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Theoretical Analysis of the Addition of Nucleophiles to (η^4-Diene)ML$_n$ Complexes

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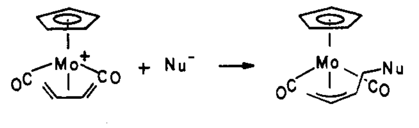
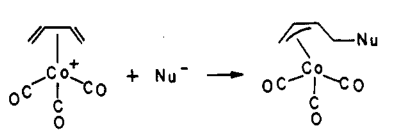
Perturbational theory using extended Hückel molecular orbitals has been used to analyze the reactions of nucleophiles with (η^4-diene)ML$_n$ complexes. The interaction of nucleophiles with the complexes ML$_n$ = $Co(CO)_3^+$ and $PdCl_2$ is dominated by the HOMO$_{Nu}$/LUMO$_{complex}$ interaction which is maximized for most nucleophiles during attack at C1 (terminal) of the diene. When ML$_n$ = $Fe(CO)_3$ the above nucleophile/complex interaction is counterbalanced by a repulsive HOMO$_{Nu}$/HOMO$_{complex}$ interaction which favors attack at C2 (internal). The influence on regioselectivity of the nucleophile and replacement of CO ligands by phosphines is also considered. The results obtained accomodate well the available experimental observations.

The addition of nucleophiles to organic fragments π-coordinated to transition metals is a process of considerable generality and is often characterized by a high degree of regio and stereoselectivity. For this reason such reactions have come to have increasing application in organic synthesis[1] and have been incorporated in important industrial processes.[2] In several cases the selectivities of these reactions have been found to depend dramatically on the nature of the metal, the nucleophile, substrate substituents, auxiliary ligands, solvent, and temperature.

An interesting case in point is provided by the various reports of nucleophilic additions to (η^4-diene)ML$_n$. For example, studies by Green,[3] Faller,[4] and Pearson[5] have demonstrated that several nucleophiles including BH_4^-, stabilized enolates and enamines attack (η^4-diene)MoCp(CO)$_2^+$ regiospecificially at the diene terminus (C1, eq 1).


(1)

Other systems which, thus far, exhibit the same regiopreference include (η^4-diene)PdX$_2$ complexes examined by Akermark[6] and Bäckvall[7] and (η^4-diene)Co(CO)$_3^+$ derivatives studied recently in this laboratory (eq 2).[8] In sharp contrast, however, recent reports by Semmelhack have indicated that (η^4-diene)Fe(CO)$_3$ initially add (at low temperatures) LiC(CN)R$_2$ at C2 (conversion to the more stable η^3-adducts of C1 attack occurs at higher temperatures).[9] We were intrigued by the question of the underlying basis for this reversal of regioselectivity among these complexes, especially between the iron and isoelectronic cobalt systems.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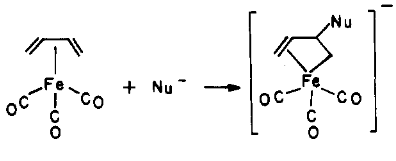
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A number of theoretical attempts have been made to analyze the factors controlling nucleophilic additions to π-coordinated hydrocarbon moieties. Early efforts considered only electronic features of the complex itself such as charge density or free valence indices. The most extensive analysis of this type was given by Davies, Green, and Mingos[10] who applied Hückel theory to additions to *cationic* complexes. Assuming *charge-controlled* processes, a set of rules for predicting regioselectivity was proposed. Although these rules hold reasonably well, there are a number of exceptions[11] and reactions of neutral compounds are not covered. INDO calculations have also been applied to reactions of η^5-cyclohexadienyl and η^6-arene complexes with limited success.[12]

In order to account for the potential influence of the nucleophile in such reactions recent studies have utilized perturbational frontier MO analysis. Extended Hückel calculations of this type have been successfully applied to the analysis of nucleophilic attack on η^2-olefin,[13] η^3-allyl,[14] and η^5-pentadienyl[15] complexes. A related EHMO methodology (self-consistent charge and configuration) which allows consideration of solvent dielectric effects and the possibility of attack at the metal or carbonyl ligands[16] has

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(1) Review: Davies, S. G. *Organotransition Metal Chemistry: Applications to Organic Synthesis*; Pergamon: Oxford, 1982; Chapter 4.

(2) Review: Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980; Chapters 4 and 6.

(3) Green, M. L. H.; Mitchard, L. C.; Silverthorn, W. E. *J. Chem. Soc. Dalton Trans.* **1973**, 1952.

(4) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 4858. Faller, J. W.; Murray, H. H.; White, D. L.; Chao, K. H. *Organometallics* **1982**, *2*, 400.

(5) Pearson, A. J.; Khan, M. N. I.; Clardy, J. C.; Cun-heng, H. *J. Am. Chem. Soc.* **1985**, *107*, 2748.

(6) Akermark, B.; Ljungqvist, A.; Panunzio, M. *Tetrahedron Lett.* **1981**, *22*, 1055.

(7) Bäckvall, J. E.; Nystrom, J. E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 3676 and references therein.

(8) Barinelli, L. S.; Tao, K.; Nicholas, K. M. *Organometallics* **1986**, *5*, 588.

(9) (a) Semmelhack, M. F.; Herndon, J. W. *J. Organomet. Chem.* **1984**, *265*, C15. Semmelhack, M. F.; Herndon, J. W.; Springer, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 2497. (b) Semmelhack, M. F.; Herndon, J. W. *Organometallics* **1983**, *2*, 363.

(10) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047.

(11) See, e.g.: Madonik, A. M.; Astruc, D. *J. Am. Chem. Soc.* **1984**, *106*, 2437. Charles, A. D.; Divers, P.; Johnson, B. F. G.; Karlin, K. D.; Lewis, J.; Rivera, A. V.; Sheldrick, G. M. *J. Organomet. Chem.* **1977**, *128*, C30. Pearson, A. J.; Kole, S. L.; Ray, T. *J. Am. Chem. Soc.* **1984**, *106*, 6060. See also ref 14 and 9b.

(12) Kane-Maguire, L. A. P.; Honig, E. D.; Sweigart, D. A. *Chem. Rev.* **1984**, *84*, 525.

(13) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308.

(14) Curtis, M. D.; Eisenstein, O. *Organometallics* **1984**, *3*, 887.

(15) Eisenstein, O.; Butler, W. M.; Pearson, A. J. *Organometallics* **1984**, *3*, 1150.

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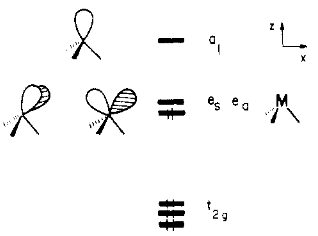


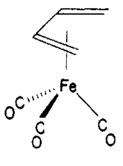
Figure 1. Frontier orbitals of the $Fe(CO)_3$ fragment.

been utilized to analyze the reactions of nucleophiles with various (η^n-polyenyl)$M(CO)_3$ complexes.[17]

No theoretical treatments have been reported which account for the remarkable metal-dependent regioselectivity of the (η^4-diene)ML_n reactions nor the possible influence of the nucleophile. The DGM rules[10] mentioned above (charge density based) predict C1 attack for additions to the *cationic* diene complexes. Previous semiempirical extended Hückel and ab initio calculations on (η^4-diene)$Fe(CO)_3$,[18,19] on the other hand, found C2 to be more electron-deficient. In order to more completely determine the factors that control the regiochemical course of these reactions, we report here the results of a perturbational analysis based on extended Hückel calculations of the reactions of nucleophiles with the complexes (η^4-butadiene)$Fe(CO)_3$, -$Co(CO)_3{}^+$, and -PdX_2.

Results and Discussion

In order to better discuss the reactivity of these complexes, we need first of all to compare their electronic structures. In this part, we concentrate on the iron **1** and cobalt cation **2** complexes of butadiene.



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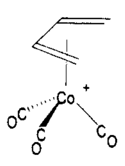

2

Numerous theoretical studies already have been devoted to ML_3–butadiene complexes, in particular by Hoffmann et al.[20] The preferred conformation (shown in **1** and **2**) has been attributed to electronic factors. However, only general features were discussed and no detailed comparison of the iron and cobalt cation complexes is available. We will focus on the shapes and energies of the molecular orbitals of these two complexes since they play a determinant role in the reactivity. For that purpose, we consider them to be made from a butadiene and an $M(CO)_3$ (M = Fe, Co^+) fragment. For the frontier orbitals of the $Fe(CO)_3$ fragment (Figure 1), one finds the usual pattern of three nonbonding orbitals originating from the t_{2g} set of the octahedron. Above this group of orbitals one has a set of three hybrids orbitals (e and a_1) that are the valence orbitals of $Fe(CO)_3$ and contain a total of two electrons. The e set is a pair of degenerate orbitals, one of them (e_s) being symmetrical with respect to the *xz* plane and the other one (e_a) being antisymmetrical with respect to it. The highest valence orbital (a_1) is of cylindrical symmetry.

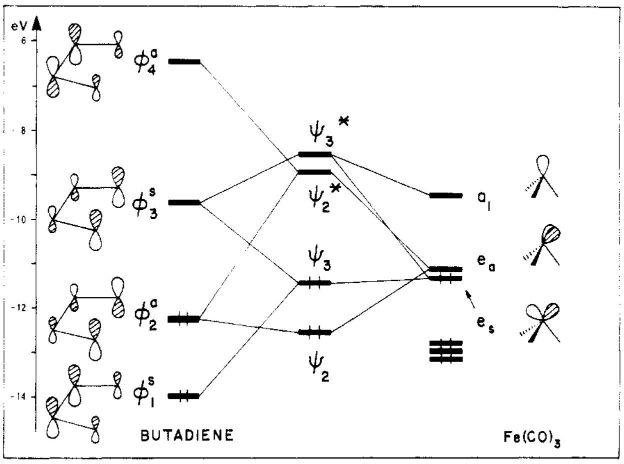

Figure 2. Simplified interaction diagram between the orbitals of $Fe(CO)_3$ and butadiene to form the frontier orbitals as well as the subjacent and superjacent frontier orbitals of (butadiene)-$Fe(CO)_3$.

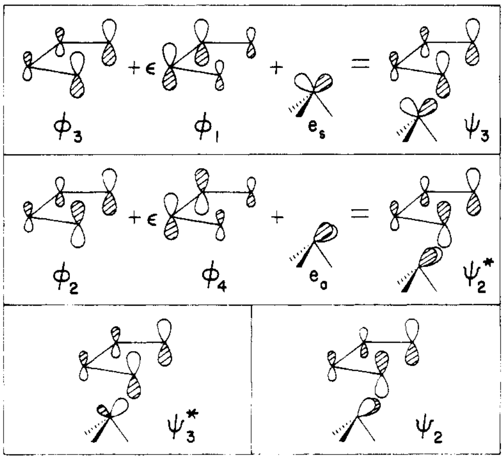

Figure 3. Shape and components of the frontier and subjacent and superjacent frontier orbitals of (butadiene)$Fe(CO)_3$.

Table I. Energy (eV) and Localization of the HOMO and the LUMO of the Butadiene and the Metal Fragments

orbital	Fe	Co^+
	LUMO	
energy	−8.8	−9.3
localization: $\phi_2{}^a$	0.21	0.29
total butadiene^a	0.25	0.32
$M(CO)_3{}^a$	0.75	0.68
	HOMO	
energy	−11.2	−11.5
localization: $\phi_3{}^a$	0.34	0.26
total butadiene^a	0.41	0.34
$M(CO)_3{}^a$	0.59	0.66

[a] Density on the fragment orbital or the whole fragment normalized to 1.

These three metal-centered orbitals, hybridized away from the CO ligands, interact strongly with the four π orbitals (ϕ_1, ϕ_2, ϕ_3, ϕ_4) of butadiene (Figure 2). The frontier orbitals of the complex come from the bonding and antibonding combinations of the e set with ϕ_2 and ϕ_3,

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[16] Brown, D. A.; Fitzpatrick, N. J.; McGinn, M. A. *J. Organomet. Chem.*, **1985**, *293*, 235.

[17] Brown, D. A.; Chester, J. P.; Fitzpatrick, N. J. *Inorg. Chem.* **1982**, *21*, 2723.

[18] El-Awady, A. A. *J. Inorg. Nucl. Chem.*, **1974**, *36*, 2185.

[19] Connor, J. A.; Derrick, L. M. R.; Hall, M. B.; Hillier, I. H.; Guest, M. F.; Higginson, B. R.; Lloyd, D. R. *Mol. Phys.* **1974**, *23*, 1193.

[20] Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.

slightly perturbed by ϕ_1 and ϕ_4. Figure 3 and Table I show the way the frontier MOs are built from these fragment MOs. The HOMO ψ_3 is the bonding combination of e$_s$ and ϕ_3 with a small contribution of ϕ_1 mixing with e$_s$ in an antibonding manner. Since the participation of ϕ_3 dominates over that of ϕ_1, the HOMO is more centered on the terminal carbon centers than on the internal ones. Below the HOMO, the subjacent orbital ψ_2 is the bonding combination of ϕ_2 and e$_a$. It is also more centered on the terminal carbon centers. The empty orbitals can be understood in a similar manner. The LUMO ψ_2^* is the antibonding combination of ϕ_2 and e$_a$ with a small admixture of ϕ_4 mixing in a bonding manner with e$_a$. The next higher empty orbital ψ_3^* is the antibonding combination of ψ_3 and e$_s$ with a significant admixture of the higher metal hybrid a$_1$. It is clear that these two empty orbitals are mostly derived from ϕ_2 and ϕ_3 on the butadiene fragment and have therefore a larger contribution on the terminal carbons than on the internal ones.

Consider now an incoming nucleophile characterized by a high-lying occupied orbital. Two types of interaction are at work between the nucleophile's occupied orbital and the substrate: (i) a two-electron attractive interaction with the empty orbitals of the complex and (ii) a four-electron destabilizing interaction with the occupied orbitals of the complex. Since the LUMO and next above orbital are mostly localized on the terminal carbons, the *attractive* interaction between the nucleophile and the butadiene complex is larger for an approach to the terminal carbon favoring the attack at the terminal center. On the other hand, since the HOMO and the next below orbital are mostly localized on the terminal carbon, the *destabilizing* interaction between the nucleophile and the butadiene complex is larger for an approach to the terminal carbon favoring the attack at the internal center. The regioselectivity is thus determined by the balance between these two contradictory effects. We will see that the difference in reactivity between the Fe and Co$^+$ complex results from a change in the relative proportion of the two interactions.

We need first to see if the shapes of the frontier orbitals (localization on terminal vs. internal carbons) vary with the metal. We have seen that there was some admixture of ϕ_4 and ϕ_1, respectively, in the LUMO and HOMO. Since these two orbitals are more concentrated on the internal carbon centers, the regioselectivity of the reaction may well be modified if the weight of ϕ_4 and ϕ_1 increases considerably in the LUMO and HOMO of the complex. This does not occur in our calculations. By varying the energy level of the d block of the metal (higher for Fe than for Co$^+$), we could not find any significant change in the relative weight of the terminal and internal coefficients in the LUMO and HOMO of the complex. It is thus clear that the HOMO always favors the addition to the internal carbon while the LUMO favors the addition to the terminal carbon, and this is for any type of ML$_3$ fragment. Note that we limit our discussion to the LUMO and HOMO since the higher empty orbital and lower occupied orbital that we have described in ψ_2 and ψ_3^* behave in the same manner.

At this point it is clear that the rationalization of the experimental facts necessitates taking into account the HOMO and LUMO simultaneously, the regioselectivity being determined by the orbital that dominates the nucleophile–substrate interaction. The model is quite simple. We are confronted with a three-orbital situation: the HOMO of the nucleophile and the HOMO and the LUMO of the substrate. By using the perturbation theory in a way that has been shown to be highly fruitful for numerous regioselectivity problems in organic chemistry, we can calculate the interaction energy ΔE arising from these three orbitals.[21] This leads us to a mathematical function in which the interaction energy explicitly depends on x, the energy of the HOMO of the incoming nucleophile. The energy of the nucleophile is varied in between that of the HOMO and LUMO of the substrate. The interaction energy is a function of the overlap between the nucleophile orbital and the two orbitals of the substrate as well as a function of the energy gaps separating the three orbitals. This function $f(S^2_{\text{LUMO}}/(E_{\text{LUMO}} - E_{\text{Nu}}), S^2_{\text{HOMO}}/(E_{\text{HOMO}} - E_{\text{Nu}})$, where S_{LUMO} (respectively S_{HOMO}) is the overlap between the LUMO (respectively HOMO) and the nucleophile, describes the following facts—when the nucleophile is close in energy to the LUMO, the LUMO–nucleophile interaction dominates whereas when the nucleophile is far in energy from the LUMO, the influence of the HOMO may dominate. The influence of each orbital increases when the overlap with the nucleophile increases and thus the percentage of butadiene character in the HOMO and the LUMO is important to consider. The curves $\Delta E = f(x)$ are shown in Figure 4 for approach to the terminal/internal carbon in the case of the iron complex.

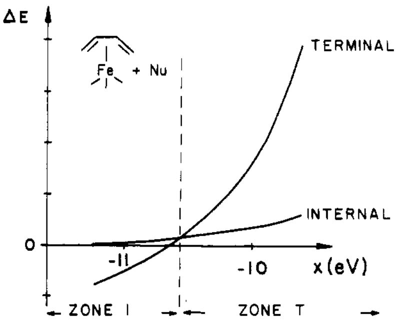

Figure 4. Interaction energy curves for terminal and internal attack on the iron complex. ΔE is in arbitrary units. x represents the energy level of the HOMO of the nucleophile. The signs have been taken such as, x being fixed, the more favored approach is the one with the greatest value for ΔE. Zone I (T) delineates the zone where the attack to the internal (terminal) carbon is favored.

These curves provide some interesting insight into the problem. The greater the interaction energy the more favored the approach is. These two curves intersect at a value x_0 so that one can expect changes in the regioselectivity with the nature of the nucleophile. It thus suggests that a nucleophile with a high-lying HOMO prefers to approach to the terminal carbon while a nucleophile with a lower lying HOMO prefers to add to the internal carbon.

The same two curves obtained in the case of the cobalt complex are shown in Figure 5. Although the overall shape of the curves is the same as in the case of iron, interesting changes have appeared. The approach to the terminal carbon is more favored in the case of cobalt since the two curves intersect for a value x'_0 which is much more negative than in the case of iron.

Another way to illustrate the same facts is to plot the difference between the two interaction energies (terminal approach–internal approach) as a function of x (Figure 6). When this function is positive (respectively negative), the approach to the terminal (respectively internal) carbon is preferred. The curve for the cobalt remains always above that for iron; i.e., there is a greater preference for the terminal attack at a given x for the cobalt complex. The

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[21] Klopman, G. *J. Am. Chem. Soc.* **1968**, *90*, 223. See chapter on ionic reactions in ref 23 for numerous applications.

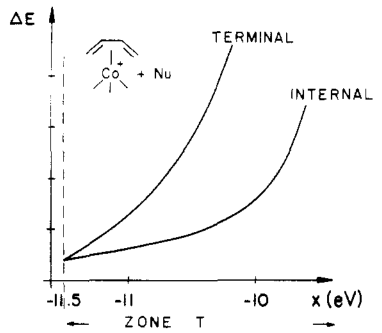


Figure 5. Interaction energy curves for terminal and internal attack on the cobalt complex. ΔE is in arbitrary units. x represents the energy level of the HOMO of the nucleophile. The signs have been taken such as, x being fixed, the more favored approach is the one with the greatest value for ΔE. Zone I (T) delineates the zone where the attack to the internal (terminal) carbon is favored.

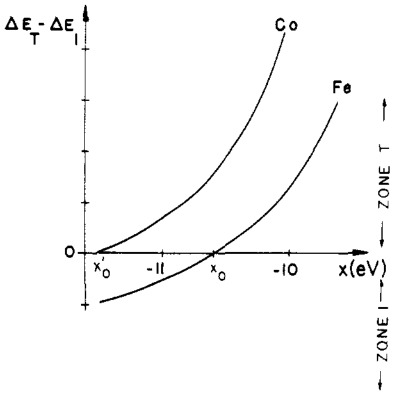


Figure 6. Interaction energy difference for nucleophilic addition to cobalt and iron complexes (terminal–internal). When $\Delta E_T - \Delta E_I$ is positive, attack to the terminal carbon is prefered (zone T). x_0 (x'_0) represents the value of the energy where the preference in regioselectivity is changed for the iron (cobalt) complex.

curve for the iron case intersects the x axis at a higher energy value ($x_0 > x'_0$). Therefore a nucleophile that prefers the internal carbon in the case of iron may attack the terminal carbon in the case of cobalt.

Our calculations show that the above regioselectivity preferences remain if more occupied and empty orbitals are included in the calculation. Since the major effect is already present in the frontier orbitals, one can discuss qualitatively the problem by considering only these two orbitals.

What is the origin of this difference in regioselectivity? It can be easily understood by looking at the way the frontier orbitals are built from ϕ_2, ϕ_3, e_s, and e_a in the Fe and Co complexes (Figure 7 and Table I). Consider first the HOMO ψ_3. As mentioned previously, it is the bonding combination of butadiene ϕ_3 and $M(CO)_3$ e_s. When the energy of e_s is lowered (Fe → Co^+), the HOMO goes lower, acquires more metal character, and loses a part of its butadiene component (Table I). Conversely, the LUMO (ψ_2*) is the antibonding combination of ϕ_2 and e_a. When the energy of e_a is lowered (Fe → Co^+), it gets closer to ϕ_2 so that the percentage of ϕ_2 into the LUMO increases (Table I). The consequence of that change in the metal/ligand localization is the following. Going from Fe to Co^+ diminishes the butadiene character in the HOMO so that the incoming nucleophile suffers less four-electron repulsion from this orbital. In addition the LUMO, itself lower in energy, is now relatively more localized on the butadiene so that the two-electron stabilization between the nucleophile and the substrate increases. So going from Fe to Co^+ makes the reaction less controlled by the HOMO and more controlled by the LUMO. Since the HOMO favors addition to the internal carbon center while the LUMO favors addition to the terminal carbon, it is clear that Co^+ prefers terminal attack.

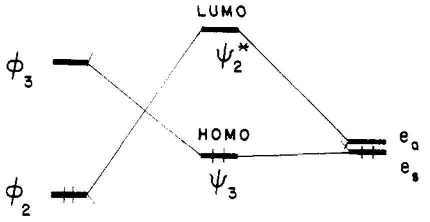


Figure 7. Simplified interaction diagram between the frontier orbitals of butadiene and $M(CO)_3$ to form the frontier orbitals of the (butadiene)$M(CO)_3$ complex.

Table II. Electronic Density on the Carbons of Coordinated Butadiene[a]

	C_{term}	C_{int}
Fe complex p_z	1.14	0.91
tot.	1.24	0.92
Co^+ complex p_z	1.03	0.82
tot.	1.13	0.88

[a] Abbreviations: P_z, π density; tot., total density; C_{term}, terminal carbon; C_{int}, internal carbon.

Our analysis was conducted by looking at the shapes and energies of the molecular orbitals. It is worthwhile to see if a charge controlled reaction would also account for the same results. As noted earlier, SCF calculations on the iron complex[18] show that the butadiene is overall negatively charged and that the negative charge is larger on the terminal carbons than on the internal ones. That the nucleophile prefers to attack the internal carbon rather than the terminal ones can be certainly related to this charge difference. However it is difficult to account for the fact that a nucleophile may want to approach an overall negatively charged ligand. The presence of low-lying empty orbitals account better for that fact. Despite that difficulty, it is informative to analyze the charge drift produced by the replacement of Fe in Co^+. In agreement with the SCF calculation the overall charge on the butadiene in the iron complex is negative (−0.08) and mostly concentrated on the terminal carbon (see Table II). π-Electronic densities follow the same trend (Table II). In contrast, the overall charge on the butadiene in the cobalt cation complex is positive (0.21). However the electron density on the butadiene is still concentrated on the terminal centers as shown by the total and π-electron density (Table II). *These facts account for the higher reactivity of the cobalt complex toward a nucleophile but cannot explain the experimentally observed regioselectivity.* π- and total electron density on the carbon centers vary in a parallel fashion when Fe is replaced by Co^+. This permits us to give a rationale of the electron drift by making use of our π-interaction diagram (Figure 3). The two occupied molecular orbitals, the bonding combination of ϕ_2 and e_a (ψ_2) as well as that of ϕ_3 and e_s (ψ_3), determine the larger part of the π-electronic charge on the butadiene. ϕ_2 loses electrons by interacting with e_a while ϕ_3 gains electrons by interaction with e_s (back-bonding). If the e set is lying at a high energy, the e_s → ϕ_3 electron transfer dominates over the other one. Lowering the e set (Fe → Co^+) makes the back-bonding less important so that the overall electron density on butadiene is less in the cobalt complex than in the iron one.

A change of the energy of the metal hybrid orbitals e can be achieved by changing the nature of the ligands. The

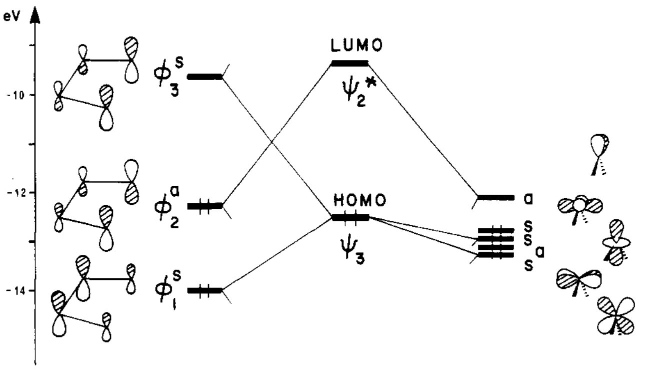
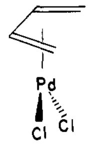


Figure 8. Simplified interaction diagram between the orbitals of butadiene and of $PdCl_2$ to form the frontier orbitals of (butadiene)$PdCl_2$.

energy of the e orbitals is sensitive to the σ-donating capability of L (they are M–L σ-antibonding). Strong σ-donating L groups will raise the energy of the set and should accordingly favor the internal (C2) attack on the coordinated butadiene. Such should be the case if CO is replaced by phosphine ligands.

The same type of analysis can be applied to diene complexes with other ML_n fragments. For instance, consider nucleophilic addition to the Pd(II) complex of butadiene, 3. Experimentally, the addition to the terminal carbon has been observed.[7] Bäckvall has interpreted this result in terms of a thermodynamically controlled reaction, thinking that kinetic control would favor addition to the internal carbon center. Our calculation shows that the addition to the terminal carbon is kinetically preferred. The system we have calculated is shown in 3, the $PdCl_2$ group being oriented in the most stable way with respect to the butadiene.



3

The interaction diagram between the butadiene and $PdCl_2$ group is given in Figure 8. The HOMO ψ_3 is the in-phase combination of the symmetric metal orbitals (s) and butadiene ϕ_3, mixing ϕ_1 in an antibonding way. The LUMO ψ_2* is the antibonding combination of ϕ_2 and the antisymmetric LUMO (a) of the $PdCl_2$ fragment. The difference with the $Fe(CO)_3$ case arises from the change of the energy levels of the metal orbitals with respect to that of butadiene. The metal orbitals that participate in the HOMO of the complex are considerably lower in $PdCl_2$ than in $Fe(CO)_3$ since they are nonbonding orbitals. As a consequence, the HOMO of the complex has less butadiene character. In addition the LUMO of $PdCl_2$ is closer in energy to ϕ_2 so that there is more butadiene character in the LUMO of the complex. The reactivity of the butadiene–$PdCl_2$ complex, like the $Co(CO)_3^+$ derivative, is therefore controlled by the LUMO. Thus, addition to the terminal carbon is preferred.

Finally, regarding the issue of regioselectivity dependence on nucleophile, it is obviously desirable to identify which nucleophiles will favor C1 (terminal) and which will favor C2 (internal) attack for a particular metal complex; i.e., what are the x values for various nucleophiles? This issue must be approached with caution because our calculations do not take specific account of the nucleophile's solvation, a factor known to be important in determining the relative reactivity and E_{HOMO} of nucleophiles.[22,23] Indeed, no satisfactory theoretical model exists which allows quantitatively reliable inclusion of this parameter. It is apparent, however, that small, highly charged (hard) nucleophiles will have their effective E_{HOMO} (x) greatly lowered by solvation whereas for larger, more polarizable (soft) nucleophiles x is less affected.[22] We associate the lower values of x (i.e. more negative) with hard, strongly solvated nucleophiles and high x values with soft (less solvated) nucleophiles. One may anticipate, therefore, that if C2 (internal) attack is to be observed at all in the (diene)$Co(CO)_3^+$ system, it will most likely occur with hard nucleophiles such as an OH^-, F^-, etc. On the other hand, C1 (terminal) attack should be preferred in the iron system with nucleophiles such as I^- and RS^-, providing these are sufficiently reactive to add. While the influence on regioselectivity of nucleophile hardness/softness and solvent had been documented in some metal–pentadienyl complexes,[11,14] no systematic experimental studies of these parameters have been conducted with metal–diene compounds. Efforts are underway to address this deficiency and to test the predictions given above.

Table III[a]

		exponents			
orbital	H_{ii}, eV	ζ_1	C_1	ζ_2	C_2
H 1s	−13.6	1.3			
C 2s	−21.4	1.625			
C 2p	−11.4	1.625			
O 2s	−32.3	2.275			
O 2p	−14.8	2.275			
Cl 3s	−30.0	2.033			
Cl 3p	−14.0	2.033			
Fe 4s	−9.10	1.9			
Fe 4p	−5.32	1.9			
Fe 3d	−12.6	5.35	0.5505	2.00	0.6260
Co 4s	−9.21	2.0			
Co 4p	−5.29	2.0			
Co 3d	−13.18	5.55	0.5680	2.10	0.6060
Pd 5s	−7.32	2.19			
Pd 5p	−3.45	2.152			
Pd 4d	−12.02	5.9836	0.5535	2.613	0.6701

[a] All calculations were performed by using the extended Hückel method[25a] using the weighted H_{ij} formula.[25b] The parameters used were taken from ref 26. Experimental geometries were taken from ref 27.

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(22) Minot, C.; Anh, N. T. *Tetrahedron Lett.* **1975**, *475*, 3905.

(23) Fleming, I. In *Frontier Orbitals and Chemical Reactions*; Wiley: London, 1976; Chapter 3.

(24) Brown, D. A.; Chawla, S. K.; Glass, W. K.; Hussein, M. F. *Inorg. Chem.* **1982**, *21*, 2726.

(25) (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. Hoffmann, R.; Lipscomb, W. N. *Ibid.* **1962**, *36*, 2179; **1962**, *37*, 177; **1962**, *37*, 2872. (b) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C. Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.

(26) Summerville, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240. See also ref 13.

(27) Eiss, R. *Inorg. Chem.* **1970**, *9*, 1650. Beddoes, R.; Lindley, P. F.; Mills, O. S. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 304. Dodman, P.; Hamor, T. A. *J. Chem. Soc., Dalton Trans.* **1974**, 1010. Evrard, G.; Thomas, R.; Davis, B. R.; Bernal, I. *Inorg. Chem.* **1976**, *15*, 52.