Effect of Ligand Asymmetry on the Structure and Reactivity of CpMLL'(allyl) and -(ethylene) Complexes

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Abstract: The electronic structure of transition metal cyclopentadienyl dicarbonyl allyl complexes is a starting point for a general theoretical analysis of the remarkable regioselectivity observed in nucleophilic attack on such complexes which are made asymmetric by substitution of a nitrosyl for a single carbonyl. Highly specific conformational preferences of CpMLL'X, X = acetylene, ethylene, carbene, are a function of the donor and acceptor properties of the different ligands L and L'.

This work was stimulated by the remarkable stereoselectivity observed in the reactions of cationic η^3 allyl complexes of the formula $CpMo(CO)(NO)(allyl)^+$.[2] These compounds exhibit endo-exo isomerism, but more importantly act as efficient substrates for addition by a wide range of nucleophiles. The addition may be carried out under conditions where the exo-endo isomerism is slow but the olefin rotation in the product is rapid. Scheme I shows the possible stereochemical consequences of attack on the outside face of the allyl group. **a** and **c** represent additions trans to the nitrosyl, **b** and **d** cis. If olefin rotation is rapid, **a** and **d** would be interconverted, as would **b** and **c**. Thus, if the nucleophile attacked exclusively cis to nitrosyl, or if it attacked exclusively trans to nitrosyl, in either case a mixture of two isomers would be expected. In fact a single isomer was found in the highly stereoselective reaction. Its configuration was not known at the time this study was initiated, but the fact that only one isomer was found by itself pointed to the intriguing conclusion that addition had taken place cis to nitrosyl in one epimer, trans to nitrosyl in the other. Subsequently it was determined that the product was **a** = **d**.[2b,3]

This interesting stereospecificity persists in the face of other substitution on the allyl group. An unusual electronic effect of asymmetry in the CpM(CO)(NO) fragment is indicated, and was explored in a series of calculations which led to the prediction of the observed reaction product. This and the development of a more general theory of the propagation of electronic asymmetries in organometallic complexes are the subjects of this paper.

$CpM(CO)_2$(allyl) Complexes

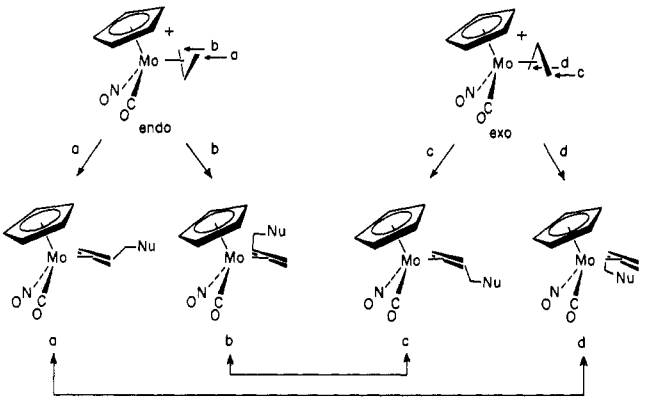
We begin with an analysis of the "symmetric" allyl complex $CpMo(CO)_2$(allyl), drawing upon our general study of $CpM(CO)_2$(ligand) compounds in the accompanying paper.[4] $CpM(CO)_2$(allyl) complexes have been subject to a range of conformational investigations,[5] but only few structural data are available.[6] In the systems where the crystal structure has been determined the allyl moiety is in general part of a larger organic system.[6]

In this study the allyl group has been idealized, kept planar, with the plane of the organic ligand parallel to the plane of the carbonyl groups. This orientation was maintained when rotating the π system about the metal-allyl axis. Two views of the exo and endo isomers are shown in **1** and **2**.

exo endo

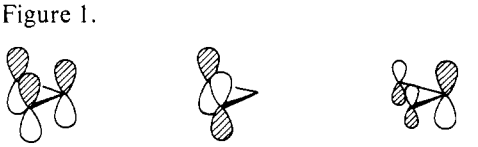
1 **2**

Scheme I



Into an analysis of the electronic structure of the complex (Figure 1) there enter the orbitals of a $CpM(CO)_2^+$ fragment and those of an allyl anion. The $CpM(CO)_2$ orbitals have been discussed in detail in the accompanying paper,[4] and are sketched at the left in Figure 1. There are three low-lying d-block orbitals, 1a', 2a' and a'', and a higher lying 3a' which carries the coordinative unsaturation of the isolated fragment. The a'' and one combination of 1a' and 2a', named a'_π, are responsible for the π-bonding capability of the fragment, in the *xz* and *yz* planes, respectively. A major point that emerged from our previous analysis is that the π-bonding strength in the two planes differs, with that in the *xz* plane, corresponding to interaction with a'', being stronger. This is the main factor behind the equilibrium orientation of carbene, acetylene, and ethylene groups, and will carry over to the allyl ligand in the symmetrically substituted (CpMLL vs. CpMLL') case.

The allyl group has three π-type orbitals of importance. These are shown below, labeled as a bonding π, a nonbonding n, and an antibonding π^*. Only the lower two appear at the right in Figure 1.



π n π^*

The interaction diagram for the allyl complex in the endo orientation (Figure 1) is very similar to that in the exo. The primary interaction is between a'' and the allyl nonbonding orbital. The calculated difference in energy between the two rotamers is slight, favoring the endo form. It is derived from the slightly different repulsive interaction between the lower allyl π and $CpM(CO)_2$ 1a' and 2a'. Figure 1 shows the iron system, whereas the complex with M = Mo has two electrons less. There is a substantial calculated barrier of 46 kcal/mol

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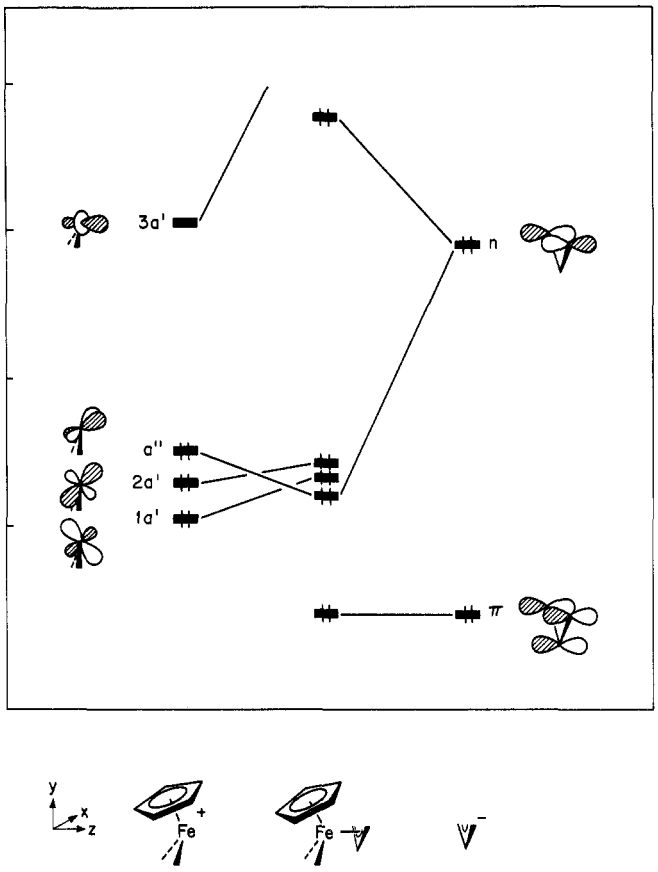
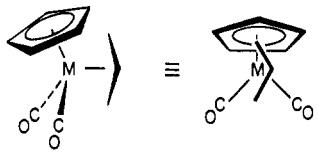


Figure 1. The orbital interaction diagram for $CpFe(CO)_2^+$ and $allyl^-$ in the endo conformation. The text discussion centers on the Mo analogue, which has two electrons less.

in $CpMo(CO)_2$(allyl) to a simple rotation about the M–allyl axis. The waypoint along such a rotation is **3,** in which the favorable interaction of a″ and n is lost. Clearly this is not a preferred mechanism for exo–endo interconversion. The structure was not optimized for **3**; thus, alternative modes for



3

isomerization which involve major distortions of the $CpMo(CO)_2$ fragment, π–σ–π rearrangement, or metallocyclobutenyl ring puckering may present lower energy pathways, but have not yet been studied by us.

In $CpMo(CO)_2$(allyl) the d-block levels are filled through the symmetric 2a′. The lowest empty orbital is the antibonding combination of the allyl n and a″, **4.** This acceptor orbital is

4

concentrated on the terminal carbons of the allyl. According to a frontier orbital argument,[7a] one would anticipate nucleophilic attack predominantly at one of the two symmetry-equivalent terminal carbons.[7b] This we probed by bringing up a hydride ion 1.75 Å from the central or terminal carbon. The resulting overlap population, shown in **5** and **6,** clearly is

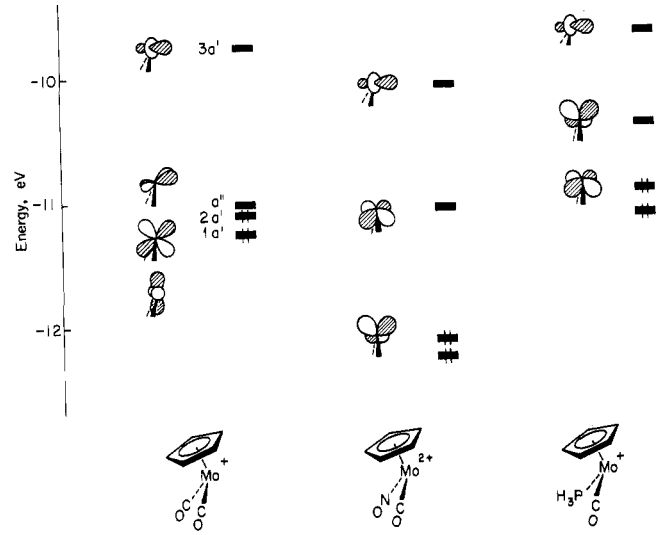
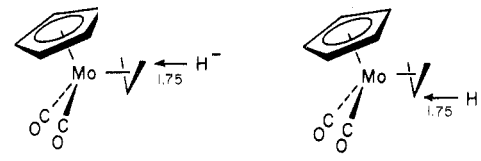


Figure 2. A comparison of the valence orbitals and the associated energy levels for the symmetric $CpMo(CO)_2^+$ and the substituted systems, $CpMo(CO)(NO)^{2+}$ and $CpMo(CO)(PH_3)^+$.



5 **6**

Overlap populations 0.1026 0.0479

higher, the allyl–H bond therefore more fully developed at this reaction waypoint, for terminal attack.

Our concern with this reaction mode anticipates the eventual aim of the analysis—the symmetry of the two ends of the allyl will be destroyed in $CpMo(NO)(CO)(allyl)^+$. We begin by analyzing the orbitals of the fragment CpM(CO)L′ using the symmetric system as a basis. The influence of the asymmetry on the bonding capability of the fragment and how the change in the ligand L′ modifies the electronic structure of the incoming polyene ligand are then studied.

The CpM(CO)L′ Fragment

The molecular orbitals of the asymmetric fragment can easily be related to the orbitals of the $CpM(CO)_2$ fragment. We recall that the frontier orbitals for the symmetric fragment consisted of a low-lying empty orbital, almost pure d_{z^2}, designated 3a′, and a group of three orbitals descending from $x^2 - y^2$, xz, and yz. The orbitals determining the conformation of the resulting complex were this group of three, the highest a″, a tilted xz, and two symmetric orbitals, 1a′ and 2a′. In the case of molybdenum 2a′ is almost pure yz and close in energy to a″, whereas 1a′ is mostly $x^2 - y^2$ and less active in bonding to L.

When the symmetry is broken, the character of these orbitals changes, and the introduction of different ligands with varying donor and acceptor capabilities will affect the position of the energy levels. The cases we will consider are with L′ = NO, PH_3, models for better and worse π-acceptor capability relative to CO. Let us first look at the CpMo(CO)(NO) fragment. Here the carbonyl of the parent compound has been substituted by a better π acceptor, nitrosyl. This results in breaking the near degeneracy of a″, **7,** and 2a′, **8,** as well as reorienting the orbitals. This latter effect is achieved by mixing the two orbitals to maximize overlap to the carbonyl and nitrosyl π*'s. The

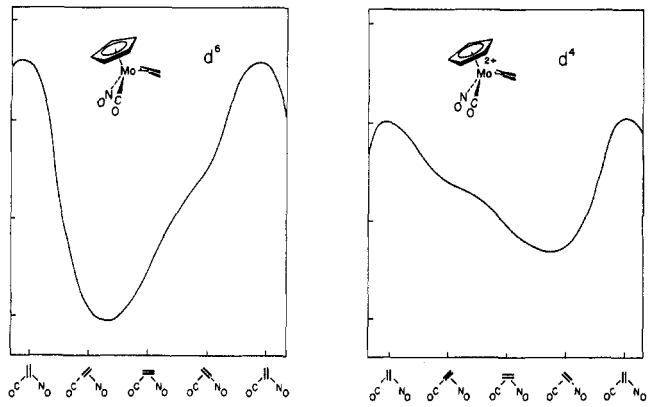


Figure 3. The energy profile for the rotation of ethylene about the metal-olefin bond in the d^6 and d^4 systems, CpMo(CO)(NO)(ethylene) and CpMo(CO)(NO)(ethylene)$^{2+}$

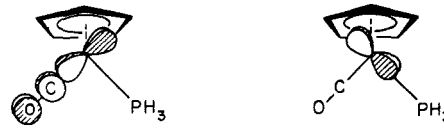
resulting MOs are shown in **9** and **10**. Their relative position is shown in the energy diagram in Figure 2 middle. As NO is a better π acceptor than carbonyl, the MO where the major interaction is with nitrosyl π^* is lowered considerably. The

7 **8**

9 **10**

orbital below this is also lowered in energy for the same reasons. What were nearly degenerate π-bonding levels, 2a′ and a″, are now well separated in energy and quite different in their orientation. The specific orientation in space will turn out to have a significant influence on the orientation and charge distribution of additional ligands, a fact which will have chemical impact when reactivity is considered.

The change in fragment orbitals discussed above was a consequence of the nitrosyl ligand being a better π acceptor than carbonyl. We now look at a ligand such as PH_3 where CO is the better π acceptor of the two. This would indicate a reversal of the above picture. The splitting of the two orbitals is indeed observed, but in this case a good π acceptor has been substituted by a mild donor, and the level not interacting with the π^* of the remaining carbonyl has actually gone up in energy. A comparison of the three systems is shown in Figure 2. Once again the orbitals reorient, the lower energy one, **11**, pointing along the M–CO axis, the higher energy one, **12**, along



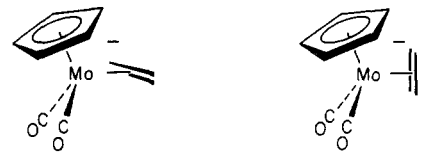
11 **12**

M–P. The reorientation of the orbitals in CpMoLL′ is best probed by attaching a conformationally sensitive group which is a single-faced π acceptor, for instance an ethylene. This is examined in the next section.

Ethylene Complexes

The preferred orientation of an ethylene ligand in the symmetric dicarbonyl systems was found to have the ethylene bisecting the molecular mirror plane.[8] This orientation is altered, however, either for steric reasons[9] or for electronic ones, as in the carbonyl–nitrosyl complexes. Crystal structures of several substituted ethylene derivatives of the type CpMo(CO)(NO)(olefin)[2b] show the ethylene twisted toward the carbonyl. The details of the structure of another nitrosyl complex are less apparent,[3] but the substituted ethylene is positioned somewhere between the bisecting orientation and parallel to CO.

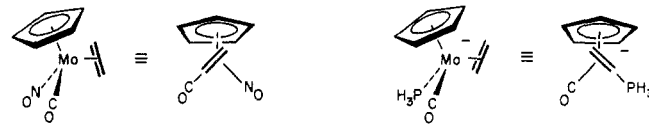
Before we discuss the influence of the asymmetry on the orientation of the ethylene, let us recall the reasoning behind the presence of a barrier to rotation in the symmetric complexes. The orbital mainly responsible for the stabilization of **13** relative to **14** is the a″, stabilized more in the conformation



13 **14**

13 by the π^* of ethylene. The interactions of the symmetric orbitals are very similar in the two conformations. The barrier thus calculated is 26 kcal/mol for the molybdenum complex and 21 kcal/mol when the metal is iron. Optimization of the structure of **14** to minimize the energy should lower the barriers.

Applying the standard perturbation argument to an asymmetric system such as CpMoL(CO)(ethylene), L = NO^+, PH_3, we would argue that the best π bonding would occur between ethylene π^* and the highest occupied efficiently overlapping π MO of the metal fragment. This is the one associated with the direction of the poorer donor, **9** or **12**. The preferred conformations should then be near **15** and **16**. When



15 **16**

the calculations are performed on CpMo(CO)(NO)(C_2H_4), the actual minimum does not occur in conformation **15** but with the ethylene between the bisecting position shown in **13** and the one shown in **15**. The deviation from the expected structure **15** amounts to 15°, but the ethylene is unmistakably twisted from the bisecting position.

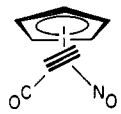
With two less electrons in the system the minimum is shifted toward the conformation with the ethylene parallel to the M–NO bond. This is understandable as the molecular orbital responsible for the orientation **15** is no longer occupied. The filled fragment MO appropriate for back-bonding into the π^* is now the lower partner of the pair, oriented toward NO, resulting in a minimum energy position approximately 90° off from what was found in the d^6 case. More precisely, it is twisted 35° from the bisecting position toward the NO bond. The energy profile for the d^6 and the d^4 systems is shown in Figure 3.

The barrier to rotation of the ethylene is found to be 30 kcal/mol for the d^6 system and 16 kcal/mol for d^4. The barrier in the neutral system is larger than what is found for the symmetric molybdenum system, 26 kcal/mol. This increase in barrier can be understood easily when we recall that the introduction of the better π acceptor not only reoriented the MOs, but also increased their splitting in energy drastically.

The interaction of π^* with the other partner in the unfavorable position is thus better in the symmetric system. The barrier in the d^4 complex is less pronounced, since the pertinent metal orbital is further removed and interaction consequently less in both conformations. In all the above calculations no attempt has been made to optimize the geometry; hence the excessively large barriers. But the trend is clear as to which conformation is the preferred. For a phosphine probe replacing the nitrosyl the situation is entirely reversed, as expected. The trends are less clear, which is to be expected since the orbital splittings are less than in the nitrosyl case (see Figure 2).

Other systems with similar π-accepting capabilities, such as acetylenes, behave in a similar fashion. The splitting and reorientation of the metal donor orbitals of π-type symmetry govern the conformational preferences of the ligand. The size of the barrier to rotation is also influenced by the reduction of symmetry. The experimentally measured rotational barriers for Mp-acetylene complexes mostly involve asymmetric systems like CpW(CO)(R)(acetylene)[10] where the barrier is found to be 16–18 kcal/mol or CpCr(NO)(CO)(acetylene)[11] with a barrier of 12–14 kcal/mol. For a monopositive diphos-substituted symmetric complex of molybdenum the barrier is approximately 14 kcal/mol.[12]

For the neutral CpMo(CO)(NO)(acetylene) system where both **9** and **10** are filled the most stable calculated conformation has the acetylene twisted away from the bisecting position toward the carbonyl, with an energy minimum at a 20° twist, **17**. This behavior is a compromise between the favorable in-



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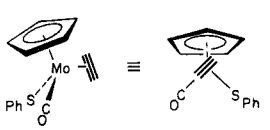
teraction of π^* with **9** and the less well disposed interaction with the two lower orbitals. Again the calculated minimum falls somewhat removed from the parallel position, but without doubt rotated from the bisecting conformation.

For the neutral system the barrier is found to be 35 kcal/mol, considerably higher than what was found for the dicarbonyl system (13 kcal/mol). The reasoning behind this change is similar to what was discussed in the ethylene case. CpMo(CO)(NO)(acetylene)$^{2+}$ has a barrier of 22 kcal/mol, somewhat lowered, as is expected since the metal MO involved in back-bonding is far away in energy from the π^*.

The barrier for CpMo(CO)(PH_3)(acetylene)$^+$ is calculated to be 30 kcal/mol, slightly smaller than the barrier in the nitrosyl system. The smaller splitting between the two π-type metal orbitals makes this reasonable. The complex for which experimental studies have been reported is the isoelectronic CpW(CO)(R)(acetylene) where R = CH_3, Ph.[10] The methyl system is calculated to be very similar to the phosphine. The position and shape of the fragment orbitals are almost identical and, expectedly, the characteristics for the energy profile are quite similar.

An interesting example of an asymmetric acetylene system where the orientation of the acetylene is altered with changes in the ligands is the complex **18**.[13] Here the acetylene is parallel to the M–CO bond. When carbonyl is substituted by oxygen, the orientation changes to **19**.[13] If we consider the CpMo(CO)(SF) fragment as a model, the orbitals do indeed suggest a conformation like **18**. The filled MO appropriate for



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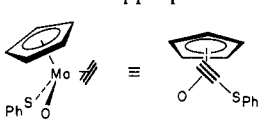

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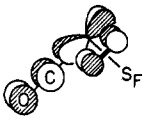
interaction with π^* is directed toward the carbonyl **20**. It might be of interest here to note that the empty orbital, rotated from **20** by 90°, is set up nicely to interact with the filled π of acetylene, as shown in **21**. The calculations do give this confor-



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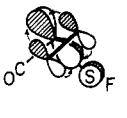

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mation as a minimum. When the two ligands are oxygen and sulfur, the calculations no longer give such a clear answer. The ligands are sufficiently alike that the minimum conformation calculated by us is the bisected analogue of **13**. The conformation next in energy, however, has the acetylene parallel to the metal–sulfur bond, the structure which is observed.

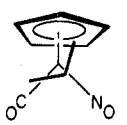
It should be noted that theoretical arguments very similar to ours for explaining the varying favored conformations of coordinated acetylenes have already been presented in the literature in the context of the experimental studies which established these structures.[11,13]

Asymmetric Allyl Complexes

We finally return to the experimental observations which stimulated this work—the remarkable regioselectivity described in the introduction and Scheme I. Nucleophilic attack on both epimers of CpMo(CO)(NO)(allyl)$^+$ leads through cis (to the nitrosyl) attack on the exo form and trans attack on the endo form to the single product **a** = **d** in Scheme I.

As in the acetylene case, it might be helpful to review briefly the bonding pattern of the symmetric systems. The two conformers, exo and endo, were calculated to be very similar in energy, this because the main interaction was with the allyl nonbonding orbital which does not differ for the two orientations. When a carbonyl is substituted by a nitrosyl, the frontier orbitals of the Mp fragment change in energy and orientation, as was discussed above. When an allyl is introduced, the lack of symmetry makes mixing of all three important allyl orbitals, n, π, and π^*, possible. This mixing is the reason for the electronic polarization in the allyl.

Before we discuss the endo and exo systems in detail, we should consider whether in fact these are the stable conformations of the allyl. Assuming the nonbonding orbital of allyl to be the important partner in bonding, an argument similar to that which was used in the asymmetric ethylene system would lead to the conclusion that the allyl group should rotate away from the idealized exo or endo positions in the direction of **22** and **23**. A calculation does lead to a relatively low energy



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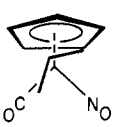
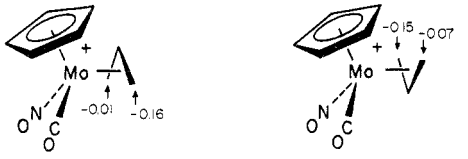


23

for these two orientations, but the overall minimum is the idealized endo form with exo at almost the same energy. At the maximum the terminal carbons are positioned perpendicular to what is the case for exo and endo. The barrier is large, around 90 kcal/mol, a value which most likely could be lowered if the geometry were optimized. We have chosen to keep the allyl planar, parallel to the plane of the carbonyl–metal–nitrosyl, keeping in mind that the problem of interest involves a difference between the two terminal carbons. The energy profile calculated supports the idea that the conformers experimentally observed are close to the idealized exo and endo structures.

The interaction diagrams for the two isomers are almost identical, and similar to Figure 1. There is no symmetry in the system, so in principle every interaction is allowed. To say the least this complicates the analysis, but a fragment molecular orbital (FMO) approach[14] allowed us to single out the primary interactions, which are those between the metal fragment and the allyl nonbonding orbital mixing with π and π^*. n is stabilized by the lowest empty orbital of the fragment, **9**, the lowering in energy of this orbital modified by the mixing in of lower fragment orbitals and allyl π. The antibonding partner of this interaction is the next lowest empty orbital, which has large orbital coefficients on the terminal allyl carbons, a factor of importance when a nucleophile attacks the organic ligand. The fact that a nucleophile should attack a terminal carbon over the center atom was already noted in the symmetric system, precisely because the acceptor orbital of the complex is descended from the allyl nonbonding orbital. If the interactions are in fact nearly identical, as far as energetics go, in the two orientations, what then accounts for the regioselectivity?

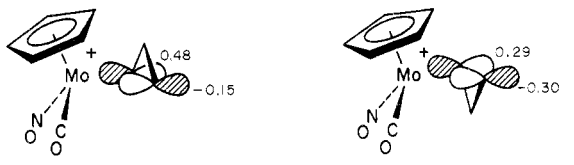
Let us examine phenomenologically in what ways the differences are manifested. The net charges calculated on the terminal carbons of the allyl not only differ within the allyl group, but change when going from exo to endo, as indicated in **24** and **25**. In exo the carbon trans to NO is most negative; in endo this is reversed.



24 **25**

A simple argument based on charges would thus predict attack by a nucleophile to occur at different carbons in the two conformers. But an actual reaction with a nucleophile will involve overlap and energy considerations as well.[7] The empty orbital mostly centered on the terminal carbons and the one most heavily involved in bonding to an approaching nucleophile is the next lowest empty orbital, the antibonding combination of **9** with the allyl n. Here again the two conformers differ in the orbital coefficients on the carbons.

There is a clear trend in exo, consistent with the charge distribution, whereas endo has only a slight differential, but in the same direction as the charge. It must here be kept in mind that a large net charge comes from an electron concentration on that center in the filled orbitals. Thus the trend shown by **24** and **25** is found in the bonding counterparts, not illustrated, of **26** and **27**. A possible tilting of the allyl may produce some change in the magnitude of the coefficients. However, we are concerned with the relative size at the terminal carbons, a feature which should be less sensitive to a tilting motion.

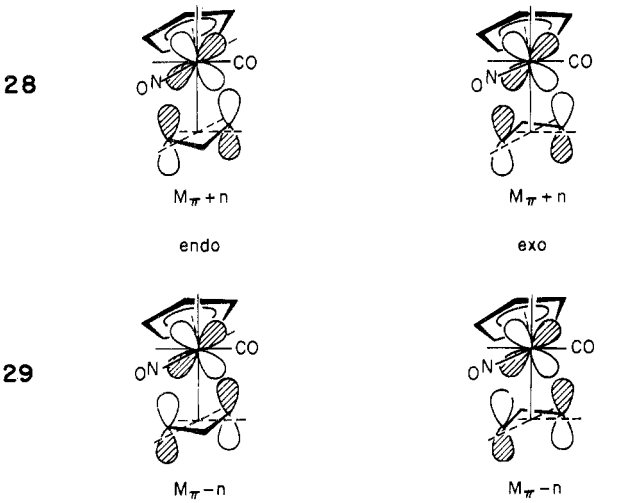


26 **27**

A nucleophile is expected to react at the center with electron deficiency and a large empty orbital coefficient or lobe. The information so far presented indicates an attack cis to NO in exo and trans to NO in endo. To confirm this expectation calculations with a model nucleophile were done, using a hydride as the attacking species. The geometry of the complex was kept constant, only varying the carbon–hydride distance. This should give the correct trends, if not quantitatively good results. The energy profile for attack is net repulsive, but changes in overlap populations give a good indication of the favored pathway. Table I shows changes in overlap population for the different modes of attack. The energies follow the overlap populations, so that more bonding results in lower energy. As would have been expected from the orbital coefficients, there is only a tiny difference for the two pathways in the endo system, but still the stronger bond is formed trans to NO. The picture is clear for the exo isomer where hydride bonds preferentially cis to NO.

These results agree nicely with the experimental findings, and in fact constituted a prediction of the regioselectivity. But probing deeper we still have not explained the reason for the variation in orbital coefficients and charges. This we now proceed to do.

The empty fragment orbital interacts with the allyl nonbonding orbital to give a lower energy occupied bonding orbital, **28**, and an empty antibonding level, **29**. The terminal carbons of the allyl overlap equally well with this metal fragment orbital, M_π, in exo and endo conformations. Any asymmetry in orbital coefficients (and resulting from that, in the charge) is due to mixing in of π and π^* of allyl. Let us first concentrate on the antibonding MO, the orbital that is most important in the interaction with an incoming nucleophile. The π^* will mix into this lower energy MO in a bonding manner, the π from below in an antibonding way.



The sign of the mixing is given by the general second-order perturbation expression[15] for orbital 1 mixing into 2 via 3:

$$c''_{12} = \frac{H'_{23} H'_{31}}{(E_2 - E_1)(E_2 - E_3)} \qquad (1)$$

The original phases of the MOs are chosen so as to give positive overlaps, where the dominant role is played by the center atom of the allyl, as shown below.

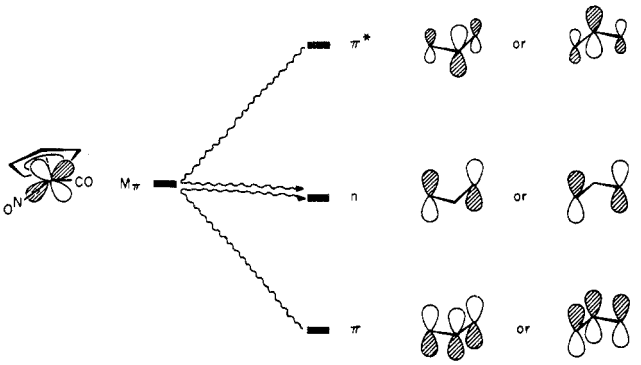


Table I. Hydride-Allyl Carbon Overlap Populations, at a C-H Distance of 1.75 Å in $CpMo(NO)(CO)(allyl)^+ + H^-$

	exo	endo
cis to NO	0.1870	0.1627
trans to NO	0.1034	0.1636

Table II. Hydride-Allyl Carbon Overlap Populations, at a C-H Distance of 1.75 Å in $CpMo(PH_3)(CO)(allyl) + H^-$

	exo	endo
cis to PH_3	0.0644	0.0884
trans to PH_3	0.0904	0.0870

For the mixing of allyl π and π^* into n through the metal orbital M_π the signs are then determined as in (2) and (3):

$$c''_{\pi,n} = \frac{H'_{nM_\pi} H'_{M_\pi\pi}}{(E_n - E_\pi)(E_n - E_{M_\pi})} = \frac{(+)(+)}{(+)(-)} = (-) \quad (2)$$

$$c''_{\pi^*,n} = \frac{H'_{nM_\pi} H'_{M_\pi\pi^*}}{(E_n - E_{\pi^*})(E_n - E_{M_\pi})} = \frac{(+)(+)}{(-)(-)} = (+) \quad (3)$$

The polarization that results is shown graphically in **30** and **31**. Thus the interaction, bonding or antibonding, of the center carbon in π and π^* with the metal fragment orbital determines

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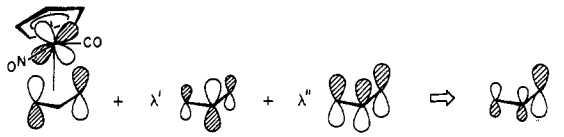

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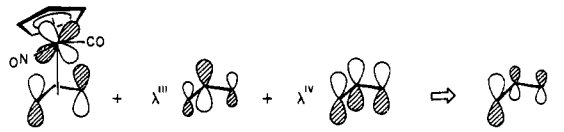
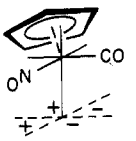


the difference in coefficients on the two terminal carbons. The sign of that interaction is in turn determined by the phase of the fragment orbital in the different quadrants of the plane parallel to the nitrosyl-carbonyl plane, **32**. The central allyl



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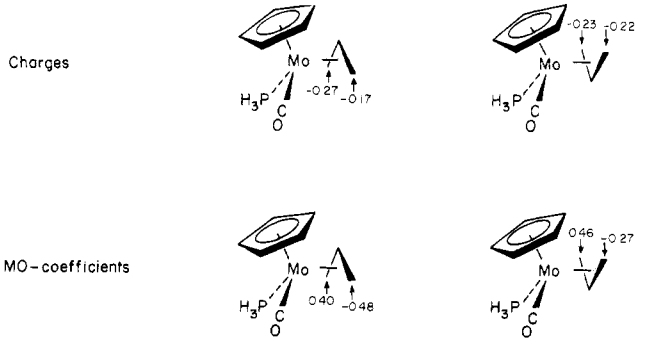
carbon will interact with lobes of different sign in the exo and endo cases, resulting in the difference in mixing.

This has been a simplified picture insofar as several metal-fragment orbitals mix into the actual MO dominating the direction of attack. But an inspection of the signs of the lobes in the manner sketched above reveals that the same sign relation as in the orbital discussed dominates. The mixing pattern shown above is maintained.

The analysis of the nitrosyl-carbonyl-allyl complex leads to the question whether one can selectively influence the polarization of the allyl by choice of ligand and thus control the



33 **34**

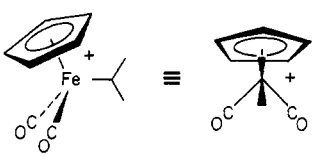
regioselectivity of the reaction. To probe this the phosphine system was studied. The fragment has already been discussed above. One would expect a reversal of behavior from the NO system. Charges and orbital coefficients for the empty MO in the two conformations are shown in **33** and **34.** From these indicators we would indeed conclude that nucleophilic attack should occur trans to PH_3 in exo, cis in endo. Overlap populations for an approaching hydride, Table II, concur. The result is opposite from the nitrosyl system. Thus one should be able to reverse the regioselectivity of the reaction. Though the phosphine substituent probe may not be the most effective one in terms of maintaining the reactivity of the complex, the general line of reasoning is clear: Substitution of one carbonyl in $CpM(CO)_2(allyl)$ by a poorer π acceptor than CO should produce a regioselectivity reversed from that observed in the nitrosyl case.

The previous discussion provides a theoretical basis for understanding important aspects of the influence of electronic asymmetry; nevertheless, other factors may make significant contributions. Alternative explanations of the observed selectivity can be constructed.[2] The electronic asymmetry of the metal may distort the allyl and tend to localize the π-electron density between the carbon atoms trans to NO. There may be some tilting of the allyl, as shown in **23**. Furthermore, the stability of conformations of the olefin complex, **15**, in the transition state may provide some directing influence. It remains to be seen what role is played by these factors. While no one could claim that an explanation grounded on second-order perturbation theoretic arguments is simple, we find the resolution of the problem satisfying. For in solving this problem we have developed a methodology for treating all problems of asymmetrically induced reactivity in organometallic complexes.

Carbene Complexes

The carbene complex offers an alternative system where one could envisage asymmetrically induced stereoselective attack. A polarization of the empty p orbital on the carbene CRR' could result in specific nucleophilic attack on one side of the enantiotopic carbon. Calculations on the substituted system, however, do not lead to any significant polarization of this MO and a model hydride therefore bonds approximately equally well to the two sides of the carbene plane.

Before discussing the lack of asymmetry of the acceptor orbital, let us consider the conformation of the carbene complex. As was the case for the previously mentioned single-faced π acceptors, the orientation of the carbene is determined by the acceptor orbital of p symmetry, the carbene p orbital. In the symmetric complex the preferred orientation was found to be the upright position, **35**,[16] where maximum overlap with a'' is achieved.



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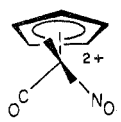
In line with the arguments presented for the olefins this orientation should shift toward a twisted form when the sym-

Table III. Parameters Used in Extended Hückel Calculations

orbital		H_{ii}, eV	ζ_1	ζ_2	c_1[a]	c_2[a]
Fe	3d	−12.70	5.35	1.80	0.5366	0.6678
	4s	−9.17	1.90			
	4p	−5.37	1.90			
Mo	4d	−10.50	4.54	1.90	0.6097	0.6097
	5s	−8.34	1.96			
	5p	−5.24	1.92			
C	2s	−21.4	1.625			
	2p	−11.4	1.625			
N	2s	−26.0	1.950			
	2p	−13.4	1.950			
O	2s	−32.3	2.275			
	2p	−14.8	2.275			
F	2s	−40.0	2.425			
	2p	−18.1	2.425			
P	3s	−18.6	1.600			
	3p	−14.0	1.600			
S	3s	−20.0	1.817			
	3p	−13.3	1.817			
H	1s	−13.6	1.30			

[a] Contraction coefficients used in the double ζ expansion.

metry is broken. This is indeed the case, and the lowest energy conformation of the nitrosyl complex has the plane of the carbene almost coinciding with the nitrosyl bond, **36**, ap-



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proaching the position of optimal interaction with **9**. In the phosphine-substituted complex, which has been studied experimentally,[17] the calculated minimum has the carbene rotated toward the phosphine bond.

An attacking nucleophile would be involved with the p orbital on the carbon center. As in the allyl complex, the empty orbital with a large contribution on carbon is the out of phase combination of the carbene p and **9**. A polarization of the p orbital would come from an addition of s character through mixing with other carbene orbitals.

We must, however, here recall the particular character of the metal orbital **9**. This MO is an almost pure mixture of xz and yz, and one of the symmetry operations which can be applied is a C_2 rotation about the carbon–metal axis, under which the orbital is antisymmetric. Any two points related to one another through the same symmetry operation will "feel" the MO identically. A specific example is the allyl n orbital centered on the symmetry-related terminal carbons. This MO is likewise antisymmetric and, although the overlap is superb, no polarization can occur. That was a result of mixing with π and π^* which have terminal contributions that are symmetric under a C_2 operation. Overlap through the terminal carbons will thus cancel and only the center atom dominates.

The s orbital on the carbene is similarly symmetric and, assuming a pure xz,yz mixture for the metal orbital, no overlap is observed. Mixing symmetric carbene MOs into p through **9** is not possible, and the antisymmetric p stays nonpolarized. In the actual system the metal MO has some symmetric contribution and there is overlap with the carbene σ orbital. But the mixing is insignificant and the s contribution is small; consequently the resulting acceptor orbital is virtually nonpolarized.

Hence, an attack of a hydride on the carbene in the nitrosyl complex does not lead to any preference in bonding to the carbon when measured by overlap populations. The phosphine system gives a slight preference, not as a consequence of a polarization of the empty p, but rather through orbitals involving more symmetric metal orbitals where mixing of the carbon p and other carbene orbitals is more pronounced.

Acknowledgment. We are grateful to the National Science Foundation for its support of this research through Grant CHE 7606099 and to D. L. Lichtenberger and T. A. Albright for their comments. The drawings were expertly done by J. Jorgensen and the typing by E. Kronman.

Appendix

The calculations were carried out using the extended Hückel method.[18] The parameters listed in Table III were taken from earlier work.[19,20] The CpMLL'L'' complex was kept pseudooctahedral with the cyclopentadiene ligand occupying three coordination sites and with metal–C(O), –N(O), and –L angles of 90°. The M–C(O) distances were 1.75 and 1.97 Å for Fe and Mo, respectively; the M–N(O), M–P, M–S, and M–O bond lengths were 1.8, 2.5, 2.39, and 1.68 Å. The distance from the metal to the plane of the olefin ligand and to the carbene carbon was kept at 2.0 Å. The C–C bond distances in acetylene, ethylene, and allyl were 1.29, 1.37, and 1.39 Å, and all C–H bonds were 1.09 Å.

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