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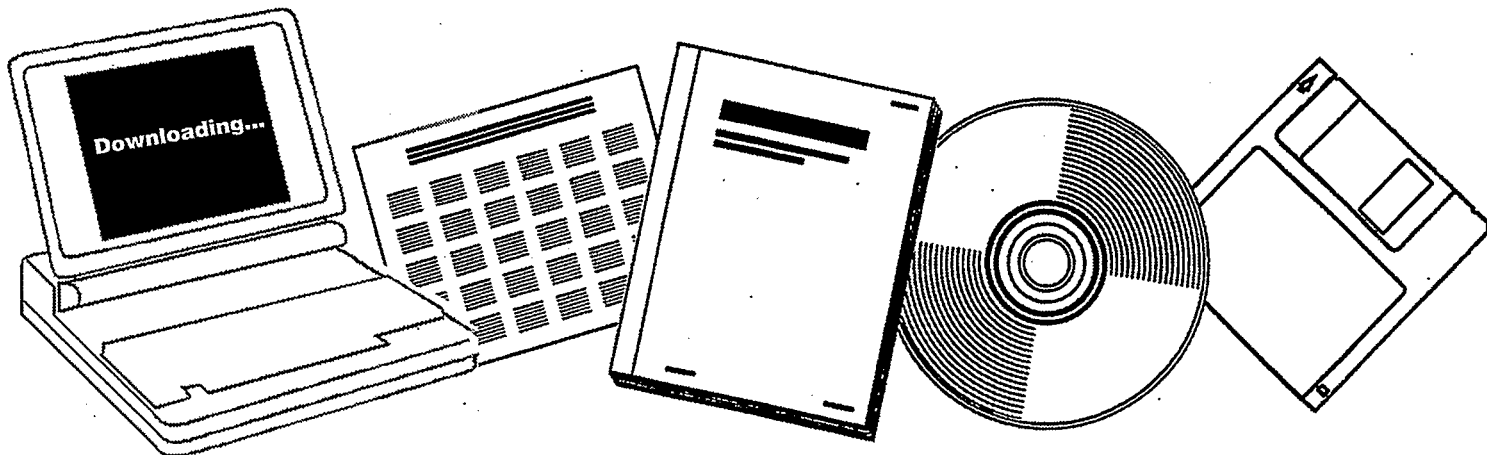
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**CATALYTIC HYDROGENATION OF CARBON
MONOXIDE. TECHNICAL RESEARCH PROGRESS
REPORT, DECEMBER 15, 1992--DECEMBER 14,
1993**

PENNSYLVANIA UNIV., PHILADELPHIA

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National Technical Information Service

CATALYTIC HYDROGENATION OF CARBON MONOXIDE

Technical Report - Research Progress Report

December 15, 1992 - December 14, 1993

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December, 1993

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TECHNICAL REPORT

Grant No. DE-FG02-86ER13615

Project Title

"Catalytic Hydrogenation of Carbon Monoxide"

Abstract

The primary focus of this project is on developing new approaches for the hydrogenation of carbon monoxide to produce organic oxygenates at mild conditions. Our strategies to accomplish CO reduction are based on the favorable thermodynamics manifested by rhodium macrocycles for producing a series of intermediates implicated in the catalytic hydrogenation of CO. Metalloformyl complexes from reactions of H₂ and CO, and CO reductive coupling to form metallo α -diketone species provide alternate routes to organic oxygenates that utilize these species as intermediates.

Thermodynamic and kinetic-mechanistic studies are used in guiding the design of new metallospecies to improve the thermodynamic and kinetic factors for individual steps in the overall process. 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. Non-macrocyclic ligand complexes that emulate the favorable thermodynamic features associated with rhodium macrocycles, but that also manifest improved reaction kinetics are promising candidates for future development.

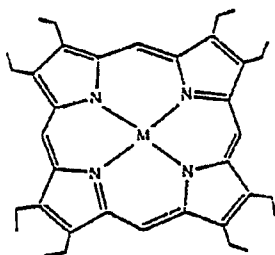
RESEARCH PROGRESS REPORT

12/15/92 - 12/14/93

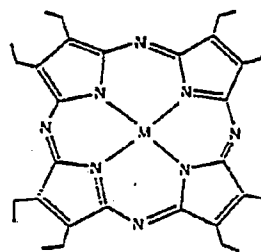
This program is focused on exploring strategies for the activation of carbon monoxide which can provide pathways for the reductive hydrogenation of CO at mild conditions. One of the major objectives is to define the scope of metal complexes capable of manifesting favorable thermodynamic parameters (M-H, M-C, M-O bond enthalpies) to produce the metallo intermediates (M-H, M-CHO, M-CH₂OH, M-C(O)CH₂OH) associated with a formyl pathway to CO hydrogenation. The most thermodynamically challenging portion of this sequence is the reaction of H₂ and CO with a metal complex to produce a metalloformyl which requires that the M-CHO BDE be greater than ~ 47 kcal mol⁻¹ and not more than ~ 9 kcal mol⁻¹ smaller than the M-H BDE. If a metal complex accomplishes production of the metalloformyl then favorable thermodynamics to form the subsequent intermediates is virtually assured. Octaethylporphyrinato rhodium(II) dimer, [(OEP)Rh]₂, and related rhodium(II) porphyrins accomplish many of the desired organometallic reactions including formation of metalloformyl species from reactions of H₂ and CO, CO reductive coupling and hydrocarbon activation. A primary focus during the prior budget period has been to explore the range of non-porphyrinic ligands that can be used with Rh(II) in accomplishing aspects of CO hydrogenation.

Tetraazaporphyrins

OEP and OETAP are structurally and thus sterically virtually identical. Substitution of N for the methine C-H units in OEP reduces



(OEP)

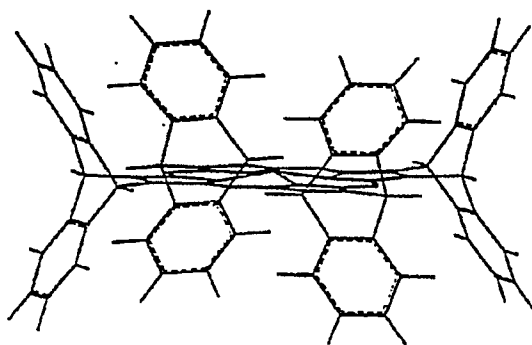


(OETAP)

the hole size and lowers the energy of the ligand pi system. These changes in the macrocycle electronic properties should produce either or both a decrease in the metal dπ electron energy and

increased $d\pi$ to macrocycle delocalization, which is expected to produce an increase in M-C relative to the M-H bond dissociation enthalpies. $[(\text{OETAP})\text{Rh}]_2$ has been prepared and a comparative study with $[(\text{OEP})\text{Rh}]_2$ is in progress. An important feature that has emerged is that the Rh-Rh bond dissociation energy in $[(\text{OETAP})\text{Rh}]_2$ is substantially larger than in $[(\text{OEP})\text{Rh}]_2$ and this reduces both the rate and scope of organometallic reactivity.

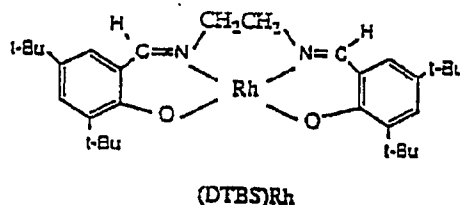
The tetraazaporphyrin derivative (TNAP) has large steric demands that will prohibit Rh-Rh bonding and is one of our current target molecules for evaluation.

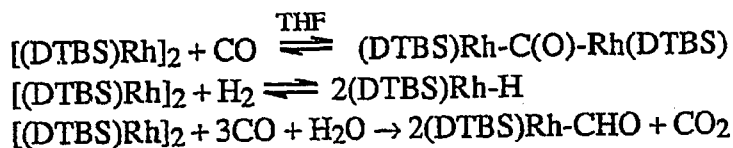


TNAP

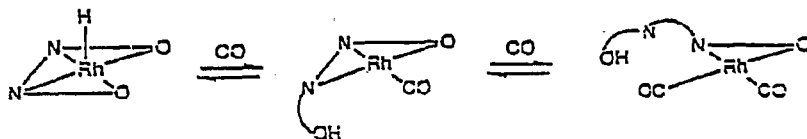
Salen (2N2O ligands) and 4N Ligands

Prior attempts to study the reactivity of $[(\text{Salen})\text{Rh}^{\text{II}}]_2$ in hydrocarbon solution were hampered by the poor solubility of the complex and the relatively large Rh-Rh bond enthalpy associated with this complex. In order to circumvent these problems a new salen derivative ligand with two t-butyl groups attached to each phenyl ring has been synthesized, 3,5-di-t-butyl-salicylaldimine, $\text{H}_2(\text{DTBS})$. Preliminary studies with the Rh^{II} complex indicate that $(\text{DTBS})\text{Rh}^{\text{II}}$ is a weakly bonded dimer which manifests several desirable reactivity features in THF and benzene solvents.

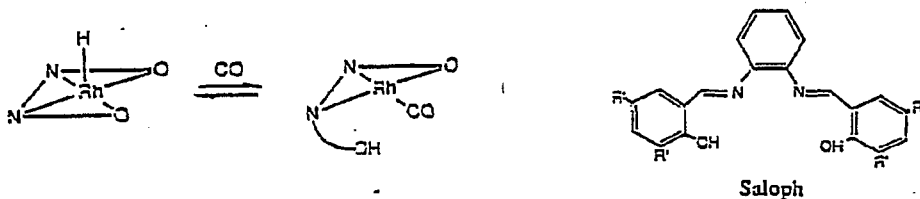


Reactions of [(DTBS)Rh]₂

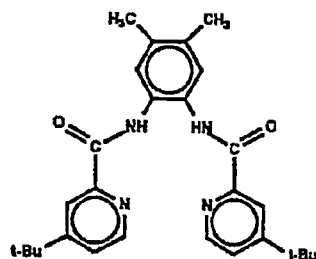
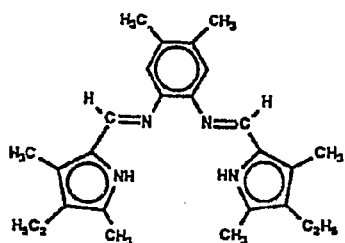
Formation of metalloketone and metalloformyl complexes are particularly significant and represent the first non-macrocyclic complex to accomplish these types of CO reduction and hydrogenation reactions. (DTBS)Rh^{II} reacts with H₂ to form a hydride (DTBS)Rh-H, but in the presence of H₂ and CO in benzene results in reduction to a Rh^I dicarbonyl complex, (HDTBS)Rh(CO)₂.



The dicarbonyl does not add H₂ to give observable quantities of a dihydride presumably because the CO ligands provide thermodynamic preference for the lower rhodium oxidation number. We are currently using a more rigid bridge between the nitrogen donor sites such that only a monocarbonyl can form. This strategy for blocking the undesirable reduction process is being tested by evaluating the Saloph derivative of DTBS.



Non-macrocyclic ligands containing 4 nitrogen donors have been designed to incorporate the most desirable features for both



thermodynamic and kinetic factors. The ligands illustrated above have been prepared and the formation and reactivity of the Rh(II) derivatives will be a focus of interest during the next budget period.

Publications Associated with DOE/ER 13615-7

"Formation and Reactivity of Tétramesitylporphyrinato Rhodium(II) Monocarbonyl: A Bent Rh(II) Complex that Reacts like an Acyl Radical," B.B. Wayland, A.E. Sherry, G. Poszmik and A.G. Bunn, *J. Am. Chem. Soc.*, 1992, 114, 1673.

"Activation of Carbon Monoxide by Metalloradicals," B.B. Wayland, A.E. Sherry, and V.L. Coffin in "New Science in Homogeneous Transition Metal Catalyzed Reactions," W. Moser and D.W. Slocum, eds. Advances in Chemistry Series No. 230, chapter 10, American Chemical Society: Washington, D.C. 1992.

"Reactions of H₂ (D₂) with a Rhodium(II) Metalloradical: Kinetic Evidence for a Four-Centered Transition State," B.B. Wayland, S. Ba and A.E. Sherry, *Inorg. Chem.*, 1992, 31, 148.

"Rh-C Bond Dissociation Enthalpies for Organometallic Derivatives of Rhodium Porphyrins," B.B. Wayland in "Energetics of Organometallic Species," Martinho Simões Ed., Kluwer, 1992, pp. 69-74.

"One Electron Activation and Coupling of Ethene by Rhodium(II) Porphyrins: Observation of an η^2 Ethene-Metalloradical Complex," A.G. Bunn and B.B. Wayland, *J. Am. Chem. Soc.*, 1992, 114, 6917.

Papers Accepted for Publication

"EPR Studies of 1:1 Complexes of Rhodium(II) and Cobalt(II) Porphyrins with σ Donor and π Acceptor Ligands: Origins of Rh(II) Metalloradical Reactivity," B.B. Wayland, A.E. Sherry, and A.G. Bunn, *J. Am. Chem. Soc.*, 1993, 115.

"Reactions of Isocyanides with Rhodium Porphyrins: Formation of Formimidoyl and Carbamoyl Complexes and CN-R Bond Cleavage," G. Poszmik, P.J. Carroll, and B.B. Wayland, *Organometallics*, 1993, 12.

Financial Report

The funding level as originally recommended for the period December 15, 1993 through December 14, 1994 are unchanged and appropriate for the work to be performed.

It is estimated that no funds will remain unexpended or uncommitted at the end of the 12/15/92-12/14/93 budget period.