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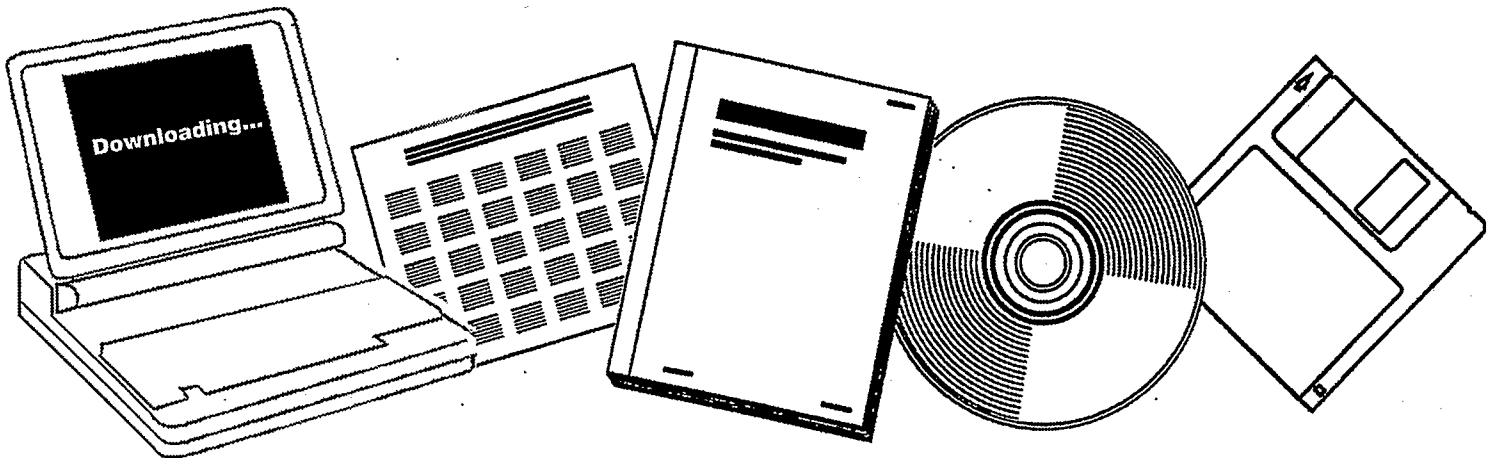
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**CATALYTIC HYDROGENATION OF CARBON  
MONOXIDE: FINAL PROGRESS REPORT, SEPTEMBER  
15, 1988-SEPTEMBER 14, 1989**

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CATALYTIC HYDROGENATION  
OF CARBON MONOXIDE

Final Research Progress Report  
September 15, 1988 – September 14, 1989

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The Trustees of the University of Pennsylvania  
Philadelphia, Pennsylvania 19104

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September, 1989

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## FINAL TECHNICAL REPORT

Grant No. DE-FG02-86ER13615

## Project Title

"Catalytic Hydrogenation of Carbon Monoxide"

## Abstract

This project is focused on developing strategies to accomplish the hydrogenation of carbon monoxide to produce organic oxygenates at mild conditions. Our approaches to this issue are based on the recognition that rhodium macrocycles have unusually favorable thermodynamic values for producing a series of intermediates implicated in the catalytic hydrogenation of CO. Observations of metalloformyl complexes from reactions of H<sub>2</sub> and CO, and reductive coupling of CO to form metallo  $\alpha$ -diketone species have suggested a multiplicity of routes to organic oxygenates that utilize these species as intermediates. Thermodynamic and kinetic-mechanistic studies are used in constructing energy profiles for a variety of potential pathways, and these schemes are used in guiding the design of new metallospecies to improve the thermodynamic and kinetic factors for individual steps in the overall process. Variation of the electronic and steric effects associated with the ligand arrays along with the influences of the reaction medium provide the chemical tools for tuning these factors. Current studies are directed toward the use of non-macrocyclic ligand complexes that emulate the favorable thermodynamic features associated with rhodium macrocycles, but that also manifest improved reaction kinetics. Multifunctional catalyst systems designed to couple the ability of rhodium complexes to produce formyl and diketone intermediates with a second catalyst that hydrogenates these intermediates are promising candidates to accomplish CO hydrogenation at mild conditions.

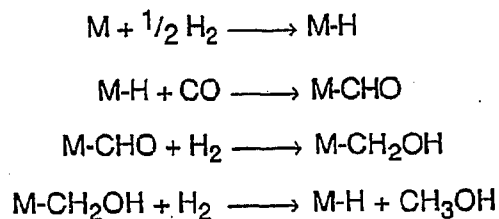
RESEARCH PROGRESS REPORT

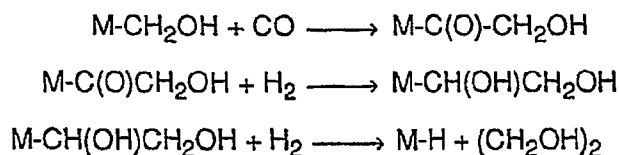
Catalytic conversion of CO and H<sub>2</sub> into organic oxygenates at mild conditions (P<sub>H<sub>2</sub></sub>, P<sub>CO</sub> ~ 1 atm; T < 100°C) and with product specificity provides a set of major technological goals for energy research. Achievement of these goals depends on the thermodynamic and kinetic factors that control the formation and conversion of intermediates which subsequently determine the rate and degree of specificity of product formation. Organometallic-catalysis studies provide a systematic approach to accomplishing these goals by revealing both the scope of thermodynamically accessible metallo-intermediates and the structural and electronic factors that contribute to their rate of formation and reaction.

This research program is focused on establishing general criteria for a metallo species to form the essential intermediates for a series of reaction pathways that could be used in the hydrogenation of CO at mild conditions. This proposal specifically addresses two very different general pathways to accomplish CO hydrogenation which we call the "formyl" and "α-diketone" mechanisms.

The formyl mechanism is generally accepted as the probable route for metallo-systems that are currently recognized to catalytically hydrogenate CO to form organic oxygenates. One version of this mechanism that produces CH<sub>3</sub>OH and (CH<sub>2</sub>OH)<sub>2</sub> is outlined below.

## A) formyl mechanism



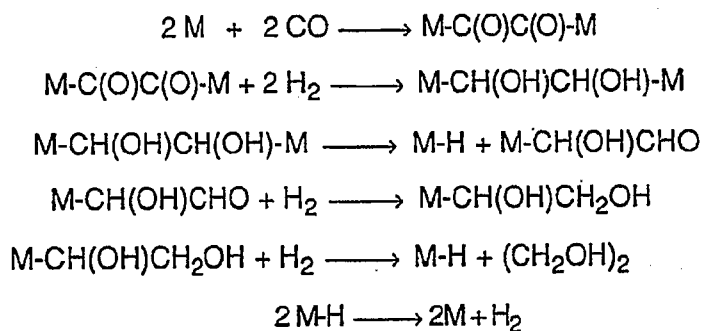


Studies of metalloformyl complexes have occupied a prominent position in organometallic-catalysis research because formyl species are the first organometallic intermediate in the hydrogenation of CO. Subsequent formation and reaction of hydroxymethyl and hydroxyacyl intermediates direct the formation of methanol and or ethylene glycol. The original stimulation for this research program arose from our observation that octaethylporphyrin rhodium(II) dimer, [(OEP)Rh]<sub>2</sub>, reacts reversibly with H<sub>2</sub> and CO at low gas pressures (P<sub>H<sub>2</sub></sub>, CO < 1 atm; T = 298K) to produce large equilibrium concentrations of a metallo formyl complex, (OEP)Rh-CHO.<sup>1</sup> This observation provided the first example of a metallo-species that could manifest the necessary thermodynamic factors to produce observable quantities of an η<sup>1</sup> carbon bonded metalloformyl species from H<sub>2</sub> and CO, and further suggested the feasibility of producing organic oxygenates from hydrogenating CO at mild conditions. Continuing studies of rhodium porphyrins and related systems have resulted in observation of an extensive series of suspected intermediates in CO hydrogenation including unusual hydroxymethyl (Rh-CH<sub>2</sub>OH)<sup>2</sup>, hydroxyacyl (Rh-C(O)CH<sub>2</sub>OH)<sup>3</sup> and α,β-dihydroxyethyl (Rh-CH(OH)CH<sub>2</sub>OH)<sup>4</sup> complexes. Reactivity, thermodynamic and mechanistic studies on these systems are guiding the future directions of this program and contributing to the development of general criteria for the design of metallo species to accomplish CO hydrogenation at mild conditions.

Recent observations in this laboratory have suggested that reductive coupling of CO to form a metallo-α-diketone intermediate could be a route for selective formation of two carbon organic oxygenates.<sup>5,6</sup> In the "α-diketone"

pathway, C-C bond formation occurs by CO coupling prior to hydrogenation, which ensures formation of two carbon products.

B)  $\alpha$ -diketone mechanism



A series of rhodium(II) porphyrin species have been shown to react reversibly with CO to form 1,2 ethane dionyl complexes, (por)Rh-C(O)C(O)-Rh(por).<sup>5,7</sup> Thermodynamic studies that are in progress on these systems are suggesting general criteria for obtaining this new form of CO reductive coupling and directing our search for further classes of metallo species that can accomplish this potentially important type of reactivity. Exploring strategies to hydrogenate the  $\alpha$ -diketone intermediate is a prominent new direction for this program.

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