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CATALYTIC HYDROGENATION OF CARBON MONOXIDE. PROGRESS REPORT, SEPTEMBER 15, 1985-SEPTEMBER 14, 1986

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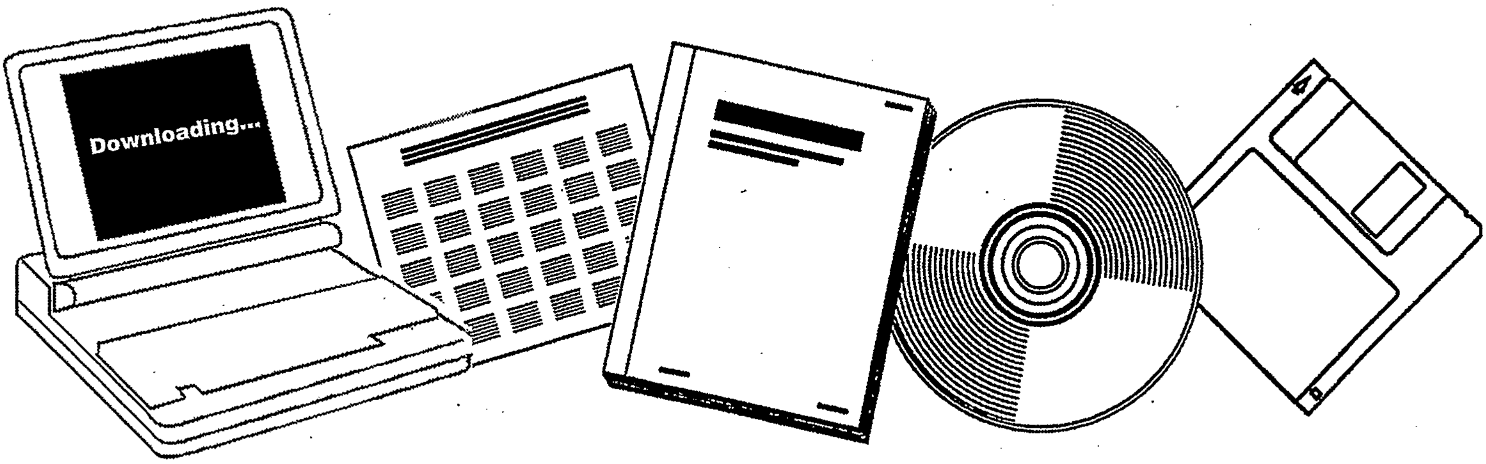

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CATALYTIC HYDROGENATION OF CARBON MONOXIDE

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Research Progress Report
September 15, 1985-September 14, 1986

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TECHNICAL REPORT

Contract No. DE-AC02-83ER13133

Project Title

"Catalytic Hydrogenation of Carbon Monoxide"

Abstract

The principal objective of this program is to learn how to utilize the unique properties of Rhodium porphyrins 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 the first intermediate in the hydrogenation of CO and provide a realistic opportunity to participate in the catalytic hydrogenation of CO at low gas pressures. Several catalytic schemes are proposed which take advantage of the unique reactivity of Rhodium porphyrins coupled with the aldehyde-like character of the metallo formyl 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 will be explored as one means for tuning the thermodynamic and kinetic parameters for optimum catalytic behavior. Comparative studies are used in identifying the essential features required to obtain a catalyst system based on metallo macrocycles.

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Research Progress Report

The principal focus of this project is to gain insight into the sequence of events that occur in the metal catalysed hydrogenation of carbon monoxide and to use this information in designing effective catalyst systems.

Metal catalysed hydrogenation of carbon monoxide is considered to occur through a series of organometallic intermediates including a metallo formyl (M-CHO) and hydroxymethyl ($M\text{-}CH_2OH$) species. Subsequent CC insertion reactions, carbonyl reduction and elimination reactions result in organic products. One possible scheme for production of glycol aldehyde, ethylene glycol and methanol is given by equations 1-9.

1) $M\text{-}M + H_2 \rightleftarrows 2\ M\ H$

2) $MH + CO \rightleftarrows M\text{-}CHO$

3) $MCHO + H_2 \rightleftarrows MH + CH_2O$

4) $MH + CH_2O \rightleftarrows M\text{-}CH_2\ OH$

5) $MCH_2OH + CO \rightleftarrows M\text{-}C(O)CH_2OH$

6) $M(C(O)\ CH_2OH) + H_2 \rightleftarrows M\text{-}CH(OH)CH_2OH$

7) $MCH(OH)CH_2OH \rightarrow MH + CH(O)CH_2OH)$

8) $MCH(OH)CH_2OH + MH \rightarrow M\text{-}M + (CH_2OH)_2$

9) $MCH_2OH + MH \rightarrow M\text{-}M + CH_3OH$

Previous studies from this laboratory have demonstrated that rhodium porphyrin dimers activate dihydrogen to form metallo hydrides that insert carbon monoxide to produce metalloformyl complexes at equilibrium conditions (steps 1 and 2). Present investigations are focused on the following issues.

1) hydrogen reduction of the metalloformyl and acyl complexes and subsequent formation of metallo α-hydroxyalkyl intermediates (steps 3, 4, 6)
2) chain lengthening by CO insertion reactions (step 5)
3) reductive elimination reactions that produce organic products (step 7-9)
4) photo promoted production of H_2CO and CH_3OH
5) design, synthesis, and evaluation of new metallo catalyst materials

1) H_2 reduction of a metallo formyl

A major focus of our current work is in exploring the hydrogen reduction of metallo formyl and related acyl species (reactions 3 and 5) ($M\text{-}CHO + H_2 \rightarrow MCH_2OH$). The purpose of this work is to discover a low energy pathway for the reaction $M_2 + 3\ H_2 + 2CO \rightarrow 2\ MCH_2OH$. The thermodynamic feasibility of this reaction for the case of rhodium porphyrins has been clearly demonstrated by the reaction of the metallo hydrides with formaldehyde.

$$\text{Rh porphyrin (H)} + H_2CO \rightleftarrows \text{Rh porphyrin } (CH_2OH)$$

Our strategy for accomplishing the H_2 reduction of the coordinated formyl group is to use a second metallo species that functions as a hydrogen transfer catalyst. We have prepared a series of bimetallic complexes that have a metal-metal bond between a rhodium porphyrin and a second metallo species with smaller steric requirements.

$$\text{por Rh} - M' \qquad M' = CO(CO)_4,\ Mn\ (CO)_5,\ Re(CO)_5,\ Fe\ (CO)_2\ Cp,\ Ru(CO)_2\ Cp,\ Mo(CO)_3Cp$$

The following set of reactions illustrates the behavior that we are searching for.

a) $\text{por Rh} - M' + H_2 \rightleftarrows \text{por Rh(H)} + M'\text{-}H$

b) $\text{por Rh(H)}^{\cdot} + CO \rightleftarrows \text{por Rh(CHO)}$

c) $\text{por Rh (CHO)} + M'\ H \rightleftarrows \text{por Rh-}M' + CH_2O$

d) $\text{por Rh(H)} + H_2CO \rightleftarrows \text{por Rh}(CH_2OH)$

We are currently in the process of evaluating the reactivity of por Rh–M′ compounds with H_2 and CO.

One specific example is OEP Rh–$Co(CO)_4$ which reacts reversibly with CO and H_2 (P_T=lat.) to produce the precursors to the hydroxymethyl complex.

$$\text{OEPRh} - Co(CO)_4 + H_2 + CO \rightarrow \text{OEPRh(CHO)} + H\ Co\ (CO)_4$$

The other bimetallic complexes have similar reactivity and these systems will be evaluated at elevated pressures and temperatures ($P<100$ at.; $T<150°C$).

The current focus of this work is on the reactivity of OEP Rh–$Ru(CO)_2Cp$ because $H\ Ru\ (CO)_5\ Cp$ is known to be an effective catalyst for the H_2 reduction of aldehydes to alcohols. If successful, this study will result in formation of the first hydroxymethyl complex prepared from H_2, CO and a metal complex.

We are presently extending the bimetallic materials to include early transition metals (Zr, Hf) and post transition series metals (In, TI, Sn).

2) <u>Carbon monoxide insertion</u> (chain lengthening)

One means of producing two carbon and larger organic molecules operates through CO insertion reactions (reaction 5).

$$M(CH_2OH) + CO \rightarrow M(C(O)CH_2OH)$$

This type of reaction has been demonstrated to occur for Rhodium porphyrin alkyls.

$$\mathrm{RhOEP(CH_3)} + \mathrm{CO} \rightleftarrows \mathrm{RhOEP(CO)CH_3}$$

This reaction is currently being evaluated for $\mathrm{RhOEP(CH_2OH)}$ in order to obtain the precursor to glycolaldehyde.

3) Reductive elimination reactions

Uni and bi molecular elimination reactions are needed to produce organic products from the organometallic intermediates (reactions 7-9). Both types of eliminations have been demonstrated for Rhodium porphyrin organometallic molecules.

unimolecular

$$\mathrm{RhOEP(CH_2CH_3)} \rightarrow \mathrm{RhOEP(H)} + \mathrm{CH_2 = CH_2}$$

$$\mathrm{RhOEP\ (CH_2OH)} \rightarrow \mathrm{RhOEP(H)} + \mathrm{CH_2 = O}$$

bi molecular

$$\mathrm{RhOEP\ (CH_3)} + \mathrm{RhOEP(H)} \xrightarrow{h\nu} \mathrm{(RhOEP)_2} + \mathrm{CH_4}$$

$$\mathrm{RhOEP(CH_2OH)} + \mathrm{RhOEP(H)} \xrightarrow{h\nu} \mathrm{(RhOEP)_2} + \mathrm{CH_3OH}$$

The bi molecular elimination of CH_4, and CH_3OH demonstrates the feasibility of producing alcohols and aldehydes from rhodium porphyrin catalyst systems.

Although catalytic formation of organic molecules from H_2 and CO has not yet been observed at mild conditions, results from this program are establishing criteria and aiding in the development of new strategies to attain this goal.

4) Photo promoted production of H_2CO and CH_3OH

When a solution of $[\mathrm{Rh(OEP)}]_2$ in contact with H_2 and CO ($P_{CO} + P_{H_2} < 1$ atm) is irradiated ($\lambda > 300$ nm) observable quantities of H_2CO are produced (figure 1).

Photo assisted catalytic formation of CH_3OH is found to occur at slightly elevated temperatures (figure 2).

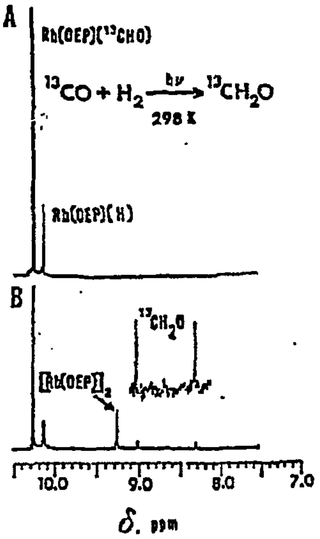


Figure 1

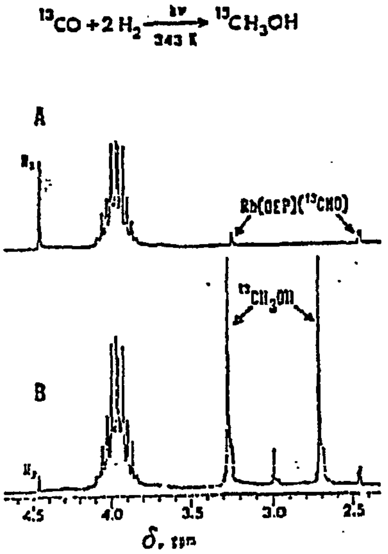
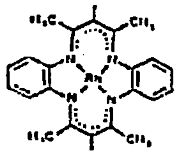


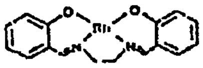
Figure 2

5) Design, synthesis and evaluation of new metallo catalyst materials

We have prepared a series of macrocycle and multidentate ligands and evaluation of several of the desired rhodium complexes is in progress.



Rh(TMTAA)



Rh(Salen)

Results from this exploratory work have already determined that the aromatic π system of the macrocycle (porphyrin) is not essential. One of our studies has utilized the TMTAA macrocycle. Both the porphyrin and TMTAA ligand systems are tetradenate N_4 macrocycle that coordinate in the form of dianions with metal ions. While the porphyrin dianion is a planar π-electron aromatic species, the TMTAA dianion is a 16 π-electron antiaromatic species which significantly deviates from planarity by rotation about the N-C bonds of σ-phenylenediamine portion of the macrocycle. The TMTAA macrocycle is found to form a metal-metal bonded rhodium complex $[Rh(TMTAA)]_2$ which has reactivity patterns that closely parallel those of the rhodium porphyrin systems. The Rh-Rh bonded macrocycle complex $[Rh(TMTAA)]_2$ accomplishes the desired reactivity with H_2 and CO to produce metallohydride and formyl complexes.

$$[Rh(TMTAA)]_2 + H_2 \rightleftarrows 2Rh(TMTAA)(H)$$

$$Rh(TMTAA)(H) + CO \rightleftarrows Rh(TMTAA)(CHO)$$

This system provides the first successful extension of this type of reactivity beyond the rhodium porphyrin complexes.

Similarity of the organometallic chemistry of Rh(TMTAA) and Rh(porphyrin) complexes indicates that the conjugation and planarity of the porphyrin macrocycle are not essential aspects of the unusual organometallic reactivity of the rhodium center. 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. Systematic variation of ligand steric and electronic factors can now be used in tuning theromodynamic factors such as M-M, M-H and M-C bond energies. Ligand arrays can also be selected to produce open cis coordination sites that permit conventional reaction pathways for oxidative addition, reductive elimination and CO insertion reactions which are effectively excluded to rhodium porphyrin reactions. Results from this program provide optimism that new metallo complexes can be designed to produce catalytic hydrogenation of carbon monoxide at mild conditions.

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Financial Report

The proposed funding levels as originally anticipated for the periods September 15, 1984 through September 14, 1985 and September 15, 1985 through September 14, 1986 are unchanged and adequate for the work to be performed.

It is estimated that no funds will remain unexpended or uncommitted at the end of the final budget period.