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TECHNICAL PROGRESS REPORT

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Division of Chemical Sciences
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Title: "Studies Relevant to the Catalytic Activation of Carbon Monoxide"

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ABSTRACT: Research activity during the 1990-91 funding period has included continued mechanistic investigations of the nucleophilic activation of carbon monoxide such as homogeneous catalysis of the water gas shift and key steps in the relevant catalytic cycles. Other investigations of related processes included the application of fast reaction techniques to prepare and to investigate quantitatively reactive organometallic intermediates relevant to the activation of hydrocarbons toward carbonylation and other functionalizations.

CONTENTS:

MASTER

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A. Research Activities:

Water Gas Shift Catalysts: Over the past several years we have worked with long time collaborator Robert Rinker of the UCSB Department of Chemical Engineering to apply continuous flow techniques in probing the kinetics of a WGSR catalyst ($H_2O + CO \dashrightarrow CO_2 + H_2$) based on a precursor solution of $RhCl_3$ trihydrate in aqueous 4-picoline. This system, which had also been the subject of recent batch reactor studies here (Pardey, A. J.; Ford, P. C. *J. Mol. Cat.,* **1989**, *53* , 247), ranks among the most active WGSR catalysts having long term stability, a property of critical importance both for continuous flow investigations and for practical applications. The personnel recently involved in this studies are **Benedito Lima Neto** and **Milan Mdleleni**. Benedito was a "sandwich student" from the Institute of Physics and Chemistry of the Sao Carlos campus of the University of Sao Paulo, Brazil with fellowship support for several years from the Conselho Nacional de Desenvolvimento Cientifico e Technologico of Brazil. As a "sandwich student" his work here was used as the basis for a Ph.D. thesis (see sec. B, # 8) at the University of Sao Paulo upon his return to Brazil this year. He is now a member of the faculty of the USP Institute of Physics and Chemistry, Sao Carlos. Milan is a black S. African student and is a first year Ph.D candidate in this department with fellowship support from a private foundation.

Benedito's studies are summarized in the publication # 5 in part B. His careful kinetics investigations of the WGSR activity from $RhCl_3$/aq. 4-picoline catalyst system in the continuous-flow reactor system (combined with results from earlier students) demonstrated that this interesting catalyst is present as a combination of mononuclear and dinuclear complexes, each of which is an active WGSR catalyst, although the monomer is clearly the more reactive. Milan is continuing the continuous-flow reactor studies; however, the catalysts that he is probing are based on metal complexes absorbed on polystyrene polymers which have been functionalized with different ligand chelating groups. These polymers have been custom synthesized by Dr. T. M. Suzuki (a former postdoc in this laboratory) of the Government Industrial Research Institute, Sendai, Japan. Previous (incomplete) studies in this laboratory have demonstrated that these "heterogenized" catalysts have some promising properties. Milan's goal is to optimize catalytic activities as well as to explore possible WGSR related catalysis (e.g. Reppe hydroformylation) which may have unusual selectivities or activities due to the special properties of Suzuki's remarkable polymers.

Nucleophilic Activation of Carbon Monoxide : The water gas shift is an example of CO activation by nucleophiles. On a broader scale, a number of catalytic processes based on metal carbonyls employ anionic nucleophilic promotors, e.g., halides and alkoxides, and have been proposed to occur via the formation of nucleophile carbonyl adducts (e.g., $\mathrm{M\text{-}CO + Nu \rightleftharpoons M\text{-}C(O)Nu}$). In this context, we have examined the quantitative aspects of the formation and reactions of adducts of nucleophiles such as alkoxide and hydroxide to $Ru_3(CO)_{12}$ and other group VIII carbonyls, in part, because of the numerous catalytic systems which have been reported involving these carbonyls (P.C. Ford and A. Rokicki, *Advances in Organometallic Chemistry*, **28**, 139-218 (1988); T. Chin-Choy,G. D. Stucky, P. C. Ford, *Inorg. Chem.*, **28**, 2028-2029 (1989).)

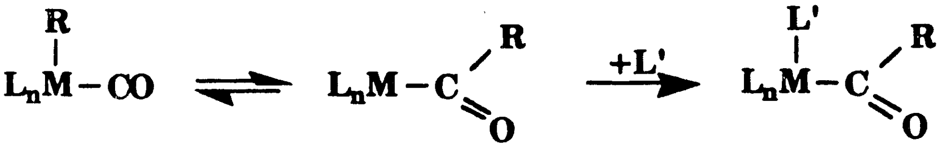
Notably, in solvents like tetrahydrofuran which do not solvate anions strongly, even anions such as halides add readily to the metal carbonyl clusters to labilize CO and to activate these clusters. **Jerome Lillis** , a fifth year graduate student, has been carrying out a very careful spectroscopic and kinetics investigation of the reactions of several halides with $Ru_3(CO)_{12}$ and of the subsequent labilities of the resulting adducts. Jerome's studies have been fraught with monumental problems of catalysis by spurious impurities and of surprising solvent instabilities under these conditions. However, he has worked with diligence and skill and is succeeding (where others have failed in extending beyond erudite speculation) in elucidating the relevant mechanisms of the formation and subsequent reactions of the halide adducts (see below). He has shown the reaction to be somewhat inhibited by CO and to be markedly solvent sensitive. The latter observation can be attributed to the response of Cl^- nucleophilicity to different solvents while the former suggests that, under the conditions used in the kinetics studies, the first two steps in the sequence shown are reversible.

$$\mathrm{Cl^- + Ru_3(CO)_{12} \rightleftharpoons [Ru_3(CO)_{11}(COCl)^-] \xrightleftharpoons{-CO} [Ru_3(CO)_{10}(COCl)^-]}$$

$$\mathrm{\dashrightarrow Ru_3(CO)_{11}(Cl)^- \xrightleftharpoons{-CO} Ru_3(CO)_{10}(\mu\text{-}Cl)^-}$$

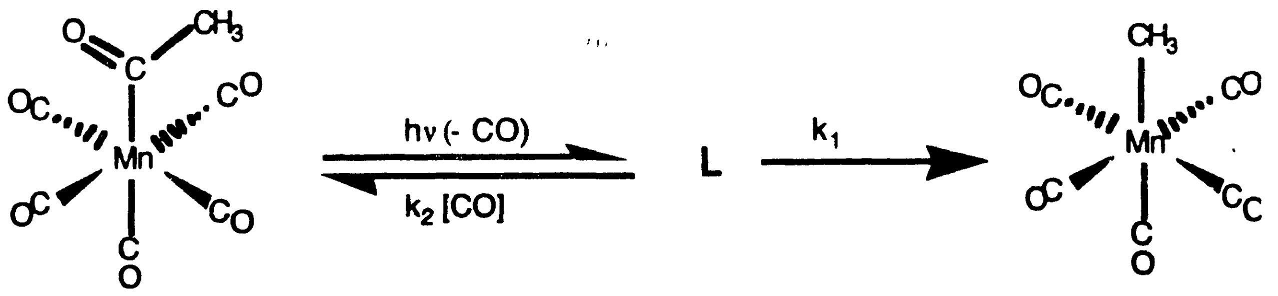
Quantitative Studies of Reactive Intermediates: We have also been concerned with quantitative investigations of fundamental metal complex reactions which have relevance to the homogeneous catalysis. These investigations include applications of fast reaction methodologies, principally laser flash photolysis with time resolved infrared (TRIR) or optical detection techniques to prepare and to interrogate the dynamics of reactive intermediates proposed as key species in the catalytic activation of CO and other C_1 compounds. Owing to their reactivity, such species are generally formed in very low steady state concentrations; thus, while their presence can be inferred from kinetics or other mechanistic information, they are often not directly detected under catalysis conditions.

One fundamental organometallic reaction commonly invoked in proposed schemes for such catalytic cycles is "migratory insertion" of CO into a alkyl-metal bond, e.g.,

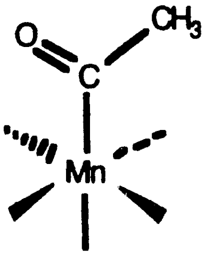


(I)

Although migratory insertion mechanisms have been extensively probed via traditional physical-organic/ physical-inorganic methods for several model compounds, evidence regarding the nature and kinetic behavior of the key intermediate I has remained indirect. In this context, quantitative flash photolysis studies of the spectral and kinetics behavior of intermediates in carbonylations of the metal-alkyl bonds of the prototype molecules $Mn(CO)_5(CH_3)$ (see sec. B #'s 2 & 3) and $CpFe(CO)L(CH_3)$ (Cp = η^5-C_5H_5, L= CO or phosphine) (sec. B, #'s 3, 6 & 7) have been the focus in this laboratory of ongoing studies by **Dr. Simon T. Belt** (SERC Postdoctoral Fellow from England), **David Ryba**, a fifth year graduate student and **Brian Lee**, a first year graduate student. In these studies we have been able to characterize the reaction dynamics of intermediates analogous to I by using a retrosynthetic strategy, namely by photolabilizing a CO from the acyl complexes , for example:



Some possible structures for L and for the analogous intermediates formed by the flash photolysis of $CpFe(CO)_2(CH_3CO)$ are illustrated below. Time resolved IR spectra suggest that, if a single intermediate structure is present, that species must be the solvated intermediate S. The kinetics studies show that in cyclohexane solutions the intermediate L undergoes isomerization to the alkyl complex and in competition to being trapped by CO. The remarkable feature is the relative stability of L in hydrocarbon solutions; the reaction with CO is several orders of magnitude slower than was seen for the analogous reaction of *cis*-$Mn(CO)_4(S)(CH_3)$ with CO in cyclohexane. Among possible explanations of this unusual behavior is that in hydrocarbon solutions, the chelated η^2-carbonyl species C is the dominant form, while in more donor solvents S is the predominant form. Ongoing flash photolysis studies of other metal acyl complexes as well as low temperature spectroscopic studies (liquid xenon solutions) in cooperation with R. G. Bergman at UC, Berkeley are designed to address this issue.



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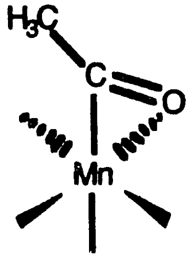

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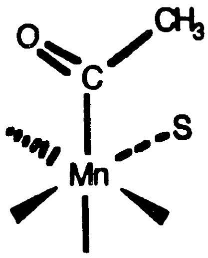

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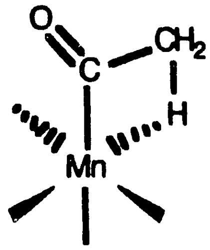

B

B. 1990-1991 Publications/Theses based on work supported by the Division of Chemical Sciences, DOE-OBES

1. "Dynamics of Reactive Intermediates as Probed by Flash : The Rhodium(I) Complexes $RhCl(CO)L_2$ ($L = PPh_3$, $P(p\text{-tolyl})_3$ or PMe_3)", P. C. Ford, T. L. Netzel, C. T. Spillett, and D. B. Pourreau, *Pure and Applied Chemistry, 62,* 1091-1094 (1990)

2. "Reactivities of Intermediates Relevant to Metal Alkyl Carbonylation. Flash Photolysis of $CH_3Mn(CO)_5$ Studied by Time Resolved Infrared and Optical Detection", S. T. Belt, D. W. Ryba and P. C. Ford, *Inorg. Chem., 29,* 3633-3634 (1990)

3. "Flash Photolysis Studies of Reactive Intermediates Relevant to Homogeneous Catalysis by Organometallic Complexes", P. C. Ford and S. T. Belt, *ACS Advances in Chemistry Series,* in press, 1991

4. "Catalysis of the. Water Gas Shift Reaction" Chapter 7 in "Electrochemical and Electrocatalytic Reduction of Carbon Dioxide", ed. by B. Patrick Sullivan, Elsevier Press, in press 1991.

5. "A Study of the Water Gas Shift Reaction Catalyzed by Rhodium Chloride in Aqueous Picoline by Use of a Continuous-Flow Stirred Reactor", Benedito S. Lima Neto, Katherine H. Ford, Alvaro J. Pardey, Robert G. Rinker, and Peter C Ford, *Inorg. Chem.,*in press

6. "Reactive Intermediates in the Photolytic Decarbonylation of the Acyl Complex $(\eta^5\text{-}C_5H_5)Fe(CO)_2(COCH_3)$ as Studied by Time-Resolved Infrared Spectral Techniques", Simon T. Belt, David W. Ryba and Peter C. Ford*, *J. Am. Chem. Soc., in press*

7. "Reactive Intermediates in the Carbonylation of Metal Alkyl Bonds Studied by Time-Resolved Infrared Spectral Techniques", Peter C. Ford*, David W. Ryba and Simon T. Belt, *ACS Advances in Chemistry Series Volume "Photosensitive Metal-Organic Systems: Mechanistic Principles and Recent Applications",* submitted (on invitation of the volume editor)

8. "Reacao de Delocamento do Gas D'Agua: Sstudos de Catalisadores Homogeneos de Complexos de Metals do Gropo da Platina" Benedito Dos Santos Lima Neto (Ph.D. Dissertation submitted to the Instituto de Fisica e Quimica de Sao Carlos, Universidade de Sao Paulo, Brazil), April 1991

Reprints of Items 1 and 2 are appended.*

* not included

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