



DE88017098

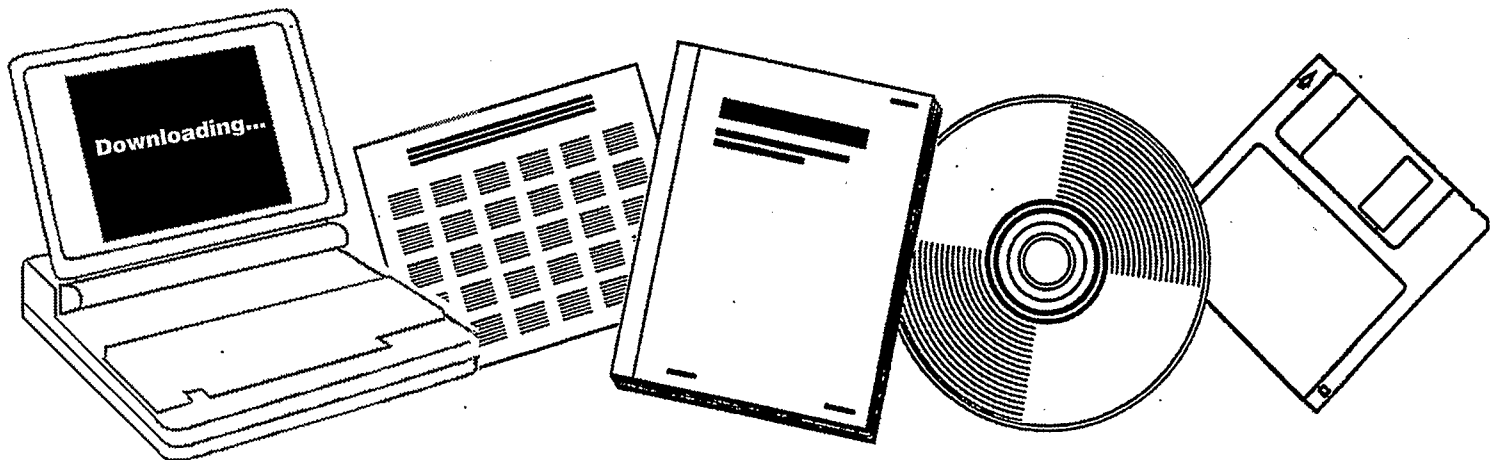
NTIS

One Source. One Search. One Solution.

**CATALYTIC HYDROGENATION OF CARBON
MONOXIDE: RESEARCH PROGRESS REPORT,
SEPTEMBER 15, 1987--SEPTEMBER 14, 1988**

PENNSYLVANIA UNIV., PHILADELPHIA. BOARD
OF TRUSTEES

1988



U.S. Department of Commerce
National Technical Information Service

DOE/ER/13615--2

DE88 017098

CATALYTIC HYDROGENATION
OF CARBON MONOXIDE

Research Progress Report
September 15, 1987-September 14, 1988

Bradford B. Wayland

The Trustees of the University of Pennsylvania
Philadelphia, Pennsylvania 19104

N O T I C E

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assumes any legal liability of responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately-owned rights.

September, 1988

Prepared for

The U.S. DEPARTMENT OF ENERGY
AGREEMENT NO. DE-FGO2-86ER13615

TECHNICAL REPORT

Grant No. DE-FG02-86ER13615

Project Title

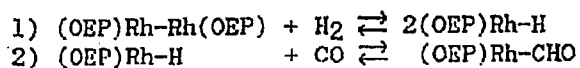
"Catalytic Hydrogenation of Carbon Monoxide"

Abstract

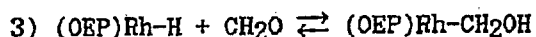
This project is focused on developing strategies to accomplish the hydrogenation of carbon monoxide to produce organic oxygenates at mild conditions. Our approaches to this issue are based upon the recognition that rhodium macrocycles have unusually favorable thermodynamic values for producing a series of metallo intermediates implicated in the catalytic hydrogenation of CO. Thermodynamic and kinetic-mechanistic studies are used in constructing energy profiles for metal promoted conversion of H₂ and CO to oxygenates, and these schemes are used in guiding the design of new metallospecies that could 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. We have successfully used this general approach to establish thermodynamic criteria for metal promoted reductive coupling of carbon monoxide, which resulted in our recent observation that rhodium porphyrins can accomplish this important reaction. 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.

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, [(OEP)Rh]₂, reacts with hydrogen and carbon monoxide, (P_{H₂} + P_{CO} < 1 atm) to produce large equilibrium concentrations of a metalloformyl complex, (OEP)Rh-CHO. (equations 1, 2).

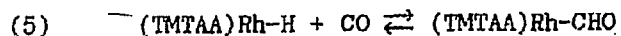
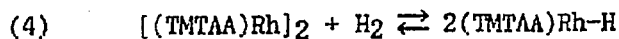


The metallohydride, (OEP)Rh-H, also reacts with formaldehyde to form a hydroxymethyl complex, (OEP)Rh-CH₂OH, (equation 3).



Metalloformyl and hydroxymethyl species are implicated as the first two organometallic intermediates in the formation of organic oxygenates from H₂ and CO. Formation of large equilibrium concentrations of these organometallic intermediates (reactions 1-3) illustrates the potential importance of these materials in attaining hydrogenation of CO at mild conditions. These reactions have now been expanded to a series of porphyrin and phthalocyanine ligand systems.

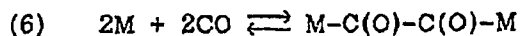
We have recently observed that the Rh-Rh bonded macrocycle complex (TMTAA)Rh)₂ accomplishes the desired reactivity with H₂ and CO to produce metallohydride and formyl complexes (equations 4 and 5). This system provides



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

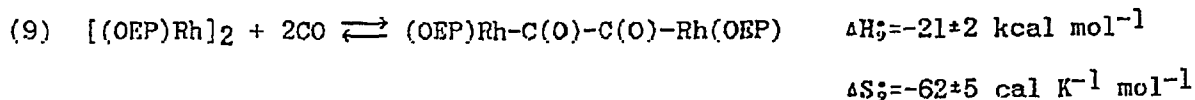
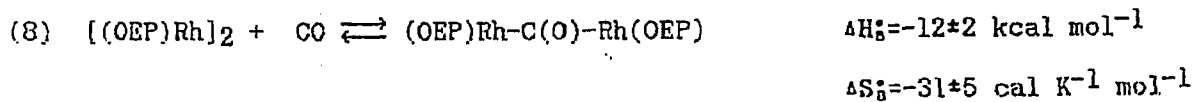
complexes with conventional macrocycle and chelating ligand arrays may be effective in promoting the initial steps in the hydrogenation of CO. Ligand arrays are now being selected that can produce open cis coordination sites which permit conventional reaction pathways and thus more favorable kinetic factors.

A new direction for this program has been to examine possible reaction pathways to form C-C bonded species from CO. One of the pathways considered for selective formation of two carbon organic molecules involves the initial reductive coupling of CO (equation 6) and subsequent reaction with hydrogen to yield organic products. This is an attractive route to provide selectivity,



but this type of reductive coupling for CO is unprecedented in organometallic chemistry.

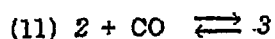
We have recently observed that octaethylporphyrin rhodium (II) dimer, [(OEP)Rh]₂ reacts with CO in toluene to produce three CO containing species in equilibrium (equation 7-9). Terminal CO adduct formation yields a mono CO adduct, [(OEP)Rh]₂CO, 1, and insertion of CO into the Rh-Rh bond gives a



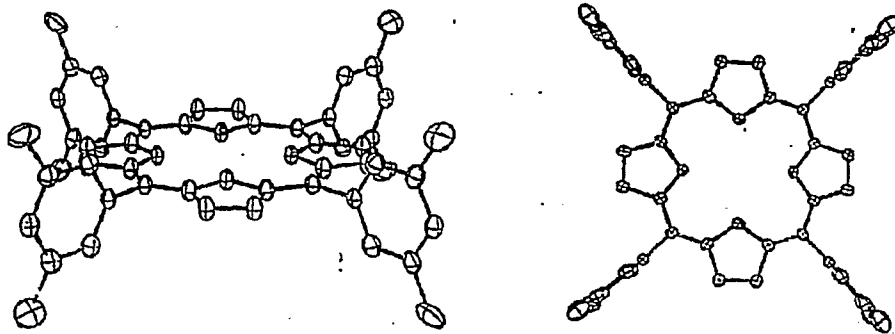
a dirhodium ketone, (OEP)Rh-C(O)-Rh(OEP), 2, and a species assigned as the

product of double CO insertion, $(\text{OEP})\text{Rh}-\text{C}(\text{O})-\text{C}(\text{O})-\text{Rh}(\text{OEP})$, 3. The proposed 1, 2 dionyl complex, 3, occurs as a significant fraction of the CO containing species only at relatively high CO pressures and lower temperatures ($P_{\text{CO}} > 10 \text{ atm}$, $T < 280\text{K}$).

Thermodynamic studies of reactions 7-9 indicate that the extent of conversion to the reductively coupled CO product ($P_{\text{CO}} \sim 1 \text{ atm}$, $T \sim 298\text{K}$) (equation 9) is limited by the presence of the monocarbonyl species 1, 2, in equilibrium with 3, (equations 10, 11) as well as the energy associated with dissociating the Rh-Rh bond.



Our next goal was to design a new ligand system that would inhibit both Rh-Rh bond formation and the monocarbonyl species and yet not seriously interfere with the required strong Rh-C bonding. We designed and prepared tetraxylporphyrin (TXP) as our initial effort to achieve these effects.

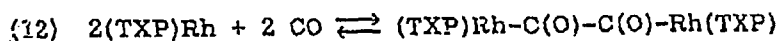


Molecular structure of TXP

Rhodium tetraxylporphyrin is found to react with carbon monoxide ($P_{\text{CO}} = 650$

torr, T = 295K) to produce the reductive coupling product,

(TXP)Rh-C(O)-C(O)Rh(TXP), as the exclusive CO containing species (equation 12)



Observation of two CO stretching frequencies at 1778 and 1767 cm^{-1} which shift to 1738 and 1727 cm^{-1} in the ^{13}C derivative are indicative of a non planar dionyl unit. A survey of potential reduction reactions of this d-diketone species is in progress.

Observation of reaction 12 verifies our general thermodynamic analysis of CO reductive coupling to form dionyl species. An implication of this analysis is that metallospecies that have M-C bond energies greater than $\sim 44 \text{ kcal mol}^{-1}$, when properly designed to inhibit M-M bond formation, have the capacity to promote CO reductive coupling. Although our observation that rhodium porphyrins reductively couple CO to dionyl species is unprecedented, it appears probable that many new complexes can be designed to fulfill the thermodynamic criteria to form d-diketone species. Incorporation of a CO reductive coupling step into a catalytic cycle has become a new major objective for this research program.