond to the end points of a rotational process. Standard perturbation theoretic arguments are used to pinpoint the differences in the conformations considered. Our actual calculations are of the extended Hückel type, with parameters specified in the Appendix.

Detailed discussions of the frontier orbitals of ML_n fragments have been given elsewhere.[5] Here we shall describe only their salient features, emphasizing those orbitals which eventually lead to a conformational distinction. The valence orbitals of four ML_{2-5} fragments are shown in Figure 1. Three of the fragments bear carbonyl ligands, the fourth a C_{2v} chloride intended as a precursor for the important class of olefin complexes of the Zeise's salt type. The C_{3v} pyramidal ML_3 fragment, and the barriers it engenders, has been discussed elsewhere.[4] The four fragments in Figure 1 are arranged not in order of coordination number, but to exploit a similarity to be discussed below, between ML_3 and ML_5 on one hand, and ML_2 and ML_4 on the other. The electron counts will also vary with the actual complex, but the typical situations are antici-

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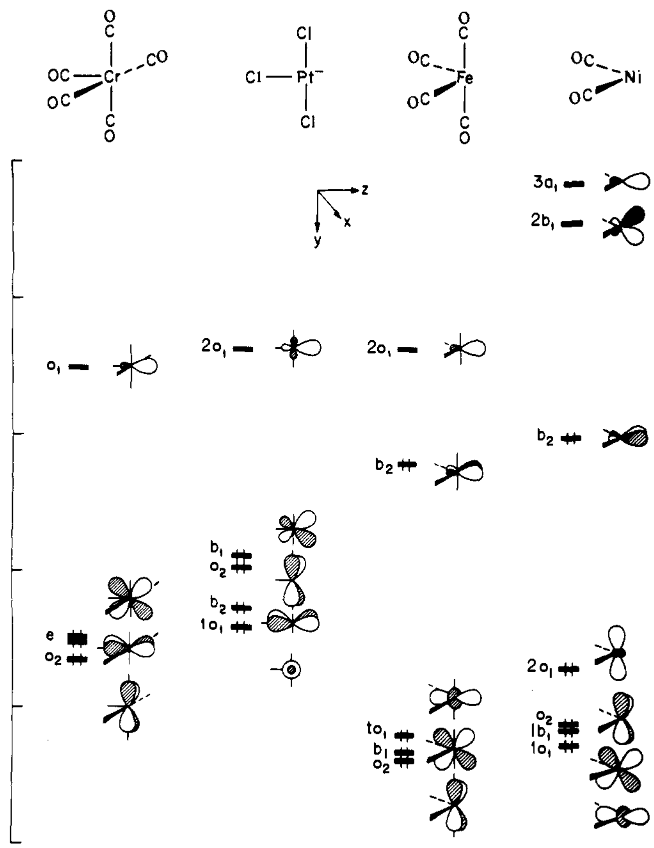


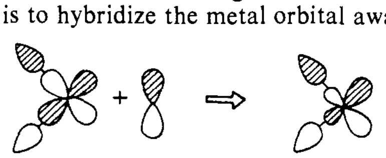
Figure 1. Important valence orbitals of some metal fragments. The energy scale markings are in eV.

pated in Figure 1 by specifying a d^6 ML_5, d^8 ML_3 and ML_4, and d^{10} ML_2.

For each of the fragments there is a high-lying a_1 orbital comprised mainly of z^2, s, and z on the metal. In the ML_{2-4} fragments there is also a filled a_1 orbital at low energy. These orbitals are cylindrically symmetrical and consequently cannot give rise to a barrier of rotation. Aside from the high-lying a_1 orbital the fragments differ, and yet certain important similarities will be found. We discuss each case in sequence.

In the $Ni(CO)_2$ fragment there is a nest of four low-lying, occupied levels. There is only a small energy difference between two of these, $2a_1$ and a_2. Since both have δ symmetry with respect to an incoming polyene, the two when taken together will not lead to a significant conformational preference. This leaves us with $1b_1$ and b_2. There is a large energy gap between them. If a polyene possesses a π orbital which is antisymmetric with respect to the yz plane (see the coordinate system in Figure 1), then it will interact with b_2. Upon rotation by 90° this π orbital will interact with $1b_1$. Because of the large energy gap between $1b_1$ and b_2, the polyene π level will preferentially interact with one of these orbitals, depending on whether its energy lies above b_2 or below $1b_1$ and the number of electrons in the system.

There is also an important difference in the spatial extent or hydridization of b_2 and $1b_1$. The carbonyl σ orbitals interact with xz in an antibonding manner in b_2, which is the reason for its high energy. However, the metal x orbital mixes in in such a way as to alleviate the antibonding character. The net effect, shown in **1**, is to hybridize the metal orbital away from the



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attached carbonyls and toward the incoming polyene. On the other hand b_1 is made up mainly of metal yz with some carbonyl π^* mixing in a bonding fashion. There is essentially no metal y that mixes into this level. This means that the overlap of b_2 with a polyene π orbital will be larger than that between $1b_1$ and π. Figure 1 shows another high-lying orbital which we have labeled $2b_1$. It is mainly carbonyl π^* (81%), although we have only shown the metal component. This orbital is hybridized in a sense similar to b_2—bonding to metal x, antibonding to metal yz.[5d] Because of its relatively high energy and small metal character it will not be a significant factor in setting conformational preferences. To reiterate, it is the b_2–$1b_1$ difference in energy and hybridization that will set a conformational preference in polyene–ML_2 complexes. We shall see examples of this in action in the following sections of this paper.

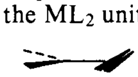
There is a marked resemblance between the valence orbitals of the $Ni(CO)_2$ and $Fe(CO)_4$ fragments, as seen in Figure 1. For $Fe(CO)_4$ again there is a large energy and hybridization difference between b_1 and b_2. The $2a_1$ orbital ($x^2 - y^2$) in $Ni(CO)_2$ is destabilized tremendously with the addition of two axial ligands in $Fe(CO)_4$ and does not even appear in Figure 1. To stress the similarity between the valence orbitals in these two fragments a slice of the wave functions in the yz plane for $Ni(CO)_2$ and $Fe(CO)_4$ is presented in Figure 2. The hybridization inherent in b_2 but absent in b_1 can clearly be seen in both cases. Notice also that there is almost no difference in the shapes of the orbitals of these two fragments around the metal atom, with the exception of $2a_1$ in $Ni(CO)_2$, which does not have a partner in $Fe(CO)_4$.

The $Cr(CO)_5$ fragment in Figure 1 is most clearly related to an octahedral complex.[5a] There is a lower set of three levels, e + a_2, descended from the octahedral t_{2g}. At much higher energy (not shown in Figure 1) is $x^2 - y^2$, which together with $1a_1$ formed the e_g in ML_6. The hybridization of $1a_1$ has been discussed in detail elsewhere.[5a] The orbitals of $PtCl_3^-$, shown in a contour diagram in Figure 3, are similar. At low energy there are three orbitals, b_1, b_2, and a_2, which correspond to e + a_2 in $Cr(CO)_5$. The $1a_1$ orbital can be viewed as derived from $x^2 - y^2$ in $Cr(CO)_5$, greatly stabilized by removal of two ligands. It now lies low in energy and is occupied by the two electrons added in going from $Cr(CO)_5$ to $PtCl_3^-$. This $1a_1$ level, of course, becomes the familiar z^2 orbital in Zeise's salt, using the more conventional coordinate system. Note that the $PtCl_3^-$ fragment bonding orbitals are at higher energy than those of the three carbonyl-containing fragments. This is a consequence of the π donation of the chloride ligand relative to the acceptor character of the carbonyl.

The important point to note is that there is little or no difference in hybridization or energy between b_1 and b_2 in the ML_5 and ML_3 fragments [in $Cr(CO)_5$ they are degenerate]. There is a substantial difference between this orbital pair in $Fe(CO)_4$ and $Ni(CO)_2$. With this in mind we now turn our attention to the ethylene complexes. The reader is referred to an important paper by Mingos[6] in which ideas similar to those presented here were independently developed.

Ethylene–ML_2 Complexes

A large number of X-ray structures[7] have shown that the most stable conformation of ethylene–ML_2 complexes is the trigonal "in-plane" one in which the ethylene carbons lie in the plane of the ML_2 unit as in **2**. The structures typically show



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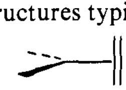

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small twists of the olefin away from the plane. This appears to be the result of crystal packing forces and minimization of

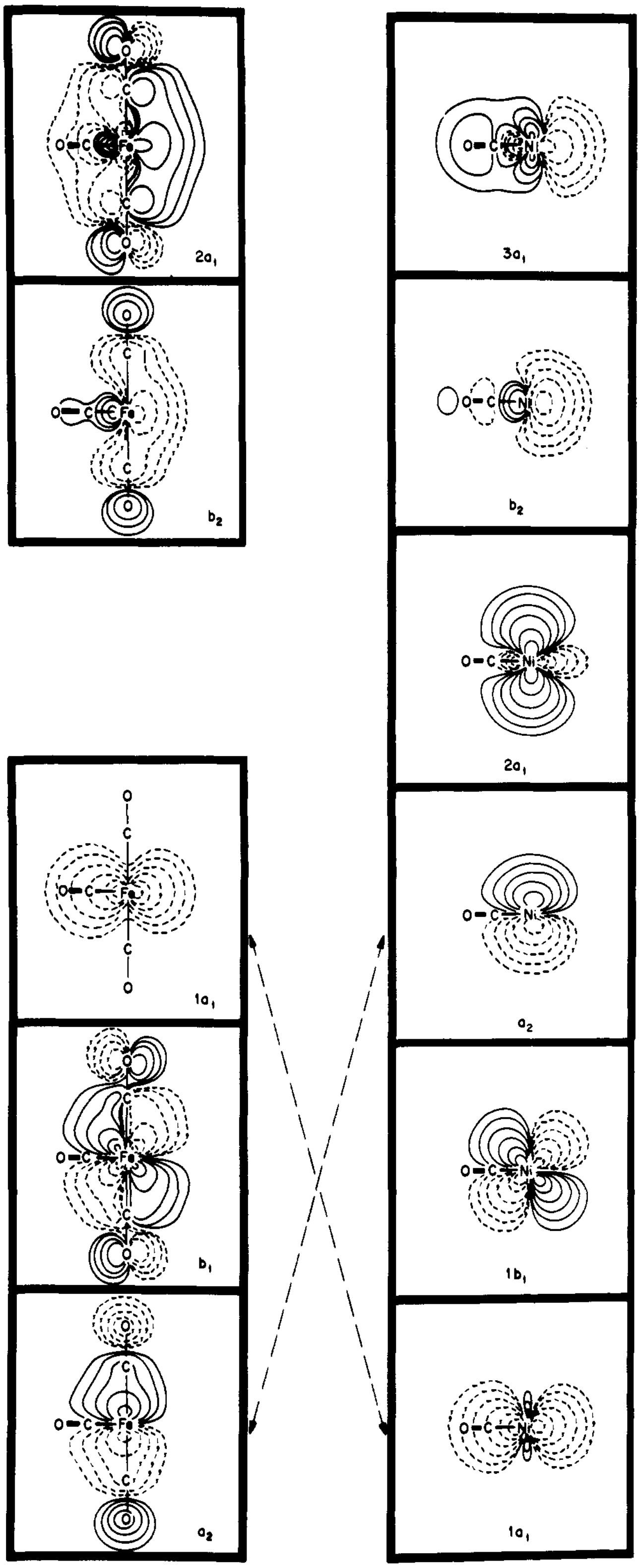


Figure 2. Contour diagram of the valence orbitals of $Fe(CO)_4$ (left) and $Ni(CO)_2$ (right). The values of ψ plotted are 0.4, 0.2, 0.1, 0.05, and 0.025. The solid lines indicate positive phase, the dashed lines negative. The orbitals are shown in the yz plane, except for b_2 and a_2, where a slice parallel to that plane and 0.5 Å away was taken. The $2b_1$ orbital of $Ni(CO)_2$ is omitted.

intramolecular close contacts.[7a] Replacement of the methylene units by heteroatoms causes no change in the conformation. The ML_2 unit lies always approximately in the plane of the π system. Examples of this are known for ML_2 complexes of imines, azo compounds, oxygen, ketones, etc.[8] The trigonal

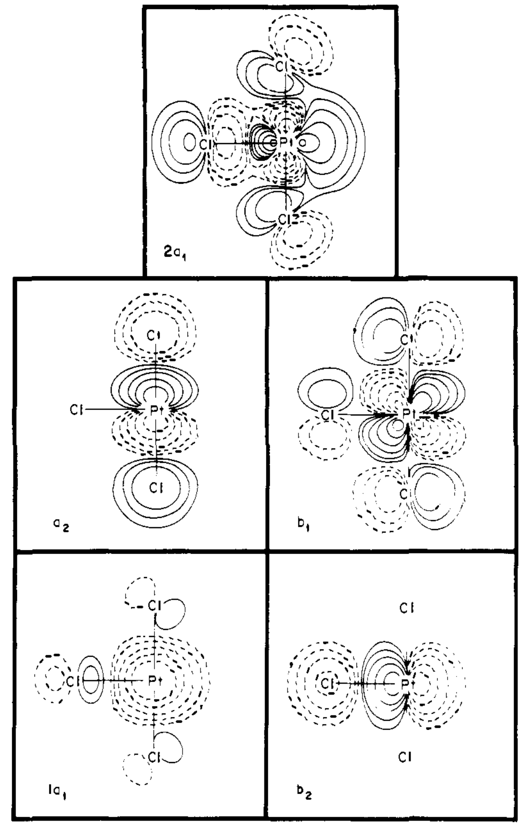


Figure 3. Contour diagram of the valence orbitals of $PtCl_3^-$. The ψ values and planes are given in the caption to Figure 2.

conformation is also found for all known acetylenes[9] and allene[10]-ML_2 complexes. Experimental estimates[7a,f,11] have indicated a barrier of 18–25 kcal/mol on going from the in-plane conformation, **2**, to the "upright" one, **3**, for a d^{10} metal complex.

To understand this large conformational preference consider the interaction of an ethylene with the ML_2 fragment in the two extreme orientations, **2** (in-plane) and **3** (upright), in Figure 4. In both conformations the ethylene π donor orbital, a_1, interacts with $1a_1$ and $3a_1$ of the ML_2 unit. Since these orbitals are approximately cylindrically symmetrical, the orbitals after interaction do not change much in energy on going from **2** to **3**. The $2a_1$ and a_2 orbitals of the ML_2 are essentially nonbonding and do not give rise to a conformational preference. The major bonding for trigonal ethylene-ML_2 complexes occurs between b_2 and the ethylene π^* orbital which is also of b_2 symmetry. However, upon rotation to **3** the interaction with b_2 is lost since the π^* orbital is now of b_1 symmetry. Now π^* forms a bonding combination with $1b_1$ of the ML_2 fragment. The $2b_1$ orbital (see Figure 1) does not significantly interact with the $1b_1 + \pi^*$ bonding combination for the reasons mentioned in the previous section. For reasons of clarity we have omitted it from Figure 4. There is a great difference between stabilization of b_2 in **2** vs. $1b_1$ in **3**. In the usual perturbation theoretic expression[12] for the stabilization energy:

$$\Delta E = \frac{|H_{ij}|^2}{E_i - E_j} \qquad (1)$$

the in-plane conformation is favored through the denominator (b_2 is above $1b_1$ in the fragment) and the numerator (b_2 is better than $1b_1$ for overlap with π^*).

In a model calculation on ethylenenickel dicarbonyl, with an angle between the carbonyls of 100°, we calculate a barrier of 23.6 kcal/mol. This corresponds to rigid rotation of the ethylene unit with respect to $Ni(CO)_2$. The hydrogens of the

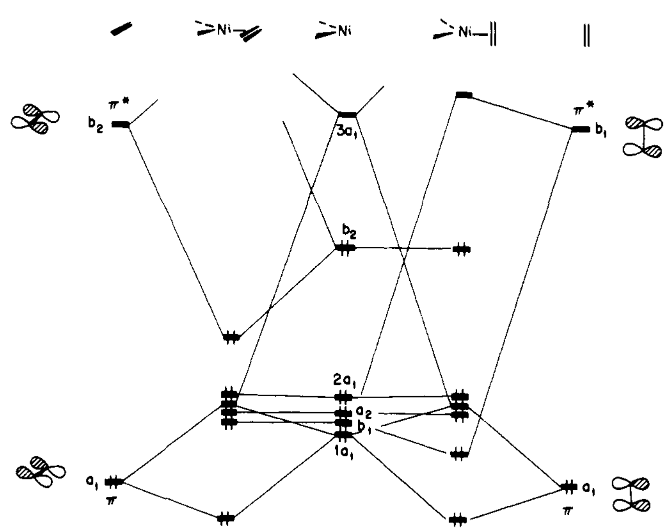
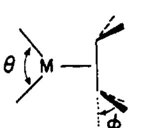


Figure 4. Interaction diagram for $(CO)_2Ni(ethylene)$ in in-plane (left) and upright (right) conformations.

ethylene have also been held coplanar with the carbon–carbon bond up to now. In fact the groups substituted on the ethylene are always bent back,[7] as shown in **4**. If we hold θ again con-



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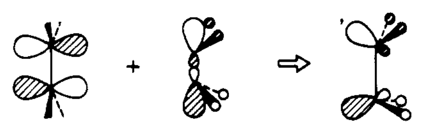
stant at 100° but let ϕ assume its average value[7a] of 25°, then the calculated barrier rises to 33.7 kcal/mol. The reason for this increase in the barrier is twofold. When the hydrogens are bent back, π^* mixes in a higher lying σ antibonding level, **5**, to give **6**. The π^* orbital is hybridized toward the ML_2 unit by

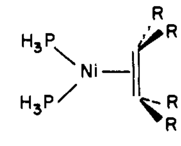


5 **6**

this mixing.[13] This increases the overlap of b_2 with π^* and also lowers it in energy. Both of these factors contribute to the increase in the barrier.

One reason that the upright geometry is so energetically unfavorable is due to the high-lying, nonbonding b_2 level (see Figure 4). Its energy can be lowered by allowing the L–M–L angle, θ, in **4** to increase in the upright conformation. In ethylenenickel dicarbonyl θ for the in-plane geometry was optimized to be 112°. However, in the upright conformation θ opens up to 130° (ϕ was held constant at 25°). The rotational barrier now drops back to 23.3 kcal/mol. A calculation on ethylenenickel biphosphine, perhaps a better model for the available complexes, yields similar results. We calculate θ to be 114 and 126° in the in-plane and upright conformations, respectively. The barrier with ϕ held constant at 25° was 21.6 kcal/mol. This is in reasonable agreement with experimental estimates.[7a,f,11]

The barrier of rotation in these complexes can be tuned to some extent. In particular, is there a possibility whereby the electronic structure is modified to the extent that **3** becomes more stable than **2**? Let us first change the substituents on the olefin. In the series of molecules **7** the R groups were bent back 25° in each case and θ was allowed to vary for both conformations. These calculations show that there is a relationship between the energy of π^* and the barrier height. As the energy



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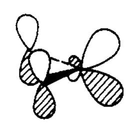
	R	π*	calc. barrier
7 a	CN	−10.7 eV	23.7 kcal/mol
b	H	−8.6	21.6
c	Cl	−6.2	14.6

of π^* goes up from **7a**, R = CN, to **7c**, R = Cl, the barrier decreases. In theory one could push the energy of π^* so high that there would be no barrier in going from the in-plane to the upright conformation. However, since the b_2 π^* interaction accounts for so much of the bonding in these complexes, it is doubtful whether one could prepare such a complex with superlative π donors on the ethylene and still have it bound.

Another strategy to lower the barrier in these complexes is to enlarge the L–M–L angle θ. This will decrease the energy and the p admixture in the b_2 (see **1**), thus making it more like $1b_1$. In test calculations the rotational barrier does fall almost linearly with increasing θ, down to ~15 kcal at θ = 130°. Thus ligands designed to enforce a large bite size[14] should decrease the olefin rotational barrier.

Still another way to minimize the b_2–$1b_1$ difference is by the use of ligands which are good π donors but poor σ donors. This will cause the energy of $1b_1$ to rise while keeping the energy of b_2 relatively constant. Furthermore, $1b_1$ will be hybridized in a manner analogous to b_2 as shown by **8**. Such π-donor



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substituents could also be viewed as pushing the system part way toward $L_2M(C_2H_4)^{2-}$. In such a hypothetical molecule a two-electron stabilizing b_2, π^* or $1b_1$, π^* interaction would be changed into a four-electron destabilizing one. The most stable conformation should then be the one with least interaction,[15] i.e., the upright one. A calculation in fact showed it to be more stable by 78 kcal/mol. Another way to see this result is to think of full donation of an electron pair from ML_2 to ethylene, converting the latter into a bidentate $C_2H_4^{2-}$ ligand. Then the neutral compound $L_2Ni(C_2H_4)$ becomes formally a d^8 complex, "square planar", whereas $L_2Ni(C_2H_4)^{2-}$ is d^{10}, "tetrahedral" as expected.

Acetylene–ML_2, or for that matter any ML_2 complex of an organic ligand characterized by an orbital similar to π^*, will also have a large rotational barrier, for the same reasons that were outlined above. For example, a 28.6 kcal/mol barrier is calculated for acetylenenickel dicarbonyl. This value corresponds to bending the hydrogens back 35°. Again θ opens from 112° in the in-plane geometry to 130° in the upright conformation. The reader is referred to an important qualitative analysis of L_2M(acetylene) bonding by Greaves, Lock, and Maitlis.[16]

Allene–ML_2 complexes also are predicted to have large barriers. Here the ML_2 unit can migrate from one π bond to another, which can give an overall result of rotation if the allene is symmetrical. We will discuss this fluxional process elsewhere.

Ethylene–ML_4 Complexes

We emphasized the analogy between the orbitals of the ML_2 and C_{2v} ML_4 fragments in a previous section. Referring back to Figure 1, there is a high-lying b_2 orbital on the ML_4 fragment and a b_1 orbital at considerably lower energy. This, as was the case for ethylene–ML_2 complexes, will cause a marked

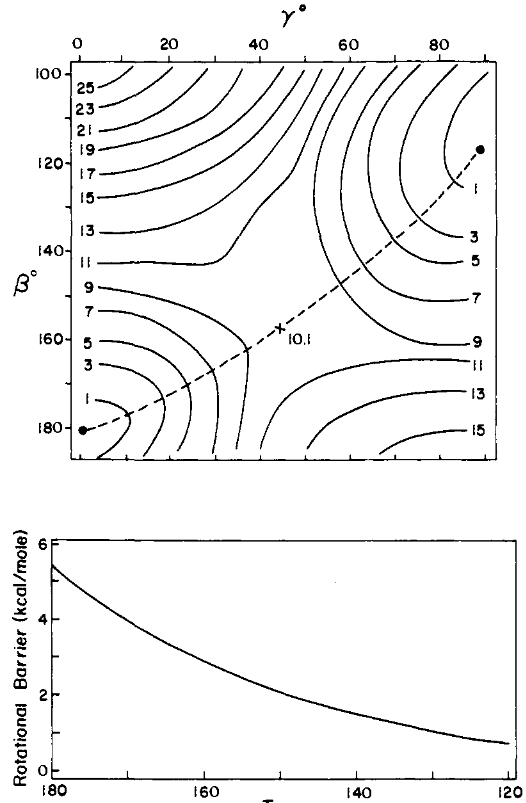
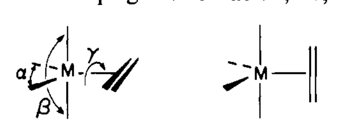


Figure 5. (a) Energy contours, in kcal/mol, for the coupled rotation-pseudorotation pathway in $Fe(CO)_4$(ethylene). The angles are defined in **9**. (b) Rotational barrier in a square pyramidal $Fe(CO)_4$(ethylene) as a function of the trans basal angle τ, defined in **13**.

preference for the coordinated ethylene to lie in the equatorial plane as in **9**, over the upright orientation, **10**, where the eth-



9 **10**

ylene lies along the axis. All of the available structural data is consistent with this, not only for coordinated ethylenes,[17] but also acetylenes,[18] and compounds where a heteroatom has been substituted for one or both of the methylene units.[19] Likewise, there are a number of compounds[20] with two or three ethylenes which conform to the orientation in **9** rather than **10.**

In a model compound, ethyleneiron tetracarbonyl, holding the angle between the equatorial carbonyls, α, and axial carbonyls, β, constant at 90 and 180°, respectively (the ethylene hydrogens were bent back 20°), **9** was calculated to be 32 kcal/mol more stable than **10.** An ab initio calculation obtains 31 kcal/mol for the same process.[20] However, NMR measurements put the rotational barrier (or the barrier to ligand-ligand interchange) at ~10–15 kcal/mol for substituted ethylene- or acetylene-ML_4 complexes.[21] Given the approximate nature of our calculations, we would not have been unhappy with the disparity between the experimental and theoretical numbers. Yet the situation is better than that. The reason for most of the discrepancy is that we have held α and β constant during the rotational process. If we vary these angles, as well as the angle of rotation, γ (γ = 0° for **9** and 90° for **10**), then it is found that the ethyleneiron tetracarbonyl complex undergoes a pseudorotational process in concert with rotation. This is shown schematically by the sequence of eq 2.

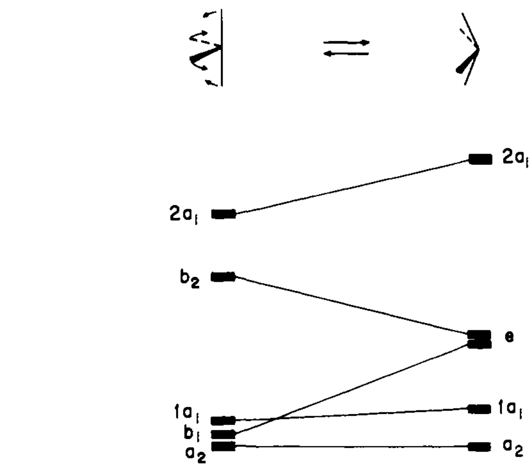
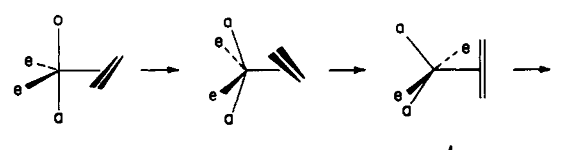


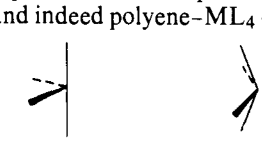
Figure 6. Schematic evolution of the orbitals of an $M(CO)_4$ fragment along a Berry pseudorotation coordinate.

 (2)

11 **12** **11′**

Independent variation of the three angular variables led to the surface shown in Figure 5a. Each point for β, γ on this surface represents an optimum value of α. The dashed line corresponds to the interconversion of **11** to **11′**. The transition state, **12**, is given by a cross in the figure. The optimum ground-state structure, **11**, was calculated to have α = 118°, β = 181°, γ = 0° while **12** is defined by $\alpha = \beta$ = 157°, γ = 45°. Our calculations give an activation energy of 10 kcal/mol for this pseudorotation-rotation itinerary. Ab initio calculations using assumed geometries along a similar path have given a barrier of 12 kcal/mol.[2p]

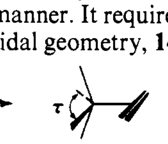
It is instructive to examine this process in greater detail. Our previous discussion of the ML_4 fragment kept it in a C_{2v} geometry **13a**. The pseudorotation requires examination of a C_{4v} fragment **13b**, and indeed polyene-ML_4 complexes, to be ex-



13a **13b**

amined later, often possess ML_4 fragment geometries intermediate between these two extremes. The evolution of the fragment orbitals along the pseudorotation itinerary, Figure 6, is easily understood. The a_2 and a_1 levels remain approximately constant in energy along the distortion coordinate. The slight rise for $2a_1$ is a result of increased antibonding from the carbonyl σ levels. The most important change is that b_2 drops in energy while b_1 rises to form an e set. As the bond angle α between the equatorial carbonyls increases, the antibonding between carbonyl σ and metal xz decreases. Likewise, as the angle between the axial carbonyls β is decreased, antibonding between carbonyl σ and metal yz is turned on. Consequently, b_1 rises in energy.

Returning to the ML_4-ethylene complex, let us examine the barrier in a stepwise manner. It requires 7.5 kcal/mol to distort **11** to a square pyramidal geometry, **14**, with γ held at 0°, and

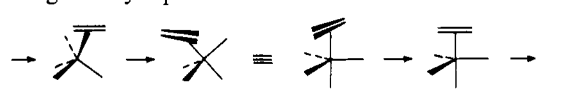
11 →  → **12**

14

a further 2.6 kcal/mol to rotate the ethylene from **14** to **12.** Remembering the crucial role of the b_2 orbital, we may refer back to Figure 6 and note that it becomes a less effective donor in the square pyramidal geometry. The b_2 orbital also loses some of its metal x character as α increases. Both of these factors are responsible for the larger initial increment on going from **11** to **14.**

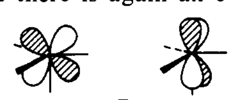
The energetics of the next step, olefin rotation over a square pyramidal fragment, have little to do with π bonding. Note that in the C_{4v} fragment b_2 and b_1 merge into an e set, whose overlap with ethylene π^* is independent of conformation. Now it is the ethylene π whose repulsive interactions with other orbitals vary somewhat with orientation. In both **14** and **12** π interacts approximately equally with $1a_1$ and $2a_1$. But in conformation **12** an additional repulsive interaction with the filled a_2 orbital is turned on. It is this two-orbital-four-electron repulsion which causes the barrier. In Figure 5b we see that this barrier is somewhat sensitive to the square-pyramidal geometry with which we start. As the trans carbonyl angles, τ (see **14**), are increased, the barrier rises. This is due to the fact that at large values of τ there is not only significant overlap of π with metal xy in a_2 but also with carbonyl π^*. We shall see below that these same factors are responsible for the rotational barrier in ethylene–ML_5 complexes.

Prompted by some experimental studies of Faller and co-workers,[22] we have also considered a turnstile rotation mechanism given by eq 3 for the rotation and interconversion of

11 →  (3)

15 **16a** **16b**

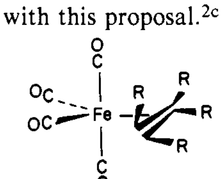
carbonyls. It is found that going from **11** to **15** requires 14.4 kcal/mol. Furthermore, it appears that **16a,** rather than **15,** represents a local transition state for this rearrangment mode. The sixfold barrier in going from **16a** to **16b** is very small—0.3 kcal/mol (with **16b** more stable). Experimental data is consistent with a small barrier for an axial ethylene.[21e] The stabilization of **16a** or **16b** is due to the fact that in the C_{3v} $Fe(CO)_4$ fragment there is again an e set, **17,** which can



17

back-bond with ethylene π^* (the interested reader is referred to ref 5a for a detailed discussion of the orbitals for this fragment). The e set in **17** is stabilized considerably by back-bonding from carbonyl π^*, making the energy gap between ethylene π^* and **17** much larger than the b_2–π^* gap in **11.** Also the hybridization present in b_2 is lost in **17.** Because of the approximations made within the extended Hückel method, we cannot conclusively rule out eq 3 as the low-energy rearrangement mode. However, the ab initio calculations of Veillard and co-workers[2p] have put the barrier of **11** to **16a** at 21 kcal/mol, also a high value.

The substitution of either π donors or π acceptors on ethylene raises the barrier for the combined rotation–pseudorotation by our calculations. There is some experimental data which is consistent with this proposal.[2c] In **18** the R groups



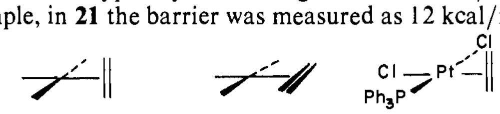
18

	R	calc. barrier
18 a	H	10.1 kcal/mol
b	Cl	11.9
c	CN	12.8

were bent away from the metal by 20° in each case. Instead of calculating the full surface for **18b** and **18c** we have only optimized α for the trigonal bipyramid (conformation **11**) and τ for the square pyramidal structures corresponding to **12** and **14.** Using the reasoning of the previous section, one might have expected the donor substitution in tetrachloroethylene to lower the barrier instead of raising it. So it does for a pure rotation, but the situation for the combined rotation–pseudorotation is more complicated. In **18c** most of the barrier is contained within the first step, distortion to the square pyramid. On the other hand, in **18b** the barrier is mainly due to rotation within the square-pyramidal geometry. There are a number of reasons for this trend and we do not wish to take the space here to discuss it in detail. Suffice it to say that, as the bonding with ethylene π^* becomes more important, the energy loss on going from **11** to **14** is greater. Likewise, as the energy of ethylene π is increased, the repulsion between it and a_2 increases in going from **14** to **12.**

Ethylene–ML_3 Complexes

X-ray structures of Zeise's salt and related square-planar ethylene–ML_3 complexes,[23] as well as complexes of acetylene,[24] consistently show the olefin oriented in or near the upright geometry, **19,** rather than the in-plane conformation, **20.** The barrier of rotation in these complexes as measured by NMR[25a–d] is typically in the range of 10–20 kcal/mol. For example, in **21** the barrier was measured as 12 kcal/mol.[25a]

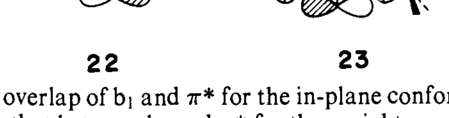


19 **20** **21**

We will argue that the main factor which determines the equilibrium orientation of the olefin in these complexes is steric and not electronic. This has also been the conclusion of the Johnson and Lewis group from their experimental studies,[25a] and of some other theoretical work as well.[2r] Consider the interaction diagram for Zeise's salt, in the upright conformation **19,** in Figure 7. The major bonding interactions in this complex are between $2a_1$ and ethylene π along with back-bonding from b_2 into π^*. Upon rotation to the in-plane conformation it is now b_1 which will interact with π^*. In the ML_2 fragment there was a large energy and hybridization difference between b_2 and b_1. But, as one can see from Figure 1 or 7, there is essentially no hybridization and only a small energy difference (0.4 eV) for the $PtCl_3$ fragment. Furthermore, since b_1 lies marginally higher in energy than b_2, one might even suppose, as has been noted previously by Lewis and co-workers,[25a] that the most stable conformation would be the in-plane one.

This is not so. The calculations reproduce the correct upright geometry, but appear to overestimate the barrier considerably, yielding a value of 34 kcal/mol.[26] This will be reduced considerably when the constraint of rigid rotation is removed, but for the moment let us proceed with the analysis of the barrier.[27]

Essentially all of this barrier comes from interactions of the cis chlorines with the ethylene. For example, approximately 70% of the barrier is due to the increased repulsion between ethylene π (and the carbon–carbon σ bonding orbital) and a relatively high-lying, filled orbital comprised mainly of Cl lone pairs, **22.** About 10% of the barrier is a consequence of the fact



22 **23**

that the overlap of b_1 and π^* for the in-plane conformation is less than that between b_2 and π^* for the upright geometry (the

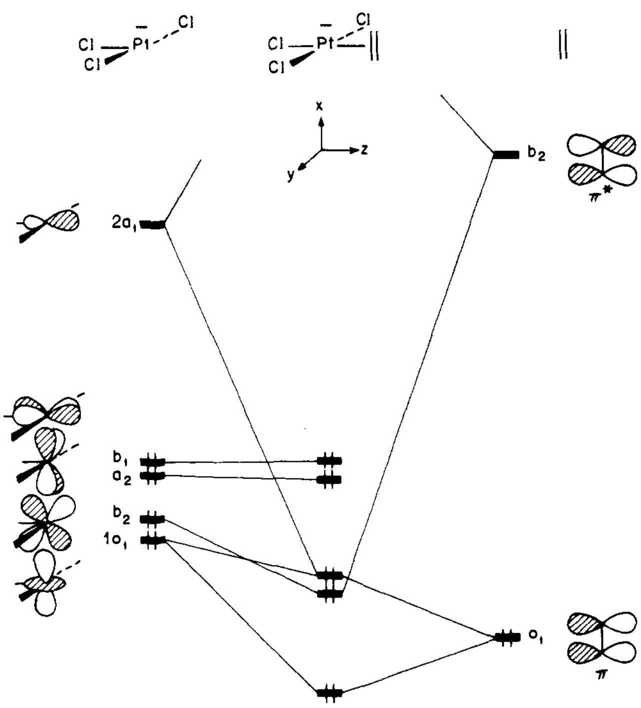
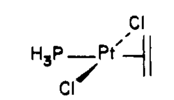


Figure 7. Interaction diagram for $PtCl_3(ethylene)^-$.

group overlaps between these fragment orbitals were 0.0903 and 0.1503, respectively). Behind this difference is not a hybridization change at the metal, but the fact that b_2 is not simply a *yz* orbital, but contains Cl p orbitals mixed out of phase. These then diminish the net group overlap with the π^*, as shown in **23**. The remaining barrier contributions arise from similar interactions. Note that there is no fundamental distinction between steric and electronic effects, and indeed we could have termed both of the factors above electronic. But, if steric interactions are to be found anywhere in one-electron molecular orbital calculations, it is in four-electron repulsions and secondary ligand-ligand interactions.

An obvious way to diminish the barrier is to allow the cis chlorines to bend back, away from the ethylene, for the in-plane conformation. If this is done, they bend back 7°, and the barrier is reduced to 22 kcal/mol. The extended Hückel calculation still overestimates the barrier.

The steric sources of the barrier can be probed by varying the bulk of the trans or cis ligands. Putting a phosphine in the trans position, as in **24**, raises the barrier to 27 kcal/mol. However, in the isoelectronic compound, **25**, where the rela-



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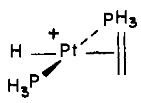


25

tively small hydride occupies the trans position, the calculated barrier is lowered to a small 5 kcal/mol. This low barrier is solely due to the ability of the phosphine ligands to bend toward the hydride in the in-plane conformation, since the barrier was calculated to be 31 kcal/mol with rigid rotation. Similarly, substitution of hydrides cis to the olefin lowers the rotational barrier, an important consideration in the mechanism of the ethylene insertion reaction.[28] It should also be noted that, if the hydrogens on ethylene are not bent back away from the metal, as is experimentally the case for Zeise's salt,[23a] then a maximum is reached on the potential surface for rotation somewhat before the in-plane orientation is reached[20] (this corresponds to a rotation of 67° in our calculations). At this point the hydrogens eclipse these cis chlorines. However, this maximum disappears when the hydrogens are bent back.

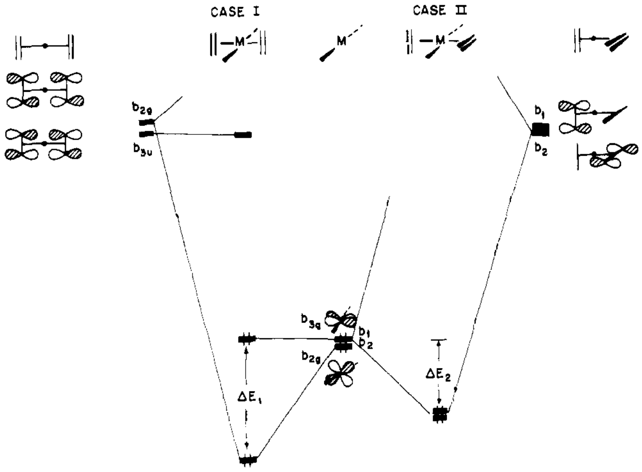
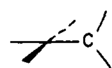


Figure 8. Interaction diagram for two conformations of a trans $PtCl_2(ethylene)_2$.

Our notion that the barrier in square-planar ethylene-ML_3 complexes is set by steric rather than electronic factors is further supported by the fact that most square-planar carbene-ML_3 complexes adopt the conformation given by **26** rather than **27**.[29] The carbene ligand has a donor function **28**



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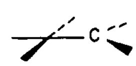


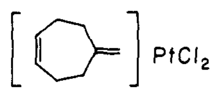
27

28

29

which is topologically equivalent to the ethylene π orbital and an acceptor p orbital, **29**, equivalent to π^*. If there would be electronic advantages to bonding with b_2, then one would expect **27** to be more stable. But this conformation is sterically more encumbered than **26**. One carbene complex does indeed adopt the "wrong" conformation, **27**, by virtue of the fact that it is tied into a five-membered heterocyclic ring which also incorporates the metal.[30]

Anytime that one has a steric rationale for a preferred conformation one should be able to think of a steric strategy for reversing the conformational preference, for making the molecule uncomfortable in the previously favored geometry. Molecules where a Zeise's salt-type upright conformation is impossible may be at hand, for instance, the 5-methylenecycloheptene complex,[31] **30**, in which, if it is monomeric, both ethylenes cannot be upright. It also should be possible to make molecules of the type **31**, where, so to speak, the steric table is turned on the upright conformation. **32** appears to be less



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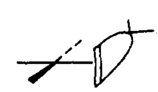

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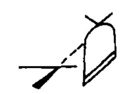
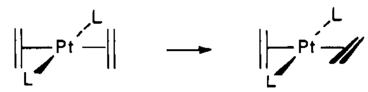


32

hindered. Still another maneuver, mentioned above, is to try to put sterically small groups trans to the olefin.

Another probe of the source of the orientational preference may be found in bis(olefin) complexes, and takes advantage of the fact that two ethylenes, trans to each other, will prefer to bond with orthogonal metal orbitals rather than the same one. Consider the two cases shown in Figure 8. In case I the two olefins are oriented in the normal upright geometry. The ethylene π^* orbitals produce two combinations, b_{3u} and b_{2g} in the D_{2h} symmetry of the molecule. The two metal orbitals which are important in this discussion are of b_{2g} and b_{3g} symmetry. Therefore one of the metal orbitals, b_{2g}, is of correct symmetry to interact with one of the π^* combinations. However, the other metal orbital, b_{3g}, remains nonbonding. We will label the amount that metal b_{2g} is stabilized by ΔE_1. In case II one ethylene is in the upright geometry and the other adopts the in-plane orientation. The ethylene and metal orbitals now transform as b_1 and b_2 in the C_{2v} geometry of the complex. Thus *both* metal orbitals are stabilized by ΔE_2. It has been shown previously[2a,32] for other related examples that, although $\Delta E_1 > \Delta E_2$, $2\Delta E_1 < 4\Delta E_2$ when there is appreciable interaction between π^* and metal d orbitals. In other words, disregarding all other factors, case II represents the more stable bonding arrangement. In order to test this hypothesis calculations were carried out on the interconversion of **33** to **34**. The

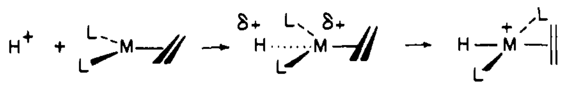


a) L = Cl
b) L = H

33 **34**

barrier on going from **33a** to **34a** (with optimization of the L-Pt-L angle) was found to be 22 kcal/mol, which is considerably reduced from that calculated for, say, the phosphine complex **24**. Furthermore, it is found that **33b** is only 0.4 kcal/mol more stable than **34b**. It appears that there are no known examples of trans bis(ethylene) complexes to experimentally test the hypothesis. Presumably this is a consequence of the trans effect, but perhaps it is possible to prepare these with a bidentate ligand which must span trans positions.

The astute reader will have noted that there is a connection that can be drawn between the barrier problems in ethylene-ML_2 and -ML_3 complexes. Consider the hypothetical protonation reaction given by **35–37**. As the "innocent" ligand,



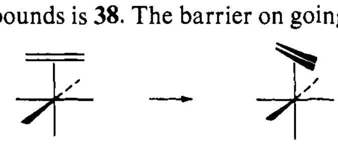
35 **36** **37**

H^+, attacks the trigonal ethylene-ML_2 complex, the L-M-L angles open and the ethylene reverses its conformational preference. The s orbital of the proton cannot interact, by symmetry, with either b_1 or b_2 on the metal. However, the conformational integrity of the trigonal ethylene in **35** is lost since the b_2-b_1 energy and hybridization difference is decreased by opening the L-M-L angle. At some point along this protonation coordinate the rotational barrier will vanish.

Before leaving this section we would like to make it clear that our conviction that there is a steric origin to the Zeise's salt-type complexed ethylene orientation does not vitiate the basic features of the Dewar-Chatt-Duncanson model. The primary bonding features of this system are indeed set by a_1, π and b_2, π^* interactions, both of comparable magnitude.

Ethylene-ML_5 Complexes

Our last example, the rotational barrier in ethylene-ML_5 complexes, is really a straightforward adaptation of the mode of argument cited above for square-pyramidal ethylene-ML_4 complexes. It has been shown from NMR studies[33a] and a recent X-ray structure[33b] that the most stable conformation of these compounds is **38**. The barrier on going from **38** to **39**



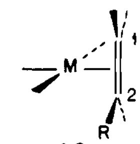
38 **39**

lies in the range of 7–10 kcal/mol.[33] We calculate that the barrier for ethylene-$Cr(CO)_5$ (with the hydrogens pinned back 20°) is 10 kcal/mol with **38** more stable than **39**. The reason behind this barrier does *not* lie in preferential bonding of ethylene π^* to a metal d orbital. Referring back to Figure 1, it is seen that π^* can bond with one member of the 1e set in the $Cr(CO)_5$ fragment for conformation **38**. Upon rotation to **39** π^* bonds to a linear combination of the two orbitals in the e set. Consequently, the energy difference between the two conformations cannot come from this source, but rather from the repulsion between ethylene π and a_2 in **39**. We could have anticipated this result from Figure 5b and the discussion around it. The ligand trans to the ethylene does nothing to the barrier except to force the four cis ligands to lie in a common plane.

There is in the literature an interesting structure of an iron(II) cyclobutene complex which is *constrained* to orientation **39**.[33c] It has a short C=C bond and Fe—C distances much longer than in most olefin complexes. We interpret this as a manifestation of the repulsive interaction discussed above superimposed on normal metal-metal bonding.

Unequal Bonding in Substituted Olefin-ML_n Complexes

The subset of complexes containing unsymmetrically substituted olefins behaves according to our earlier discussion, but possesses the interesting structural feature of potential and actual inequality in the metal-olefinic carbon bond lengths. Experimental data (Table I) for square-planar olefin-ML_3 complexes, **40**, show that the metal-carbon bond to the carbon

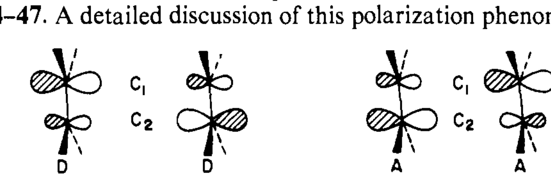


40

carrying the substituent (C_2) is longer than that to the unsubstituted carbon (C_1), whether the substituent is a π donor (**40a–f**) or a π acceptor (**40i**).[34] Often this bonding asymmetry is accompanied by a shift of the entire ethylene "down", so that the center of the C_1-C_2 lies below the coordination plane.

Results for substituted olefin-ML_2 and -ML_4 complexes are collected in Table II. Unfortunately only good π-accepting substituents appear in the list. The M-C_2 bond is again the longer one, except in two cases (**43b,d**). The metal-nitrogen bond lengths in the imine-ML_2 complexes **42a,b** are longer than the metal-carbon bond lengths, even though nitrogen should have a smaller atomic radius than carbon. This has been noted previously.[7a] Similarly, in the NiL_2 complex of hexafluoroacetone, **42c**, the Ni-C and Ni-O bonds are of approximately equal length. We shall show now that all these observations are reflections of perturbations in the π and π^* levels of the polyene.

When a π acceptor or π donor is substituted on ethylene, the π and π^* orbitals become polarized in the sense shown in **44–47**. A detailed discussion of this polarization phenomenon



44 donor **45** **46** acceptor **47**

has been given elsewhere.[35] Model calculations on a donor system 1,1-dichloro-, an acceptor 1,1-dicyano-, and a mixed case, 1,1-dichloro-2,2-dicyanoethylene, generally confirm this pattern. As far as the energy levels are concerned, acceptor substitution lowers the energy of π and π^*, while donor substitution raises both.

Calculations were next carried out with the ethylenes complexed to $PtCl_3^-$ (**48**) and $Ni(PH_3)_2$ (**49**). In the platinum complex both metal-carbon bonds were 2.13 Å, in the nickel complex both 2.10 Å. The assumption was made that changes in the overlap populations for the metal-carbon bonds would be indicators of actual bond length effects, an increase in

Table I. Pt–C Bond Lengths in Olefin–PtL_3 Complexes

olefin[a]	no.	Pt–C_1, Å	Pt–C_2, Å	ref
$CH_2{=}C(OMe)_2$	**40a**	2.086 (28)	2.798 (30)	23m
$CH_2{=}CHOH$	**40b**	2.098 (10)	2.222 (9)	23r
$CH_2{=}CHOEt$	**40c**	2.128 (7)	2.208 (7)	23s
$CH_2{=}CH(OR)$	**40d**	2.12 (3)	2.20 (3)	23o
$RCH{=}CH(OR)$	**40e**	2.13, 2.04 (2)	2.32, 2.33 (2)	23p
$CH_2{=}CHPhNMe_2$-*p*	**40f**	2.137 (17)	2.262 (16)	23n
$CH_2{=}CHPh$	**40g**	2.188 (8)	2.219 (9)	23f
$CH_2{=}CHPh$	**40h**	2.180 (12)	2.236 (10)	23n
$CH_2{=}CHPhNO_2$-*p*	**40i**	2.174 (13)	2.216 (11)	23n
$CH_2{=}CHEt$	**40j**	2.163 (25)	2.173 (23)	23k
$CH_2{=}CH$-*i*-Bu	**40k**	2.17 (5)	2.26 (5)	23l
$CH_2{=}CHR$[b]	**40l**	2.11 (1), 2.17 (3)	2.14 (2), 2.19 (3)	23u

[a] In the olefin the first carbon as written is C_1, the second is C_2. [b] R = $CH_2CH_2CH_2NH_3^+$. The two entries refer to two crystalline modifications, one orange, the other yellow.

Table II. M–C Bond Lengths in Olefin–ML_2 and –ML_4 Complexes

olefin[a]	M	no.	M–C_1, Å	M–C_2, Å (M–X)	ref
$CH_2{=}CHCN$	Ni	**41a**	2.016 (10)	1.911 (10)	7l
$Cl_2C{=}C(CN)_2$	Pt	**41b**	2.00 (2)	2.10 (2)	7c
$CH_2{=}N(Me)_2^+$	Ni	**42a**	1.884 (5)	1.920 (4)	8e
$(CF_3)_2C{=}NN{=}C(CF_3)_2$	Pt	**42b**	2.02 (1)	2.112 (9)	8d
$(CF_3)_2C{=}O$	Ni	**42c**	1.89 (2)	1.87 (1)	8f
$CH_2{=}CHC(O)OMe$	Fe	**43a**	2.092 (2)	2.106 (2)	17e
$CH_2{=}CHCN$	Fe	**43b**	2.10 (1)	2.09 (1)	17p
$CH_2{=}C(C(O)R)(R')$	Fe	**43c**	2.098 (5)	2.127 (4)	17k
$CH_2{=}C<$ (cyclopropane ring with $CH(CO_2CH_3)$, $CH(CO_2CH_3)$)	Fe	**43d**	2.092 (7)	2.024 (5)	17f

[a] In the complexed π ligand the first atom (C) as written is numbered 1, the second (C, N, or O) is labeled 2.

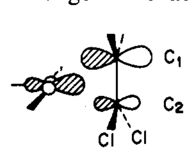
Table III. Calculated Overlap Populations in Olefin–$PtCl_3^-$ and Olefin–$Ni(PH_3)_2$ Complexes

		olefin–$PtCl_3^-$			olefin–$Ni(PH_3)_2$	
olefin[a]	no.	Pt–C_1	Pt–C_2	no.	Ni–C_1	Ni–C_2
$CH_2{=}CH_2$	**48a**	0.1083	0.1083	**49a**	0.2324	0.2324
$CH_2{=}C(Cl)_2$	**48b**	0.1639	0.0311	**49b**	0.2115	0.2011
$CH_2{=}C(CN)_2$	**48c**	0.1168	0.0408	**49c**	0.2465	0.1515
$Cl_2C{=}C(CN)_2$	**48d**	0.1346	0.1657	**49d**	0.2041	0.1264

[a] In the olefin the first carbon as written is C_1, the second is C_2.

overlap population corresponding to a decrease in bond lengths. The results, shown in Table III, nicely reflect the experimental data cited in Tables I and II.

The general pattern can be understood from the interaction diagrams (Figures 4 and 7) and the polarization pattern and energetics that follow from substitution. In ethylene–$PtCl_3^-$ (Figure 7) there are two strong, approximately equal, orbital interactions: between the filled π orbital of ethylene and the empty $2a_1$, and between the filled b_2 and empty π^*. A π donor raises the π and π^* energies, so that the $2a_1$, π interaction becomes stronger. In that interaction, illustrated in **50a**, the



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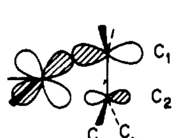
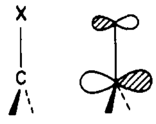


50b

C_1 coefficient is larger, and so the Pt–C_1 bond will be stronger. On the other hand, for a π acceptor the π and π^* are both lowered. This emphasizes the b_2, π^* interaction, **50b**, which again leads to a shorter Pt–C_1 bond. Not surprisingly, donor and acceptor substituents on opposite ends of the ethylene tend to cancel each other's effects. The olefin–ML_5 case should be quite similar.

The situation is slightly different for olefin–ML_2 (and the similar –ML_4) complexes. The high energy of b_2 (see Figure 4) makes the b_2, π^* interaction much more important than the $3a_1$, π interaction. This accentuates the effect of a π-acceptor substituent, so, as in olefin–ML_3 complexes, the bond from the metal to the unsubstituted carbon should shorten, in agreement with Table III and the experimental data of Table II. Substitution by π donors, however, will produce variable results. The effect of polarizing the π orbital is diminished by the weakness of the $3a_1$, π interaction. For a superlative π donor one might see a shortening of the bond to the unsubstituted carbon. But our results on a moderate π donor, chlorine (Table III, **49b**), show relatively little differentiation between the Ni–C_1 and Ni–C_2 overlap populations. With π donors at one end of the ethylene, π acceptors at the other, the acceptor dominates because of the strong b_2, π^* interaction. The M–$C_1(Cl_2)$ bond is calculated to be stronger, and it is shorter.

When a more electronegative heteroatom replaces carbon in ethylene, both the π and π^* levels go down in energy.[12,36] Furthermore, π^* becomes polarized so that the coefficient at the less electronegative carbon is increased, **51**. So there is a



51

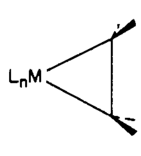
natural tendency for the M-C bond to be shorter than the M-X bond, disregarding all other factors. This is probably the source of the interesting bond lengths of **42a-c** in Table II. The same effect should be operative in imine-$PtCl_3$ complexes.

Calculations were also carried out on the Feist's acid complex **43d**, whose Fe-C bond length differentiation does not fit the general pattern. The calculated overlap populations from a computation with equal M-C bond lengths agree with the observed bond length trends, but we have not yet been able to construct an explanation for the result.

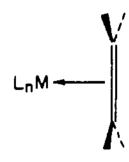
Asymmetric π bonding to an olefin and the associated slipping of the olefin unit are of course signs of an easy transformation to a zwitterionic π-bonded form, with important consequences on the olefin reactivity.[37] In at least one of the cases cited, **40a**, the olefin displacement and asymmetry are so great that the σ-bonded extreme is approached.

Metallocyclopropanes or Olefin π Complexes?

The answer we would give, which will not satisfy some, is "both". The question, of course, is an old one. Is the best representation of olefin complexes **52a** or **52b**? To deal with this



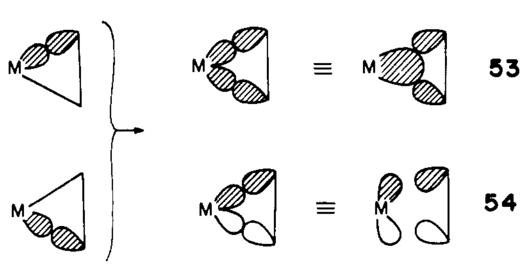
52a



52b

problem we must be clear about the meaning of the two symbolisms. On the face of it **52b** implies π donation to the metal, but of course the Dewar-Chatt-Duncanson model extends this to include back-donation from a metal orbital (b_2 or b_1) to ethylene π^*.

What is a metallocyclopropane? Taking the localized bonding scheme seriously, we begin with two localized M-C σ bond orbitals. These must be symmetry adapted, and this is trivially done by forming in- and out-of-phase combinations **53** and **54.** These are seen to be the two components of the



π-complex model, bonding ($a_1 + \pi$) and back-bonding (b_2 or $b_1 + \pi^*$).

So the two pictures are equivalent. What does vary is the extent of the admixture of metal and ethylene orbitals in **53** and **54**. These drawings, totally arbitrarily, give the impression of equal mixing. This will be true, and then only approximately so, in cyclopropane itself, i.e., where ML_n is CH_2. In any organometallic case there will be a range of interaction from little (**53** mainly π, **54** mainly metal b_2, ethylene reasonably intact with a short C=C and hydrogens not pinned back) to great (**53** and **54** both carrying substantial metal and olefin character, C—C approaching a single bond, hydrogens bent back). The best we can say from a calculation, or better still from observed structures, is roughly where along the continuum a given type lies. Thus cyclopropane and heteroatom-substituted cyclopropanes are clearly cases of strong mixing (see the interesting case of ethylene sulfide, sulfoxide, sulfone[27a]), the d^{10} $L_{2,4}M$-ethylenes of less interaction, the d^8 L_3M-ethylenes of still less. But, given the wide range of substituents which can modify the electronic structure within a given class, it would be counterproductive to deny the existence of a continuum of interaction, and to attempt to pigeonhole these complexes as being of one type and not another.[38]

Table IV. Parameters Used in Extended Hückel Calculations

orbital	H_{ii}, eV	ζ_1	ζ_2	C_1[a]	C_2[a]
Cr 3d	−11.22	4.95	1.60	0.4876	0.7205
4s	−8.66	1.70			
4p	−5.24	1.70			
Fe 3d	−12.70	5.35	1.80	0.5366	0.6678
4s	−9.17	1.90			
4p	−5.37	1.90			
Ni 3d	−12.99	5.750	2.00	0.5683	0.6292
4s	−8.86	2.100			
4p	−4.90	2.100			
Pt 5d	−12.59	6.01	2.70	0.6334	0.5513
6s	−9.08	2.55			
6p	−5.48	2.55			
C 2s	−21.40	1.625			
2p	−11.40	1.625			
N 2s	−26.00	1.95			
2p	−13.40	1.95			
P 3s	−18.60	1.60			
3p	−14.00	1.60			
O 2s	−32.30	2.275			
2p	−14.80	2.275			
Cl 3s	−26.30	2.033			
3p	−14.20	2.033			
H 1s	−13.60	1.30			

[a] Coefficients in double ζ expansion.

Acknowledgment. We are grateful to the members of our group for numerous discussions, and to Paul Dobosh for a careful reading of the manuscript and some suggestions. Helpful discussions with J. A. Ibers and L. J. Guggenberger are also acknowledged, as is the hospitality extended to R.H. by the Department of Organic, Inorganic and Theoretical Chemistry of the University of Cambridge, where this work was completed. The drawings and typing were skillfully done by J. Jorgensen and E. Kronman, respectively. Our research at Cornell was generously supported by the National Science Foundation through Grant CHE-7606099.

Appendix

All calculations were performed using the extended Hückel method.[37] The H_{ii}'s for chromium and iron were taken from previous work.[4] The H_{ii}'s for nickel and platinum were obtained from charge iterative calculations on ethylene-$Ni(CO)_2$ and ethylene-$PtCl_3^-$. The metal orbital exponents for the d functions are those given by Richardson, Basch, et al.,[40] while those for the 4s and 4p functions are taken from previous work.[41] The values for the H_{ii}'s and orbital exponents are listed in Table IV. The modified Wolfsberg-Helmholz formula was used.[42] The following idealized bond distances were used: C-H, 1.09; C-O, 1.14; Ni-P, 2.15; P-H, 1.42; C-C(N), 1.45; C-N, 1.16; C-Cl, 1.70 Å. Also all C-C-C, C-C-H, M-C-O, and Ni-P-H angles were set at 120, 120, 180, and 123.1°, respectively. The M-C(O) distances were set at Cr, 1.84; Fe, 1.78; Mn, 1.80; Ni, 1.82 Å. The geometries for ethylene-

$Ni(PH_3)_2$,[7a] ethylene–$PtCl_3^-$,[23a] and ethylene–$Fe(CO)_4$[17i] were adapted from experimental structures. The Cr–ethylene bond in the $Cr(CO)_5$ complex was fixed at 1.88 Å.

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Polyene–ML_2 and –ML_4 Complexes. Conformational Preferences and Barriers of Rotation

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Received September 19, 1978

Abstract: Rotational barriers in acyclic and cyclic polyene–ML_2 and –ML_4 complexes are analyzed by subdividing the molecules into polyene and ML_n fragments. In C_nH_n–ML_2 the inherently small rotational barrier may be strongly perturbed by substitution patterns which create an electron density asymmetry. Slipping and geometrical deformations of the coordinated polyene may also occur. In acyclic polyene–ML_2 complexes generally large barriers are to be expected, with well-defined equilibrium conformations. The analysis of ML_4 complexes follows similar lines, but is complicated by a geometrical degree of freedom which relates C_{4v} and C_{2v} ML_4 fragment geometries.

In several preceding papers we have analyzed the bonding, conformational preferences, and rotational barriers in polyene–ML_3[1] and ethylene–ML_{2-5} transition metal complexes.[2] The barrier to internal rotation about the metal–ligand coordination axis is a most direct probe of the bonding in these compounds. In this paper we study the important class of

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0002-7863/79/1501-3812$01.00/0