FINAL TECHNICAL PROGRESS REPORT

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Division of Chemical Sciences
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Title: **"Studies Relevant to Catalytic Activation of CO and Other Small Molecules"**

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Abstract:

This report summarizes the technical progress accomplished over the tenure of Grant No DE-FG03-85ER13317 and briefly describes the personnel who contributed to this research.

Contents:

Summary

Detailed annual and triannual reports describing the progress accomplished during the tenure of this grant were filed with the Program Manager for Catalysis at the Office of Basic Energy Sciences. To avoid unnecessary duplication, the present report with provide a brief overview of the research areas that were sponsored by this grant and list the resulting publications and theses based on this DOE supported research. The scientific personnel participating in (and trained by) this grant's research are also listed.

Research carried out under this DOE grant was largely concerned with the mechanisms of the homogeneous catalytic and photocatalytic activation of small molecules such as carbon monoxide, dihydrogen and various hydrocarbons. Much of the more recent effort has focussed on the dynamics and mechanisms of reactions relevant to substrate carbonylations by homogeneous organometallic catalysts. A wide range of modern investigative techniques were employed, including quantitative fast reaction methodologies such as time-resolved optical (TRO) and time-resolved infrared (TRIR) spectroscopy and stopped flow kinetics. Although somewhat diverse, this research falls within the scope of our long-term objective of applying quantitative techniques to elucidate the dynamics and understand the principles of mechanisms relevant to the selective and efficient catalytic conversions of fundamental feedstocks to higher value materials

Of particular interest has been the mechanism of the carbon-carbon bond formation via CO migratory insertion into metal alkyl bonds of manganese carbonyl models as well as of cobalt carbonyl phosphine analogs of the "Shell catalyst" for hydroformyation of higher alkenes. The time-resolved spectroscopic techniques involve the use of pulsed laser excitation of appropriate precursors or, in the some cases, rapid mixing techniques to prepare reactive intermediates that are potentially relevant to the catalysis mechanisms. The spectra and temporal behavior of such species are then interrogated using optical (UV/Vis) light sources and detection or infrared light sources and detection. Both methods give important information regarding the identity and dynamics of these transient species; however, for organometallic complexes, the TRIR technique provides especially valuable information regarding the structure of species with strong IR chromophores. Development of a high pressure/variable temperature sample flow cell for these studies has generated the opportunity to examine such reactivities under conditions closer to those likely to be employed by industrial catalysts. In addition, the HPVT cell provides exceptional control over the reactant gas pressures and the temperature, therefore allowing the accurate measurements of activation parameters.

A related topic of investigation has been the time-resolved spectroscopic investigations of rhodium and iridium halo carbonyl complex intermediates proposed in methanol carbonylation catalysts.. These studies were carried out with the goal of interrogating reactive intermediates relevant to the commercially important "Monsanto" and "Cativa" catalysts for methanol carbonylations to acetic acid.

Other investigations during this period of effort include a detailed time-resolved spectroscopic studies of the C-H bond activation by Rh(I) phosphine complexes. Reports that the phosphine complexes *trans*-$RhCl(CO)L_2$ ($L = PR_3$) are precursors to catalytic and photocatalytic hydrocarbon functionalization[32] rekindled our interest in probing the fundamental chemistry of these systems. Our detailed TRIR and TRO spectroscopic reexamination of intermediates

generated by ns flash photolysis to outline dominant steric and electronic factors determining the initial C-H activation pathways. The rhodium(I) phosphine complexes are especially interesting given their ability to participate in catalytic hydrocarbon functionalization.

Earlier studies during the tenure of this grant were concerned with the design of new catalysts for the water gas shift reaction and for utilizing water gas shift chemistry to carry out the hydrogenation or hydroformylation of selected substrates using carbon monoxide as the key reductant and water as the hydrogen source. A particularly interesting development was the discovery of a rhodium based system effective for the hydrodehalogenation of chlorocarbons of the type that are persistent environmental pollutants. Extensive mechanistic studies were carried out on several catalytic systems including those based on ruthenium carbonyl clusters and on rhodium carbonyl halide complexes

In addition, two newer areas of inquiry relevant to selective catalytic conversions were initiated and these represent continuing research in these laboratories. The first is concerned with the characterization and dynamics of metal-based radicals of the type proposed to be intermediates in an unusual molybdenum carbonyl catalyst for ethene hydrocarboxylation. While falling within our group's long-term interest in carbonylation chemistry, this catalytic system draws additional interest from the proposal that it proceeds via metal-based free radical intermediates. Elucidating the pathways of generating such species and their reaction dynamics under conditions relevant to catalysis has the potential of providing insight into the design of new catalysts. The other effort is concerned with using our time-resolved spectroscopic techniques to investigate the oxygen transfer reactions of metal-NO_x complexes with the longer term goal of evaluating the potential applications of such species as mediators for the selective and controlled oxidation of organic substrates by dioxygen.

The following listing of publications supported by this grant are separated by area into the various topics indicated above. In addition, a large number of invited and contributed oral and poster presentations were made at national and international scientific meetings describing the DOE supported studies.

DOE SUPPORTED PUBLICATIONS AND THESES 1986-2003

A. Time resolved spectroscopic studies of carbonylation catalytic mechanisms

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

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Flash Photolysis Studies of Reactive Intermediates Relevant to Homogeneous Catalysis by Organometallic Complexes, P. C. Ford and S. T. Belt, *ACS Adv. Chem. Ser. 230*, 105-122 (1992)

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Pressure Effects on the Photoreactions of the Iron Acyl Complex $(\eta^5\text{-}C_5H_5)\text{-}Fe(CO)_2(COCH_3)$. Mechanistic Implications Regarding Competitive Reactions of the Solvento Intermediate $(\eta^5\text{-}C_5H_5)Fe(CO)(Sol)(COCH_3)$, David W. Ryba, Rudi van Eldik and Peter C. Ford, *Organometallcs, 12,* 104-107 (1993)

Photocatalysis Involving Metal Carbonyls, P. C. Ford, W. Boese, B. Lee, K. L. McFarlane, Cpt. in "Photosensitization and Photocatalysis by Inorganic and Organometallic Compounds" ed. by M. Graetzel and K. Kalyanasundaram, Kluwer Academic Publishers, the Netherlands, 1993, pp 359-390

Time Resolved Infrared Observation of a Long-Lived Transient in the Photo Decarbonylation of $Mn(CO)_5C(O)CH_3$: Potential Relevance to the CO Migratory Insertion Mechanism, William T. Boese, Brian Lee, David W. Ryba, Simon T. Belt and Peter C. Ford*, *Organometallics,12,* 4739-4741 (1993))

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Intermediates Relevant to the Carbonylation of Manganese Alkyl Complexes Interrogated by Time Resolved Infrared and Optical Spectroscopy, William T. Boese and Peter C. Ford**J. Am. Chem. Soc., 117*, 8381-8391 (1995)

Time Resolved Infrared Studies of Migratory Insertion Mechanisms in Manganese Carbonyls, Peter C. Ford and William T. Boese, *ACS Adv. Chem. Ser. , 253*, 221-238 (1997)

Photochemistry as a tool for elucidating organometallic reaction mechanisms, W. Boese, K. McFarlane, B. Lee, J. Rabor and P. C. Ford, *Coord. Chem. Rev., 159*, 135-152 (1997)

Room Temperature Reactions of the Intermediate(s) Generated by Flash Photolysis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$, Karen L. McFarlane, Peter C. Ford, *Organometallics,* 17, 1166-1168 (1998)

Time Resolved Infrared Spectroscopy as a Technique to Study Reactive Organometallic Intermediates, Karen McFarlane, Brian Lee, Jon Bridgewater and Peter C. Ford, invited article to a special edition of *J. Organomet. Chem. 554*, 49-61 (1998)

Reactive Intermediates in the Photodecarbonylation of the Cyclopentadienyl and Indenyl Complexes $CpFe(CO)_2(C(O)CH_3)$ and $IndFe(CO)_2(C(O)CH_3)$ ($Cp = \eta^5$-C_5H_5; $Ind = \eta^5$-C_9H_7), Karen L. McFarlane, Brian Lee, Wenfu Fu, Rudi van Eldik and Peter C. Ford* *Organometallics 17*, 1826-1834 (1998)

Photochemical Strategies for Investigating Organometallic Intermediates Relevant to Catalysis Mechanisms. P. C. Ford, Jon. S. Bridgewater, S. Massick, J. Marhenke, *Catalysis Today*, 1999, *49*, 419-430.

A Time-Resolved Infrared Spectroscopic Study of Reactive Acyl Intermediates Relevant to Cobalt-Catalyzed Hydroformylation. S. M. Massick, J. Rabor, S. Elbers, J. Marhenke, S. Bernhard, J. R. Schoonover, P. C. Ford, *Inorg. Chem.* 2000, *39*, 3098-3106

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Activation parameters for reactive intermediates relevant to carbonylation catalysts based on phosphine modified cobalt carbonyls. S. M. Massick, T. Büttner, P. C. Ford *Inorg. Chem.* 2003, *42*, 575-580.

A flash photolysis investigation of iridium carbonyl intermediates relevant to the Cativa catalyst for methanol carbonylaltion M. Volpe, P. Ford. in preparation

B. Catalyst development and mechanistic studies related to the water gas shift reaction.

Ligand Substitution Kinetics of the Triruthenium Hydride Ion $HRu_3(CO)_{11}^-$, D.J. Taube and P.C. Ford, *Organometallics*, **5**, 99-104 (1986).

Activation Volumes for the Substitution Reactions of the Triruthenium Cluster Anions $HRu_3(CO)_{11}^-$ and $Ru_3(CO)_{11}(CO_2CH_3)^-$", D.J. Taube, R. van Eldik and P.C. Ford, *Organometallics*, **6**, 125-129 (1987).

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The Crystal Structure of Bis(triphenylphosphine)decacarbonyltriruthenium, An Example of Unsymmetrical Semibridging Carbonyls in Substituted Clusters, T. Chin-Choy, N. L. Keder, G. D. Stucky and P. C. Ford, *J. Organometallic Chem.*, **346,** 225-236 (1988).

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Selective Activation of Small Molecules, P. C. Ford and A. Friedman, Chpt. 16 in "Photocatalysis: Fundamentals and Applications" eds. N. Serpone and E. Pelizzetti, J. Wiley and Sons, NY, 1989, pp 541-564

Quantitative Mechanistic Studies of the Photoreactions of Trinuclear Metal Carbonyl Clusters of Iron, Ruthenium and Osmium, P. C. Ford, *J.Organometallic Chem.*, **383**, 339-356 (1990)

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Hydroformylation and hydrogenation of alkenes as catalyzed by polymer anchored $RhCl_3$ under water gas shift conditions, M. M. Mdleleni, R. Rinker, P. C. Ford *Inorganica Chemica Acta* 270, 345-352 (1998)

Hydrodechlorination of 1,2-dichloroethane by rhodium catalysts under water gas shift reaction conditions. E. Trabuco, P. C. Ford. *J. Mol. Catalysis, A. Chem.*, 1999, *148*, 1-7

Homogeneous Catalysis of the Water Gas Shift Reaction. P. C. Ford, E. Trabuco, M. M. Mdleleni, *Encyclopedia of Catalysis,* Wiley-VCH Publishers, 2002.

Rhodium catalyzed reduction of nitroaromatic compounds under water gas shift conditions. M. M. Mdleleni, R. G. Rinker, P. C. Ford, *J. Molecular Catalysis A, Chemical, .in press* 2003

C. Catalytic and photocatalytic pathways to C-H activation in hydrocarbons

Flash Photolysis Studies of $RhCl(CO)L_2$ (L = Trimethyl or Tritolylphosphine). Evidence for Intermediates in the Photocatalytic Carbonylation of Hydrocarbons, C. T. Spillett and P. C. Ford, *J. Am. Chem. Soc.*, **111**, 1932-1933 (1989).

Dynamics of Reactive Intermediates as Probed by Flash Photolysis: 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)

Synthesis, Structure and Spectroscopic Properties of Ortho-metalated Pt(II) Complexes. M. M. Mdleleni, J. S. Bridgwater, R. J. Watts, P. C. Ford*, *Inorg. Chem. 34*, 2334-2342 (1995)

Time Resolved Infrared Spectral Studies of Photochemically Induced Oxidative Addition of Benzene to trans-$RhCl(CO)(PMe_3)_2$, Jon S. Bridgewater, Brian Lee, Stefan Bernard, Jon R. Schoonover and Peter C. Ford* *Organometallics, 16*, 5592-5594 (1997)

Time resolved optical and infrared spectral studies of intermediates generated by photolysis of *trans*-$RhCl(CO)(PR_3)_2$. Roles played in the photocatalytic activation of hydrocarbons. J. S. Bridgewater, T. L. Netzel, J. R. Schoonover, S. M. Massick, P. C. Ford, *Inorg. Chem.* 2001, *40*, 1466-1476.

D. Studies relevant to the role of metal-based radical intermediates in catalytic reactions

Photoreactions of $Ir_8(CO)_{22}^{2-}$. Homolytic Cleavage of an Unsupported Metal- Metal Bond Linking Two Tetrahedral Iridium Carbonyl Clusters, D. Vandenberg, A. E. Friedman, and P. C. Ford *Inorg. Chem.* **27**, 594-595 (1988).

A reinvestigation of the dynamics of "unsaturated" molybdenum carbonyl complexes. C. Kayran, M. Richards and P. C. Ford, *Inorg. Chimic Acta*, 2003

Time resolved spectroscopic studies of reactive intermediates in cobalt and rhodium catalyzed alkene and alcohol carbonylations, J. Marhenke, V. Reyes, P. C. Ford, in preparation, to be submitted to *Inorg. Chem.*

E. Oxidations involving metal NO_x complexes.

Reactions of Nitrogen Oxides with Heme Models. Characterization of Fe(TPP)(NO_2) as an Unstable Intermediate, Mark D. Lim, I. M. Lorkovic, K. Wedeking, A. W. Zanella, C. F. Works, S. M. Massick, P. C. Ford, *J. Amer. Chem. Soc.* 2002, *124*, 9737-9743.

F. New experimental techniques for the investigation of catalytic mechanisms

"Recrystallization Apparatus for Air Sensitive Compounds, A.E. Friedman and P.C. Ford, *ACS Symp. Ser.*, **357**, 68-69 (1987).

"Reaction Dynamics of Photosubstitution Intermediates of the Triruthenium Cluster $Ru_3(CO)_{12}$ as Studied by Flash Photolysis with Infrared Detection, J. DiBenedetto, D. W. Ryba and P. C. Ford, *Inorg. Chem.*, **28,** 3503-3507 (1989).

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 Proceedings 1636*, 9-16 (1992)

Photochemical Rearrangement of a Rhenium Dimetallacyclobutene Studied by Time Resolved Infrared Spectroscopy, Charles P. Casey, William T. Boese, Ronald S. Cariño, and Peter C. Ford, *Organometallics, 15,* 2189-2191 (1996)

Time Resolved Infrared Spectroscopy in Studies of Organometallic Excited States and Reactive Intermediates, Peter C. Ford, Jon S. Bridgewater, Brian Lee, *Photochem. Photobiol. 65*, 57-64 (1997)

Use of a High Pressure/Variable Temperature Infrared Flow Cell to Examine the Reaction Kinetics of the Migratory Insertion Intermediate ($\square^5$-C_5H_5)Fe(CO)$COCH_3$ by Time-Resolved Spectroscopy, S. M. Massick, P. C. Ford, *Organometallics* 1999,*18,* 4362-4366

II. Theses based on DOE supported research:

"Homogeneous Catalysis of the Water Gas Shift Reaction by Rhodium Complexes in Aqueous Heterocyclic Amine Solutions" Alvaro J. Pardey, *Ph.D. Dissertation* (UCSB, 1986)

"Catalysis Reactions of Indium Carbonyl Clusters" David Vandenberg, *Ph.D. Dissertation* (UCSB, 1986)

"The pK_a Values of Some Substituted Iron Carbonyl Hydrides in Aqueous Methanol" Katherine O. Jimison, *M.S. Dissertation* (UCSB, 1986)

"Mechanistic Investigations of the Photoreactions of $HRu_3(CO)_{10}(COCH_3)$" Alan E. Friedman, *Ph.D.Dissertation*, (UCSB, 1988)

"Kinetics Study, Spectral Characterization and Structural Determination of Substituted and Nucleophilic Adducts of $Ru_3(CO)_{12}$" Tyrena K. Chin, *Ph.D. Dissertation* (UCSB, 1989)

"A Study of the Water Gas Shift Reaction Catalyzed by Soluble Organometallic Complexes in a Continuous-Flow Stirred Reactor" Katherine Howland Ford, *Ph.D. Dissertation* (UCSB, 1989) (R.G. Rinker, Dept of Chemical Engineering, co-Research Advisor)

I. "Flash Photolysis Investigations of Rhodium(I) Phosphine Complexes" II. "Acid Equilibrium Studies of Rhodium(I) and Iridium(I) Complexes" CrisTina Spillett, *Ph.D. Dissertation* (UCSB, 1989) (R.G. Pearson, co-Research advisor)

"Reacao de Delocamento do Gas D'Agua: Studos 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)

"An Investigation of Coordinatively Unsaturated Metal Carbonyls, Using Time-Resolved Infrared Spectroscopy", David W. Ryba, *Ph.D. Dissertation*, UC Santa Barbara (1991)

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

"Catalytic and Spectroscopic Properties of Some Platinum Metal Complexes", Millan M. Mdleleni (United Nations Predoctoral Fellow), *Ph.D. Dissertation*, UC, Santa Barbara, 1995

"Structural and Mechanistic Investigations of Reactive Iron Carbonyl Intermediates Relevant to Migratory Insertion Reactions", Karen McFarlane, *Ph.D. Dissertation*, UC Santa Barbara, 1996

"Mechanistic Investigations of Rhodium(I) Complexes Relevant to C-H Activation Reactions", Jon S. Bridgewater, *Ph.D.*Dissertation, UC Santa Barbara, October 1998

"Synthesis of Cobalt-Acyl-Complexes of the Type $MeC(O)Co(CO)_3PR_3$; Characterization of Reactive Intermediates Using TR IR Techniques, Torsten Bütner, *Diplom thesis* submitted to the Univ. Jena, Germany based on DOE supported studies at UCSB, 2000

"Time Resolved Spectroscopic Studies of Reactive Intermediates in Cobalt and Rhodium Catalyzed Alkene and Alcohol Carbonylations, Jon Marhenke, *Ph.D. Dissertation* , UC Santa Barbara, 2002

"Synthesis and reactivity of heteronuclear metal carbonyls: study of the systems $[HCr(CO)_5]/Ln(Acac)_3.3H_2O$ (Ln= Sm or Yb) and $[HCr(CO)_5]$-/$Cu(Acac)_2$ Marizio Volpe *(Ph.D. thesis* submitted to the University of Palermo, Italy including DOE supported work partially carried out at UC Santa Barbara) 2003

UCSB Personnel Participating in Research Supported by DOE Grant DE-FG03-85ER13317

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William T. Boese (Oracle Corp.)
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Enrique Lozano-Diz (postdoctoral fellow, UCSB)
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Veronica Reyes (Amgen Corp)

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