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TECHNICAL PROGRESS REPORT

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

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ABSTRACT: Research activity during the 1991-92 funding period has been concerned with the following topics relevant to carbon monoxide activation. 1) Exploratory studies of water gas shift catalysts heterogenized on polystyrene based polymers. 2) Mechanistic investigation of the nucleophilic activation of CO in metal carbonyl clusters. 3) Application of fast reaction techniques to prepare and to investigate reactive organometallic intermediates relevant to the activation of hydrocarbons toward carbonylation and to the formation of carbon-carbon bonds via the migratory insertion of CO into metal alkyl bonds.

CONTENTS:

MASTER

A. Research Activities:

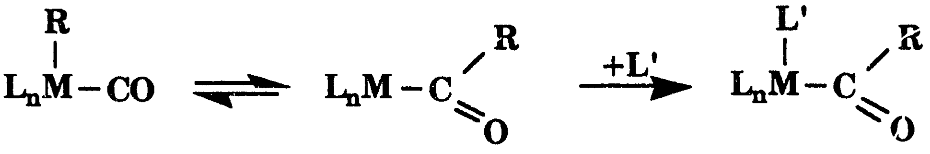
Water gas shift reaction catalysts: Over the past several years we have worked with long time collaborator Robert Rinker of the UCSB Department of Chemical Engineering to apply continuous flow techniques in probing the kinetics of WGSR ($H_2O + CO \dashrightarrow CO_2 + H_2$) catalysts, most recently one based on a $RhCl_3$ precursor in an aqueous solution of aromatic amines which ranks among the most active WGSR catalysts having long term stability (*J. Mol. Cat.*, **1989**, *53*, 247; *Inorg. Chem.*, **1991**, *30*, 3837). New catalysts we are probing are rhodium complexes absorbed on polystyrene polymers which have been functionalized with different amine ligand chelating groups, some custom synthesized by Dr. T. M. Suzuki of the Government Industrial Research Institute, Sendai, Japan. So far these materials have proved to be somewhat less active than the homogeneous catalyst noted above but are active in neutral aqueous media. Furthermore, these systems have not yet been optimized. The graduate student currently involved in this study is **Millan Mdleleni**, a black S. African student in his second year as a Ph.D candidate in this Department with fellowship support from a private foundation. He is making good progress, but like most second year students, academic requirements like written and oral research propositions and the oral candidacy exam make important demands on his time. Millan's short term goal is to optimize catalytic activities as well as to explore possible WGSR related CO activation (e.g. Reppe hydroformylation) which may have unusual selectivities or activities due to the special properties of Suzuki's polymers.

Nucleophilic activation of carbon monoxide : A number of catalytic processes based on metal carbonyls employ anionic nucleophilic promoters, e.g., hydroxide, halides or alkoxides. In this context, we have examined quantitative aspects of the formation and reactions of adducts of such nucleophiles to $Ru_3(CO)_{12}$ and other group VIII carbonyls, partially because of the numerous catalytic systems which have been reported involving these carbonyls (see Ford, Rokicki, *Advances in Organometallic Chemistry*, **28**, 139-218 (1988)). 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. Over the past year **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 ensuing adducts, e.g.,

$$Cl^- + Ru_3(CO)_{12} \overset{-CO}{=\!=\!=} [Ru_3(CO)_{11}Cl^-] \overset{-CO}{=\!=\!=} [Ru_3(CO)_{10}(\mu\text{-}Cl)^-]$$

Jerome has shown the reaction to form [$Ru_3(CO)_{11}Cl^-$] to be slightly inhibited by CO but 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, intermediates in the reaction sequence may be formed by the reversible labilization of CO. A manuscript is in preparation describing these studies. He completed his Ph.D. thesis in March and is now carrying out postdoctoral studies under the auspices of a NSF-STA Fellowship at the Institute for Physical and Chemical Research (RIKEN) in Wako, Japan.

Time resolved studies of reactive intermediates relevant to 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 intermediates 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. For example, over the past several years, we have mounted a major effort in identifying and characterizing the reaction dynamics of intermediates in the migratory insertion of CO into M-R bonds.

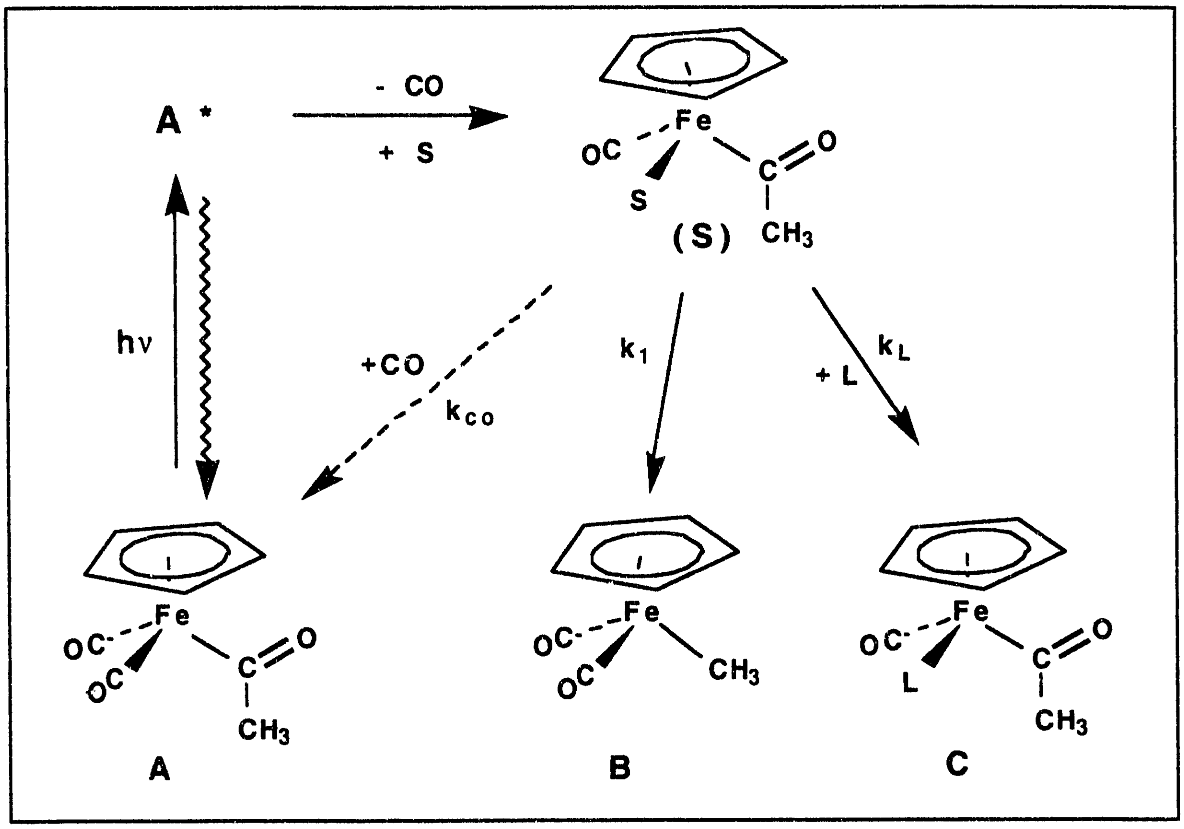


(I)

Laser flash photolysis techniques with time resolved infrared detection has allowed us to characterize such intermediates for reactions of the model compound $CpFe(CO)_2CH_3$ (*J. Am. Chem. Soc. 113,* 9524-9528 (1991), $Cp = \eta^5\text{-}C_5H_5$) and ongoing studies are addressing similar problems with derivatives of this compound as well as the manganese analog $Mn(CO)_5CH_3$ and its derivatives. Such investigations provide new insight into the mechanisms of this fundamental organometallic reaction.

David Ryba, a senior graduate student who completed his Ph.D. thesis in December but who stayed on in a postdoctoral position for several months afterwards, has been a major player in all our TRIR studies. This past January he spent about a month in Germany working collaboratively with Prof. Rudi van Eldik of the

University of Witten/Herdecke using hydrostatic pressure effects to probe the competitive reactions of intermediates in the carbonylation of $CpFe(CO)_2CH_3$, which we have identified by time-resolved spectroscopic methods (Scheme 1)



Scheme 1: Model for reactions of the intermediate S from the photolysis of $CpFe(CO)_2(COCH_3)$. In 295 K cyclohexane solution, $k_1 = 5.6 \times 10^4\ s^{-1}$, $k_{co} < 6 \times 10^5\ L\ mol^{-1}\ s^{-1}$ and $k_2 = 2.4 \times 10^6\ L\ mol^{-1}\ s^{-1}$ for L = PPh_3.

Dave was able to show that the difference between the activation volumes for the k_L and k_1 steps ($\Delta V_L^* - \Delta V_1^*$) is a remarkable $-40\ cm^3\ mol^{-1}$, an observation which strongly suggests very different mechanisms for the two pathways. On the basis of such evidence, we have proposed an associative pathway for the attack of a phosphine type ligand L and a dissociative pathway (or a concerted pathway with strongly dissociative character) for the alkyl migration to the metal center. The associative pathway for trapping with L could be accentuated by the possible role of a "ring-slip" process involving the coordinated cyclopentadienyl ligand, so we will continue our collaborative pressure studies with van Eldik using other metal acyl complexes, e.g., $Mn(CO)_5(COCH_3)$, not having the same functionality in order to test the generality of the associative pathway. Dave Ryba has accepted a postdoctoral fellowship at Washington State University.

Brian Lee and **Karen MacFarlane,** both students finishing their second year, are continuing the TRIR studies of the migratory insertion reactions. Their focus has been on the structures and reaction dynamics of the intermediates produced in the migratory insertion reactions of $Mn(CO)_5R$ and $CpFe(CO)_2R$ ($R = CH_3$, CD_3 or CF_3) under various conditions including different solvents. Both are outstanding students, and Brian in particular has developed excellent instrumentation skills. We also plan to carry out some collaborative experiments with Bruce Weiller of the Aerospace Corp. who has constructed a liquid xenon system with very fast IR detection. This will allow us to prepare some of these intermediates under low temperature conditions where they will be much longer lived and to compare these spectra to those we determine in our TRIR system to provide better insight regarding the structures of the relevant species.

Several years ago we probed the flash photolysis characteristics of the rhodium(I) phosphine complexes $RhCl(CO)L_2$ which in some cases proved to be effective photocatalysts for the carbonylations of hydrocarbons (*J. Am. Chem. Soc. 109,* 436 (1987), *111,* 1932 (1989),. Changes in personnel led to a diminished activity in this area; however, with the addition of a new postdoctoral fellow in August, we are reinitiating quantitative studies of such C-H activation with the goal of identifying the key reactive intermediates responsible for the hydrocarbon activation. **Susan Boggs**, a third year graduate student will be participating in these studies. **Jon Bridgewater**, an outstanding first year student, is also initiating exploratory studies of related platinum(II) complexes which may also prove to effective in the activation of hydrocarbons toward carbonylations or other functionalization.

Our instrumental capabilities to probe the reaction dynamics of reactive intermediates has undergone a major upgrading with the award of a 1991 University Research Instrumentation grant from the Department of Energy to purchase new nanosec and picosec YAG lasers and appropriate detection instrumentation. Jon Bridgewater and Brian Lee with the help of a former student **Dr. John DiBenedetto** (now at EG&G, Goleta) have made major strides in setting up these systems to be used as a facility for fast reaction dynamics investigations by ourselves and other DOE investigators on this campus. When fully operational, the ps system will allow us to probe reaction intermediate lifetimes three orders of magnitude shorter than does our present instrumentation.

B. 1991-1992 Publications and Theses and Presentations based on work supported by the Division of Chemical Sciences, DOE-OBES

Publications:

1. "Kinetics of the Water Gas Shift Reaction Catalyzed by Rhodium(III) Chloride in Aqueous Picoline Studied by Use of a Continuous-Flow Stirred Reactor", Benedito S. Lima Neto, K. Howland Ford, Alvaro Pardey, Robert G. Rinker, Peter C. Ford, *Inorg. Chem. 30*, 3837-3842 (1991)

2. "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, Peter C. Ford, *J. Am. Chem. Soc. 113,* 9524-9528 (1991)

3. "Flash Photolysis Studies of Reactive Intermediates Relevant to Homogeneous Catalysis by Organometallic Complexes", P. C. Ford, S. T. Belt, *ACS Adv. Chem. Ser. 230* "New Science in Homogeneous Transition Metal Catalysis", in press

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

5. "Reaction intermediates in organometallic chemistry studied by time-resolved infrared spectral techniques ", Peter C. Ford, John A. DiBenedetto, David W. Ryba, Simon T. Belt, *SPIE Vol.1636* "Applied Spectroscopy in Materials Science II", pp 9-16 (1992)

6. "Reactive Intermediates in the Carbonylation of Metal Alkyl Bonds Studied by Time-Resolved Infrared Spectral Techniques", Peter C. Ford*, David W. Ryba Simon T. Belt, *ACS Adv. Chem. Ser. Vol 238 "Photosensitive* Metal-Organic Systems: Mechanistic Principles and Recent Applications", in press

7. "Pressure Effects on the Photoreactions of the Iron Acyl Complex $(\eta^5\text{-}C_5H_5)Fe(CO)_2(COCH_3)$, Mechanistic Implications Regarding Competitive Reactions of the Solvento Intermediate $(\eta^5\text{-}C_5H_5)Fe(CO)(S)(COCH_3)$", David W.Ryba, Rudi van Eldik, Peter C. Ford, submitted for publication

Reprints of items 1, 2 and 5 are attached.

Theses:

1. "Reacao de Delocamento do Gas D'Agua: Estudos 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, 1991

2. "An Investigation of Coordinatively Unsaturated Metal Carbonyls, Using Time-Resolved Infrared Spectroscopy"
   David W. Ryba, Ph.D. Dissertation submitted to Department of Chemistry, UC Santa Barbara, 1991

3. "An Investigation of the Nucleophilic Activation of $Ru_3(CO)_{12}$"
   Jerome Lillis, Ph.D. Dissertation submitted to Department of Chemistry, UC Santa Barbara, 1992

Invited presentations:

1. "Reactive Intermediates in the Carbonylation of Metal Alkyl Bonds Studied by Time-Resolved Infra-Red Spectral Techniques" presented to symposium on *Photosensitive Metal-Organic Systems*, **Fourth Chemical Conference of North America,** New York, August 1991

2. "Reaction intermediates in organometallic chemistry studied by time-resolved infrared spectral techniques ", **International Symposium on Lasers, Sensors and Spectroscopy** (SPIE-International Society for Optical Engineering) Los Angeles, January 1992

3. "Nucleophilic Activation of Metal Carbonyls: Applications to Homogeneous Catalysis of the Water Gas Shift and Related Processes", **Symposium on New Molecular Catalysts and Catalysis,** Sapporo Japan, May 1992

Also, contributed oral presentations describing DOE supported studies were made this past year at the **Pacific Conference on Chemistry and Spectroscopy**, (Anaheim, 10/91); the **California Catalysis Society,** (Santa Barbara, 11/91), the **203rd National Meeting of the American Chemical Society**, (San Francisco, 4/92), and the **VII International Symposium on Relations Between Homogeneous and Heterogeneous Catalysis** (Tokyo, 5/92)

C. Plans for 1991-92

The research group has undergone significant changes in personnel this past year, a situation which offers both problems and opportunities. Two senior graduate students **Dave Ryba** and **Jerome Lillis** have finished their Ph.D. studies and have moved on to postdoctoral positions. New personnel include a very capable first year graduate student **Jon Bridgewater** and a postdoctoral fellow **William Boese** (from Alan Goldman's group at Rutgers), who will join the group this summer. In addition it is anticipated that Jeorge Schrikel, who has experience in time-resolved infrared (TRIR) spectroscopy from the M. Planck Institute in Muelheim, Germany will be joining the group as a NATO postdoctoral fellow late in 1992

Jon and Bill will both be involved in the investigations of reactive intermediates in catalytic and photocatalytic C-H activation processes involving rhodium(I) and/or platinum(II) phosphine complexes. It is anticipated that another student, **Susan Boggs,** who has been investigating certain ruthenium complexes which are capable of activating the C-H bonds of aromatic nitrogen heterocycles, will also participate in these activities.

The TRIR studies are being carried on by second year graduate students **Brian Lee** and **Karen MacFarlane.** Their focus has been on the structures and reaction dynamics of the intermediates produced in the migratory insertion reactions of $Mn(CO)_5R$ and $CpFe(CO)_2R$ ($R = CH_3$, CD_3 or CF_3) under different conditions including different solvents. We also have plans to carry out collaborative experiments with Bruce Weiller of the Aerospace Corp to prepare and study intermediates in liquid xenon and compare our TRIR spectra to the spectra of species trapped at much lower temperature.

Millan Mdleleni will continue the water gas shift related studies utilizing the custom designed polymer supported catalyst systems described in section A. These studies will be carried out using both continuous flow and batch reactor systems. He also plans to carry out exploratory studies into WGSR related reactions such as Reppe hydroformylation.

Reprints, Budget info. removed

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