

the best current route to this compound, viz., oxidative transmetalation between ytterbium metal and thallos cyclopentadienide.²⁸

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A Theoretical Analysis of the Stepwise Reduction of [(η -C₅H₅)Re(NO)(CO)(PPh₃)]⁺ to [(η -C₅H₅)Re(NO)(CH₃)(PPh₃)]

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The stepwise reduction of [(η -C₅H₅)Re(NO)(CO)(PPh₃)]⁺ to [(η -C₅H₅)Re(NO)(CH₃)(PPh₃)] is investigated from a theoretical point of view. All the rhenium complexes involved in the reaction are found to have HOMOs and LUMOs that are similar in nature. The HOMOs are mainly metal d in character, while the LUMOs appear to be antibonding combinations of rhenium d orbitals and nitrosyl π^* orbitals. In the reaction sequence being studied proton attacks have the overall effect of lowering orbital energies, while reduction destabilizes most molecular orbitals. Also investigated is the site of nucleophilic and electrophilic attack, which is found to be the nitrosyl ligand for the nucleophile and the oxygen atom at the original carbonyl site for the electrophile.

Introduction

Lately, new interest in organometallic complexes has been generated by their possible use in the transformation of coal into various organic molecules;¹ specifically, they have been studied as homogeneous² or heterogeneous^{3,4} catalysts in the reduction of CO.⁵ Gladysz has considered a variety of pseudotetrahedral⁶ organorhenium complexes, studying their role as catalysts⁷ as well as their stereoisomerism, which is important in stereospecific reactions.⁸⁻¹⁵

The chemistry involved in the synthesis and reactivity of these rhenium compounds is interesting from a theoretical point of view; the reactions studied present features that can be analyzed in a straightforward manner and at the same time reveal interesting aspects of the reactivity of organometallic compounds.

In a previous paper¹⁶ one of these organorhenium complexes, [(η -C₅H₅)Re(NO)(CO)(PPh₃)]⁺, and its reduction to the neutral formyl [(η -C₅H₅)Re(NO)(CHO)(PPh₃)] have been analyzed in detail. The present work proposes to take that analysis further, following in a stepwise fashion the reaction that leads to the complete reduction of the formyl ligand to a methyl ligand.⁷

Experimentally,⁷ Gladysz has shown that the reduction of the formyl complex to the methyl species can occur: (1) by addition of BH₃·THF to the formyl compound, (2) by the reaction of the carbonyl complex (which is the precursor to the formyl ligand) with NaBH₄ in THF/H₂O, and (3) by electrophile-induced disproportionation of the formyl complex by either CH₃SO₃F or CH₃CO₂H. In an excellent series of experimental studies, Gladysz demonstrated that all three reaction sequences are equivalent to a series of alternating nucleophilic and electrophilic attacks. This sequence of reactions can thus provide information as to how the energetics of the rhenium complex change upon gradual reduction and what the role of the alternating electrophilic attack is. In addition, previous work has shown that reduction of CO to CHO in the same rhenium complex occurs via the nitrosyl ligand, which is energetically more apt to form a coordinate-covalent bond with the attacking nucleophile.¹⁶ In this paper it will be

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Table I. Comparison of Molecular Orbital Energies for the Seven Rhenium Complexes^a

	$[\text{Rp}(\text{CO})]^+$ ^b	$[\text{Rp}(\text{CHO})]$	$[\text{Rp}(\text{CHOH})]^+$	$[\text{Rp}(\text{CH}_2\text{OH})]$	$[\text{Rp}(\text{CH}_2\text{OH}_2)]^+$	$[\text{Rp}(\text{CH}_2)]^+$	$[\text{Rp}(\text{CH}_3)]$
	-4.36	1.19	-4.78	2.07	-2.37	-5.56	2.33
	-5.71	0.02	-6.02	0.46	-3.62	-7.30	0.68
LUMO	-7.68	-1.64	-6.68	-1.12	-5.25	-9.72	-0.93
HOMO	-15.15	-8.21	-14.89	-7.84	-12.29	-16.46	-7.59
SHOMO	-16.36	-9.06	-15.71	-9.85	-14.18	-16.86	-9.72
	-16.66	-10.60	-16.01	-10.38	-14.62	-18.15	-10.16
	-19.70	-10.94	-18.63	-11.06	-18.03	-20.25	-13.32
	-19.77	-14.06	-19.45	-11.89	-18.73	-20.65	-14.21
	-22.46	-14.50	-20.48	-14.35	-20.84	-22.87	-15.27

^aThe values of the energy levels are valid only relative to one another and are expressed in units of electronvolt. The effect of counterions on cationic levels has not been taken into account. ^b $\text{Rp} = (\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)$.

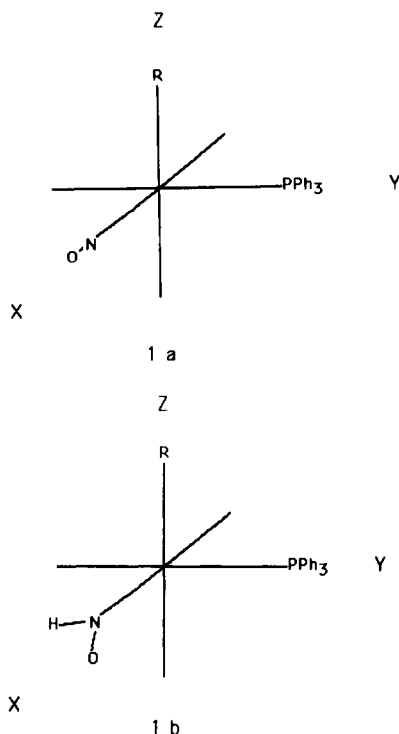


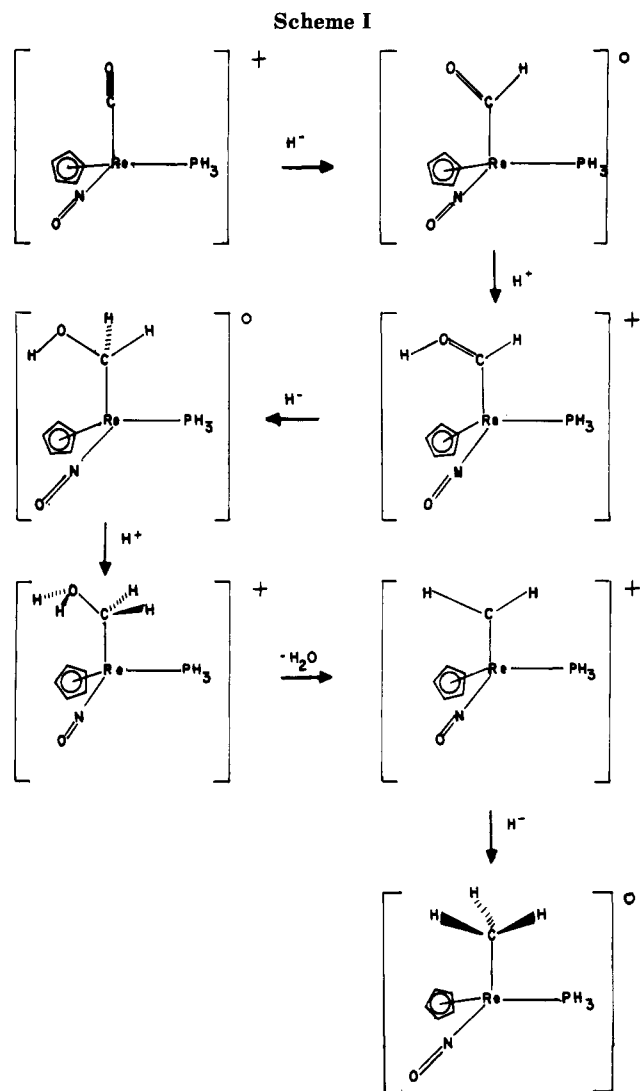
Figure 1. Coordinate system used in the calculations. The centroid of the Cp ring (not shown) is located in the octant bounded by the $-x$, $-y$, and $-z$ axes.

possible to investigate whether further reduction in the complex also occurs via the nitrosyl ligand or directly at the formyl ligand.

Computational Procedure

Calculations have been carried out by using the Fenske-Hall nonempirical method¹⁷ on a Harris/7 computer. The average time required for calculations on each rhenium complex was between 15 and 20 min of cpu time. Atomic basis functions were employed; for oxygen, carbon, nitrogen, and phosphorous Clementi's double- ζ functions were used,¹⁸ except for 1s and 2s functions, which were curve-fit to single ζ by using the maximum overlap criterion.¹⁹ The hydrogen exponent was set to 1.16. The rhenium(0) functions were taken from the results of Richardson et al.,²⁰ the 6s and 6p exponents were set to 2.30 to avoid working with metal outer functions that are too diffuse, which often leads to meaningless results.

The geometry used for $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})(\text{PPh}_3)]^+$ and $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CHO})(\text{PPh}_3)]$ was taken from the



actual X-ray structures determined by Gladysz et al.²¹ and idealized to pseudooctahedral symmetry (see ref 6 and Figure 1); the geometry of the remaining rhenium complexes was extrapolated from that of the precursor. For simplicity of interpretation and greater ease in the calculations, the triphenylphosphine group present in each of the complexes has been substituted with a phosphine group and the attacking nucleophile and electrophile have been represented by H^- and H^+ , respectively.

Results and Discussion

Scheme I shows the sequence of complexes from $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})(\text{PPh}_3)]^+$ to $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CH}_3)]$.

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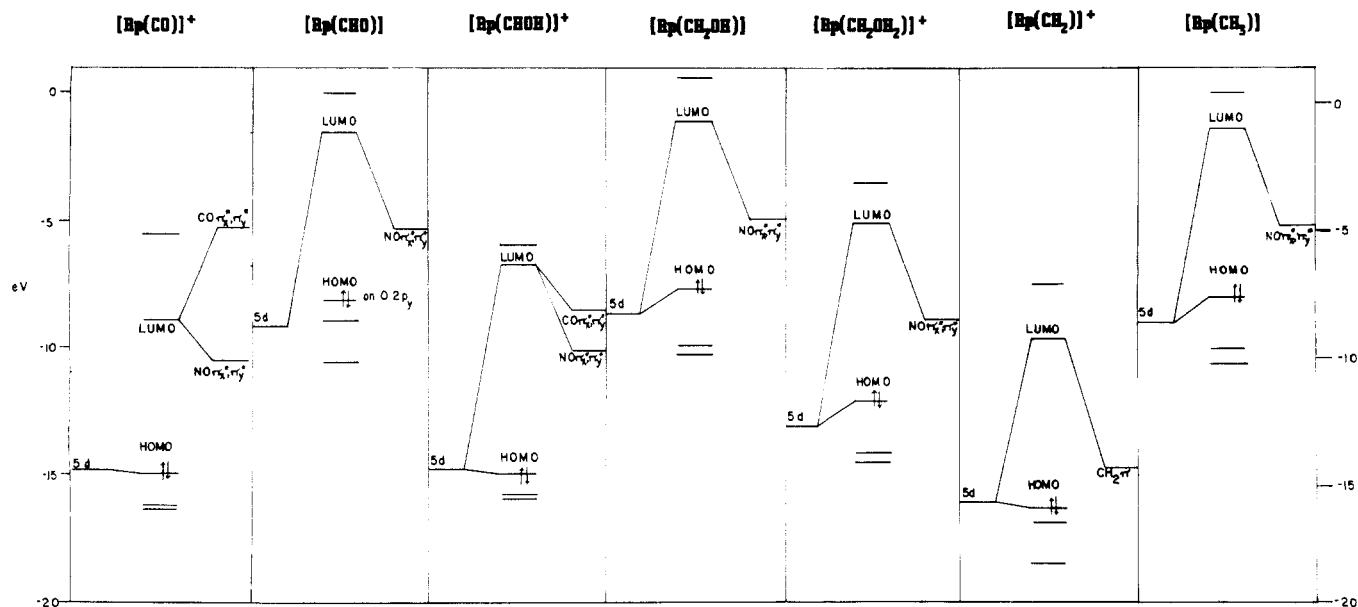


Figure 2. Energy diagrams for the seven organorhenium complexes. In each diagram, the diagonal terms of the metal d basis functions are shown on the left-hand side, the molecular orbitals in the center, and the diagonal terms of the ligands' basis functions on the right-hand side. The complexes have been labeled as in Table I.

(PPh₃)] that are formed in the succession of alternating proton and hydride attacks. Both nucleophilic and electrophilic attacks result in the addition of a hydrogen atom at the site originally occupied by the carbonyl ligand; when CH₂OH₂ is formed, a water molecule splits off and the ligand rearranges to a carbene.

As stated in the Introduction, the gradual reduction of [(η-C₅H₅)Re(NO)(CO)(PPh₃)]⁺ to [(η-C₅H₅)Re(NO)(CH₃)(PPh₃)] presents two interesting aspects: the pattern of energy changes in the rhenium complex as the reaction proceeds and the question of the site of nucleophilic attack. First, let us consider the energetics of the complexes involved in the reaction and how they are modified by either nucleophilic or electrophilic attack.

Energy Patterns in the Rhenium Complexes. Trends in frontier molecular orbitals, and especially in the HOMO and LUMO, are important in the understanding of reactivity of molecules, since these are the orbitals that are most likely to be involved in interactions with other molecules.²² Table I shows a comparison of energy values for several frontier molecular orbitals in each of the compounds. Examination of the relative positions of the HOMOs and LUMOs indicates that hydride attacks have an overall destabilizing effect, while the addition of a proton tends to lower orbital energies. This observation can be explained in terms of electron-electron repulsion and nuclear attraction: while a proton introduces in the molecule just an additional nucleus that can help stabilize and delocalize electron charge, a hydride also contributes a pair of electrons and negative charge, which increase electron-electron repulsion. The proton attacks that intercalate reduction can therefore be interpreted as necessary to stabilize the molecule and prepare it for the next reduction step.

Figure 2 again shows a comparison of the principal molecular orbitals in the seven molecules and, in addition, the major contributions to each orbital from the metal and ligands. From this figure the nature of the HOMOs and LUMOs of the complexes can be determined, which in turn is important in the evaluation of their chemical reactivity. All complexes, with the exception of [(η-C₅H₅)Re(NO)-

Table II. Metal and Ligand Contributions to the HOMOs of the Complexes

	contribution	
	major	minor
[(η-C ₅ H ₅)Re(NO)(CO)(PPh ₃)] ⁺	metal d _{zz}	CO π*
[(η-C ₅ H ₅)Re(NO)(CHO)(PPh ₃)]	formyl O lone pair	
[(η-C ₅ H ₅)Re(NO)(CHOH)(PPh ₃)] ⁺	metal d _{yz}	CO π*, Cp ⁻ π
[(η-C ₅ H ₅)Re(NO)(CH ₂ OH)(PPh ₃)]	metal d _{yz}	
[(η-C ₅ H ₅)Re(NO)(CH ₂ OH ₂)(PPh ₃)] ⁺	metal d _{yz}	
[(η-C ₅ H ₅)Re(NO)(CH ₂)(PPh ₃)] ⁺	metal d _{xz} , d _{xz}	NO π*
[(η-C ₅ H ₅)Re(NO)(CH ₃)(PPh ₃)]	metal d _{yz}	

(CHO)(PPh₃)],²³ have HOMOs that are mainly metal d in character. In general, this results from the fact that at least one of the metal d orbitals has very little or no stabilizing interaction with the ligands, so as to remain fairly high in energy. Given that all complexes have the same symmetry and similar ligands, the fact that the rhenium d orbitals show comparable bonding patterns is not surprising. A tabulation of the various contributions to each molecule's HOMO can be found in Table II.

The LUMOs also show similarities, but with some variations. All molecules, except for [(η-C₅H₅)Re(NO)(CO)(PPh₃)]⁺, receive a sizeable contribution from metal d orbitals also to their LUMOs; but, contrary to what is observed in the HOMOs, it is usually a linear combination of orbitals rather than a single one. The recurring feature, though, is the significant contribution of NO π_x* and π_y* orbitals, which occurs in all molecules except [(η-C₅H₅)Re(NO)(CH₂)(PPh₃)]⁺.²⁴ A significant contribution from the carbon-containing ligand, on the other hand, is found only in [(η-C₅H₅)Re(NO)(CO)(PPh₃)]⁺ and [(η-C₅H₅)Re(NO)(CHOH)(PPh₃)]⁺. Table III summarizes these data. In general, then, the LUMO can be characterized as being for the most part an antibonding combination of metal d and nitrosyl π* orbitals, with the bonding counterpart usually found just below the HOMO of the molecule.

(23) See ref 15 for a more in-depth discussion of the HOMO in [(η-C₅H₅)Re(NO)(CHO)(PPh₃)].

(24) The LUMO of [(η-C₅H₅)Re(NO)(CH₂)(PPh₃)]⁺ has been found to be an antibonding combination of metal d and carbon p orbitals, confirming the results already obtained by Gladysz et al.⁸

Table III. Metal and Ligand Contributions to the LUMOs of the Complexes^a

	metal d	NO	C-containing ligand
$[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})(\text{PPh}_3)]^+$		π_x^* : 10.05% π_y^* : 34.21%	π_x^* : 16.95%
$[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CHO})(\text{PPh}_3)]$	$d_{x^2-y^2}$: 8.51% d_{xy} : 10.52% d_{xz} : 10.95% tot: 33.83%	π_x^* : 21.34% π_y^* : 21.19%	
$[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CHOH})(\text{PPh}_3)]^+$	tot: 25.40	π_x^* : 20.19% π_y^* : 16.47%	π_y^* : 16.85%
$[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CH}_2\text{OH})(\text{PPh}_3)]$	$d_{x^2-y^2}$: 8.91% d_{xy} : 11.52% d_{xz} : 10.35% tot: 35.89%	π_x^* : 21.66% π_y^* : 19.64%	
$[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CH}_2\text{OH}_2)(\text{PPh}_3)]^+$	$d_{x^2-y^2}$: 9.14% d_{xy} : 11.37% d_{xz} : 9.53% tot: 33.09%	π_x^* : 22.77% π_y^* : 19.04%	
$[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CH}_2)(\text{PPh}_3)]^+$	d_{xz} : 31.48% tot: 35.46%		Cp_x : 51.97%
$[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CH}_3)(\text{PPh}_3)]$	$d_{x^2-y^2}$: 8.60% d_{xy} : 10.88% d_{xz} : 10.82% tot: 36.21%	π_x^* : 21.08% π_y^* : 20.61%	

^a Percentages should be viewed only on a comparative basis. Also, the total metal d contribution to the LUMO is usually larger than the sum of the individual d orbital contributions, since it includes minor contributions from the other d orbitals that have not been listed.

From the foregoing analysis, it can be concluded that the organorhenium complexes under consideration show marked similarities in the nature of both their HOMOs and LUMOs, together with a downward shift in orbital energies following each electrophilic attack. These features are easily explained by simple physical arguments, like the ones used above; but there is a peculiarity about the nature of these frontier orbitals, which is the lack of contribution from the carbon-containing ligand. On the contrary, since most of the chemistry appears to occur at the original CO site, this ligand would be expected to make a significant contribution to the HOMO and LUMO. This problem leads to the question of where attack actually occurs in the molecule, which is the other focus of this paper.

Sites of Nucleophilic and Electrophilic Attack.

This aspect of the problem will be approached from two different points of view: one involving qualitative frontier orbital arguments and the other, more quantitative, which employs perturbation theory. It will be shown that both approaches lead to the same conclusions with respect to sites of attack; these results will then be applied specifically to each step in Scheme I.

Nucleophilic attacks generally involve that part of the molecule which is low in electron density and presents an empty lobe apt to receive a pair of electrons.²⁵ Frontier orbital arguments²⁶ suggest that such a site coincides with the ligand on which the LUMO of the molecule is localized, since the nucleophilic attack will result in filling this lowest unoccupied molecular level. This has in fact been found to be the case for nucleophilic attack on η^3 -allyl complexes.²⁷ On the other hand, an electrophile would be expected to attack a site with an excess of negative charge, which can be easily donated when forming the dative bond.

From these simple arguments involving electron density distribution and from the energetics of the complexes being studied (discussed above), some predictions can be made

about the sites of nucleophilic and electrophilic attack in this series of reactions. The hydride would be expected to attack the ligand which contributes most to the LUMO of the molecule, and, to determine the site of electrophilic attack, it is necessary to analyze the Mulliken population of each atom in the molecule and determine which one carries the largest negative charge. While doing the latter, it would appear logical to also take into consideration the role of the HOMO, the same way in which that of the LUMO was used in relation to nucleophilic attack. It should be remembered though that in the molecules being studied the HOMO is mostly localized on the central metal atom, which is far less accessible to the incoming electrophile than any of the ligands.

Another approach that can be used to determine the sites of attack is to consider the relative energies of the nucleophile or electrophile with respect to that of the substrate. Klopman has studied the general problem of reactivity between two molecules from a molecular orbital point of view by using perturbation theory.²⁸ His approach is a particularly valid one because it takes into consideration the energetics of both interacting molecules, although the perturbation created by the interaction has to be small for the theory to be valid. Applied to the problem at hand, this theory suggests that it is not sufficient to look solely at the HOMO and LUMO of any of the rhenium compounds to predict its reactivity; rather, it is necessary to consider the nucleophile or the electrophile also involved in the reaction.

By using this approach, Klopman has been able to place most reactions in one of two categories: charge-controlled reactions and orbital-controlled reactions.²⁸ The former category includes reactions that are mainly ionic in type and are characterized by a large energy difference between the HOMO of one molecule and the LUMO of the other. On the other hand, orbital-controlled reactions usually involve strong electron transfer and occur when the molecular orbitals involved in the reaction are nearly degenerate. Therefore, to decide whether the reactions of interest in this paper are orbital- or charge-controlled, it is

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Table IV. Comparison of HOMO and LUMO Orbital Energies of the Rhenium Complexes with Those of a Nucleophile and an Electrophile^a

	nucleophilic attack		electrophilic attack	
	HOMO	LUMO	HOMO	LUMO
BH ₄ ⁻	-7.64		H ⁺	-13.6
[(η -C ₅ H ₅)Re(NO)(CO)(PPh ₃)] ⁺		-7.68	[(η -C ₅ H ₅)Re(NO)(CHO)(PPh ₃)]	-8.21
[(η -C ₅ H ₅)Re(NO)(CHOH)(PPh ₃)] ⁺		-6.68	[(η -C ₅ H ₅)Re(NO)(CH ₂ OH)(PPh ₃)]	-7.84
[(η -C ₅ H ₅)Re(NO)(CH ₂)(PPh ₃)] ⁺		-9.72		

^aThe energy values are expressed in units of electronvolt.

necessary to compare the HOMO or the LUMO of each rhenium complex with the HOMO of the nucleophile or the LUMO of the electrophile performing the attack.

As previously stated, H⁺ and H⁻ have been used as reagents in the calculations so far, but experimentally BH₄⁻ has usually been employed;⁷ therefore, for the purpose of this comparison, it is more meaningful to use BH₄⁻ as the nucleophile. Since either H⁺ has been the experimental electrophile or the complexes were observed to undergo electrophile-induced disproportionation, H⁺ will still be employed as a model electrophile. In Table IV, the energy of the HOMO of the electron-donating BH₄⁻ is compared to that of the LUMOs of the complex cations, while the energy of the LUMO of the electrophile is compared to that of the HOMOs of the neutral rhenium complexes. It is obvious from the numbers shown that the reduction steps are orbital-controlled reactions, while the electrophilic attacks can be categorized as being charge-controlled. In an orbital-controlled reaction, it is either the HOMO or the LUMO that determine the site at which reaction will occur and, in the case of nucleophilic attack, the site of reaction would be where the LUMO of the molecule is localized. On the other hand, in a charge-controlled reaction the site of attack is determined by the charge on individual atoms and electrophilic attack would occur at the site which carries the largest negative charge. Therefore, the approach used by Klopman leads to the same conclusions reached previously by the earlier set of arguments. These findings can now be employed to determine the sites of nucleophilic or electrophilic attack in each of the steps shown in Scheme I.

Reduction of [(η -C₅H₅)Re(NO)(CO)(PPh₃)]⁺ to [(η -C₅H₅)Re(NO)(CHO)(PPh₃)] will occur via the nitrosyl ligand, since it is on this ligand that the LUMO is mostly localized. This confirms the conclusions reached in a previous paper,¹⁶ where this reduction step has been studied in detail. In the following step, the electrophile should attack the atom with the largest negative charge, which, in [(η -C₅H₅)Re(NO)(CHO)(PPh₃)], is by far the oxygen atom of the formyl ligand. This conclusion is strengthened by the fact that this oxygen is also the atom where the HOMO is localized. The reduction which follows should occur at the LUMO of [(η -C₅H₅)Re(NO)(CHOH)(PPh₃)]⁺, which Table II shows to be mainly metal d and NO π^* in character. As in [(η -C₅H₅)Re(NO)(CO)(PPh₃)]⁺, the LUMO's greatest contribution comes from the nitrosyl ligand, which would then be the site of attack. The mechanism of the rearrangement that produces [(η -C₅H₅)Re(NO)(CH₂OH)(PPh₃)]⁺ from [(η -C₅H₅)Re(NHO)(CHOH)(PPh₃)]⁺ has not been investigated in this work, but the presence of some hydroxymethylidene character in the LUMO of [(η -C₅H₅)Re(NHO)(CHOH)-

(PPh₃)]⁺ suggests that a proton shift might occur within this molecular orbital. The last electrophilic attack should occur again at the oxygen atom of the CH₂OH ligand, which carried the largest negative charge in the molecule, and reduction from the carbene to the methyl complex will probably proceed through the -CH₂ ligand. One of the p orbitals on the carbene ligand, in fact, makes up more than half of the LUMO in [(η -C₅H₅)Re(NO)(CH₂)(PPh₃)]⁺, as Gladysz et al. have previously shown.⁸

In summary, the electrophilic and nucleophilic attacks shown in Scheme I follow a very specific pattern, which is the one suggested by both the frontier orbital and the perturbation theory approaches: with the exception of the carbene complex, reduction occurs via the nitrosyl ligand and this is immediately followed by a rearrangement to the observed thermodynamically favored configuration, in which the H⁻ is attached to the carbon-containing ligand. In [(η -C₅H₅)Re(NO)(CH₂)(PPh₃)]⁺, frontier orbital considerations indicate that nucleophilic attack occurs directly at the carbene carbon, in accord with previous calculations.⁸ The site of electrophilic attack is always the oxygen atom of what originally was the carbonyl group.

Conclusions. The organorhenium complexes that have been studied in this paper show marked similarities in the nature of their HOMOs and LUMOs. The HOMOs seem to be mainly metal d in character, while the LUMOs add a large NO π^* contribution to the significant metal d percentages. Although the alternating nucleophilic and electrophilic attacks do not seem to have much effect on the nature of most frontier orbitals, they tend to shift the overall energy of the molecule. Electrophilic attacks lower orbital energies by introducing additional positive charge, which helps delocalize electron density.

The second aspect of Scheme I that has been investigated is the question of where in the molecule the reagent attacks. It was found that nucleophilic attacks are in this case orbital-controlled, while electrophilic attacks are charge-controlled. This subdivision leads to the conclusion that the electrophile always attacks at the oxygen of the ligand that starts out as a carbonyl, while reduction occurs via the nitrosyl ligand. The latter finding is consistent with the conclusions previously reached about the reduction of [(η -C₅H₅)Re(NO)(CO)(PPh₃)]⁺ to [(η -C₅H₅)Re(NO)(CHO)(PPh₃)].¹⁶

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Registry No. [Rp(CO)]⁺, 70083-72-6; Rp(CHO), 70083-74-8; [Rp(CHOH)]⁺, 72343-49-8; Rp(CH₂OH), 104198-48-3; [Rp(CH₂OH₂)]⁺, 104198-49-4; [Rp(CH₂)]⁺, 71763-21-8; Rp(CH₃), 71763-18-3.