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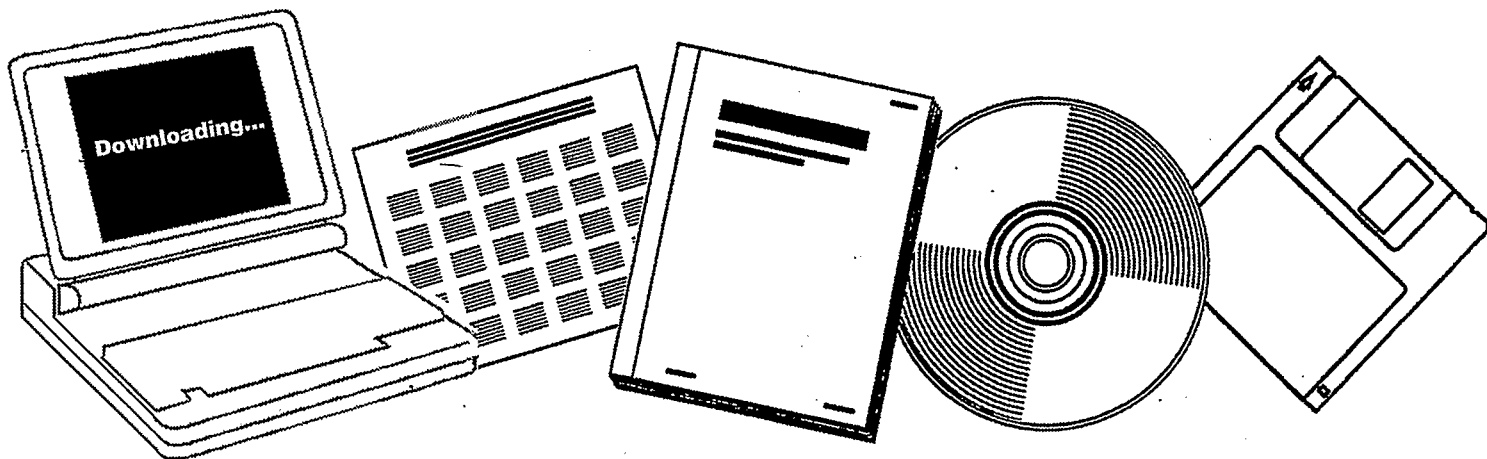
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**CATALYTIC HYDROGENATION OF CARBON
MONOXIDE. TECHNICAL PROGRESS REPORT,
DECEMBER 15, 1990-DECEMBER 14, 1991**

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CATALYTIC HYDROGENATION OF CARBON MONOXIDE

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Technical Report - Research Progress Report

December 15, 1990 - December 14, 1991

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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 materials for future development.

RESEARCH PROGRESS REPORT

12/15/90 - 12/14/91

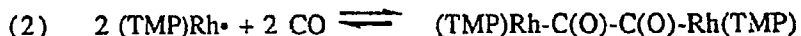
This program is focused on exploring strategies for the activation of carbon monoxide which can provide pathways for the reduction and hydrogenation of CO at mild conditions. The most important advances in this research during the last grant period have resulted from recognition of one electron metalloradical activation of both CO and H₂, and the development of new multidentate ligands that emulate organometallic reactivity previously unique to rhodium porphyrins.

One Electron Activation of CO and H₂*CO Activation*

One of our objectives has been to determine whether metalloradicals (M•) can react with CO to form intermediate complexes ([MCO]•), that exhibit one electron carbonyl carbon reactions in analogy with the acyl radical (CH₃CO•). A feature that distinguishes our goal from previous work is that the one electron activating species (M•) is present at thermal equilibrium, which provides an opportunity to have an equilibrium source of one electron activated CO [MCO]•.

The search for metal complexes capable of one electron activation of CO was focused on Rh(II) and Ir(II) porphyrins which have sufficiently strong M-C bonds to justify CO rehybridization. Reactivity studies of CO with octaethylporphyrin rhodium(II) dimer, [(OEP)Rh]₂, revealed the formation of dimetal ketone ((OEP)Rh-C(O)-Rh(OEP)) and dimetal α-diketone complexes. These products have a formal relationship to acetone (CH₃-C(O)-CH₃) and biacetyl (CH₃-C(O)-C(O)-CH₃) that result from the reaction of CH₃• with CO and suggested that the desired type of CO complex could be an intermediate in these CO reductions. Efforts to observe the proposed intermediate complex directly by EPR were not successful, but recent investigations of the reaction of CO with the monomeric tetramesitylrhodium(II) complex, (TMP)Rh•, have now resulted in the direct observation of (TMP)Rh-CO.

(TMP)Rh• reacts with CO to form a mono CO complex, (TMP)Rh-CO, and an α -diketone (TMP)Rh-C(O)-C(O)-Rh(TMP) (equations 1,2). A dimetal ketone (M-C(O)-M) is not observed for the (TMP)Rh system because of the large

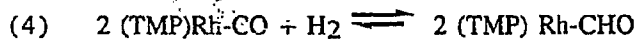


steric requirements of tetramesitylporphyrin. Observation of three g values in the methylcyclohexane glass EPR spectrum indicates that the Rh-CO unit is bent. The isotropic ^{13}C coupling constant of 312 MHz in (TMP)Rh ^{13}C O approaches the value for the formyl radical (365) MHz and corresponds to a C_{2s} spin density of 0.10 electrons compared to a ρ_{2s} of 0.12 in the formyl radical. (TMP)Rh-CO thus contains a bent partially rehybridized Rh-CO unit where the unpaired electron occupies a σ molecular orbital ($d_z^2 + \text{CO}\sigma$).

Reversible dimerization of (TMP)Rh-CO through C-C bond formation to produce a 1,2-ethanedionyl complex, (TMP)Rh-C(O)-C(O)-Rh(TMP), illustrates a carbonyl carbon centered one electron reaction that can be viewed as an organometallic analog of formyl radical coupling ($2 \text{HCO} \rightarrow \text{H-C(O)-C(O)-H}$) (equation 3). The type of CO reductive coupling



depicted by equation 3 is presently known only for reactions of rhodium (II) porphyrins with CO. Reactions of (TMP)Rh-CO with H_2 and $\text{CH}_2=\text{CH}_2$ are further illustrations of one electron carbon centered reactions (equations 4, 5).

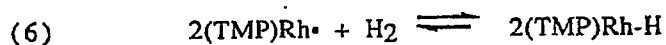


H₂ and D₂

Metal catalyzed hydrogenation of substrates involves addition of hydrogen to the metal center as an obligatory step. The importance of this

class of reactions has stimulated efforts to understand the scope of mechanistic pathways operative in reactions of H₂ with metal complexes.

Benzene solutions of (TMP)Rh• react with H₂ (P_{H2} = 0.2 - 1.0 atm.) to form the hydride complex, (TMP)Rh-H, (equation 6), which is identified in solution by appearance of the characteristic hydride NMR ($\delta_{\text{Rh-H}} = -40\text{ppm}$, $J_{103\text{Rh-H}} = 44\text{Hz}$).



The rate for reaction 6 is observed to have a second order dependence on the molar concentration of (TMP) Rh• at conditions where the process is pseudo zero order in hydrogen. Variation of the H₂ concentration (P_{H2} (296K) = 0.2 - 0.9 atm) demonstrates a first order rate dependence on the molar concentration of H₂ and an overall third order rate law for reaction 6 ($\text{rate}_6 = k_6[(\text{TMP})\text{Rh}\cdot]^2[\text{H}_2]$). Temperature dependence of the third order rate constant (k_1) was used in deriving estimates for the transition state and Arrhenius activation parameters ($\Delta H_{\ddagger}(\text{H}_2) = 4.9 \text{ kcal mol}^{-1}$, $\Delta S_{\ddagger}(\text{H}_2) = -40 \text{ cal K}^{-1} \text{ mol}^{-1}$). Parallel studies for the reaction of D₂ with (TMP)Rh• provide the kinetic isotope effect on the rate ($k(\text{H}_2)/k(\text{D}_2)(296 \text{ K}) = 1.6 \pm 0.3$; $k(\text{H}_2)/k(\text{D}_2)(353 \text{ K}) = 1.3 \pm 0.01$) and activation parameters ($\Delta H_{\ddagger}(\text{H}_2) = 5.5 \text{ kcal mol}^{-1}$, $\Delta S_{\ddagger}(\text{H}_2) = -39 \text{ cal K}^{-1} \text{ mol}^{-1}$).

The rate law for reaction 6, ($\text{rate}_6 = k_6[(\text{TMP})\text{Rh}\cdot]^2[\text{H}_2]$) establishes that the transition state contains two (TMP)Rh• metalloradicals and H₂. A large negative activation entropy ($\Delta S_{\ddagger} = -40 \text{ kcal mol}^{-1}$) and small activation enthalpy ($\Delta H_{\ddagger} = 4.6 \text{ kcal mol}^{-1}$) are also consistent with organizing three molecules into a transition state (TS) where evolution of two Rh-H bonds substantially compensates for the H-H bond breaking.



The kinetic isotope effect is relatively small, but this result cannot at this time be used in differentiating between linear and bent transition states because of the inability to determine both the vibrational structure of the TS and the contribution of tunneling to $k(\text{H}_2)/k(\text{D}_2)$. Linear four centered transition states can be expected to produce substantially smaller kinetic isotope effects, $k(\text{H}_2)/k(\text{D}_2)$, than the better known linear three centered TS because of the larger number of isotope sensitive vibrations in the TS. Bonding and steric considerations suggest that a linear four centered TS is preferable, but

confirming experimental evidence is lacking. The most important conclusion arising from studies of metalloradicals reacting with substrates like H₂ and CH₄ is that when atom abstraction is thermodynamically unfavorable, the reaction can be accomplished by an alternate low activation enthalpy pathway involving the concerted reaction of two radicals through a four centered TS.

New Macrocyclic and Multidentate Ligand Systems

Substantial effort is being directed toward expanding the range of materials capable of producing formyl complexes and general CO reduction reactions. The classes of ligands investigated include phthalocyanines, non-aromatic macrocycles and tetradentate chelating agents.

Rhodium(II) phthalocyanines including tetra-*t*-butyl derivatives do not produce observable quantities of formyl complexes from H₂ and CO, dimetal ketone or CO reductive coupling products. This behavior is tentatively ascribed to the presence of relatively strong Rh-Rh bonds in the rhodium(II)phthalocyanine complexes investigated.

The dimeric complex [(TMTAA)Rh]₂ (TMTAA = dibenzotetramethylaza[14]annulene dianion) reacts with mixtures of hydrogen and carbon monoxide gases to produce a metallo hydride, (TMTAA)Rh-H and an η¹-metallo formyl complex, (TMTAA)Rh-CHO. [(TMTAA)Rh]₂ also reacts with CO to produce a dimetal ketone, but does not accomplish CO reductive coupling. If substituent steric effects can be used to reduce the Rh-Rh bond energy then derivatives of this system should emulate all of the observed rhodium porphyrin reactions.

N,N' ethylene *bis* (3,5-di-*t*-butylsalicylaldehyde) forms a Rh(II) complex with a weak Rh-Rh bond. The Rh(II) derivative reacts with CO to yield a dimetal ketone and with H₂ to form a hydride complex. This system provides promise for extending the formyl and CO reduction reactions to a non-macrocyclic ligand system and is a current focus of interest.

Publications Associated with DE-FG02-86 ER 13615

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Formation and Reactivity of Tetramesitylporphyrinato Rhodium(II) Monocarbonyl: A Bent Rh(II)CO Complex that Reacts like an Acyl Radical, Bradford B. Wayland and Alan E. Sherry, *J. Am. Chem. Soc.*, 1991.

Reactions of H₂(D₂) with a Rhodium(II) Metalloradical: Kinetic Evidence for a Four-Centered Transition State, B.B. Wayland, S. Ba, A.E. Sherry, *Inorg. Chem.* 1991.

Pending Publications:

Organometallic Reactivity of Rhodium Phthalocyanine, K.J. Balkus, S. Ba, and B.B. Wayland, *Organometallics*, 1992.

Reactions of CO and H₂ with Rhodium(II) Salen Derivatives, A.G. Bunn, and B.B. Wayland, *Inorg. Chem.*, 1992