

ligand (Scheme IIa) and to a lesser extent to C₁ of 2 to produce a 2-alkyne ligand (Scheme IIb). For diene and alkene adducts, the H atom is transferred predominantly to C₁ of the π-allyl group (1, Scheme Ia). Alkene complexes also rearrange to a lesser extent by H transfer to C₁ of the π-allyl fragment (Scheme Ib). Allene complexes probably rearrange after vinylic and allylic insertions.

If no β-H is available after allylic insertion, several higher energy pathways become accessible. The iron ion probably causes isomerization of the multiple bond via a 1,3-H shift so that upon allylic insertion, β-H abstraction is possible or inserts into vinylic bonds when no alternative pathways exist.

The abundance of Fe⁺ relative to other fragment ions formed upon collisional activation is a measure of the propensity of the metal ion to add oxidatively to C-C bonds. A relatively low abundance of Fe⁺ (50% or less) is indicative of the presence of a highly reactive propargylic or allylic bond. If the allylic bond is deactivated because it is also a vinylic or terminal C-C bond and isomerization is not possible, then less oxidative addition occurs as signaled by a relative abundance of Fe⁺ between ca. 50 and 100%. Dienes or alkynes with vinylic bonds and a limited number of carbon atoms are relatively inert toward oxidative addition, and Fe⁺ becomes the most abundant CAD

product (100%). The other CAD products obtained from these stable adducts probably result from high-energy processes involving direct decompositions of the organic ligand.

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Registry No. Fe⁺, 14067-02-8; FeCO⁺, 35038-14-3; Fe(CO)₂⁺, 35038-15-4; 1,4-octadiene, 5675-25-2; 4-octyne, 1942-45-6; 1-octyne, 629-05-0; 1,3-octadiene, 1002-33-1; 1,7-octadiene, 3710-30-3; 2,4-octadiene, 13643-08-8; 3-octyne, 15232-76-5; cyclooctene, 931-88-4; 2,6-octadiene, 4974-27-0; 2-octyne, 2809-67-8; allene, 463-49-0; 1-pentyne, 627-19-0; 1-hexyne, 693-02-7; 1-heptyne, 628-71-7; 1,2-pentadiene, 591-95-7; 1,5-hexadiene, 592-42-7; 1,2-hexadiene, 592-44-9; propyne, 74-99-7; 1,3-hexadiene, 592-48-3; 1,3-butadiene, 106-99-0; 2-butyne, 503-17-3; 1,2-butadiene, 590-19-2; 2-heptyne, 1119-65-9; 2-hexyne, 764-35-2; 3-hexyne, 928-49-4; 1-butyne, 107-00-6; 3-heptyne, 2586-89-2; 3-nonyne, 20184-89-8; 2-pentyne, 627-21-4; 2,3-pentadiene, 591-96-8; 1,3-pentadiene, 504-60-9; 1,4-pentadiene, 591-93-5; isoprene, 78-79-5; 1,4-hexadiene, 592-45-0; 5-decyne, 1942-46-7.

Proposed Mechanism for Nucleophilic Attack in [(η-C₅H₅)Re(NO)(CO)(PPh₃)]⁺

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A molecular orbital analysis of [(η-C₅H₅)Re(NO)(CO)(PPh₃)]⁺ and its reduction to [(η-C₅H₅)Re(NO)(CHO)(PPh₃)] shows that the site of nucleophilic attack is not the one suggested by the product. It is proposed that the nitrosyl ligand is the energetically favored position for attack, which leads to formation of [(η-C₅H₅)Re(NHO)(CO)(PPh₃)]. We further contend that this kinetic product is thermodynamically unstable and it rearranges to form the formyl complex.

Introduction

In the past few years there has been a considerable amount of work done on the synthesis, characterization, and reactivity of a variety of pseudotetrahedral organorhenium complexes, Gladysz being one of the principal investigators.¹⁻⁸ In particular, neutral formyls have generated a great deal of interest because of their presumed

role in catalytic processes.^{9,10} The rhenium formyl [(η-C₅H₅)Re(CHO)(NO)(PPh₃)] has been investigated in more than one laboratory¹¹⁻¹³ and especially by Gladysz, who has found two different routes to synthesize it from its precursor [(η-C₅H₅)Re(NO)(CO)(PPh₃)]⁺.¹⁴ This carbonyl cation has also been used by Gladysz as the starting material in a series of reactions involving alternating nucleophilic and electrophilic attacks.¹⁴

Both of these studies are interesting from a theoretical point of view since the chemistry involved is relatively straightforward and yet presents some challenging questions. This paper will be devoted to an analysis of the

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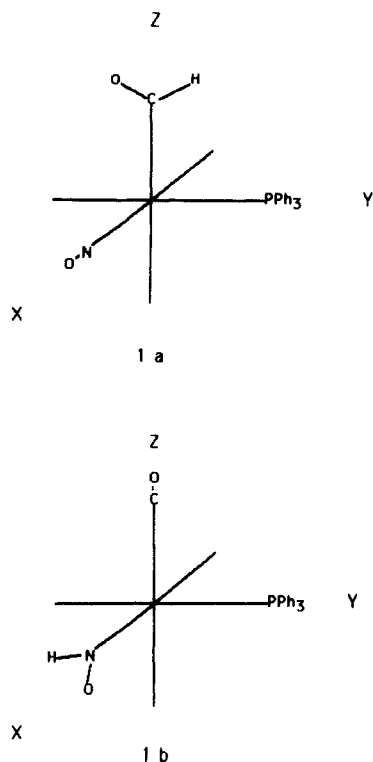


Figure 1. Orientations of the ligands relative to the master coordinate system of the rhenium atom. In each case the centroid of the Cp ring is located in the octant bounded by the $-x$, $-y$, and $-z$ axes.

reduction of the carbonyl rhenium cation to form the neutral formyl; investigation of the multistep synthesis that takes the cation gradually to a methyl species will be deferred to a future publication.

Computational Procedure

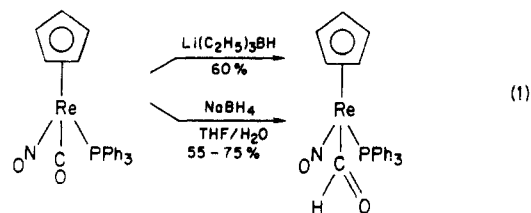
Calculations have been carried out by using the Fenske-Hall nonempirical method¹⁵ on a Harris/7 computer. The average time required for calculations on each rhenium complex was under 15 min of cpu time. Atomic basis functions were employed; for oxygen, carbon, nitrogen, and phosphorus Clementi's double- ζ functions were used,¹⁶ except for 1s and 2s functions, which were curve-fit to single ζ by using the maximum overlap criterion.¹⁷ The hydrogen exponent was set to 1.16. The rhenium functions were developed by the method of Bursten et al.¹⁸ in which Slater functions are fitted to the numeric functions generated by X α methods for atomic orbitals. 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 the rhenium complexes was taken from the actual X-ray structure determined by Gladysz et al.¹⁹ and idealized to pseudo- C_{3v} symmetry; the geometry of $[(\eta-C_5H_5)Re(NHO)(CO)(PPh_3)]^+$ had to be extrapolated from that of $[(\eta-C_5H_5)Re(NO)(CHO)(PPh_3)]^+$ (see Figure 1). For simplicity of interpretation and a greater ease in the calculations, the triphenylphosphine group present in each of the complexes has been substituted with a phosphine group.

Results and Discussion

$[(\eta-C_5H_5)Re(NO)(CO)(PPh_3)]^+$. Gladysz has shown that $[(\eta-C_5H_5)Re(NO)(CO)(PPh_3)]^+$ can be synthesized

from $(\eta-C_5H_5)Re(CO)_3$ in a three-step reaction. The product can then be reduced to the neutral formyl by using either $Li(C_2H_5)_3BH$ or $NaBH_4$ as the reducing agent,¹⁴ as indicated by eq 1. Equation 1 presents an intriguing



problem, since several considerations suggest that the nitrosyl ligand should be the favored site of nucleophilic attack and the predicted product would then be $[(\eta-C_5H_5)Re(NHO)(CO)(PPh_3)]$.

The first in the series of arguments that lead to the above conclusion is a comparison of the nitrosyl cation and the carbonyl ligands, which are isoelectronic. Both have a σ occupied orbital with a lobe directed toward the metal and two empty π orbitals which are the antibonding counterparts to the p-p π -bonding orbitals between carbon or nitrogen and oxygen. While the σ orbital donates electron charge to the metal, the empty orbitals are energetically available to receive electron density that the metal donates back.^{20,21}

Despite similarities between the two ligands in the HOMO and LUMO shapes and functions, the levels of CO and NO^+ are at quite different energies. Since nitrogen is more electronegative than carbon, its atomic orbitals are at a lower energy: this results in a corresponding shift in the NO^+ energy levels with respect to those of CO. The effect is also enhanced by the positive charge that the nitrosyl carries, which "tightens" the orbitals around the nuclei and stabilizes the energy levels of NO^+ relative to those of CO.

Finally, the calculations performed on $[(\eta-C_5H_5)Re(NO)(CO)(PPh_3)]^+$ confirm that, even though the ligands' energy levels are perturbed by interaction with the metal and with one another, the nitrosyl π^* levels are still lower in energy than the carbonyl ones. The separation between NO^+ and CO energy levels has been greatly reduced from that found in the free ligands, but their order remains the same. Because of the relative energies of the ligand orbitals in $[(\eta-C_5H_5)Re(NO)(CO)(PPh_3)]^+$, the π^* levels of NO^+ should be the lowest antibonding orbitals in the complex. Figure 2 shows a molecular orbital diagram for the rhenium cation: the LUMO of the complex does receive its most significant contribution from the nitrosyl ligand (44%), together with some minor ones from the carbonyl and the cyclopentadienyl ligands (18% and 10%, respectively). The nitrosyl ligand contributes with a linear combination of its p_x-p_x (π_x^*) and p_y-p_y (π_y^*) antibonding orbitals, so that the lobes of the resulting molecular orbital are at approximately the dihedral angle with respect to $x-z$ and $x-y$ planes.

Given the energy and nature of the molecular orbitals of $[(\eta-C_5H_5)Re(NO)(CO)(PPh_3)]^+$, more than one theoretical approach found in the literature suggests that nucleophiles, such as the borohydrides used in the synthesis of the neutral formyl, would attack the nitrosyl rather than the carbonyl ligand. Fukui has used frontier orbital arguments to predict reactivity in aromatic compounds. One of the postulates of his theory is that nucleophilic attack will occur at that site which will have the highest electron

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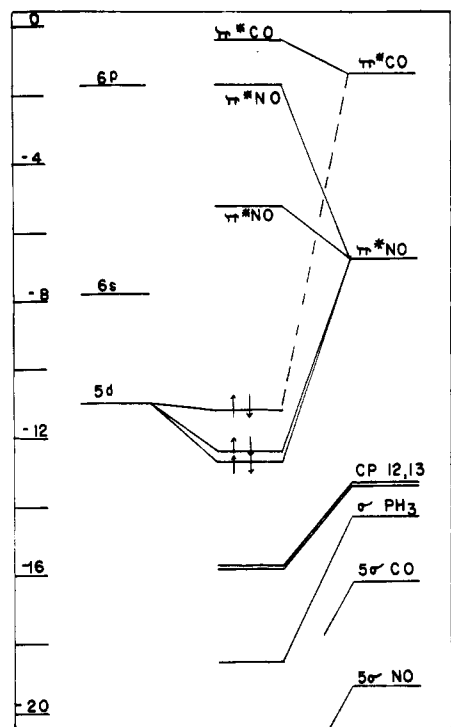


Figure 2. Molecular orbital diagram for $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})(\text{PPh}_3)]^+$. Splitting of the two NO^+ π^* orbitals in the molecule is caused by interaction with the Cp^- ring. All energy levels have been shifted up 4 eV so that nonbonding orbitals of the cation match those of the neutral formyl. This makes the comparison between the two molecules not dependent on the overall charge.

density when the two donated electrons occupy the LUMO in the ground state of the molecule.^{22,23} Since the LUMO of the rhenium complex is mostly nitrosyl in character, according to this theory $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NHO})(\text{CO})(\text{PPh}_3)]$ would be the predicted product. Other authors have based reactivity predictions on the difference in orbital energies between the nucleophile and the substrate.^{24,25} More specifically, if the energy difference between the HOMO of the nucleophile and the LUMO of the substrate is large, the reaction is said to be charge controlled; if it is negligible, the reaction will be orbitally or frontier controlled.²⁶ In the first case nucleophilic attack occurs at the position carrying the largest positive charge; in the latter case, it occurs at the site where the LUMO is localized. One of the reducing agents that has been used by Gladysz is BH_4^- ¹⁴ with the HOMO at -7.64 eV and the LUMO of the rhenium cation is at -7.68 eV. The small energy difference shows that the reaction is orbitally controlled, which confirms the earlier prediction.

Now that $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NHO})(\text{CO})(\text{PPh}_3)]$ has been shown to be the expected product, the question remains as to why the formyl complex is formed and how.

$[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CHO})(\text{PPh}_3)]$ and $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NHO})(\text{CO})(\text{PPh}_3)]$. Recent work by Bergman, Diel, and Brown furnishes some insight into the problem; Brown at the University of Dublin has done studies on addition reactions of soft and hard nucleophiles to metal carbonyl complexes. He has observed that, in the case of kinetically controlled reactions, the initial nucleophilic attack does not always lead to the thermodynamically stable prod-

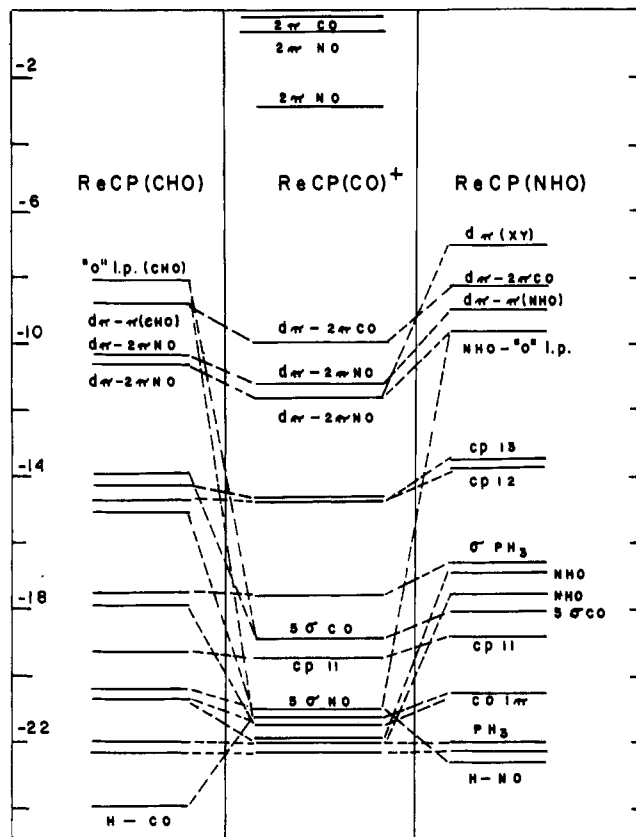


Figure 3. Comparison of the energetics of $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})(\text{PPh}_3)]^+$, $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CHO})(\text{PPh}_3)]$, and $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NHO})(\text{CO})(\text{PPh}_3)]$. Again, energy values have been adjusted for a more meaningful comparison. For convenience, CP represents both $(\eta\text{-C}_5\text{H}_5)$ and PH_3 ligands.

uct.^{25,27} It is then conceivable that a similar argument could apply to the rhenium cation complex and that the kinetically favored product $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NHO})(\text{CO})(\text{PPh}_3)]$ is not observed because it is thermodynamically less stable than $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CHO})(\text{PPh}_3)]$. Further experimental evidence that nitrosyl groups are feasible sites of attack comes from studies on nitrosyl migratory insertions in organo-transition-metal complexes. Both Bergman²⁸ and Diel²⁹ have observed migration of alkyl groups to nitrosyl groups to yield ligands of the type $\text{RN}=\text{O}$; although these alkyl-nitroso complexes are thermally sensitive and quite reactive, they can be isolated.²⁸ This suggests that the formation of $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NHO})(\text{CO})(\text{PPh}_3)]$ is certainly possible, but the reduced rhenium complex could be unstable and subsequently rearrange to the formyl configuration.

The question of kinetically vs. thermodynamically stable products which has been raised by the experimental data discussed above can be probed further by a direct comparison of $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CHO})(\text{PPh}_3)]$ and $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NHO})(\text{CO})(\text{PPh}_3)]$. Specifically, the thermodynamically unstable molecule is expected to have molecular orbitals that are higher in energy than those of the stable form and therefore to have a higher total energy.

Calculations have been performed on the phosphine equivalents of both molecules in order to compare their total energies. The relative geometries of the relevant ligands in the final set of calculations are as indicated in Figure 1. The results confirm that $[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NHO})$

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(CO)(PH₃) is less stable than [(η -C₅H₅)Re(NO)(CHO)(PH₃)]³⁰. Figure 3 shows a comparison of energy levels for [(η -C₅H₅)Re(NO)(CO)(PH₃)]⁺, [(η -C₅H₅)Re(NHO)(CO)(PH₃)], and [(η -C₅H₅)Re(NO)(CHO)(PH₃)].³¹ It is obvious from the diagram that hydride attack at the nitrosyl is on the whole more destabilizing than attack at the carbonyl: from the low-lying CHO and NHO bonding orbitals all the way to the LUMOs, [(η -C₅H₅)Re(NHO)(CO)(PH₃)] energy levels are generally higher than [(η -C₅H₅)Re(NO)(CHO)(PH₃)] levels.

In addition to this general trend, it is interesting to consider in detail how the third highest occupied molecular orbital of the rhenium cation is affected by hydride attack. This orbital is mainly metal d and nitrosyl π^* in character, and it allows for some of the charge localized on the metal to be back-donated to the ligand. Interaction of the cation with the hydride nucleophile affects this molecular orbital in different ways depending on the position of attack. In [(η -C₅H₅)Re(NHO)(CO)(PH₃)] there is a loss of metal-ligand interaction and the molecular orbital is split into two entities: a primarily d orbital on the metal and a molecular orbital on the nitrosyl ligand, which is localized on the oxygen atom. The metal d orbital is therefore left without any stabilizing interaction, and its energy is sufficiently high to become the HOMO of [(η -C₅H₅)Re(NHO)(CO)(PH₃)]. In [(η -C₅H₅)Re(NO)(CHO)(PH₃)], on the other hand, there is not much change in the character of the orbital since the hydride affects mostly the carbonyl ligand.

In contrast with the foregoing analysis, the HOMO of the formyl complex is formed in quite a different way. Two of the occupied molecular orbitals in the rhenium cation, one a linear combination of metal d_{z^2} , σ CO, and

Cp⁻ orbitals and the other with some NO and PH₃ character, interact to form, in part, two orbitals which are localized on the formyl ligand. The one at higher energy resembles an oxygen lone pair and becomes the HOMO of [(η -C₅H₅)Re(NO)(CHO)(PH₃)]; the other, at a much lower energy, is mostly a C-H bonding interaction.

From the above analysis and Figure 3 it is clear that not only does the interaction of the hydride with the nitrosyl ligand result in a larger upward shift in the molecular orbital energies than is observed when attack occurs at the carbonyl but also the HOMOs of the two molecules are totally different in nature. This latter feature is of interest when studying alternating hydride and proton attacks starting with the same rhenium cation, and it will be further investigated in a future paper.

Since the [(η -C₅H₅)Re(CO)(PPh₃)] complex that results from hydride attack is unstable with respect to its formyl counterpart, there is probably an inter- or intramolecular mechanism that allows rearrangement from the initial configuration to the final one. Analysis of the [(η -C₅H₅)Re(NHO)(CO)(PH₃)] molecular orbitals suggests a possible pathway. The SHOMO (second highest occupied molecular orbital) in particular has some interesting characteristics: while having a large metal d character, it also receives equal contributions from both the NHO and CO ligands. An intermolecular shift between the two ligand sites would then be possible within this molecular orbital, which offers a sort of "link" between the two ligands. At this point, though, there is no concrete evidence that this is the mechanism involved and further studies need to be carried out.

Conclusions

By examination of the reduction of [(η -C₅H₅)Re(NO)(CO)(PPh₃)]⁺ through a molecular orbital approach, the reaction has been shown to be orbitally controlled. This means that nucleophilic attack will occur at the LUMO of the molecule, which in the rhenium cation is localized at the nitrosyl ligand. But the kinetic product thus formed, [(η -C₅H₅)Re(NHO)(CO)(PPh₃)], is thermodynamically unstable, and it rearranges to the observed formyl product.

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Registry No. [(η -C₅H₅)Re(NO)(CO)(PPh₃)]⁺, 70083-72-6; (η -C₅H₅)Re(NO)(CHO)(PPh₃), 70083-74-8.

(30) A question naturally arises as to the proper orientation of the HNO ligand in the molecule. Two reasonable alternatives have been considered: one with the ligand in the x - y plane and the other with the ligand in the x - z plane. They differ from one another by approximately 5 eV in their total energies. Either rotamer of [(η -C₅H₅)Re(NHO)(CO)(PPh₃)], though, was found to be higher in energy than [(η -C₅H₅)Re(NO)(CHO)(PPh₃)]; for the lower energy configuration, which has all three atoms in the x - y plane, the difference is 0.65 eV and the other rotamer gives an even larger energy difference (5.70 eV). The diagram in Figure 3 presents the energy levels of the most favorable orientation. This is in accord with the results of Bergman et al.,²⁸ who have characterized the structure of CpCo(CH₃CH₂NO)PPh₃ and found the plane defined by the centroid of the Cp ligand, Co, and N and that defined by N, O, and CH₂ to be almost coplanar.

(31) The higher energy configuration of [(η -C₅H₅)Re(NHO)(PPh₃)] is used in this comparison.