

PROGRESS REPORT

for

Highly Nucleophilic Acetylide, Vinyl, and Vinylidene Complexes

DOE Grant No. DE-FG02-85-ER13323

June 15, 1992

This past year has been an extremely busy and productive one for this research program. Three DOE-supported graduate students finished their Ph.D. theses last year, and as a consequence several projects were completed and a number of manuscripts based on this research were submitted for publication. Copies of all those manuscripts are being sent to DOE headquarters (Dr. Stephen Butter) along with a copy of this report. Those students are Tom Snead, who is now with Dr. Lanny Liebskind as a post-doctoral fellow, Dr. David Ramage, now with Dr. Jack Norton as a post-doctoral fellow, and Dr. Colleen Kelley, who spent six months with Dr. Jean-Marie Lehn as a post-doctoral scholar before being called to military duty (she was a ROTC student as an undergraduate). The present members of my research group working on DOE-supported research include four graduate students (Melinda Rau, Christine Kretz, Lisa Mercado, and Michael Terry), a post-doctoral scholar (Chae Yi, Ph.D. with Chuck Casey at Wisconsin), and two undergraduate scholars (Sharon Niezgoda and Anne Kaplan). Our research efforts are augmented by a NATO travel grant with Noël Lugan in Toulouse, France, who worked in my laboratory at Penn State on some of the chemistry described below. As part of this DOE/NATO effort, I have sent one student each year to Toulouse for one-month visits, and these have been enormously productive. We have used the stay of the student in Toulouse to explore a wide range of "new" ideas, and some of those exploratory studies have subsequently led into full-scale research projects.

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I. Studies of the Nucleophilic and Chiral Acetylide Complex [Cp(CO)(PPh₃)Mn-C≡CR]:

This work is now complete and is described in full in a comprehensive paper in press in *J. Am. Chem. Soc.* entitled "Addition and Cycloaddition Reactions of the Chiral and Highly Nucleophilic Alkynyl Complex [(η^5 -C₅H₄Me)(CO)(PPh₃)Mn-C≡CMe]." This study is one of the more significant pieces of work performed in the Geoffroy group in recent years, and we are most grateful to the Department of Energy for its support.

II. Nucleophilic Addition of Carbene Anions to Organic Ligands on Electrophilic Complexes.

This work is also complete and is described in a full paper entitled "Nucleophilic Addition of Chromium Carbene Anions to the Coordinated Olefin in [Cp(CO)₂Fe(η^2 -olefin)]⁺ Complexes and to the Cyclohexadienyl Ligand in [(η^5 -cyclohexadienyl)(CO)₃Fe]⁺" which I was invited to write for the special 200th volume of *Inorg. Chim. Acta* and is in press.

III. Halide-promoted Carbonylation of Imido Ligands.

These studies have also been completed and are described in a full paper entitled "Halide-Promoted Carbonylation of the Imido Ligand in Os₃(μ_3 -NPh)(CO)₁₀" which was published in *Organometallics* earlier this year. A spin-off of this DOE-supported study was also recently published as a full paper in *Inorganic Chemistry* entitled "Preparation of the Triiron Phosphinidene-Imido Clusters Fe₃(μ_4 -PBU')(μ_3 -NPh)(CO)₉ (R = Et, Ph) and Their Reactions with Alkynes".

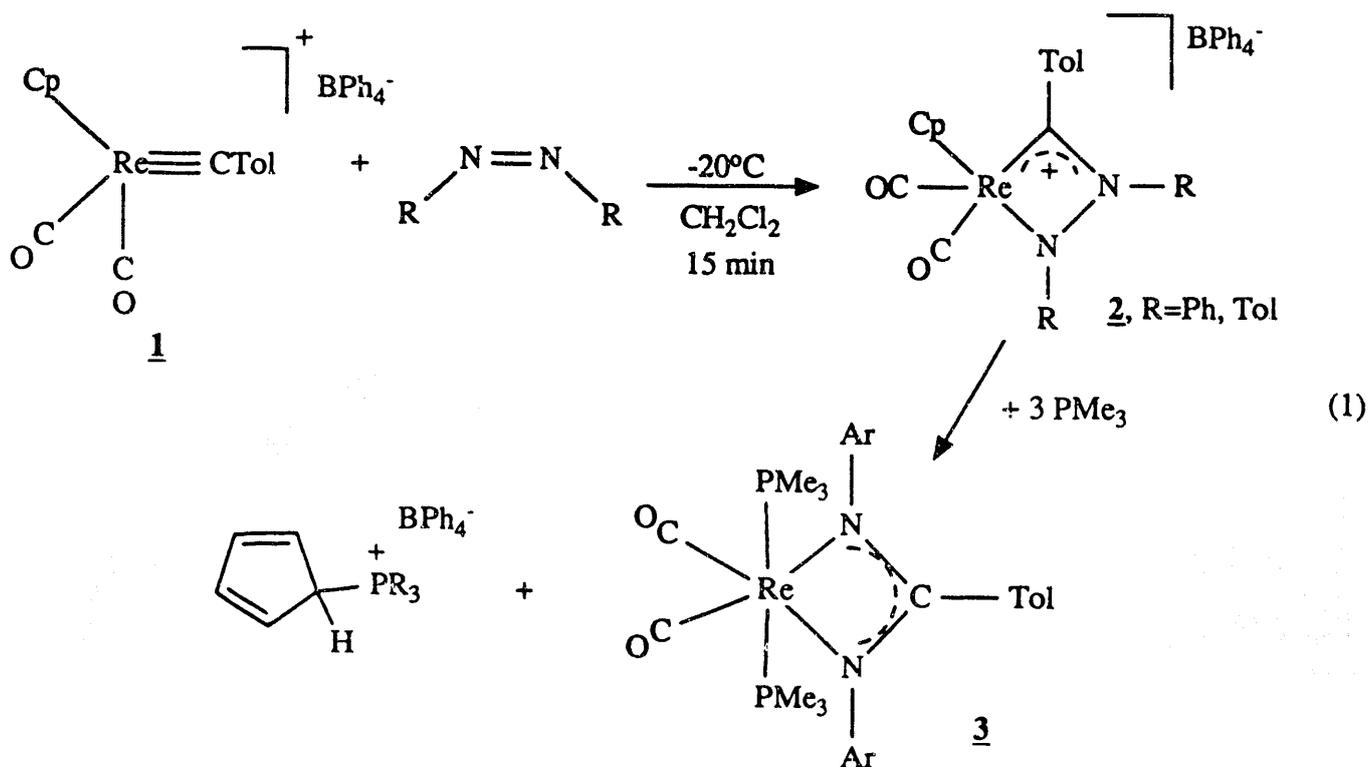
VI. Binuclear Fe₂ Complexes with Bridging Organonitrogen Ligands.

This project has also been completed, and two full papers describing these results are currently in press in *Organometallics*. They are entitled "Formation of Substituted Ferracyclopentadiene Complexes by The Reaction of Alkynes with Protonated Diferra- μ -Azaallylidene Complexes" and "Formation of Substituted Ferracyclopentadiene Complexes by the Reaction of Alkynes with

Protonated DiFerra-μ-azaallylidene Complexes."

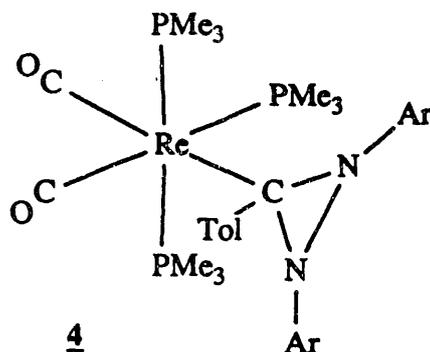
V. Addition and Cycloaddition Reactions of the Carbyne Complex [Cp(CO)₂Re≡CTol]⁺.

This study, part of which was described in last year's report, is now almost complete and is being written up as a full paper and as part of Lisa Mercado's Ph.D. thesis which is to be submitted this summer. In the past year we have worked out many of the mechanistic details of these reactions, but there is still one very interesting puzzle which we are trying to sort through. As detailed in last year's report, we had shown that carbyne complex 1 underwent cycloaddition of *cis*-azobenzene to give the new metallacyclic complex 2, eq. 1. As illustrated, we have since



found that 2 readily reacts with PMe₃ to displace the Cp ring as a phosphonium salt and form the new complex 3 in which the connectivity within the metallacycle has changed so as to place the tolyl-substituted carbon *between* the two nitrogen atoms. We have just recently isolated an intermediate in this process and are in the process of assigning its structure, with the preliminary

spectroscopic data consistent with the structure 4 shown below. To complete our study of



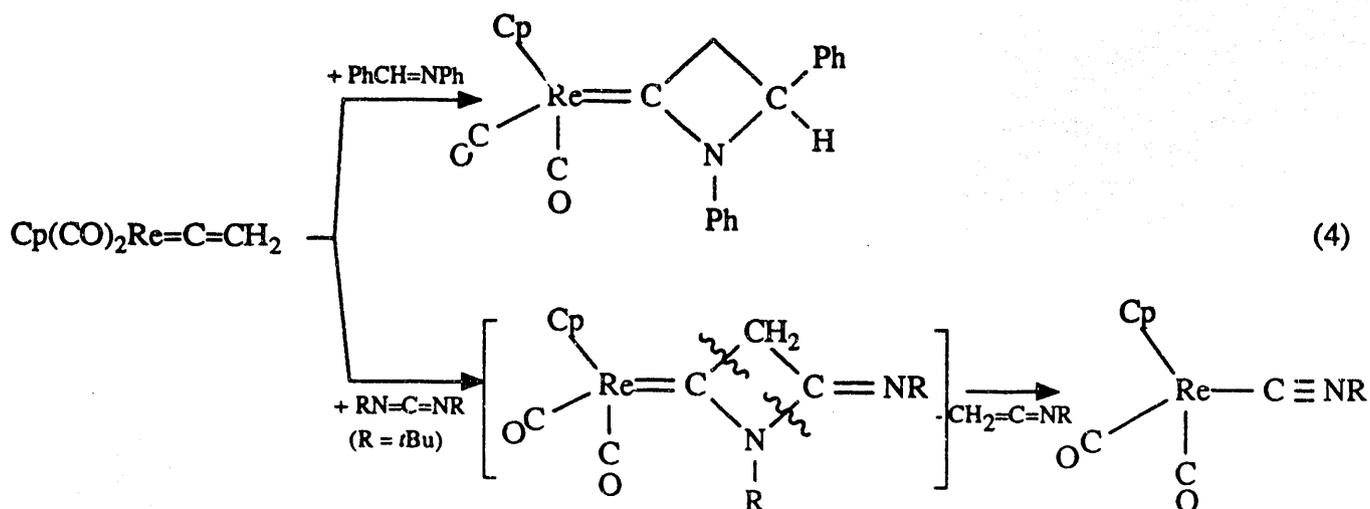
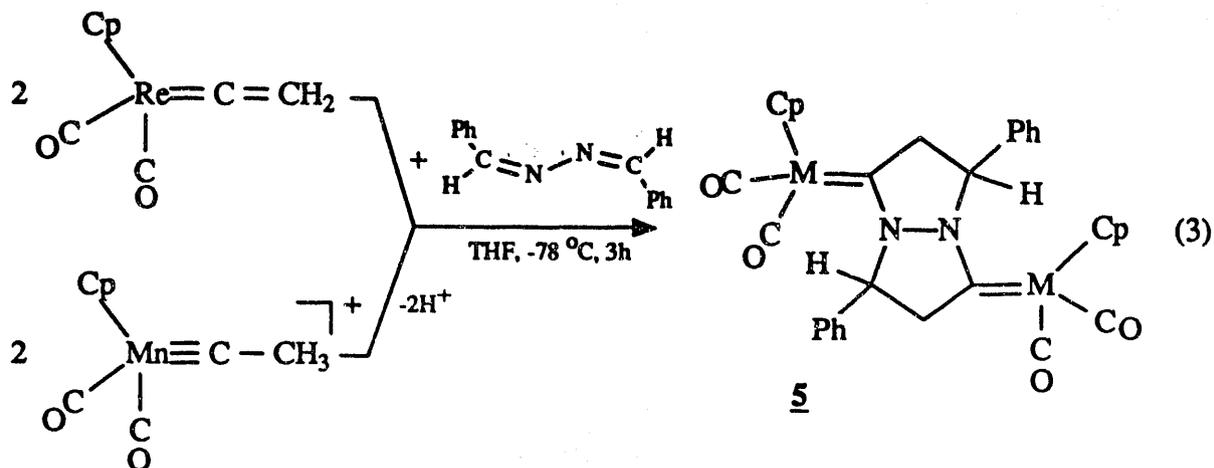
carbyne complex 1, we need to finish the characterization of 4 and tie up a few other loose ends, including some key mechanistic questions, and we anticipate that all of that will be done by the end of the summer, 1992.

VI. Addition and Cycloaddition Reactions of the Methylcarbyne Complexes [Cp(CO)₂M≡CCH₃]⁺ and the Vinylidene Complexes Cp(CO)₂M=C=CH₂ (M = Mn, Re).

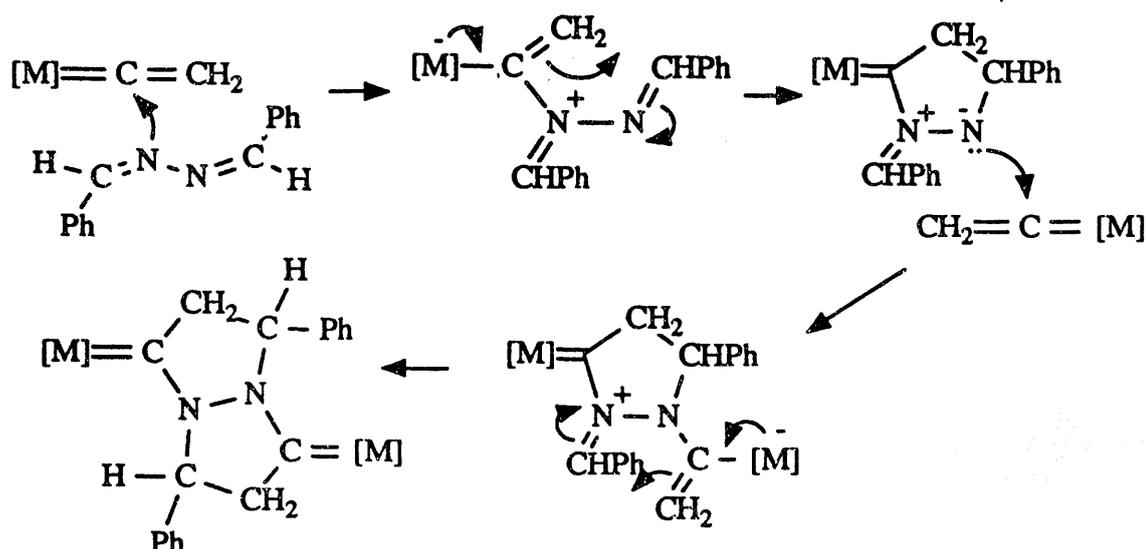
In last year's report, it was noted that we had just discovered that the *methylcarbyne* complexes [Cp(CO)₂M≡C-CH₃]⁺ (M = Mn, Re) undergo facile deprotonation to form the new vinylidene complexes Cp(CO)₂M=C=CH₂, eq. 2. This deprotonation may be accomplished by treating the



carbyne complexes with Et₃N, although the rhenium complex is sufficiently acidic to deprotonate spontaneously upon dissolution in CH₂Cl₂ or THF. These vinylidene and methylcarbyne complexes are extremely reactive towards a series of organic substrates capable of giving addition and cycloaddition products. Our preliminary results have been written up as a communication which is now in press in *Angew. Chem., Int. Ed. Engl.* and entitled "An Organometallic Analogue of the "Criss-Cross" Cycloaddition Reaction." The key reactions described in that paper are summarized in equations 3 and 4, and Scheme I summarizes the proposed mechanism of the unusual "criss-cross" cycloaddition reaction to form 5 which occurs by sequential [2+3] cycloaddition reactions.



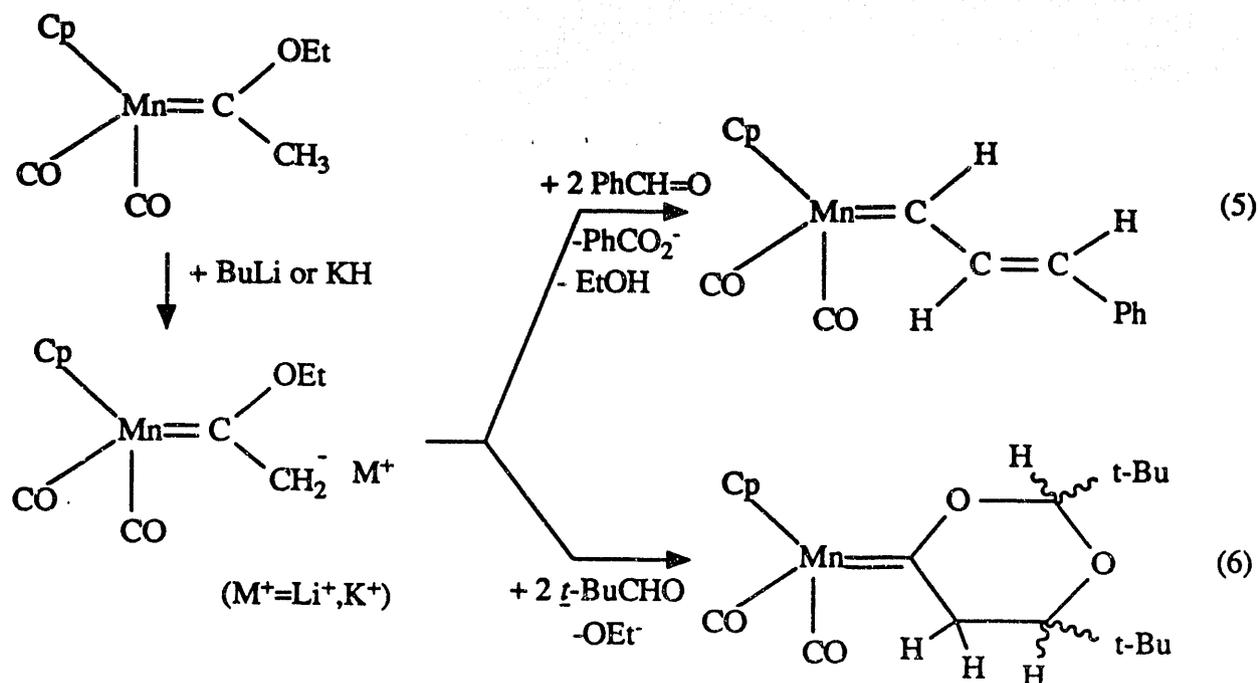
The above reactions demonstrate that the vinylidene complex $\text{Cp}(\text{CO})_2\text{Re}=\text{C}=\text{CH}_2$ and the carbyne complex $[\text{Cp}(\text{CO})_2\text{Mn}\equiv\text{CCH}_3]^+$ are highly reactive species, and in particular the [2+3] cycloaddition reactions with benzalazine indicate that these complexes are potent 1,3-dipolarophiles which should be capable of undergoing cycloadditions with a variety of other substrates. Interestingly, the manganese vinylidene complex $\text{Cp}(\text{CO})_2\text{Mn}=\text{C}=\text{CH}_2$ does not readily react with benzalazine, imines, and $t\text{BuN}=\text{C}=\text{N}t\text{Bu}$, implying a decreased electrophilicity of the vinylidene α -carbon compared to its rhenium analogue. However, the much more electrophilic carbyne complex $[\text{Cp}(\text{CO})_2\text{Mn}\equiv\text{CCH}_3]^+$ does react rapidly with each of these substrates to give, after

Scheme I ([M] = Cp(CO)₂Re)

treatment with Et_3N , products analogous to those formed with $Cp(CO)_2Re=C=CH_2$. Thus, in the manganese reactions, deprotonation must be accomplished after substrate addition, but in the rhenium case it occurs before addition. We are continuing to examine the reactivity of these complexes and anticipate that they will show a rich cycloaddition and addition chemistry with a variety of unsaturated organic substrates.

VII. Studies of the Generation and Reactivity of Vinylcarbene Complexes Formed from the Reaction of Manganese Carbene Anions and Aldehydes.

In last year's report, we described the generation and reactivity of a series of vinyl-substituted carbyne complexes, $[Cp(CO)(PPh_3)Mn\equiv C-CMe=CRR']^+$ via the addition of aldehydes to the PPh_3 -substituted acetylide complex $[Cp(CO)(PPh_3)Mn-C\equiv CMe]^-$. That work is now being readied for publication, but as an extension we sought the preparation of similar vinylcarbyne complexes that did not have a PPh_3 ligand, thinking these species would be more electrophilic and thus more prone to cycloaddition reactions with nucleophilic and unsaturated organic substrates. In the course of those attempts, we discovered some remarkable transformations of carbene anions with aldehydes, as illustrated in eqs. 5 and 6. Reaction 5 occurs with aromatic

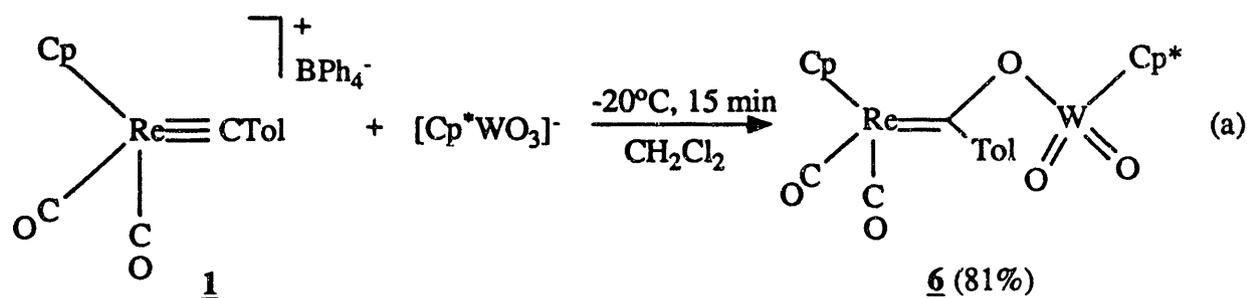


aldehydes and requires two equivalents for complete reaction. It represents a condensation of the aldehyde with the carbene anion, loss of EtOH, and transfer of the oxygen atom from one aldehyde to another (with loss of the hydrogen atom) to form PhCO_2^- . The second reaction involves coupling of the carbene anion with two equivalents of aliphatic aldehyde with concomitant loss of the ethoxide group. We have explored the mechanisms of both of these remarkable and unprecedented reactions, and believe we now have a good understanding of how they proceed. We are currently writing these results up to submit as a communication to *J. Am. Chem. Soc.*, and are extending these studies to other aldehydes, ketones, esters, and amides and to an examination of the reactivity characteristics of the vinylcarbene and cyclic carbene complexes produced in these reactions.

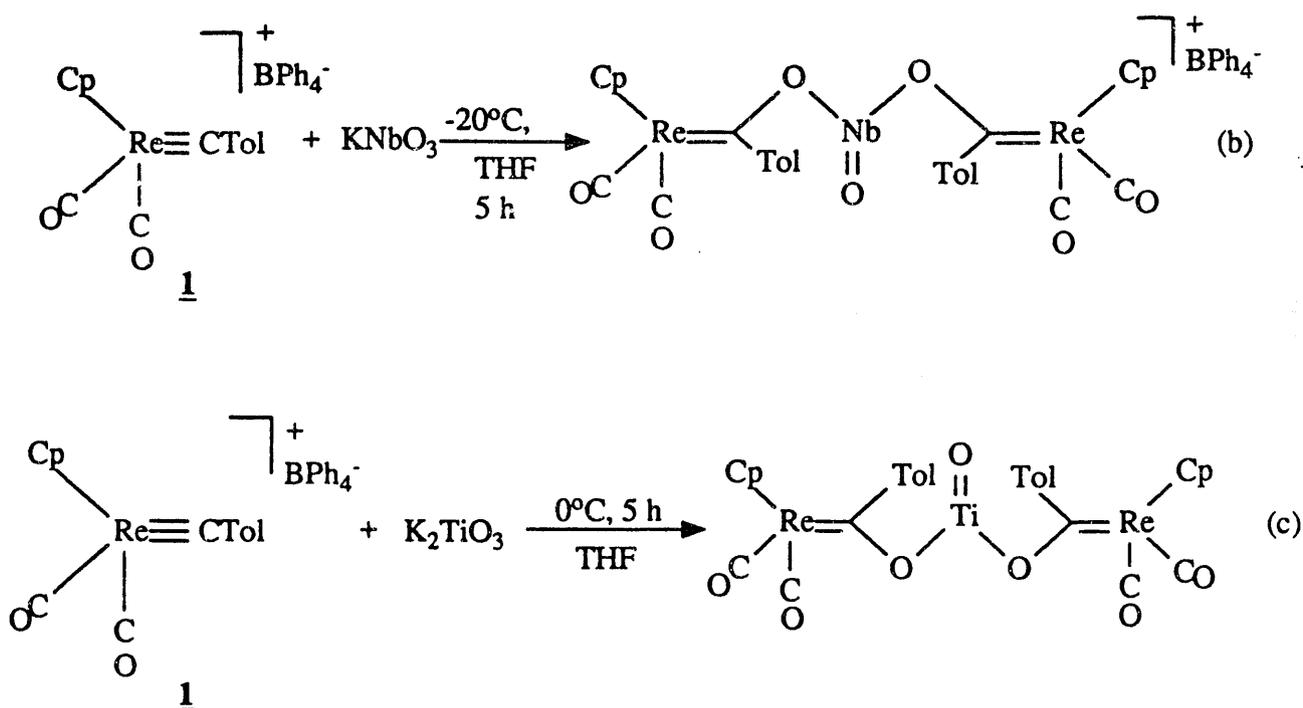
VIII. Addition of Oxo Ligands of Nucleophilic Oxo Complexes to Organic Ligands on Electrophilic Metal Centers.

In an effort to understand how metal complexes assist the oxidation of organic substrates, we have begun to study the reactions of a series of nucleophilic oxo complexes with organic ligands

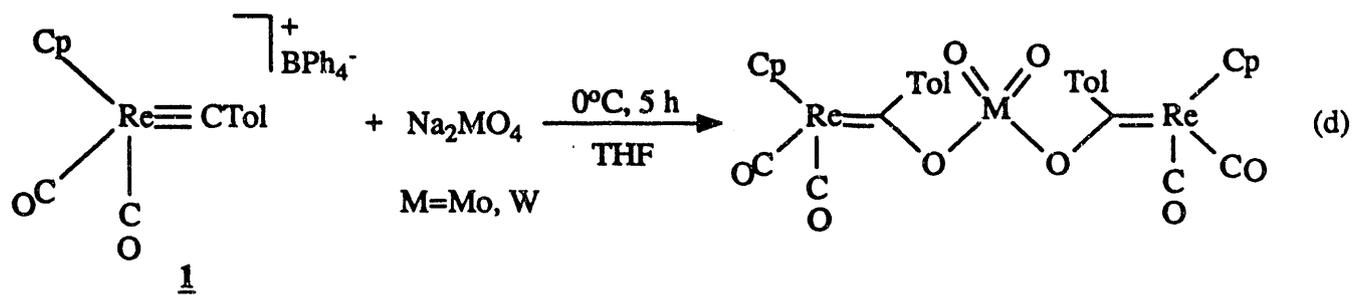
attached to electrophilic metal complexes. One such compound available in our laboratories was the anion $[\text{Cp}^*\text{WO}_3]^-$, and it has been found that this species readily adds to the carbyne carbon of $[\text{Cp}(\text{CO})_2\text{Re}\equiv\text{CTol}]^+$ to form the new carbene complex **6**, eq. a. It has also recently been found



that carbyne complex **1** slowly reacts with suspensions of KNbO_3 , K_2TiO_3 , Na_2MoO_4 , and Na_2WO_4 in THF to form the bi- and trimetallic carbene complexes shown in eq. b-d. Each of



these new oxo-carbene complexes have been isolated as thermally unstable solids and spectroscopically characterized. We are currently examining their reactivity properties, particularly with a series of unsaturated organic substrates, with the aim of inducing cycloaddition reactions of the metal-carbene functionality or between the carbene carbon and an oxo ligand of



the metal-oxo functionality.

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