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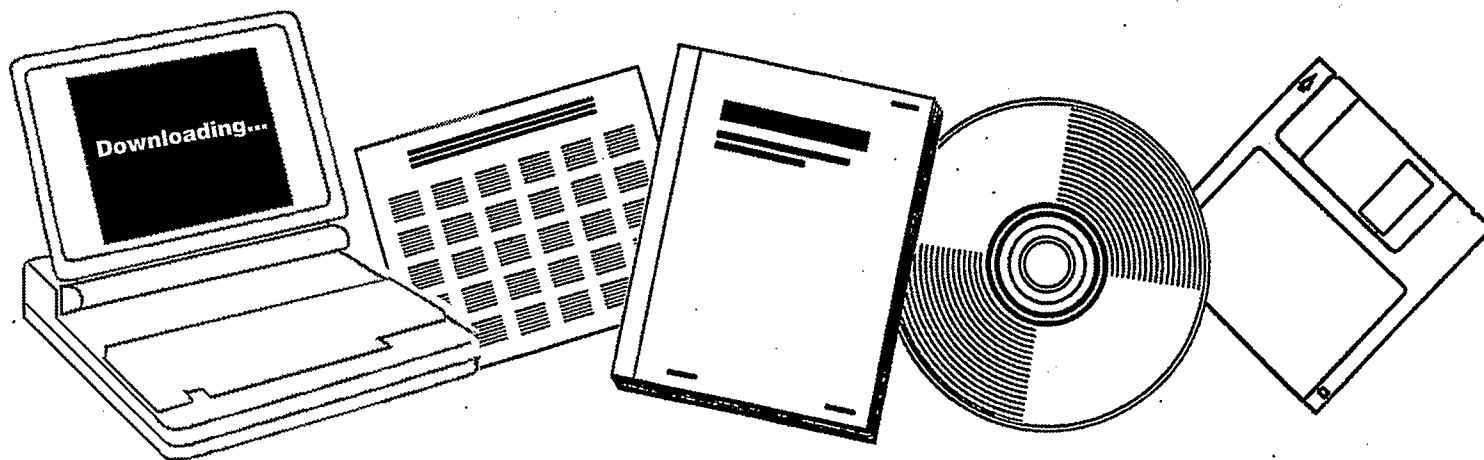
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**CATALYTIC HYDROGENATION OF CARBON
MONOXIDE: RESEARCH PROGRESS REPORT,
SEPTEMBER 15, 1986-SEPTEMBER 14, 1987**

PENNSYLVANIA UNIV., PHILADELPHIA. DEPT.
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CATALYTIC HYDROGENATION
OF CARBON MONOXIDE

Research Progress Report
September 15, 1986-September 14, 1987

Bradford B. Wayland

The Trustees of the University of Pennsylvania
Philadelphia, Pennsylvania 19104

N O T I C E

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Project Title

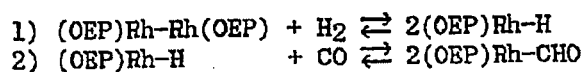
"Catalytic Hydrogenation of Carbon Monoxide"

Abstract

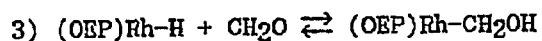
The principle objective of this program is to learn how to utilize the unique properties of rhodium porphyrins and related metallo species in achieving catalytic hydrogenation of carbon monoxide at mild conditions. Rhodium porphyrins react with H_2 and CO at pressures less than one atmosphere to produce a metalloformyl complex which is a primary intermediate in the hydrogenation of CO. Several catalytic schemes are proposed which take advantage of the unique reactivity of rhodium porphyrins coupled with the aldehyde like character of the metalloformyl intermediate. Multifunctional catalysts that utilize rhodium porphyrins and a second catalyst known to promote the hydrogenation of aldehydes are particularly promising candidates for achieving low pressure hydrogenation of CO. Solvent effects are being explored as one means of tuning the thermodynamic and kinetic parameters for optimum catalytic behavior. Results from studies of the rhodium porphyrin system provide a guide in designing new materials that retain the favorable thermodynamic factors but that have improved reaction kinetics. Comparative studies utilizing variation of the ligand array and central metal (Co,Rh,Ir) are being used to optimize the desired catalyst behavior.

Research Progress Report

The principal focus of this project is to develop strategies to accomplish catalytic hydrogenation of carbon monoxide at mild conditions. Initial motivation for this program came from the observation that rhodium octaethylporphyrin dimer, $[(\text{OEP})\text{Rh}]_2$, reacts with hydrogen and carbon monoxide, $(\text{P}_{\text{H}_2} + \text{CO} < 1 \text{ atm.})$ to produce large equilibrium concentrations of a metallo formyl complex, $(\text{OEP})\text{Rh}-\text{CHO}$. (equations 1, 2).

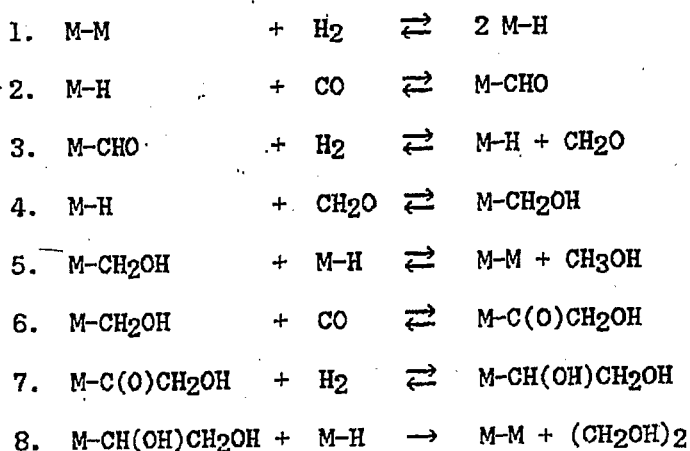


The metallo hydride, $(\text{OEP})\text{Rh}-\text{H}$, also reacts with formaldehyde to form a hydroxymethyl complex, $(\text{OEP})\text{Rh}-\text{CH}_2\text{OH}$, (equation 3).



Metallo formyl and hydroxymethyl ~~species are implicated~~ as the first two organometallic intermediates in the formation of organic oxygenates from H_2 and CO . Formation of large equilibrium concentration of these organometallic intermediates (reactions 1-3) illustrates the potential importance of these materials in attaining hydrogenation of CO at mild conditions.

A model scheme for metal complex catalyzed hydrogenation of CO to organic products (CH_3OH , $(\text{CH}_2\text{OH})_2$) is given by reaction steps 1-8.



This scheme is used in guiding and focusing our studies on the most important intermediate steps in the hydrogenation of carbon monoxide. Each of the steps 1-8 has been observed as either a thermal or photoprocess for the rhodium porphyrin system. Reactions 1, 2, 4, 5 and 8, occur by thermal routes ($T < 80^\circ\text{C}$) while reactions 3, 6 and 7 occur by photolytic pathways ($\lambda > 350\text{ nm}$). The rhodium porphyrin catalysed photopromoted formation of CH_2O and CH_3OH from H_2 and CO are illustrated in figures 1 and 2.

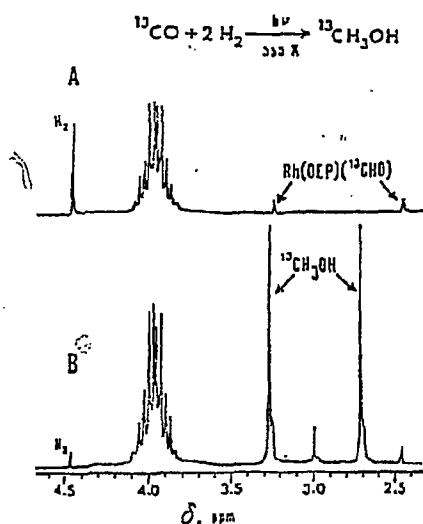


Figure 1. ^1H NMR spectra of rhodium octaethylporphyrin species in C_6D_6 under H_2 and ^{13}CO .
A. Thermal Equilibrium ($T = 353\text{ K}$; $P_{\text{H}_2} + P_{^{13}\text{CO}} = 600\text{ torr}$).
B. Products from photolysis of solution A ($\lambda = 300\text{ nm}$; $t = 36\text{ h}$; $T = 353\text{ K}$). $\delta^{13}\text{CH}_3\text{OH} = 2.99\text{ ppm}$; $\delta^{13}\text{CH}_2\text{OH} = 50.2\text{ ppm}$; $J_{^{13}\text{C-H}} = 140\text{ Hz}$.

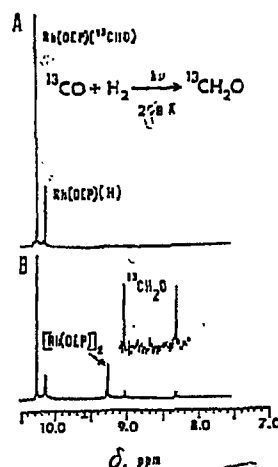


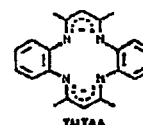
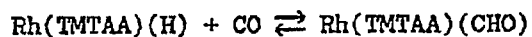
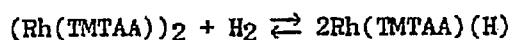
Figure 2. ^1H NMR spectra of rhodium octaethylporphyrin species in C_6D_6 under H_2 and ^{13}CO .
A. Thermal Equilibrium ($T = 298\text{ K}$; $P_{\text{H}_2} + P_{^{13}\text{CO}} = 600\text{ torr}$).
B. Products from photolysis of solution A ($\lambda = 300\text{ nm}$; $t = 45\text{ min}$; $T = 298\text{ K}$). $\delta^{13}\text{CH}_2\text{OH} = 8.68\text{ ppm}$; $J_{^{13}\text{C-H}} = 176\text{ Hz}$.

Organometallic reactions of rhodium porphyrins have unusual thermodynamic and mechanistic features. The unprecedented organometallic reactivity of rhodium porphyrins is a consequence of an unusual set of Rh-C (55-60 kcal) and Rh-H (~60 kcal) bond energies. Near equivalence of the Rh-C and Rh-H bond energies provides favorable thermodynamics for addition reactions of $(\text{por})\text{Rh-H}$ to C-O multiple bonds. The rigid porphyrin macrocycle occupies the four binding sites adjacent to the Rh-X ($\text{X}=\text{H},\text{R}$) bond and provides a barrier to the pathways utilizing a *cis* coordination site that are generally associated with migratory

insertion, oxidative addition, reductive elimination and β -H eliminations. As a consequence, many organometallic reactions for rhodium porphyrins proceed by bond homolysis or heterolysis, which are relatively high energy pathways.

Many of the unusual organometallic species produced by rhodium porphyrin complexes are key intermediates in the formation and transformation of organic compounds and would have considerable utility if the product forming mechanisms were not inhibited by the coordination properties of the porphyrin ligand. Our primary goal for next year is to identify complexes that manifest favorable thermodynamic factors to produce the desired reaction intermediates coupled with more favorable kinetic pathways to form organic products. The initial approach is simply to choose ligands with donor properties similar to that of a porphyrin ligand, but that have adequate structural flexibility to provide the opportunity for reaction mechanisms that utilize an open coordination site *cis* to the M-H or M-C bonds.

We have recently observed that the Rh-Rh bonded macrocycle complex $(\text{Rh}(\text{TMTAA}))_2$ accomplishes the desired reactivity with H_2 and CO to produce metalhydride and formyl complexes.



This system provides the first successful extension of this type of reactivity beyond the rhodium porphyrin system, and it now seems evident that a large class of rhodium complexes with conventional macrocycle and chelating ligand arrays may be effective in promoting the initial steps in the hydrogenation of CO. Ligand arrays are now being selected that can produce open *cis* coordination sites which permit conventional reaction pathways and thus more favorable kinetic factors.

Publications associated with DOE/ER 13615

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