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Synthesis and Catalysis for Alcohol Fuels

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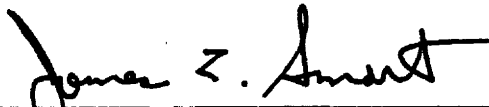
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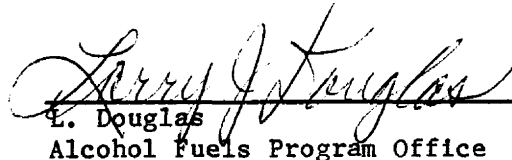
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PREFACE

This progress report describes the chemical synthesis of new materials and their evaluation as homogeneous and heterogeneous catalysts for the conversion of biomass-derived syngas (H_2/CO) to alcohol fuels and fuel additives. This research was conducted by Alex Miedaner, Calvin Curtis, and James Smart of the Photoconversion Branch, Solar Fuels Division, SERI, and David Wickham and Scott Cowley of Colorado School of Mines.



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SUMMARY

Objective

Active and selective catalysts are needed for the conversion of biomass-derived syngas (H_2/CO) to alcohol fuels and fuel additives. The synthesis, characterization, and evaluation of selected dinuclear organometallic complexes of zirconium for reactions with H_2/CO have been completed in an effort to develop new homogeneous syngas catalysts.

Discussion

Screening studies and preliminary results have been obtained with heterogeneous modified alumina-supported palladium catalysts for the production of higher alcohols from syngas. Following the recent discovery that selected early transition metal organometallic complexes with hydride ligands will stoichiometrically reduce carbon monoxide to coordinated ethylene glycolate, a two-carbon alcohol, we have demonstrated that dinuclear analogues of these complexes are even more reactive. We have studied the synthetic organometallic chemistry of dinuclear zirconium complexes with bridging fulvalene ligands. Reactions with H_2 and CO yielded reactive zirconium hydride and carbonyl derivatives that were isolated and characterized. Combined H_2/CO reactions and in situ Fourier transform nuclear magnetic resonance (FT-NMR) studies demonstrate that low pressure and temperature reduction of coordinated CO can be accomplished. This important step in the development of a catalytic CO hydrogenation cycle has led us to develop new technical approaches to this catalysis problem, based on the synthetic and reaction studies presented in this report. Future work is outlined on both homogeneous and heterogeneous catalysis.

TABLE OF CONTENTS

	<u>Page</u>
1.0 Introduction.....	1
2.0 Synthesis, Characterization, and Reaction of Organometallic Complexes.....	9
2.1 Organic Synthesis of Ligands.....	9
2.2 Synthesis of Dinuclear Zirconium Complexes.....	9
3.0 Conclusions and Recommendations.....	15
4.0 References.....	23
Appendix.....	25

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SECTION 1.0

INTRODUCTION

The development of catalysts for syngas (H_2/CO) conversion that are both active at low temperatures and pressures and selective for higher alcohols is being actively investigated in academic, industrial, and government laboratories in virtually all developed countries [1,2]. Such catalysts will be particularly important in the production of oxygenated hydrocarbon fuels and fuel additives from relatively small-scale biomass-based gasifiers that yield syngas. Even if most of the syngas produced from such biomass conversion plants is converted to methanol (CH_3OH), there will be a need for higher alcohols and derived ethers for use as fuel additives to improve the octane value of methanol or serve as cosolvents in methanol/gasoline blends.

This report presents an overview of our FY 1984 research and development studies on new homogeneous and heterogeneous catalysts for syngas conversion to oxygenated hydrocarbons. A more detailed introduction to the important industrial role of homogeneous catalysis in the production of fuels and chemicals was presented in our report for FY 1983 (SERI/PR-233-2231, February, 1984).

Figure 1-1 represents an overview of existing and proposed technologies that convert biomass to syngas (H_2/CO), or syngas and ethylene ($H_2/CO/C_2H_4$), followed by catalytic liquefaction to alcohols. Current coal-based processes involve partial oxidation of coal to syngas followed by catalytic "shift" conversion, by the water-gas shift reaction, to a suitable $H_2:CO$ ratio. Catalytic liquefaction of the syngas by Fischer-Tropsch catalysis then yields a mixture of alcohols and alkanes. This overall process is not particularly efficient and yields a wide variety of Fischer-Tropsch products. However, this technology is appealing in situations where hydrocarbon fuels from coal are required. In contrast to heterogeneous iron-based Fischer-Tropsch catalysts, the well-developed heterogeneous Cu-ZnO catalysts for the conversion of syngas to methanol are remarkably selective. Suitable heterogeneous catalysts for the selective production of higher alcohols from syngas do not exist. These alcohols are currently being produced from H_2/CO and olefins such as ethylene by homogeneous "oxo" catalysis. In this process the formation of aldehydes by the hydroformylation reaction is followed by hydrogenation to yield alcohols that are one carbon higher than the starting olefin. Both reactions are catalyzed by soluble cobalt or rhodium complexes in homogeneous solution. Suitable heterogeneous catalysts do not exist for the production of "oxo" alcohols.

Table 1-1 lists some general comparisons between homogeneous and heterogeneous catalysts and indicates the different operating conditions of the various processes that utilize H_2/CO .

Homogeneous catalysts or catalyst precursors are soluble compounds, often transition metal complexes, that combine reactant molecules in a series of stoichiometric transformations to yield stable products and regenerated catalysts. The intermediate species in such a catalytic cycle have varying degrees of kinetic stability, and a detailed understanding of such transformations forms the molecular basis for the design and synthesis of new and

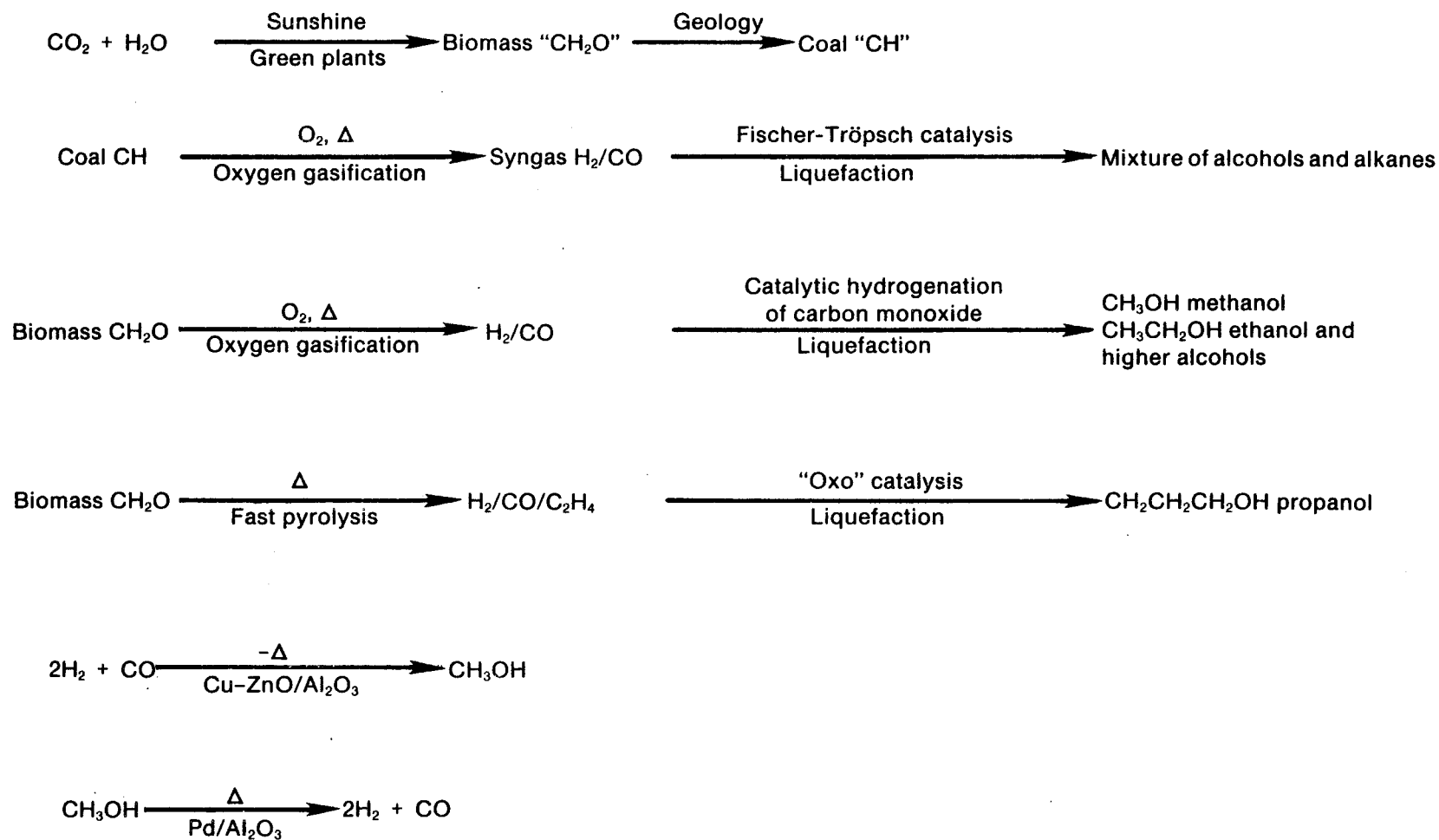


Figure 1-1. Ways to Convert Biomass to Syngas and then to Alcohols

Table 1-1. Comparison of Homogeneous and Heterogeneous Catalysts

Homogeneous Catalysts

In single-phase systems, reactants, products, and catalysts--typically a transition metal complex--are dissolved in an organic solvent. Compared with heterogeneous catalysts, they

- Are more active at lower temperatures and pressures
- Are more active per metal center
- Are more selective in products formed
- Allow for better heat transfer
- Use discrete, well-defined catalytic species that are more easily studied and modified
- Operate at 50^o-150^oC and 50-500 psi to produce H₂/CO

Heterogeneous Catalysts

In two-phase systems, gaseous or liquid reactants and products and a solid catalyst material--typically a metal or metal oxide--are often dispersed on ceramic supports. Compared with homogeneous catalysts, they

- Are thermally more stable, because they
 - Allow higher reaction rates at higher temperatures
 - Have longer catalyst lifetime
 - Regenerate the catalyst in situ
 - Produce reactants and products that are more readily separated from catalyst
 - Operate at 200^o-300^oC and 500-1500 psi to produce H₂/CO
-

improved homogeneous catalysts. Compared with heterogeneous catalysts, homogeneous catalysts are usually more active and allow transformations to take place at lower temperatures and pressures. For this reason, and because of their well-defined molecular composition and structure, homogeneous catalysts tend to be much more selective in the products they form.

Heterogeneous catalysts are solid materials, typically transition metals on ceramic supports, that react with gaseous reactants to yield gaseous products. They operate at higher temperatures and pressures and usually yield a wider range of products than homogeneous catalysts do. In some areas of catalysis, such as the hydrogenation of olefins, both homogeneous and heterogeneous catalysts exist, and both are used industrially in different applications. In some areas, such as methanol synthesis from syngas, well-developed and very selective heterogeneous catalysts exist, such as Cu-ZnO/Al₂O₃, for which there

are no analogous homogeneous catalysts. In the area of "oxo" catalysis, or hydroformylation of olefins with hydrogen and carbon monoxide to yield aldehydes and higher alcohols, homogeneous cobalt and rhodium catalysts are used industrially. Analogous heterogeneous hydroformylation catalysts do not exist.

Efforts to explore the interrelationship of heterogeneous and homogeneous catalysts are increasing in various laboratories. One of the goals of our research program is to contribute to such efforts. Our expertise in inorganic and organometallic synthesis is being utilized in the synthesis and evaluation of both homogeneous and heterogeneous catalysts. This broad effort includes collaborative research with groups doing structural studies and theoretical calculations of electronic structure, spectroscopic studies, reaction and mechanistic studies, and surface analysis and characterization of heterogeneous catalysts. A specific research goal is the development of catalysts for the hydrogenation and homologation of carbon monoxide to convert "syngas" (H_2/CO) to higher (C_2-C_6) alcohols. The Synthesis and Catalysis Task of the SERI Alcohol Fuels Program combines in-house research and collaborative sub-contractual research with nearby academic institutions to develop distinctly new, as well as improved, catalysts for alcohol fuels production and utilization. A major focus of this effort has been the development of active and selective homogeneous catalysts for low-temperature, low-pressure conversion of biomass-derived syngas to oxygenated hydrocarbons containing two to six carbon atoms. This general effort seeks to efficiently utilize the inherently "clean" syngas with a suitable H_2/CO ratio that is available from biomass downdraft oxygen gasifiers.

The more specific goal of research on C_2-C_6 oxygenated hydrocarbons, in particular higher alcohols, stems from a need for octane enhancers and blending fuels for neat methanol and mixed alcohol/gasoline transportation fuels. The availability of such blending fuels from biomass-derived syngas would have a significant impact on the acceptability of alcohol-based alternate fuels. In addition, there is a long-term need for more active low-temperature and low-pressure methanol synthesis catalysts for fuels production from dispersed, small-scale biomass gasifiers. The development of either homogeneous or heterogeneous catalysts systems that yield various mixtures of methanol and higher alcohols would be particularly useful for the production of blended transportation fuels, which will require new, mixed-function catalysts if a single catalyst train is used.

Figure 1-2 outlines a general mechanism for the conversion of H_2/CO to methanol and higher alcohols at a mononuclear metal center. This catalytic cycle does not specify a metal, its oxidation state, ancillary ligands, or overall geometry of the complex. The reaction cycle depicts two kinds of metal formyl hydride intermediates $[M(CHO)(H)]$, with subsequent transfer of hydride to yield either a metal formaldehyde $[M(CH_2O)]$ or a metal hydroxycarbene $[M(C(OH)H)]$ complex. The metal formaldehyde complex with the addition of H_2 is shown to yield a methoxy metal hydride complex $[M(OCH_3)(H)]$ with an M-O bond that then eliminates methanol (CH_3OH). The metal hydroxycarbene is depicted adding H_2 to yield an intermediate hydroxymethyl metal hydride complex $[M(CH_2OH)(H)]$ with an M-C bond. This intermediate can either eliminate methanol or undergo CO coordination and migratory insertion, or carbonylation, to yield a two-carbon hydroxyacyl metal hydride complex $[M(COCH_2OH)(H)]$. Elimination or hydrogenolysis of this intermediate yields hydroxy acetaldehyde

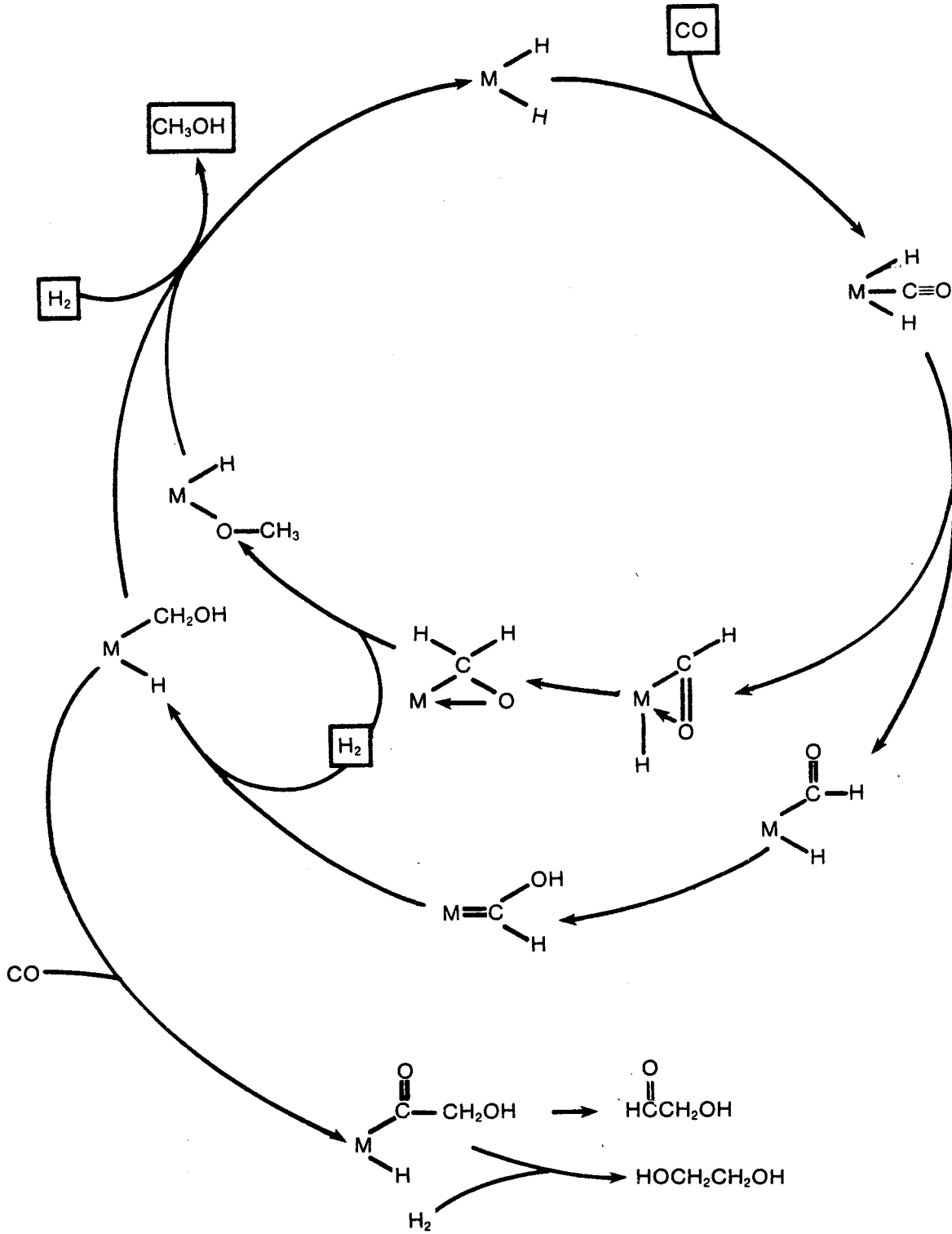
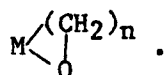


Figure 1-2. General Mechanism of H_2/CO Conversion to Alcohols with a Mononuclear Metal Catalyst

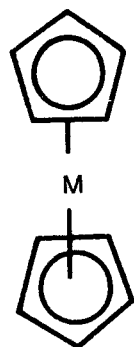
[HCOCH₂OH], which can be hydrogenated in a separate cycle with the same catalyst to yield ethylene glycol (CH₂OHCH₂OH). Dehydration followed by hydrogenation under the same reaction conditions, or in a separate cycle, will yield ethanol (CH₃CH₂OH). Higher alcohols can be formed by successive carbonylation and hydrogenation steps of the M-C bonded intermediate, with perhaps some dramatic control of the size of the product alcohol from the formation of a relatively stable metallocycle,



This precursor would yield the final product [CH₃(CH₂)_{n-1}OH] by H₂ addition.

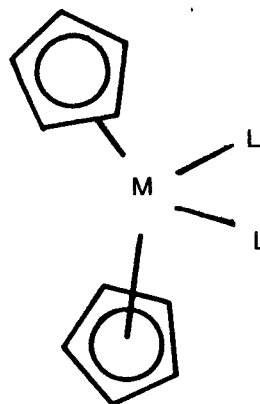
This report describes the synthesis and characterization of new soluble organometallic complexes of zirconium and a preliminary evaluation of their potential for homogeneous syngas catalysis. Figure 1-3 depicts the molecular structures of the various kinds of compounds under investigation. They include "planar" metallocenes [(C₅H₅)₂M] and "bent" derivatives [(C₅H₅)₂ML] with various additional ligands (L) that include carbon monoxide (M-CO) and hydrogen (M-H). Such complexes, with transition metal metallocenes from the left of the period table, can be prepared directly from H₂/CO under mild conditions (1-10 atm, room temperature). The stoichiometric reduction of H₂/CO to a coordinated ethylene glycolate C₂ product has been demonstrated with the very reactive complex permethyl zirconocene dihydride [(C₅Me₅)₂ZrH₂] as shown in Figure 1-4 [3]. The stability of the Zr-O products formed from the very reactive Zr-H intermediate does not allow this stoichiometric process to yield a catalytic cycle.

Figure 1-4 also depicts the structure of dinuclear analogues of the mononuclear metallocenes. The class of bimetalloenes [(C₅H₅)₂(C₁₀H₈)M₂] is presently much smaller and less explored than the bis(fulvalene)dimetal complexes [(C₁₀H₈)₂M₂]. Work to prepare such bimetallic complexes is described in this report. Future work in both homogeneous and heterogeneous catalysis is proposed.



M = V, Cr, Mn, Fe, Co, Ni
Ru
Os

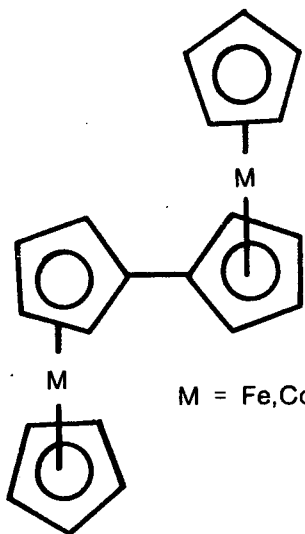
Planar metallocene
(C₅H₅)₂M



M = Ti, V
Zr, Nb, Mo

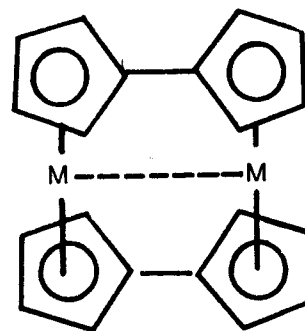
L = CO, CO₂, N₂, H₂O
H, R, OR, etc.

Bent metallocene
(C₅H₅)₂ML₂



M = Fe, Co

Bimetalloocene
(C₅H₅)₂(C₁₀H₈)M₂



M = V, Cr, Fe, Co, Ni
Mo

L = CO, H, R, OR

Bis(fulvalene)dimetal complex
(C₁₀H₈)₂M

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Figure 1-3. Molecular Structures of Metallocenes and the Bis(fulvalene)dimetal Complex

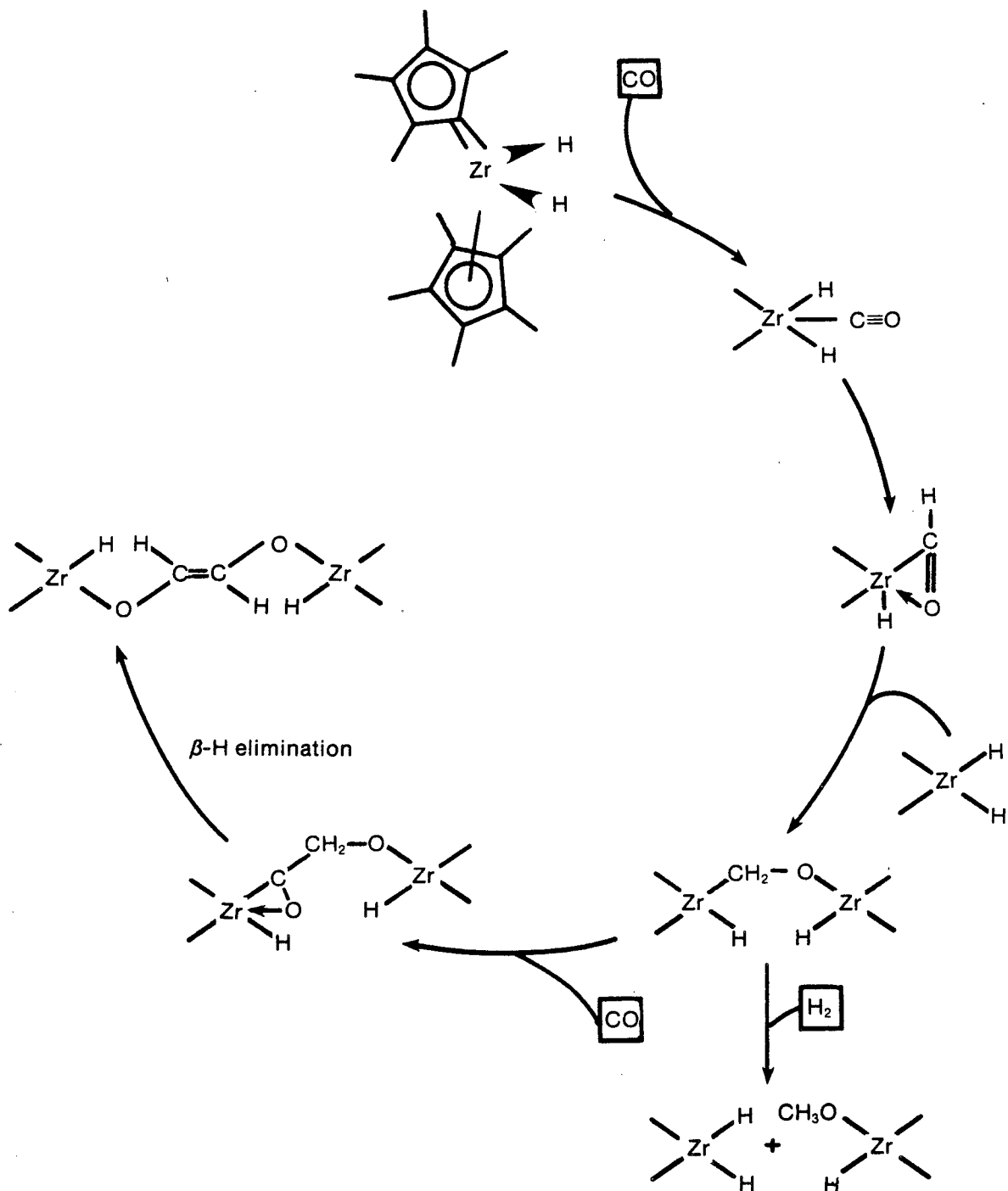


Figure 1-4. Permethylzirconocene Dihydride Reduction of CO

SECTION 2.0

SYNTHESIS, CHARACTERIZATION, AND REACTION OF ORGANOMETALLIC COMPLEXES

2.1 ORGANIC SYNTHESIS OF LIGANDS

1,2,3,4,5-Pentamethylcyclopentadiene and the derived ligand anion sodium pentamethylcyclopentadienide (NaC_5Me_5) were prepared by a previously published procedure [4]. We used these reagents to prepare the new starting complex, $(\text{C}_5\text{Me}_5)\text{ZrCl}_3$.

The bridging fulvalene or bicyclopentadienyl ligand system for the synthesis of dinuclear bimetalloocene complexes was prepared by the reductive coupling of sodium cyclopentadienide (NaC_5H_5) [5] as indicated on Figure 2-1. Deprotonation of the resulting dihydrofulvalene yields the fulvalene dianion as the lithium salt $\text{Li}_2\text{C}_{10}\text{H}_8$. A particularly important reagent for the preparation of early transition metal complexes, such as titanium and zirconium, that we have synthesized is the fulvalene bistrimethyltin derivative $\text{C}_{10}\text{H}_8(\text{SnMe}_3)_2$. An efficient, large-scale organic synthesis of this intermediate has been developed. This reagent has the potential for selective transmetalation reactions to transfer one or perhaps two fulvalene ligands to yield homodinuclear metal complexes. The reaction of $\text{C}_{10}\text{H}_8(\text{SnMe}_3)_2$ with one equivalent of *n*-BuLi yields the mixed lithio-tin reagent $\text{LiC}_{10}\text{H}_8\text{SnMe}_3$, in which the distinct differences in metal reactivity of each five-membered ring can be used to prepare heterobimetallic complexes containing two different transition metal moieties.

Characterization of these organic ligands typically includes multinuclear Fourier transform nuclear magnetic resonance spectroscopy (FT-NMR) such as ^1H , ^{13}C , ^{129}Sn , as well as infrared spectroscopy (IR) at SERI. Elemental analyses are performed commercially outside of SERI.

2.2 SYNTHESIS OF DINUCLEAR ZIRCONIUM COMPLEXES

The synthetic routes used to prepare the new zirconium fulvalene complexes are shown in Figure 2-2. A new preparation of the lithium salt of fulvalene dianion was recently developed that yields a material free of solvent and alkali metal halides. Treatment of this material with $(\text{C}_5\text{Me}_5)\text{ZrCl}_3$ in toluene produces good yields of the yellow, air stable tetrachloride complex (a). In principle, there are a number of ways to convert this chloride precursor into the desired hydride complex (c). We chose to try hydrogenolysis of a suitable tetraalkyl derivative under mild conditions in hydrocarbon solvents because we have had success with this method in similar systems. For this purpose, the tetramethyl complex (b) was synthesized by addition of methyl lithium to complex (a). However, hydrogenolysis of this material, even at hydrogen pressures up to 20 atm, was slow and seems to yield intermediate complexes with both methyl and hydride ligands rather than the tetrahydride complex. Less stable alkyls, such as the *n*-butyl, are generally more easily hydrogenolyzed, so the complex a was treated with butyllithium under a hydrogen atmosphere, and tetrahydride was produced.

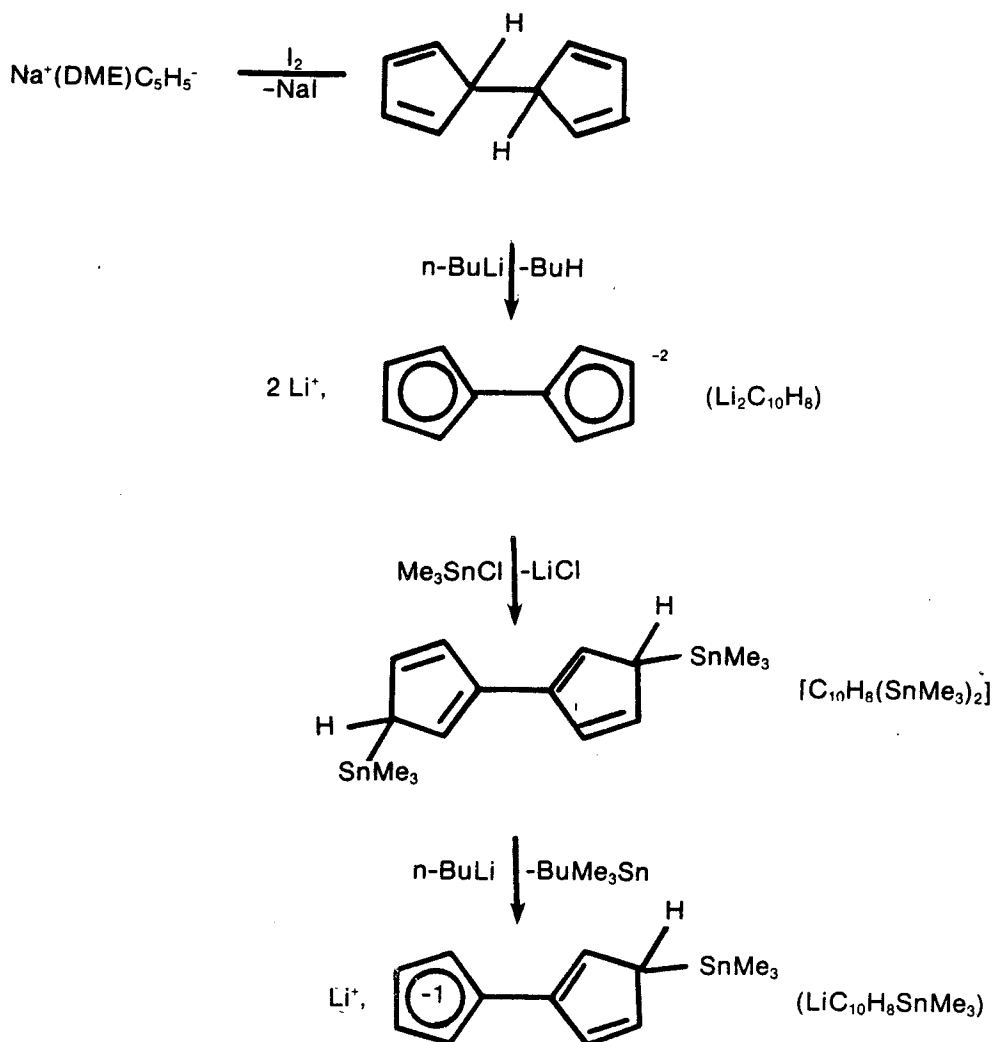
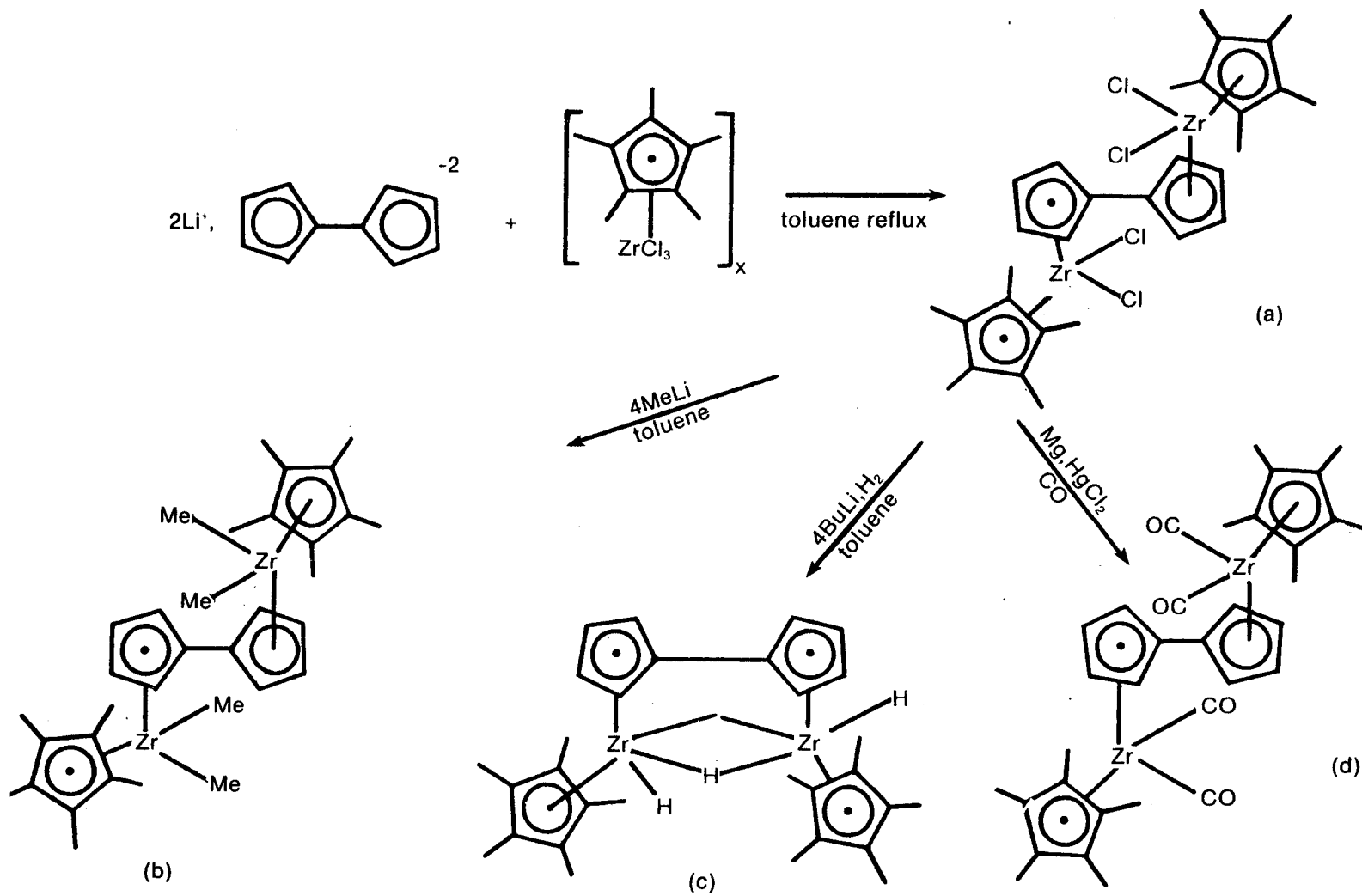


Figure 2-1. Synthesis of Dinuclear Bimetalocene Complexes

The interesting hydride bridged structure for (c) depicted in Figure 2-2 is assigned on the basis of its ^1H NMR spectrum. This complex is highly reactive, sensitive to oxygen and water, and thermally sensitive. It decomposes, even in the solid state, at room temperature, probably by loss of hydrogen. Decomposition appears to be followed by the oxidative addition of a ring methyl C-H bond to the resulting zirconium(II) center, as shown in Figure 2-3. This sequence is probably repeated to give the symmetrical, multiply bridged complex shown.

This type of reactivity suggests that complex (c) will not effectively promote the reduction of carbon monoxide. CO reduction would be expected to occur only when CO is a good enough ligand to break the hydride bridges in complex



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Figure 2-2. Synthesis of Dinuclear Zirconium Hydride and Carbonyl Complexes

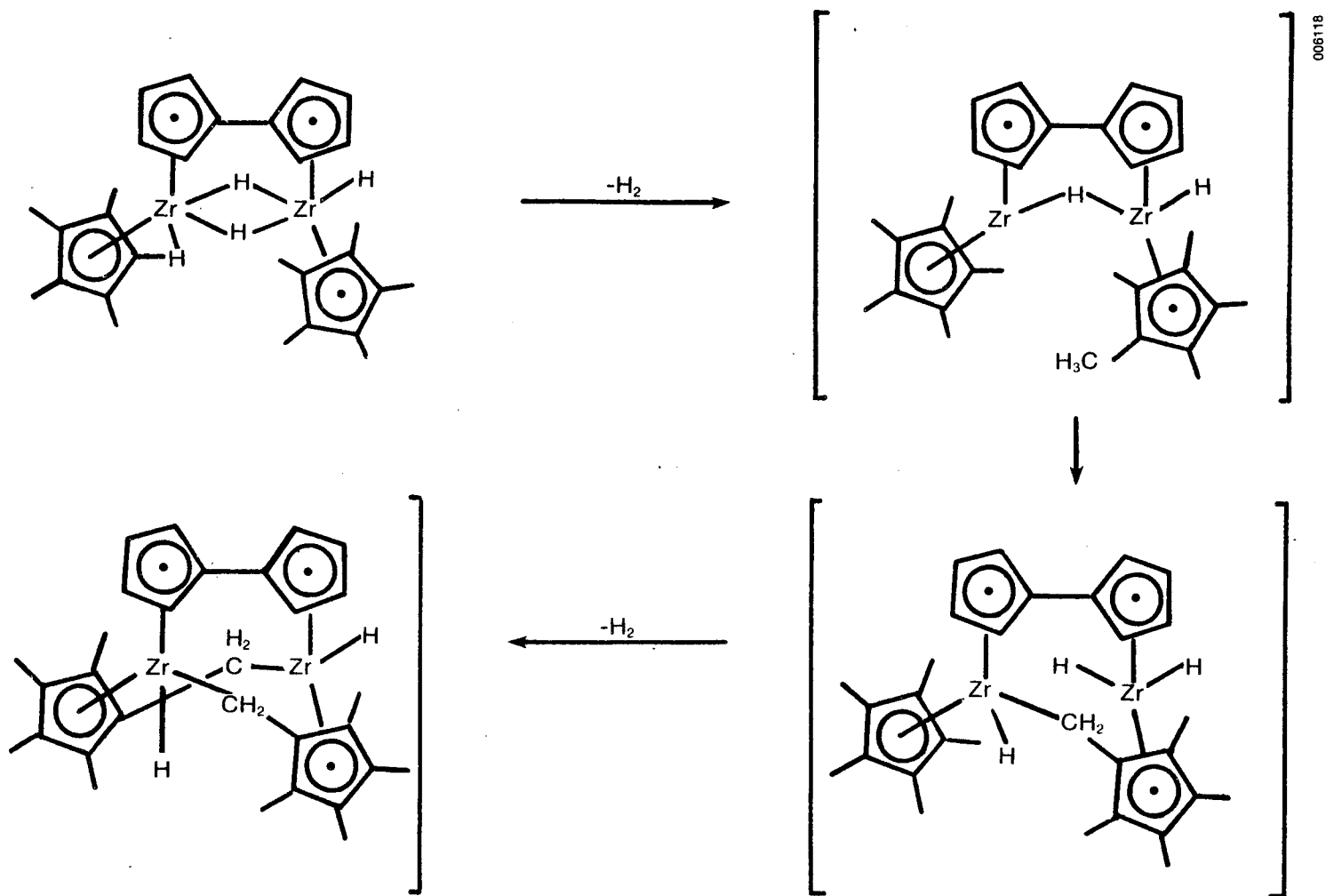


Figure 2-3. Proposed Decomposition Pathway for Complex (c) by Reductive Elimination of Hydrogen Followed by Oxidative Addition of Ring CH₃ Groups

(c) and form a strong complex at temperatures low enough to retard decomposition by hydrogen loss. It was found that CO does not react with complex (c) at low temperature and that upon warming thermal loss of hydrogen predominates.

Another useful complex for studying syngas reactions in this system is the tetracarbonyl zirconium(II) complex (d in Figure 2-2). This complex was prepared by reducing complex a with activated magnesium powder under carbon monoxide pressure. The NMR and infrared spectra of complex (d) are consistent with the structure drawn.

The other possibility for observing CO reduction in this dinuclear zirconium system involves treating the carbonyl complex (d) with hydrogen, as shown in Figure 2-4. We found that this procedure yields more promising results. When complex (d) in solution is exposed to low pressures of hydrogen, no reaction takes place until the solution is warmed to 70°C. At that temperature a reaction occurs that yields products consistent with stoichiometric reduction of carbon monoxide. Several products are obtained under these conditions, but they have not been separated and characterized. Recent efforts have been directed toward finding conditions of hydrogen pressure and temperature that will give a cleaner product, and this work is still in progress.

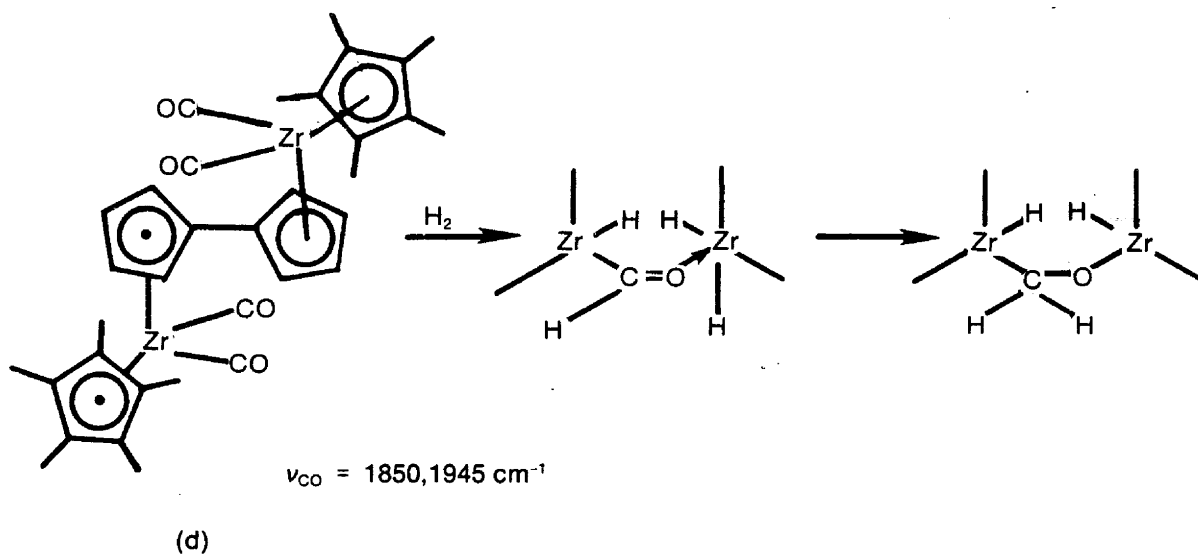


Figure 2-4. Reduction of Carbon Monoxide with the Dinuclear Zirconium Complex (d)

Related studies that should be continued involve the hydrolysis of zirconium complexes containing H_2/CO reduction products and gas chromatographic (GC) analysis of the oxygenated hydrocarbon products. Related synthetic studies with partially oxidized complexes, e.g., $Zr_2(O)(H)_2$ and $Zr_2(O)(CO)_2$, may allow CO hydrogenation to occur, followed by hydrogenolysis of the now less "oxophilic" Zr-OCH₂-Zr bonds to yield a catalytic cycle.

We hope that the low thermal stability of both hydride and carbonyl derivatives presented in this report would be found in the proposed methyl, hydride, and carbonyl oxide derivatives. Such a feature is desirable for the complexes to act as reactive precursors to begin a catalytic cycle.

SECTION 3.0

CONCLUSIONS AND RECOMMENDATIONS

We proposed to synthesize a set of dinuclear zirconium complexes with features that would make them able to promote reduction of carbon monoxide. Good synthetic routes to several complexes were developed, and two possible routes to CO reduction were examined. The first involved reaction of a dinuclear zirconium hydride complex with carbon monoxide. This route does not yield CO reduction because an unforeseen thermal decomposition reaction uses up the hydride before it can react with CO. The second route involved treatment of a zirconium carbonyl complex with hydrogen. We have evidence that CO reduction has occurred in this system, but the reduction products have not been fully characterized.

We recommend that future work will proceed in three areas. First, we will continue to examine the zirconium carbonyl plus hydrogen system to find out what the products of reduction are. Second, we will try two ways to change the zirconium hydride system so that the thermal decomposition reaction just described does not occur. One way is to remove the more reactive methyl-substituted C_5Me_5 rings in Figure 3-1, and replace them with "normal" C_5H_5 rings. The C-H bonds on these cyclopentadienyl rings should be less accessible to oxidative addition reactions than those of the methyl groups in the present complex.

The second means of circumventing the H_2 reductive elimination is to replace zirconium with hafnium (Figure 2-3). Hafnium is just below zirconium in the periodic table and is expected to exhibit analogous chemistry. However, metals from the third transition series generally form more kinetically stable complexes than do second-row analogues.

Finally, we are preparing new dinuclear complexes of metal further to the right in the periodic table. There are limited prospects for achieving catalytic rather than just stoichiometric reduction of CO with zirconium compounds. This is due to the relatively strong zirconium-oxygen bond strength. Metals further to the right will form weaker bonds to oxygen and also have lower oxidation states, which are more accessible. For this reason we are preparing dinuclear hydride complexes of vanadium and tantalum so that a balance between metal-hydride reducing power and metal-oxygen bond strength can be achieved and a catalytic CO reduction system can be designed.

The proposed research will involve the synthesis of new dinuclear metal hydride complexes using metals from group VB of the periodic table. The complexes will be of two structural types as shown in Figure 3-1. All contain a bridging fulvalene ligand to hold the two metals together. The two types differ in that the type I complexes contain a cyclopentadienyl ligand on each metal in addition to the fulvalene and hydride ligands, while the type II complexes have only two unidentate electron donor ligands in addition to fulvalene and hydrides. The latter have fewer electrons associated with the metal and are more coordinatively unsaturated than the first type. Type II complexes give us the opportunity to correlate the degree of unsaturation with the ability of a complex to reduce CO.

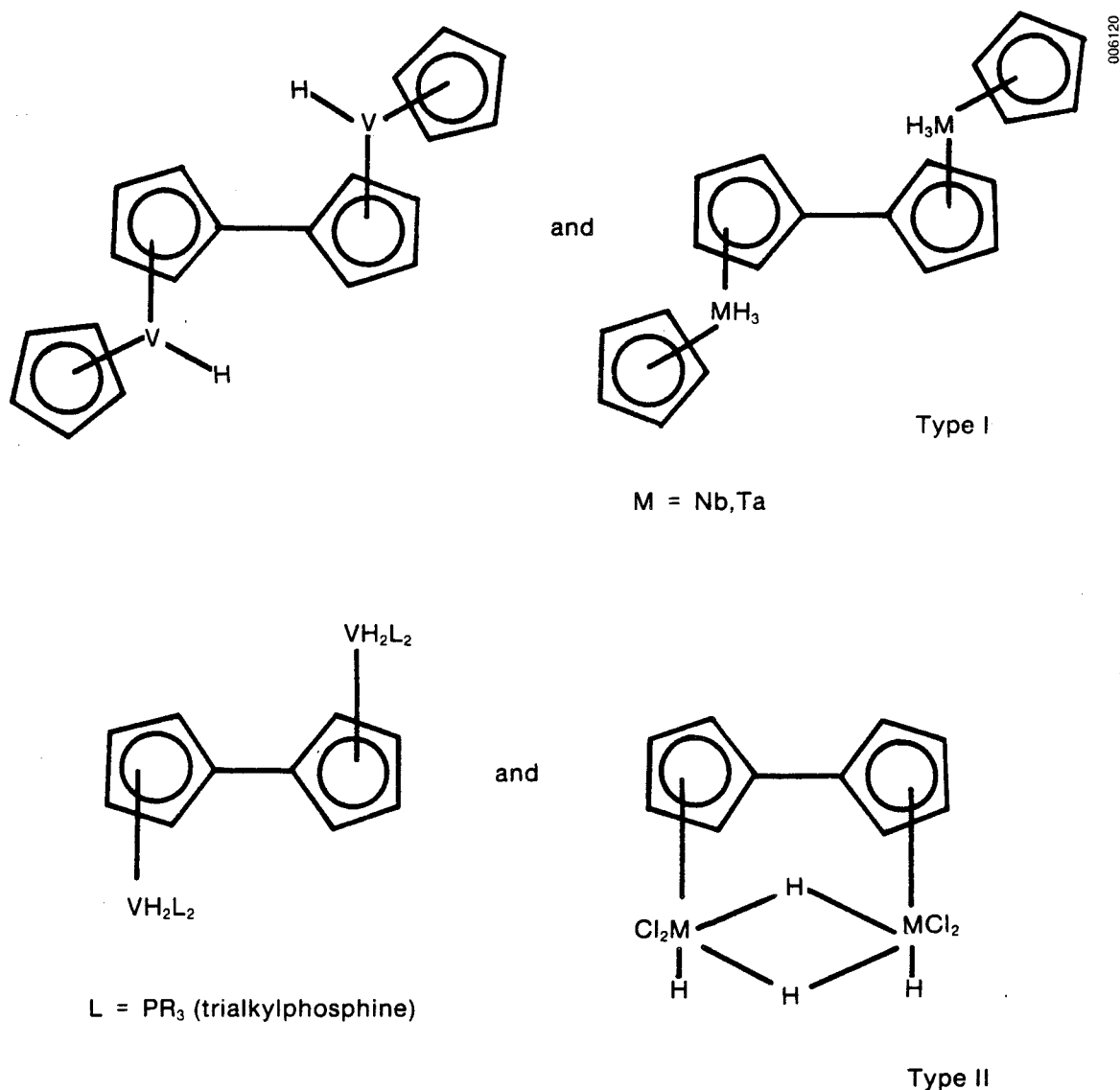


Figure 3-1. Proposed Metal Hydride Complexes

Note that the vanadium complexes in Figure 3-1 are represented in the +3 oxidation state while the niobium and tantalum complexes are shown in the +5 oxidation state. This is a reflection of the tendency for metals in the first transition series (like vanadium) to form stable compounds with lower oxidation states and coordination numbers. The metals below them in the second and third rows of the periodic chart tend to form more stable compounds with higher oxidation states and higher coordination numbers.

We have developed relatively straightforward procedures, for which precedents exist, to synthesize the proposed complexes. The strategy will be the same in all cases. Dinuclear complexes will be synthesized by nucleophilic substi-

tution reactions of the lithium salt of fulvalene dianion ($\text{Li}_2\text{C}_{10}\text{H}_8$) with known mononuclear metal halide complexes. Then the hydride ligands will be generated by hydrogenolysis reactions on suitable dinuclear metal alkyl complexes. The synthesis of vanadium complexes will be discussed first followed by the synthesis of the niobium and tantalum complexes.

The synthesis routes to the proposed vanadium complexes are shown in Figure 3-2. These reaction schemes are very similar. The starting materials, $(\text{C}_5\text{H}_5)\text{VCl}_2(\text{PMe}_3)_2$ and $\text{VCl}_3(\text{PMe}_3)_2$ [6], are known compounds that can be readily prepared on a large scale. Both are expected to react with fulvalene dianion to give the dinuclear vanadium chloride complexes shown. The halide complexes will react with alkyl lithium reagents to yield the corresponding vanadium alkyls, which should be stable when $\text{R} = \text{CH}_3$ and less stable when R is a longer chain or branched alkyl group. We do not intend to isolate them, however. Instead, the reaction will be done in a hydrogen atmosphere to yield hydride complexes directly. Under these conditions, the vanadium alkyl intermediates undergo hydrogenolysis as they are formed to yield the vanadium hydride and the alkane.

The syntheses of the proposed niobium and tantalum complexes are shown in Figure 3-3. These routes are similar to those proposed for the vanadium complexes except that with these metals the alkyl groups, which are the precursors to the hydride ligands, must be introduced into the starting complexes before the cyclopentadienyl rings are added. The starting materials for these reactions, Me_3MCl_2 [7] and Np_2MCl_3 [8] (where $\text{M} = \text{Nb, Ta}$; $\text{Me} = \text{methyl}$, $\text{Np} = \text{neopentyl}$), are known compounds that can be prepared on a large scale. The introduction of the fulvalene ligand into the complexes parallels the work of R. R. Schrock and coworkers at MIT [7,9] on the synthesis of mono- and bis(cyclopentadienyl) complexes of these metals. We have reacted the Me_3TaCl_2 with fulvalene dianion and found that it yields $(\text{C}_{10}\text{H}_8)(\text{TaMe}_3\text{Cl})_2$, as expected. The proposed hydrogenolysis reactions are expected to proceed as shown to yield the desired hydride complexes. Neopentyl ligands are proposed in the second reaction rather than methyls because neopentyl complexes undergo hydrogenolysis much faster than the analogous methyl complexes, especially when π -basic ligands such as chloride, alkoxide, or pyridene are present [10]. Schrock has demonstrated that $[(\text{C}_5\text{Me}_5)\text{TaCl}_2\text{H}]_2$ can be made by hydrogenolysis of the neopentyl ligands in $(\text{C}_5\text{Me}_5)\text{TaCl}_2\text{Np}_2$ under 40 psi H_2 at room temperature [11]. Comparable methyl complexes require much higher hydrogen pressures and higher temperatures [10].

Once the dinuclear metal hydride complexes have been synthesized, reactions with carbon monoxide will be examined. A proposed cycle for the conversion of CO/H_2 to ethylene glycol using one of the complexes is shown in Figure 3-4. Two key features of this cycle should be addressed. First, the bridging form-aldehyde complex at the bottom of the cycle will be the key to selectivity for producing a two-carbon product. If this intermediate reacts rapidly with H_2 , methanol would be produced and the starting tantalum complex would be regenerated. If the intermediate reacts rapidly with CO , then the cycle will be followed as indicated in Figure 3-4 and ethylene glycol will be produced selectively. If the intermediate reacts with H_2 and CO at comparable rates, a mixture of ethylene glycol and methanol would be produced. However, it should be possible to produce either product as the major component by adjusting the CO/H_2 ratio.

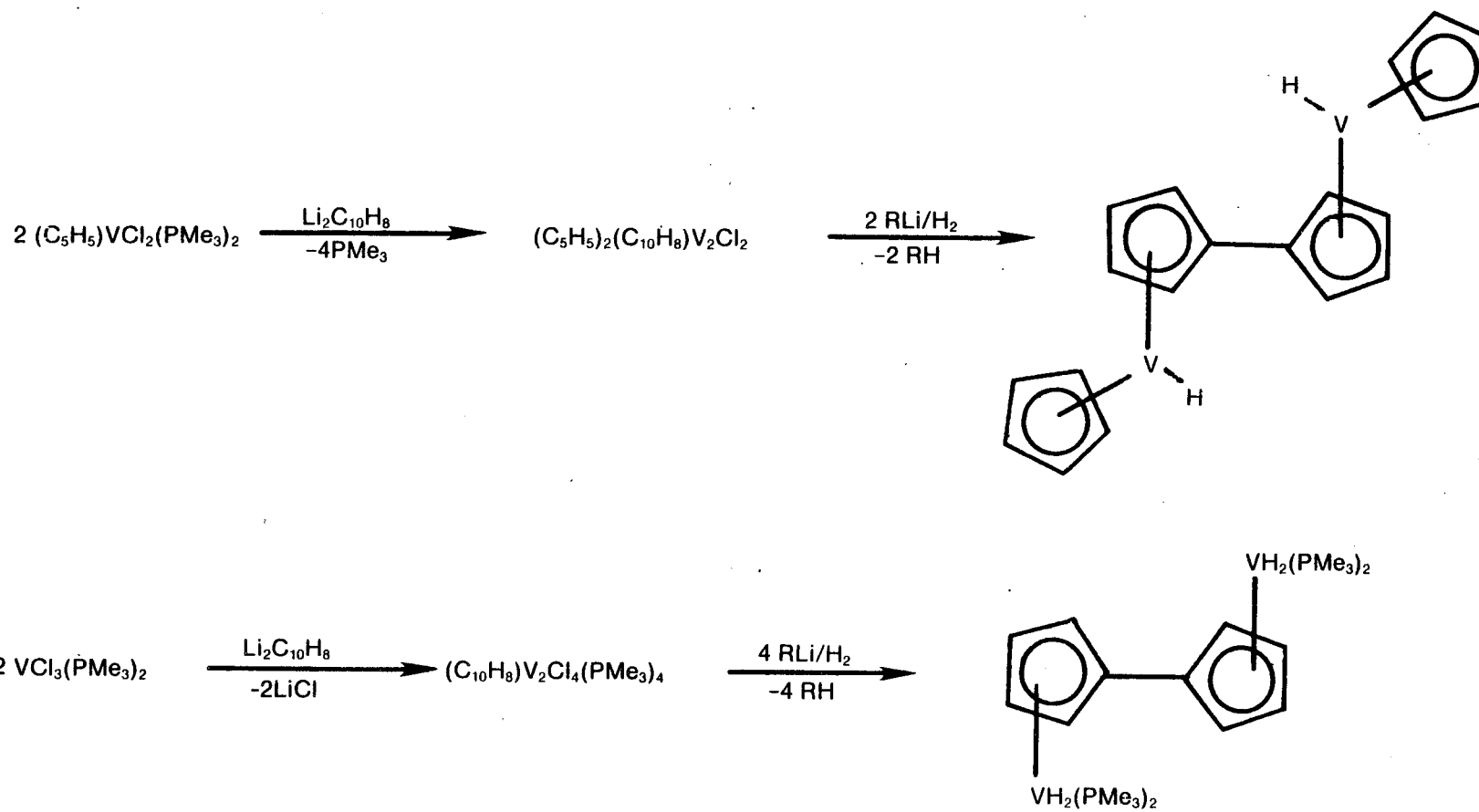


Figure 3-2. Synthetic Routes to the Proposed Vanadium Complexes

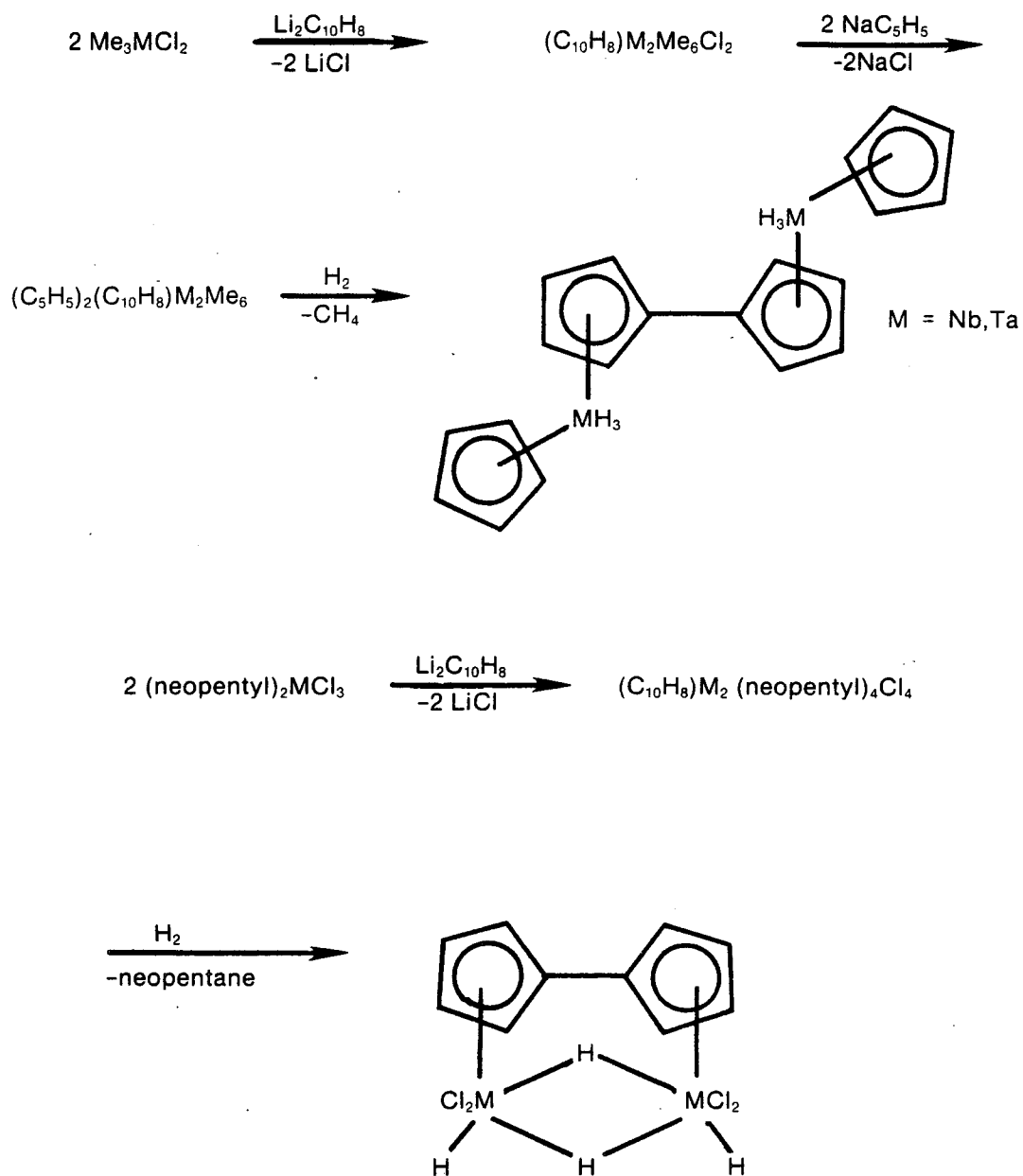


Figure 3-3. Synthetic Routes to Proposed Niobium and Tantalum Complexes

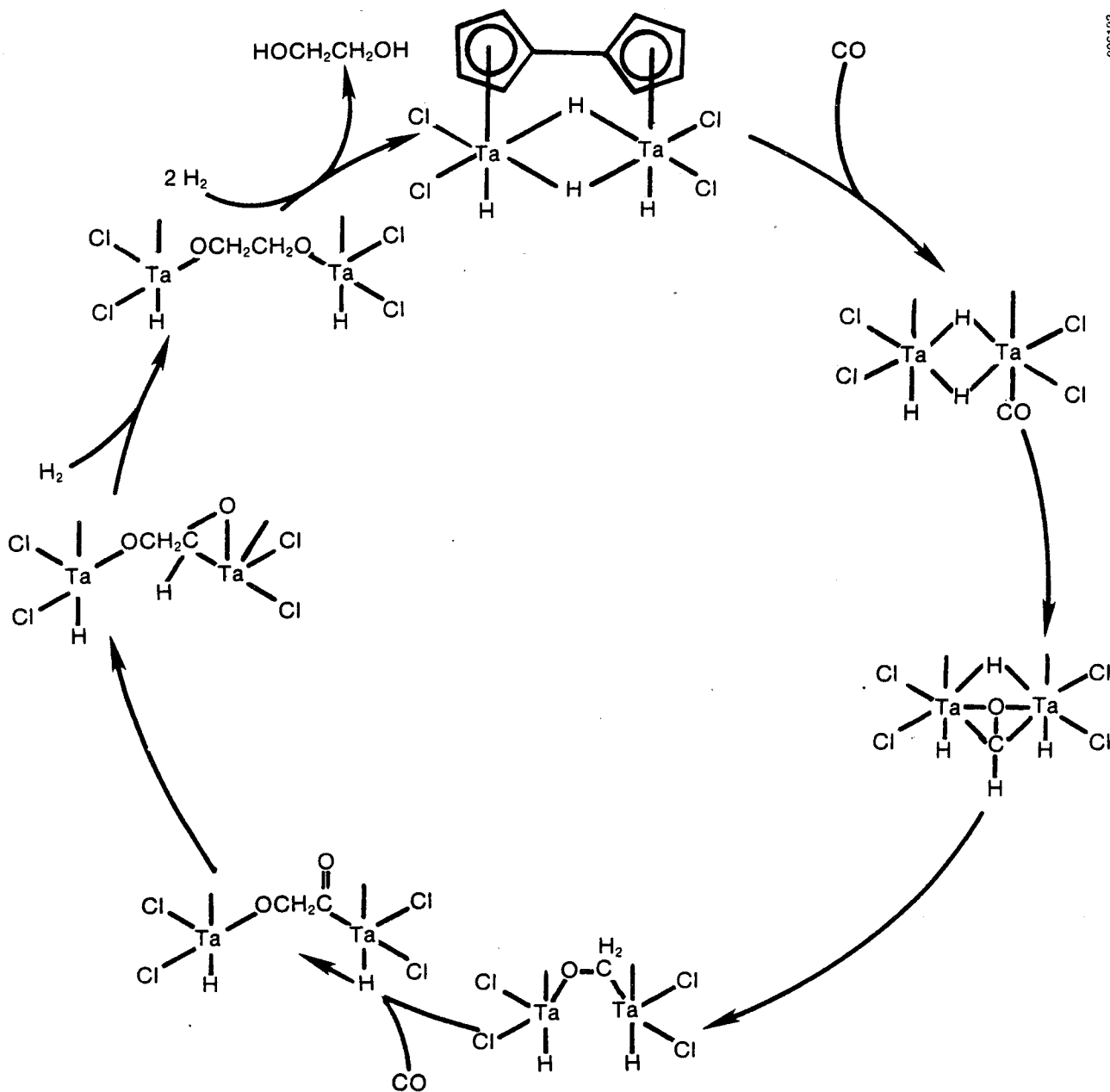


Figure 3-4. Proposed Cycle for the Conversion of CO/H₂ to Ethylene Glycol Using $(C_{10}H_8)(TaCl_2H_2)_2$. The fulvalene ligand has been omitted from all but the first structure for the sake of clarity.

The second key step in this cycle is the reaction of hydrogen with the final intermediate to yield ethylene glycol and regenerate the starting tantalum complex. There is no precedent for this reaction, so we are guardedly optimistic that it will occur. Our choice of compounds will make it possible to systematically probe this reaction. Metal-oxygen bond strength decreases from tantalum to niobium to vanadium. If the tantalum system does all but the last step in the cycle, it may be possible to use the analogous niobium or vanadium complex to achieve a catalytic cycle.

Similar cycles can be drawn for each of the proposed compounds. They differ slightly depending on the number of hydrides present in the starting complex, but the concepts are the same and the intermediates derived from CO reduction are expected to be the same for all the systems.

The major points of this proposal are as follows. Based on mechanistic analysis of systems that reduce carbon monoxide stoichiometrically, we have proposed the synthesis of new complexes that contain features which we feel are important to make the reduction catalytic. These new complexes can be prepared by the straightforward synthetic routes we have developed: the standard techniques of infrared and FT-NMR spectroscopy, elemental analysis, and, in selected cases, X-ray crystal structure analysis. Reactions of these complexes with carbon monoxide and hydrogen will be carried out, and systems that reduce carbon monoxide will be identified. In selected cases, CO-reducing systems will be examined in more detail by isotopic labeling studies using ^{13}C O and D_2 and by product analysis to determine the important mechanistic features of the reaction. All of this is done to produce a system that shows a high selectivity for the production of two-carbon products.

The demonstration of a complete catalytic cycle in a homogeneous system that reduces carbon monoxide will be a major scientific breakthrough. In addition, a detailed understanding of the mechanism of reactions of well-characterized complexes with CO will allow relationships between structure and reactivity to be developed, which will form the scientific basis for new and improved H_2/CO reduction catalysts.

The technological consequences of such a scientific breakthrough are also significant. A homogeneous catalyst should operate at lower temperatures and lower pressures of CO/H_2 , compared to possible heterogeneous analogues. Also, a homogeneous catalyst would probably be more selective in terms of the products produced. It should therefore be less costly to implement and operate using a homogeneous catalyst system than it would using comparable heterogeneous technology. This might be particularly true for small-scale biomass-based pyrolysis/indirect liquefaction plants.

In addition, the potential flexibility of producing various two-carbon products and higher alcohols would allow for various octane boosters and fuel additives to be generated for use in methanol fuel blends. For example, the catalytic studies proposed depict ethylene glycol as the resulting two-carbon product. Various catalysts and processes already exist to dehydrate this to vinyl alcohol or acetaldehyde, which can be catalytically hydrogenated further to ethanol. Such products may also be catalyzed by the complexes described in this proposal in the presence of excess hydrogen.

Vinyl alcohol is an excellent precursor to ether and mixed alcohol ethers for use as blending agents for methanol/gasoline mixtures. Catalysts for such transformations already exist in various states of development, but the most important catalyst development needed is for converting H_2/CO to two-carbon and higher oxygenated products.

SECTION 4.0

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APPENDIX

**Screening Studies of Modified Heterogeneous Catalysts for
the Production of Higher Alcohols**

FINAL REPORT

Submitted to SERI

S. W. Cowley
and
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November 20, 1984

INTRODUCTION

This nation's current economic recovery program calls for a restructuring of the synthetic fuels program, including a reduction in expenditure on coal research and development. The direct combustion of coal or coal liquids results in substantial pollution problems. Alcohol fuels do not pose the severe pollution problems generated by other synthetic fuels. Methanol is particularly attractive because it burns so cleanly. Alcohol mixtures (C_1-C_5) are also attractive fuels because they can be used as a high-octane blending stock for gasoline.

One of the advantages of alcohol fuels is that they can be produced from synthesis gas [1,2]. Synthesis gas is available from abundant resources and is produced by steam reforming coal [3] or methane or thermally decomposing biomass [4]. Biomass has advantages over coal in that it is a renewable energy source and it produces a cleaner synthesis gas that has less sulfur than syngas from coal. Current catalytic processes are very sensitive to the presence of poisons such as sulfur [5].

Methane is often produced along with petroleum at a well site. In some cases this methane can be shipped to consumers if a gas pipeline is available. However, in remote areas such as Alaska, the Middle East, or isolated areas in the western United States the methane is not utilized because pipelines to potential consumers do not exist and the cost of building them is not justified. It has been proposed that methane produced in these areas be catalytically converted into synthesis gas and catalytically converted into methanol. The methanol can be transported as a liquid using the same transportation facilities as those used for petroleum [6,7]. Methanol produced in such a fashion would be relatively inexpensive compared to petroleum. Many countries lacking in natural gas and oil resources are very interested in obtaining and using methanol as an alternate fuel to petroleum. This interest has sparked a flurry of research activity on the production of methanol for use as a fuel and a chemical feedstock.

Methanol has excellent fuel qualities and has been tested for use in both transportation and electric power generation. The use of methanol as an automotive fuel has been discussed extensively in the literature [8-12]. Methanol exhibits some important combustion qualities that give it an advantage over gasoline as a fuel. Methanol demonstrates substantially lower carbon monoxide and nitrogen oxide emissions. Also, the higher octane value of methanol allows a higher engine compression ratio to be used, which gives a better engine efficiency. Methanol has been tested for use as a boiler fuel, a turbine fuel, and a diesel fuel [13,14]. Because methanol demonstrates good combustion properties and has lower emission levels than conventional fuels, the catalytic synthesis of methanol from synthesis gas has been studied extensively [15-20].

The production of higher alcohols (C_2-C_5) is another attractive way of utilizing synthesis gas [21]. Higher alcohols are also excellent fuels. However, initially their principal use will be as high-octane blending stocks. The EPA intends to cut the use of tetraethyl lead in gasoline by 91%, beginning January 1, 1986, and to ban the use of lead completely by 1995.

Assuming that the ban of lead is inevitable, there will be a need for processes that can provide large quantities of octane boosters for gasoline. Several researchers have investigated the catalytic production of higher alcohols. Klier et al. have used Cu-ZnO catalysts doped with cesium to promote the production of higher alcohols [22]. However, copper-based catalysts are extremely sensitive to sulfur poisoning and overreduction. Recently a molybdenum-sulfide-based catalyst was developed by Dow Chemical Company [23]. This catalyst is extremely resistant to sulfur poisoning; however, it has a low surface area, which increases the cost of the catalyst significantly.

Our objective is to investigate the catalytic production of higher alcohols using the technical information we have gained from the study of methanol decomposition catalysts. It is important to find a catalyst system that will provide the necessary stability, activity, and selectivity required for the production of an alcohol mixture. Control of the alcohol product distribution is essential if higher alcohols are to be successfully used as a blending stock. After testing several catalysts, the most successful will be further investigated to establish the fundamental chemistry behind their activity and selectivity. This information will be used to improve future catalyst designs.

CATALYST TESTING RESULTS

Several catalysts were screened in a microcatalytic plug-flow reactor at the SERI catalyst laboratory, and the results are given in Tables 1 and 2. The catalysts were selected because of their expected behavior for the production of higher alcohols. It is believed that the catalyst must have some ability to synthesize CH_x surface groups to permit chain growth, which is necessary for the production of higher alcohols. Chain growth requires a catalyst that can dissociate some carbon monoxide on the surface and hydrogenate the others to the alcohol. None of the catalysts demonstrate any activity for the production of the higher alcohols as expected. Instead, methanol was the only alcohol product observed. Other products such as methane, carbon dioxide, water, and dimethyl ether were also produced. Although no higher alcohols were detected, it is possible that they were produced in quantities below the detection limit of our equipment. The higher alcohols are typically produced in very small amounts, which makes their analysis very difficult by gas chromatography. The production of methanol and methane is very encouraging and suggests that our criteria for CO dissociation and hydrogenation are achieved on this catalyst.

FUTURE STUDIES

We are planning to evaluate our analytical procedure for higher alcohols. We hope to use a quadrupole mass spectrometer to monitor the products in the future. This instrument is under construction, but progress has been slow because of funding problems.

We are planning to investigate other catalysts such as sulfided molybdenum, which looks promising because of its stability and selectivity. We plan to

Table 1. Alcohol Synthesis Catalysts

Catalyst	wt % Metals				
	La	Pd	Rh	Ru	Fe
Pd/La ₂ O ₃ /Al ₂ O ₃	5.0	4.0	0	0	0
Pd-Rh/Al ₂ O ₃	0	2.9	1.0	0	0
Rh/La ₂ O ₃ /Al ₂ O ₃	7.7	0	0.8	0	0
Pd-Rh/La ₂ O ₃ /Al ₂ O ₃	7.7	2.7	0	0	0
Pd/La ₂ O ₃ /Al ₂ O ₃ ^a	5.0	3.0	0	0	0
Ru/La ₂ O ₃ /Al ₂ O ₃	7.7	0	0	1.0	0
Pd-Ru/La ₂ O ₃ /Al ₂ O ₃	7.7	2.5	0	1.1	0
Pd-Fe/La ₂ O ₃ /Al ₂ O ₃	7.7	2.5	0	0	0.7

^aAlumina support was Norton 1/16-in. spheres. All other alumina supports were 14-30 mesh by Alfa Company.

Table 2. Alcohol Synthesis Over Various Catalysts

Catalysts ^a	Mole % Products						
	H ₂	CO	CH ₄	CO ₂	H ₂ O	CH ₃ OH	DME
Pd/La ₂ O ₃ /Al ₂ O ₃	69.1	19.0	2.4	1.6	3.6	2.9	0
Pd-Rh/Al ₂ O ₃	61.9	29.9	2.9	0	5.1	0.2	0.1
Rh/La ₂ O ₃ /Al ₂ O ₃	65.0	32.2	0.9	0	1.9	0	0
Pd-Rh/La ₂ O ₃ /Al ₂ O ₃	61.7	32.5	1.3	0.3	3.4	0.4	0
Pd/La ₂ O ₃ /Al ₂ O ₃ ^b	59.4	30.1	2.2	1.7	4.1	0.7	1.9
Ru/La ₂ O ₃ /Al ₂ O ₃	57.3	20.6	9.0	0.6	11.8	0.7	0
Pd-Ru/La ₂ O ₃ /Al ₂ O ₃	56.2	43.8	0	0	0	0	0
Pd-Fe/La ₂ O ₃ /Al ₂ O ₃	66.1	31.9	0	0.3	0.6	0.4	0.7

^aTesting conditions: temperature = 300°C; pressure = 620-640 mm Hg; feed flow = 49-83 cm³/min.

^bAlumina support was Norton 1/16-in. spheres. All other alumina supports were 14-30 mesh by Alfa Company.

impregnate the molybdenum catalysts onto the modified aluminas that were prepared for the methanol decomposition studies.

We are also planning to look at ways of making ether products in addition to the higher alcohols. Methanol is an excellent diesel fuel, but its quality is markedly improved by the addition of dimethyl ether. We are certain that the modified aluminas will serve as excellent catalysts for the controlled production of ether.

These studies provide valuable information about the Fischer-Tröpsch (FT) process in general. It would be interesting to apply some of the principles discovered during methanol decomposition and alcohol synthesis to the production of FT products.

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