ACTIVATION OF HYDROGEN AND CARBON MONOXIDE
BY TRANSITION METAL COMPLEXES

By

JAMES G. MILLER

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA
1985
To my parents, Mary and George Miller, and my wife, Nan, whose constant support and encouragement made this work possible.
ACKNOWLEDGEMENTS

I wish to express my deep appreciation to my research director, Professor Russell S. Drago, for his guidance, motivation, and understanding during my years at the University of Illinois and the University of Florida.

A very grateful thank you goes to Professor Glenn C. Vogel for his encouragement and friendship.

I would like to thank the members of the Drago research group, both past and present, for their help, discussions and friendship. Among the group Mike Desmond, Dean Oester, Pete Doan, Jim Stahlbush and especially Keith Weiss deserve special thanks. Robert King and Chris Schirmer are acknowledged for their invaluable assistance with the GC mass spectrometry and electrochemistry studies, respectively.

Financial support by the University of Illinois, the University of Florida and Professor Drago in the form of teaching and research assistantships is gratefully acknowledged.

Finally, a very special thanks go to Ginger Solano and my wife Nan for their patience and help in preparing this manuscript.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>ACKNOWLEDGEMENTS</th>
<th>iii</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>vi</td>
</tr>
<tr>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. ACTIVATION</td>
<td>4</td>
</tr>
<tr>
<td>III. IMMobilIZED</td>
<td>48</td>
</tr>
</tbody>
</table>

## I. INTRODUCTION
- Introduction: 4
- Experimental:
  - Materials: 11
  - Instrumentation: 12
  - Synthesis: 13
  - Thermodynamic Measurements: 14
  - Hydrogen Gas Flow System: 15
- Results and Discussion: 24
- Conclusion: 46

## II. ACTIVATION OF MOLECULAR HYDROGEN
- Introduction: 4
- Experimental:
  - Materials: 11
  - Instrumentation: 12
  - Synthesis: 13
  - Thermodynamic Measurements: 14
  - Hydrogen Gas Flow System: 15
- Results and Discussion: 24
- Conclusion: 46

## III. IMMobilIZED HOMOGENEOUS CARBON MONOXIDE REDUCTION CATALYSTS
- Introduction: 48
- Experimental:
  - Reagents: 59
  - Instrumentation: 59
  - Fixed Bed Flow Reactor: 60
  - Synthesis: 63
- Results and Discussion:
  - Polymer Supported $[\text{Ru}(\text{CO})_3\text{I}_3]^{-}$ and $[\text{HRu}_3(\text{CO})_{11}]^{-}$: 73
    - Synthesis and characterization: 73
    - Catalysis: 83
  - Covalently Supported $\text{Ir}_4(\text{CO})_{11}$: 83
    - Synthesis: 83
    - Infrared characterization: 86
    - Catalysis: 94
    - CH$_3$Cl catalyst development: 102

iv
Halogen sources .......................... 126
GC Mass spectrometry .................. 131
Mechanism ............................... 142

Conclusion .................................. 146

IV. IMIDAZOLE FUNCTIONALIZED SILICA GEL .... 149

Introduction ................................ 149

Experimental ................................ 153

Materials .................................... 153
Instrumentation ........................... 153
Synthesis .................................... 154

Results and Discussion .................... 158

Synthesis - Imidazole Support ......... 158
Hydroformylation .......................... 167

Conclusion .................................. 169

V. SOLUBLE BIMETALLIC COMPLEXES ............ 171

Introduction ................................ 171

Experimental ................................ 173

Materials .................................... 173
Instrumentation ........................... 173
Synthesis .................................... 177

Results and Discussion .................... 181

Ligand Preparation ....................... 181
Metalomers, Synthesis and Characterization 182
Electrochemistry ........................... 195

Conclusion .................................. 199

VI. SUMMARY AND CONCLUSION ................ 201

REFERENCES ............................... 203

BIOGRAPHICAL SKETCH ..................... 211
ACTIVATION OF HYDROGEN AND CARBON MONOXIDE BY TRANSITION METAL COMPLEXES

By

James G. Miller

December 1985

Chairman: Russell S. Drago
Major Department: Chemistry

Reported here are four studies related to the catalytic processes involving the activation of carbon monoxide and/or molecular hydrogen by transition metal complexes. The first study investigates the process of hydrogen activation by square-planar rhodium (I) complexes of the formula (P(p-tolyl)₃)_2RhClB where B is P(p-tolyl)₃, tetrahydrothiophene (THTP), pyridine and N-methylimidazole. Enthalpies were determined for the reaction of the P(p-tolyl)₃ and THTP complexes with H₂ forming cis dihydride complexes of the formula (P(p-tolyl)₃)_2RhClBH₂. Attempts to determine enthalpies for the pyridine and N-methylimidazole complexes were unsuccessful.

The metal-hydrogen dissociation energies determined from these enthalpies were found to be insensitive to the ligand variation around the rhodium center.

In the second study, ruthenium and iridium homogeneous CO reduction catalysts were immobilized on silica gel and alumina. Ionic attachment of the two ruthenium anions
[Ru(CO)₃I₃]⁻ and [HRu₃(CO)₁₁]⁻ to ammonium iodide functionalized silica gel, as demonstrated by infrared showed no syngas (CO and H₂) conversion up to 175°C and 1 atm pressure.

A physical mixture of AlCl₃ and Ir₄(CO)₁₁ covalently attached to a phosphine silane functionalized silica gel or alumina was found to selectively produce CH₃Cl from syngas under very mild conditions, 25°C, 1 atm pressure. Replacement of AlCl₃ as the chloride source by addition of HCl(g) to the syngas feed enabled production of CH₃Cl with 99% selectively at temperatures up to 100°C. The novel chemistry was demonstrated with other halogen sources: aqueous HCl, Cl₂ and HBr (producing CH₃Br). The presence of a Lewis acid and the phosphine silane linkage appeared to be important for their catalytic properties.

In the third study a 4(5) substituted imidazole functionalized silica gel support was synthesized to heterogenize a homogeneous rhodium imidazole hydroformylation catalyst. The synthesis utilizes Schiff base reactions between an aminosilane functionalized silica gel, histamine and 1,4-dihydroxy-2,5-dibenzaldehyde. The rhodium metalated support was active for the conversion of 1-hexene but suffered severe metal leaching.

In the fourth study a series of soluble bimetallic complexes of the formula [M(II)(DIOX)BF₂]₂ (M = Cu, Ni, Zn, Pd; DIOX = bis-4-tert-butyl-2,6-diformyl-phenol dioxime)
Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

ACTIVATION OF HYDROGEN AND CARBON MONOXIDE BY TRANSITION METAL COMPLEXES

By

James G. Miller

December 1985

Chairman: Russell S. Drago
Major Department: Chemistry

Reported here are four studies related to the catalytic processes involving the activation of carbon monoxide and/or molecular hydrogen by transition metal complexes. The first study investigates the process of hydrogen activation by square-planar rhodium (I) complexes of the formula \((\text{P(p-tolyl})_j)^\text{RhClB}_n\) where \(B\) is \(\text{P(p-tolyl})_j\), tetrahydrothiophene (THTP), pyridine and N-methylimidazole. Enthalpies were determined for the reaction of the \(\text{P(p-tolyl})_j\) and THTP complexes with \(H_2\) forming cis dihydride complexes of the formula \((\text{P(p-tolyl})_j)^\text{RhClBH}_2\). Attempts to determine enthalpies for the pyridine and N-methylimidazole complexes were unsuccessful.

The metal-hydrogen dissociation energies determined from these enthalpies were found to be insensitive to the ligand variation around the rhodium center.

In the second study, ruthenium and iridium homogeneous CO reduction catalysts were immobilized on silica gel and alumina. Ionic attachment of the two ruthenium anions
[Ru(CO)₃I₃]⁻ and [HRu₃(CO)₁₁]⁻ to ammonium iodide functionalized silica gel, as demonstrated by infrared showed no syngas (CO and H₂) conversion up to 175°C and 1 atm pressure.

A physical mixture of AlCl₃ and Ir₄(CO)₁₁ covalently attached to a phosphine silane functionalized silica gel or alumina was found to selectively produce CH₃Cl from syngas under very mild conditions, 25°C, 1 atm pressure. Replacement of AlCl₃ as the chloride source by addition of HCl(g) to the syngas feed enabled production of CH₃Cl with 99% selectivity at temperatures up to 100°C. The novel chemistry was demonstrated with other halogen sources: aqueous HCl, Cl₂ and HBr (producing CH₃Br). The presence of a Lewis acid and the phosphine silane linkage appeared to be important for their catalytic properties.

In the third study a 4(5) substituted imidazole functionalized silica gel support was synthesized to heterogenize a homogeneous rhodium imidazole hydroformylation catalyst. The synthesis utilizes Schiff base reactions between an aminosilane functionalized silica gel, histamine and 1,4-dihydroxy-2,5-dibenzaldehyde. The rhodium metalated support was active for the conversion of 1-hexene but suffered severe metal leaching.

In the fourth study a series of soluble bimetallic complexes of the formula [M(II)(DIOX)BF₄]₂ (M = Cu, Ni, Zn, Pd; DIOX = bis-4-tert-butyl-2,6-diformyl-phenol dioxime)
was synthesized and characterized. These complexes are formed from analogous insoluble O-H···O bridged complexes by reaction with BF$_3$·Et$_2$O. Electrochemical studies were performed on the Cu(II) BF$_2$ capped complex in acetone and DMF and illustrated strong metal site interactions.
I. INTRODUCTION

The field of catalysis is one of the most active and intensely pursued areas of chemistry research. The overriding goal of this research, driven primarily by its economic importance, is to develop better and more efficient catalysts.

Reported here are the results of four studies all related to catalytic processes (i.e. hydrogenation, carbon monoxide reduction, hydroformylation) involving the activation of carbon monoxide and/or molecular hydrogen by transition metal complexes. These studies focus on two different aspects of catalysis research: 1) gaining an understanding of chemical transformations taking place in a catalytic cycle and 2) developing new and novel transition metal catalysts. In the first study thermodynamic data were obtained on the activation of molecular hydrogen by square-planar rhodium(I) complexes of the formula \([P(p-tolyl)\_3]^\text{2}RhClB (B = P(p-tolyl)\_3, \text{THTP, Py, MeIm})\). These results provide needed information on the strength of the metal hydrogen bonds formed upon activation of molecular hydrogen by a typical hydrogenation catalyst, "Wilkinson's" catalyst\(^1\) and the sensitivity of these bonds to variation in the ligand environment around the metal center. These
results also give insight into adverse effects of additives such as pyridine to the catalytic system.

In the second study immobilized homogeneous transition metal catalysts were synthesized and tested for their use in developing selective carbon monoxide reduction catalysts which operate under mild reaction conditions. A low pressure and temperature catalytic system was discovered and described for the conversion of syngas (CO + H₂) and HCl selectively to chloromethane using a bifunctional supported iridium cluster catalyst. The active catalyst precursor consists of Ir₄(CO)₁₁ covalently attached to a phosphine silane functionalized silica gel or alumina and can be operated in the presence or absence of an AlCl₃ co-catalyst.

The third study, which relates very closely to the immobilized catalysts used in the previous study, involves the development of a 4(5) substituted imidazole functionalized silica gel support. The new support was designed to heterogenize a reported homogeneous rhodium imidazole hydroformylation catalyst of the formula [Rh(imidazole)]₃.²,³ The synthesis and characterization of this new support are reported along with preliminary tests on the hydroformylation activity of the rhodium metal loaded support.

The fourth and final study reported deals primarily with the synthesis and characterization of new soluble bimetallic macromolecules which might be capable of
facilitating bifunctional catalysis similar to that demonstrated in the second study. These complexes synthesized are of the formula \([M(DIOX)BF_2]_2\) (DIOX = bis-4-tert-butyl-2,6-diformyl-phenol dioxime and M = Cu, Ni, Zn, Pd) and contain two metal centers in close proximity allowing metal site interactions.
II. ACTIVATION OF MOLECULAR HYDROGEN

Introduction

Activation of molecular hydrogen by metals is an important fundamental process with relevance to many catalytic systems (i.e. hydrogenation of olefins,\(^4\) hydroformylation,\(^5\) and reduction of carbon monoxide by \(\text{H}_2\)) and to storage of \(\text{H}_2\) by dissolution in metals.\(^7\)

In order to develop better and more efficient catalysts, it is important to determine what metal hydrogen bond dissociation energies are needed to affect desired chemical transformations. For example, a transition metal hydride complex will not be a good hydrogenation catalyst if its M-H bond strengths are so large that it is unable to easily transfer hydrogens to an olefin.

To date, very little thermodynamic data have been reported in the literature regarding metal hydrogen bond dissociation energies and their dependence on various ligands in the metal coordination sphere. The reaction of a series of square planar rhodium (I) complexes of the formula \([\text{P}(p\text{-tolyl})_3]_2\text{RhClB} (\text{B}=\text{P}(p\text{-tolyl})_3, \text{THTP, Py, MeIm})\) with molecular hydrogen forming six coordinate rhodium (III) dihydride complexes (Equation 1) provided an excellent opportunity for this type of study.
\[ [P(p\text{-tolyl})_3]_2\text{RhClB} + H_2 \rightarrow [P(p\text{-tolyl})_3]_2\text{RhClB(H}_2) \]  

The complex \([P(p\text{-tolyl})_3]_2\text{RhClB}\), (where \(B=P(p\text{-tolyl})_3\)) often termed "Wilkinson's catalyst," has been extensively studied since it was first reported to be a good hydrogenation catalyst by Wilkinson et al.\(^1\) in 1966. To this date, a number of studies and mechanistic schemes have been published.\(^8\)-\(^12\) The most recent was proposed by Halpern et al.\(^13,14\) and is shown Figure 2-1 where \(L=P(p\text{-tolyl})_3\) or \(P(C_6H_5)_3\), \(S=\text{solvent}\), and \(\text{C}=	ext{C}^\prime\) represents some non-sterically hindered unconjugated olefin.

In concentrations of up to 0.1M excess phosphine the predominant catalytic pathway is not through direct hydrogenation of \(\text{RhClL}_3\) I but through a dissociative pathway where \(\text{RhClL}_3\) dissociates a phosphine generating the unsaturated three coordinate species \(\text{RhClL}_3\) II. This was found to activate \(H_2\) \(10^4\) times faster than \(\text{RhClL}_3\) generating another coordinately unsaturated complex \(\text{RhClL}_3(H)_2\) III which then reacts with an olefin giving the six coordinate complex IV. Stepwise hydrogen transfer to the olefin produces the alkane product and also regenerates the three coordinate complex II. The catalytic cycle then continues along the pathway contained in the dotted circle.

A number of studies have been published attempting to correlate changes in the ligand environment around the
Figure 2-1. Mechanistic scheme proposed for the hydrogenation olefins by "Wilkinson's Catalyst."
rhodium center to catalytic activity. Most of these studies involved changing all three phosphines with other phosphines and other 2 electron donating bases.\textsuperscript{15-18} When a series of para-substituted aryl phosphines were used, it was found that catalytic activity increased as the electron donating ability of the phosphine increased. This could be due to the more electron donating phosphines making the rhodium more basic improving its ability to activate $H_2$ (as well as to back bond into olefins).

When alkyl phosphines were used, which are even more electron donating than aryl phosphines, catalytic activity was diminished. These results can be interpreted in a number of ways. First, the alkyl phosphines could be making the rhodium center so basic that the rhodium hydride and rhodium olefin complex are becoming too stable. Second, steric factors may also be playing an important role. The less bulky more electron donating phosphines may be binding too tightly to the rhodium center preventing the necessary phosphine dissociation steps that provide important coordinative unsaturation. When the bulky aryl phosphines were used,\textsuperscript{19} crowding around the metal center may be increasing the tendency for ligand dissociation.

Further studies have used N, S, As and Sb donors\textsuperscript{16,17,20,21} around the rhodium center. Also, it was reported\textsuperscript{1} that large excesses of pyridine, acetonitrile and various sulfur donors added to solutions of RhCl(P(C$_6$H$_5$)$_3$)$_3$ greatly reduce catalytic activity.
Due to the complexities of a catalytic system it is difficult to predict exactly what reactions are being affected by variations imposed on the system unless each catalytic reaction step can be studied separately. This study will hopefully give some insight into one segment of the catalytic reaction, that is the effects of ligand variation on the activation of molecular hydrogen by rhodium complexes with structures similar to Wilkinson's.

A convenient and fairly simple method for making derivatives with one ligand around the rhodium center of Wilkinson's catalyst being varied was found making use of the dimer bridge cleavage reaction shown in Equation 2.

Calorimetric studies on this\(^\text{22,23}\)

\[
P_\text{Rh-P} \quad \text{Cl-} \quad \text{Rh-Cl} \quad \text{P} + 2B \xleftrightarrow{\text{2}} 2\text{Rh-P}_\text{B}\quad \text{Cl} \quad (P = P(p\text{-tolyl})_3) \quad \text{(2)}
\]

and two other chloro bridged dimer systems \([\text{RhCl(CO)}_2]_2\)\(^\text{24}\) and \([\text{RhCl(COD)}_2]_2\)\(^\text{25}\) have previously been reported by the Drago research group.

The bridge cleavage reaction of the phosphine dimer ((\([\text{RhCl(P(p\text{-tolyl})}_3]_2\)) was found to occur with nitrogen, phosphorus and sulfur donors. Attempts using oxygen donors were unsuccessful. By way of \(^1\text{H}\) and \(^31\text{P}\) NMR the geometric structure of all the monomeric base adducts formed were found to be the same; that is the base occupied a
position cis to the chlorine, as shown in Equation 2. Heats obtained for the bridge cleavage reaction were incorporated into the E, C and W correlation\textsuperscript{26,27} (Equation 3) and $E_A$ and $C_A$ parameters were generated for the three coordinate acid $(P(p$-tolyl)$_3)_2$RhCl.

$$- \Delta H = E_A E_B + C_A C_B + W \quad (3)$$

The monomeric base adducts generated in solution were also shown to react with molecular hydrogen at ambient temperature and pressure (Equation 1). The six coordinate rhodium (III) dihydride complexes formed (shown below) were found to have the same geometric structure, again using $^1$H and $^{31}$P NMR. The two inequivalent hydrides end up cis to each other and the two equivalent phosphines occupy trans positions.

This study deals specifically with the thermodynamic aspects of the activation of molecular hydrogen by Wilkinson's catalyst and its derivatives. Determination of
the ΔH for Equation 1 will provide us with a better understanding of the influence of donor strength on the activation of molecular hydrogen and on the average Rh-H bond strength.

In addition, the resulting thermodynamic data could possibly be entered into the E, C and W correlation and $E_A$ and $C_A$ parameters could be determined for the five coordinate acid "(P(p-tolyl)$_3$)$_2$RhCl(H)$_2$." By comparing these E and C parameters to the E and C parameters of the three coordinate acid "(P(p-tolyl)$_3$)$_2$RhCl," the effect of oxidative addition of H$_2$ on the acidity of the rhodium center could be quantitatively determined.

**Experimental**

**Materials**

Toluene was dried and degassed by first refluxing over CaH$_2$ for 24 hours, collected by distillation under N$_2$ and then subjected to freeze pump thawing (a minimum of 5 cycles using a mercury diffusion pump). It was then stored in an inert atmosphere box until needed. Rhodium trichloride • 3H$_2$O was purchased and used without further purification.

All bases used in this study were purchased and purified by the following methods. Tri-p-tolylphosphine was recrystallized in hot absolute ethanol followed by drying
under vacuum. Pyridine (Py) was stored over KOH pellets overnight, then distilled from BaO under N\textsubscript{2} (middle fraction taken, boiling range 112.0 - 112.5\degree C).

Tetrahydrothiophene (THTP) was fractionally distilled over CaH\textsubscript{2} at atmospheric pressure. N-methylimidazole was fractionally distilled over CaH\textsubscript{2} at 10 mmHg pressure and the middle fraction taken. Dimethylthioformamide was dried over 4A molecular sieves. All liquid bases were degassed by freeze pump thawing.

Ethylene, hydrogen and nitrogen gases used were obtained from Linde (Union Carbide); the hydrogen and nitrogen were of ultra-high purity (2 ppm O\textsubscript{2}, 3 ppm moisture).

High capacity oxygen traps were purchased from L.C. Company, Inc. These were designed to remove O\textsubscript{2} to below 0.1 ppm with a gas flow of less than 3 liters per minute. The traps contain a Mo based indicator which is blue-green when activated and grey when spent. The traps were periodically regenerated by placing them in a Lindberg (model 123-8) tube furnace at 375\degree C while passing H\textsubscript{2} gas through them at a rate of 30 cc/min for 20 minutes.

Instrumentation

All air sensitive manipulations were performed in a Vacuum Atmosphere Co. model HE-43-2 inert atmosphere box, in specially designed Schlenck-ware glassware. Elemental
analysis was performed by the Microanalytical Laboratory, University of Illinois, Urbana, Illinois.

Electronic absorption spectra were taken on a Cary 14-RI spectrometer equipped with a Varian constant temperature chamber in the sample compartment. The chamber was coupled to a Braun Thermoboy circulating temperature bath which will maintain a constant temperature to \( \pm 0.2^\circ C \). For temperatures below room temperature a cold slush bath was added to the circulating system. The bath consisted of \( \frac{1}{4}'' \times 10' \) copper tubing coil suspended in a dewar containing any number of solvent/\( CO_2 \) or solvent/\( N_2 \) slushes\(^{27}\) depending on the temperature desired. Methanol was used as the circulating liquid at low temperatures to prevent freezing and the sample compartment was continuously purged with \( N_2 \) to prevent moisture from condensing on the sample cell.

**Synthesis**

Di-\( \alpha \)-chlorotetrakis(ethylene)dirhodium(1), \([\text{Rh} (C_2H_4)_2\text{Cl}]_2\), was prepared according to a method reported by Cramer.\(^{28}\) A solution of 0.6 g (2.28 mmoles) \( \text{RhCl}_3 \cdot 3\text{H}_2\text{O} \) dissolved in 1 ml of \( \text{H}_2\text{O} \) and 7.0 ml methanol was added to a 125 ml Parr pressure bottle containing a magnetic stir bar. The mixture was then purged 5 times with ethylene and finally pressurized to 20 psi. After 15 hours of stirring the solution had changed color and an orange-yellow precipitate had formed. The solid was
filtered and washed with anhydrous methanol in a \( N_2 \) filled glove bag and dried for 2 hours over \( \text{P}_2\text{O}_5 \). (Caution, vacuum drying will result in the loss of ethylene from the complex.) The complex can be stored indefinitely under \( N_2 \) at 0°C.

Di-\( \alpha \)-chlorotetrakis(tri-p-tolylphosphine)dirhodium(I), \([\text{Rh}(\text{P(p-tolyl)}_3)_2\text{Cl}]_2\) was prepared by combined methods reported by Tolman et al. and Wilkinson et al.. In an inert atmosphere box 0.266 g \([\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2\), 0.85g of freshly recrystallized \( \text{P(p-tolyl)}_3 \) and 17 ml toluene were placed in a 50 ml round bottom flask equipped with a Vigreux column. The resulting solution was refluxed with stirring for 3 hours. While still warm, 35 ml of hexanes were added and the solution was allowed to cool. The orange precipitate that formed was filtered, washed with hexanes and dried for 12 hours under vacuum. This complex is found to decompose slowly with time and can be purified by repeated recrystallization in toluene followed by addition of hexanes. Analysis: C, 67.6; H, 5.7; Cl, 5.0. Theoretical: C, 67.5; H, 5.7; Cl, 4.8.

**Thermodynamic Measurements**

Spectrophotometric titration was used to determine the equilibrium constant of the following reaction:

\[
(P(p\text{-tolyl})_3)_2\text{RhClB} + \text{H}_2 \rightleftharpoons (P(p\text{-tolyl})_3)_2\text{RhClB(H)}_2
\]  (4)
Due to extreme O\textsubscript{2} sensitivity of the above reaction a special hydrogen gas flow system was used to vary the hydrogen partial pressure. A series of preset H\textsubscript{2}/N\textsubscript{2} gas mixtures were bubbled through a 0.1 cm UV-vis cell containing a toluene solution of (P(p-toly1)\textsubscript{3})\textsubscript{2}RhClB. Absorbance changes of the hydrogenated complex in the visible range (350-650nm) were recorded after equilibrium was reached with each hydrogen partial pressure.

Equilibrium constants were determined with the Gasuptake program developed by Beugelsdijk\textsuperscript{29} in which the best K\textsuperscript{-1} and (Eo-E) were simultaneously determined. By use of the best fit (Eo-E) calculated for each temperature equilibrium constants were generated for each absorbance change. These K's were then used in a van't Hoff analysis to determine ΔH. In determination of 90\% confidence intervals for ΔH, a degree of freedom was subtracted for each temperature used to account for holding the best fit (Eo-E) constant.

Hydrogen Gas Flow System

A specially designed gas flow system was assembled as shown in Figure 2-2. Hydrogen and nitrogen gas was first passed through L.C. Company O\textsubscript{2} traps removing O\textsubscript{2} up to 0.1 ppm. The gases then enter a Matheson (Model 7352) rotometer fitted with no. 610 tubes where the gases are accurately mixed to the desired N\textsubscript{2}/H\textsubscript{2} ratios. The no. 610 tubes are the most sensitive flow meters available
Figure 2-2. Gas flow system.
from Matheson and are essential for accurate determination of $N_2/H_2$ ratios.

The mixed gas leaving the rotometer enters a brass manifold made up of Swaglok hardware including five gas valves. From here the gas is directed to a specially designed bubbler containing a toluene solution of the rhodium chloride dimer. The bubbler saturates the gas with toluene so that when it is bubbled through the toluene solution in the UV-vis cell, there is no appreciable evaporation. The function of the oxygen sensitive rhodium chloride dimer in the bubbler was to act as a final $O_2$ trap.

The gas now saturated with toluene was bubbled through the bottom of a highly modified 0.1 cm pathlength barrel UV-vis cell (Figures 2-3, 2-4) situated in the thermostated source compartment of a Cary 14 spectrophotometer. The special cell contained a toluene solution of the solution generated monomeric rhodium base adduct. Gas exiting the cell was bubbled through a mineral oil bubbler which maintained a constant internal pressure in the system. A mercury monometer present in the system was used to determine the internal pressure.

Solutions of the various monomeric base adducts were generated by adding enough of each base to a rhodium dimer solution to cause greater than 95% cleavage of the dimer. The amount of each base added was based on equilibrium constants reported by Farris$^{30}$ and Hoselton$^{23}$ for the
Figure 2-3. UV-cell.

A. 1mm pathlength barrel cell
B. #7 O-ring joint
C. Teflon needle valves
Figure 2-4. UV-vis cell holder.

A. Thermostated cell holder
B. UV-vis cell
C. Aluminum cell holder
D. Rubber liner
bridge cleavage reaction. The general operating procedure of the hydrogen gas flow system is described below in an example experiment (refer to Figure 2-2).

The UV-vis cell and the toluene bubbler were removed from the flow system and placed in an inert atmosphere box. The cell was filled with a toluene stock solution that was $2.02 \times 10^{-3} \text{M}$ in $[\text{Rh}(\text{P}(\text{p-tolyl})_3\text{Cl}_2]$ and $8.111 \times 10^{-2}\text{M}$ in $\text{P}(\text{p-tolyl})_3$. The toluene bubbler was loaded with toluene that contained a spatula or two of $[\text{Rh}(\text{P}(\text{p-tolyl})_3\text{Cl}_2]_2$. The teflon valves were closed on both the cell and the bubbler. The cell and bubbler were then removed from the inert atmosphere box and placed back into the flow system.

Having all the valves closed except for valves #3, 6 and 9, the system was evacuated by opening valve #10 which was connected to a vacuum pump. After closing valve #10, the system was then purged with $\text{N}_2$ by opening valve #8. The evacuation-purge cycle was repeated a minimum of five times. Following the final purge with $\text{N}_2$, valves #8 and #6 were closed and valves #4, 5 and 11 were opened.

Valve #8 is opened fully and the rate of $\text{N}_2$ bubbling was now controlled by the rotometer valve. Valve #9, which is the major bypass valve, is slowly closed until a satisfactory bubble rate is achieved in the toluene bubbler. Too high a rate may cause toluene to foam over into the built in trap.
Valves on the cell, #1 and #2, were then opened fully. Valve #3, a minor bypass valve, was slowly closed until the desired cell bubble rate was achieved, about 1 bubble per second. Too rapid a bubble rate may cause evaporation. After the rhodium monomer solution had come to equilibrium with the N₂ in the system, the valves on the cell were closed and the visible spectrum was recorded.

Valve #3 was opened fully and the rotometer valves were adjusted to give the first desired hydrogen partial pressure. The bubbling through the toluene bubbler was adjusted again by valve #9 and the system was allowed to purge for 30 minutes. Following purging, the cell valves were opened and bubbling through the cell solution was adjusted using valve #3. Once the cell solution had come to equilibrium, indicated by no further change in the absorbance spectrum, the cell valves were closed and the visible spectrum was recorded. This same procedure was followed for each additional hydrogen-nitrogen gas mixture.

The rotometer was calibrated prior to the experiment using a soap bubble flow meter connected to valve #7.

Results and Discussions

Fairly extensive thermodynamic and structural studies have previously been done by Farris and Hoselton on the bridge cleavage reaction (Equation 2) of the chloro
bridged dimer \([\text{RhCl}(\text{P(p-tolyl)}_3)_2]_2\) with various sulfur, nitrogen and phosphorous donor bases. Equilibrium constants and heats of reaction obtained for the reaction are shown in Table 2-1.

Based on these results monomer solutions used for the reaction with hydrogen (Equation 1) were made by adding a sufficient quantity of base to a rhodium dimer solution to cleave the dimer by greater than 95%. The ratios of base to dimer concentration suggested by Farris were as follows: \(\text{P(p-tolyl)}_3\), 40:1; THTP, 60:1; pyridine, 40:1. The resulting monomer solutions were then loaded into the cell of the specially designed flow system.

Great care was taken to exclude \(O_2\) while preparing the monomer solutions because of their extreme oxygen sensitivity. Fresh monomer solutions were made before each experiment in an inert atmosphere box. The rhodium dimer which was also oxygen sensitive had to be recrystallized periodically to maintain its purity.

Previously, Farris\(^{30}\) had attempted to determine heats for the reaction of the various base monomers with molecular hydrogen using a variable temperature spectrophotometric titration method utilizing a static gas system. This proved unsuccessful mainly due to problems with oxygen contamination.

An alternative to a static type system is a gas flow type system which was developed for this study (Figure 2-2) and described in detail in the experimental section. The
Table 2-1. Thermodynamic Results for the Interaction of [RhCl(P(p-tolyl)3)]2 with Various Bases at 24±2°C.

<table>
<thead>
<tr>
<th>Base</th>
<th>$\Delta H^a$</th>
<th>$K^a$</th>
<th>$K^b$ (spec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(p-tolyl)3</td>
<td>$-4.7^{+0.3}_{-0.3}$</td>
<td>Large $^e$</td>
<td>-</td>
</tr>
<tr>
<td>Pyridine</td>
<td>$-4.9^{+0.2}_{-0.2}$</td>
<td>Large</td>
<td>$183^{+22}_{-22}$</td>
</tr>
<tr>
<td>THTP</td>
<td>$-1.9^{+0.2}_{-0.2}$</td>
<td>$(1.0^{+0.4}_{-0.4}) \times 10^2$</td>
<td>-</td>
</tr>
<tr>
<td>N-methylimidazole</td>
<td>$-6.6^{+0.2}_{-0.2}$</td>
<td>$(2.4^{+2.0}_{-2.0}) \times 10^4$</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Determined by Calorimetry. $^b$ Determined spectrophotometrically. $^c$ Units of Kcal/mole of monomer formed. $^d$ Reported errors are standard deviations. $^e$ $K_{eq}$ is unknown but assumed to be very large for purpose of calculating $\Delta H_{av}$. 
main advantage of this system is that a positive pressure of \( \text{H}_2 \) and \( \text{N}_2 \) is maintained throughout an experiment which reduces the chance of \( \text{O}_2 \) leaking into the system from the outside atmosphere. One disadvantage of a flow system is that care must be taken to prevent solvent evaporation due to continuously bubbling the various \( \text{H}_2: \text{N}_2 \) gas mixtures through the cell solution. This potential problem was solved first by maintaining a slow continuous bubble rate through the cell solution and second, by placing a toluene bubbler in the gas line before the cell. This aided by prior saturation of the \( \text{H}_2: \text{N}_2 \) gas with toluene minimizing any solvent evaporation due to bubbling gas through the cell.

In order to test the flow system a toluene solution of air stable tetraphenylporphyrin solution was placed in the cell of the flow system. After 2 hours of continuously bubbling \( \text{N}_2 \) through the solution, there was no significant change in its UV-visible spectrum indicating that the toluene bubbler was effectively preventing solvent evaporation.

The changes that occurred in the electronic spectra upon bubbling various partial pressures of hydrogen through solutions of \( (\text{P(p-toly1)}_3)_2\text{RhClB} \) are illustrated in Figures 2-5 and 2-6 for the bases \( \text{P(p-toly1)}_3 \) and THTP respectively. In both cases the shoulder (centered at 430nm for \( \text{P(p-toly1)}_3 \) and 420nm for THTP) on the side of
Figure 2-5. UV spectrum of a toluene solution of $1.86 \times 10^{-3} \text{M}$ $[\text{RhCl} \left( \text{P(p-tolyl)}_3 \right)_2]_2$, and $7.47 \times 10^{-2} \text{M}$ $\text{P(p-tolyl)}_3$ at $35.0^\circ \text{C}$ in equilibrium with various pressures of $\text{H}_2$. (1: $P_{\text{H}_2} = 0.00 \text{ atm}$, 2: $P_{\text{H}_2} = 0.023 \text{ atm}$, 3: $P_{\text{H}_2} = 0.045 \text{ atm}$, 4: $P_{\text{H}_2} = 0.075 \text{ atm}$, 5: $P_{\text{H}_2} = 0.145 \text{ atm}$, 6: $P_{\text{H}_2} = 0.363 \text{ atm}$, 7: $P_{\text{H}_2} = 0.909 \text{ atm}$.)
Figure 2-6. UV spectrum of a toluene solution of $2.98 \times 10^{-3} \text{M}$ [RhCl($P(p$-tolyl)$_3$)$_2$], and $5.79 \times 10^{-2} \text{M}$ THTP at $10.0^\circ\text{C}$ in equilibrium with various pressures of $H_2$. (1: $P_{H_2} = 0.00$ atm, 2: $P_{H_2} = 0.015$ atm, 3: $P_{H_2} = 0.102$ atm, 4: $P_{H_2} = 0.217$ atm, 5: $P_{H_2} = 0.965$ atm.)
a large charge transfer peak decreased in intensity as the concentration of H\textsubscript{2} increased.

An isobestic point was observed in the P(p-tolyl\textsubscript{3}) system at about 350nm probably indicating that only two chromophors were present in solution and that the rhodium monomer was being cleanly converted into the six coordinate cis-rhodium dihydride complex. This provided further evidence supporting what had previously been shown by NMR studies of the reaction. (Caution must be taken not to rely solely on the appearance of an isobestic point. An additional experimental method should be used to determine the actual reaction taking place.)

The spectral data obtained were analyzed using the Rose-Drago\textsuperscript{31} equation (Equation 5)

\[
K^{-1} = P_{H_2} \left( \frac{(A_0) b (E_0 - E)}{A - A^0} \right) - 1
\]

which was modified for the hydrogen uptake experiment.\textsuperscript{32}

In this equation \( P_{H_2} \) is the hydrogen partial pressure bubbled through the solution, \( b \) is the pathlength of the cell, \( A_0 \) is the initial concentration of the acid (Rh monomer), \( A \) is the absorbance of the cis dihydride complex, \( A^0 \) is the absorbance of the acid solution (with no H\textsubscript{2} present), \( (E_0 - E) \) is the difference in the molar absorptivity between the hydrogenated and monohydrogenated complex and \( K^{-1} \) is the inverse of the equilibrium constant for the reaction.
The spectral data and the best determined K and (Eo-E) values at various temperatures are listed in Table 2-2 for the bases P(p-tolyl)$_3$ and THTP. An equilibrium constant previously reported by Tolman et al.\textsuperscript{8} of $40 \pm 3$ atm$^{-1}$ at 25°C corresponds well with the results of this study where at 30.1°C a value of $29.9 \pm 0.26$ atm$^{-1}$ was obtained.

Attempts to study the pyridine adduct produced inconsistent results. This system, unlike the previously described base adduct systems, was not as well behaved and presented a number of complications. The first complication encountered was the extreme $O_2$ sensitivity of the pyridine system. Additional precautions to exclude $O_2$ had to be taken during the generation of the monomer solutions and when flushing the flow system.

Initial spectral results established that the equilibrium constant for the pyridine system was at least an order of magnitude greater than was observed for the P(p-tolyl)$_3$ and THTP adducts. This was a problem because the lowest possible $H_2$ partial pressure that could be accurately delivered by the rotometer was converting most of the pyridine monomer into the hydrogenated form.

To overcome this problem, another Matheson rotometer was added to the flow system. The rotometers were connected in series as illustrated in Figure 2-2. Rotometer 1 diluted the $H_2$ with $N_2$. The mixture then entered the second rotometer reducing the $H_2$ concentration with $N_2$ once again. The double dilution feature of the system allowed
Table 2-2. Thermodynamic Data for the Reaction of RhClB(P(p-toly1)3)2 + H2 &gt; RhClB(P(p-toly1)3)2H2.

<table>
<thead>
<tr>
<th>B</th>
<th>Temp (°C)</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(p-toly1)3</td>
<td>9.0</td>
<td>113.7</td>
</tr>
<tr>
<td></td>
<td>30.1</td>
<td>29.9</td>
</tr>
<tr>
<td></td>
<td>35.0</td>
<td>24.4</td>
</tr>
<tr>
<td></td>
<td>44.0</td>
<td>12.2</td>
</tr>
<tr>
<td></td>
<td>53.8</td>
<td>7.27</td>
</tr>
</tbody>
</table>

\[ \Delta H^b = 11.0 \pm 0.5^c \text{ Kcal/mole} \]

<table>
<thead>
<tr>
<th>THTP</th>
<th>10.0</th>
<th>77.4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15.0</td>
<td>47.6</td>
</tr>
<tr>
<td></td>
<td>20.6</td>
<td>33.9</td>
</tr>
<tr>
<td></td>
<td>30.0</td>
<td>21.5</td>
</tr>
<tr>
<td></td>
<td>40.0</td>
<td>13.2</td>
</tr>
<tr>
<td></td>
<td>50.0</td>
<td>5.91</td>
</tr>
</tbody>
</table>

\[ \Delta H^b = 11.6 \pm 1.0^c \text{ Kcal/mole} \]

a Best fit K. b Determined by van't Hoff analysis, based on generating an equilibrium constant for each absorbance change after the best Eo-E was determined and held constant. c 90% confidence interval.
for the accurate delivery of the very low $H_2:N_2$ ratio gas needed.

A problem encountered which was mainly responsible for the inconsistent results obtained was the observation of a slow secondary reaction occurring during the course of the hydrogen uptake experiment. As seen in the other base systems, reduction in the shoulder absorbance was observed on exposing the pyridine monomer solution to various $H_2$ partial pressures. Once the solution had come to equilibrium with a hydrogen partial pressure, the shoulder absorbance increased slowly with time instead of remaining constant. This phenomenon is attributed to a slow secondary reaction taking place, possibly due to the presence of a large excess of pyridine in solution with the newly formed rhodium dihydride complex. (As in the pyridine experiments, similar problems were encountered with the 1-methylimidazole adduct experiments.)

The two systems that could be investigated ($P(p$-toly$)\_3$ and THTP) fortunately provided a substantial variation in the strength of binding to the Rh(I) center. Enthalpies of hydrogen binding were determined by use of the van't Hoff equation where a plot of $-R\ln K$ vs. $1/T$ yields a straight line with a slope of $\Delta H$ and an intercept of $\Delta S$.

$$-R \ln K = \frac{\Delta H}{T} - \Delta S$$  \hspace{1cm} (6)
Due to the large error limits involved with calculating $\Delta H$ from a plot of only five or six points corresponding to $K$ at each temperature, a method suggested by Breese$^{33}$ was employed to utilize all of the data obtained in the equilibrium constant experiments. His method involves calculating the best $K$ and $(E_0 - E)$ at each temperature. The best $(E_0 - E)$ at a specific temperature is then substituted into the Rose-Drago equation and an equilibrium constant is calculated for each absorbance change. Thus a number of equilibrium constants were determined at each temperature (Table 2-3) instead of only one. The end result was a $\Delta H$ with a much smaller error limit. Care must be taken in determining standard deviations to reduce the degrees of freedom by one for every temperature to account for fixing the value of $(E_0 - E)$.

The van't Hoff plots obtained are shown in Figures 2-7 and 2-8 respectively for the $P(p$-tolyl)$_3$ and THTP systems. The enthalpies obtained are shown in Table 2-2. These enthalpies can be combined with the heat of dissociation of $H_2$ to produce the average metal-hydrogen bond dissociation energies (Table 2-4).

\[
\text{RhClB(P(p-tolyl)$_3$)$_2$(H)$_2$} \rightarrow \text{RhClB(P(p-tolyl)$_3$)$_2$} + \text{H}_2 \quad (7)
\]
\[
\text{H}_2 \rightarrow 2\text{H}^* \quad (104.2 \text{ kcal mole}^{-1}) \quad (8)
\]

\[
\text{RhClB(P(p-tolyl)$_3$)$_2$(H)$_2$} \rightarrow \text{RhClB(P(p-tolyl)$_3$)$_2$} + 2\text{H}^* \quad (9)
\]
<table>
<thead>
<tr>
<th>Temp.</th>
<th>( B )</th>
<th>((\text{Rh})(\text{M}))</th>
<th>( P_{\text{H}_2} ) (atm)</th>
<th>Abs</th>
<th>( K^c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.0°C</td>
<td>4.05 x 10^{-3}</td>
<td>.0246</td>
<td>.356</td>
<td>108.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Eo-E)_a = 1209</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( K_a = 113.7 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CSD = 3.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MSD/CSD_b = 1.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30.1°C</td>
<td>4.05 x 10^{-3}</td>
<td>.0237</td>
<td>.158</td>
<td>29.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Eo-E) = 951.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( K = 29.9 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CSD = .26</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MSD/CSD = 1.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35.0°C</td>
<td>3.72 x 10^{-3}</td>
<td>.0227</td>
<td>.135</td>
<td>21.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Eo-E) = 1095</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( K = 24.4 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CSD = .85</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MSD/CSD = 1.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>44.0°C</td>
<td>4.05 x 10^{-3}</td>
<td>.0224</td>
<td>.087</td>
<td>12.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Eo-E) = 1007</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( K = 12.2 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CSD = .19</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MSD/CSD = 1.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>53.8°C</td>
<td>4.05 x 10^{-3}</td>
<td>.0423</td>
<td>.090</td>
<td>6.37</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Eo-E) = 1047</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( K = 7.27 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CSD = 3.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MSD/CSD = 1.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2-3. Thermodynamic Data on \( \text{RhCl}(\text{P}(\text{p-tolyl})_3)_2\text{B} + \text{H}_2 \leftrightarrow \text{RhCl}(\text{P}(\text{p-tolyl})_3)_2\text{BH}_2 \).
<table>
<thead>
<tr>
<th>Temp.</th>
<th>(Eo-E)</th>
<th>K</th>
<th>CSD</th>
<th>MSD/CSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0°C</td>
<td>847</td>
<td>77.4</td>
<td>.99</td>
<td>1.2</td>
</tr>
<tr>
<td>15.0°C</td>
<td>667</td>
<td>47.6</td>
<td>.94</td>
<td>1.4</td>
</tr>
<tr>
<td>20.6°C</td>
<td>505</td>
<td>33.9</td>
<td>.68</td>
<td>1.5</td>
</tr>
<tr>
<td>30.0°C</td>
<td>541</td>
<td>21.5</td>
<td>1.1</td>
<td>1.8</td>
</tr>
<tr>
<td>40.0°C</td>
<td>442</td>
<td>13.2</td>
<td>.31</td>
<td>2.2</td>
</tr>
<tr>
<td>50.0°C</td>
<td>883</td>
<td>5.91</td>
<td>.31</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Table 2-3. - Continued

<table>
<thead>
<tr>
<th>B</th>
<th>(Rh)(M)</th>
<th>P_H2 (atm)</th>
<th>Abs</th>
<th>K^c</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5.66 x 10^-3</td>
<td>.0147</td>
<td>.256</td>
<td>78.0</td>
</tr>
<tr>
<td></td>
<td>5.66 x 10^-3</td>
<td>.102</td>
<td>.423</td>
<td>73.6</td>
</tr>
<tr>
<td></td>
<td>5.66 x 10^-3</td>
<td>.217</td>
<td>.453</td>
<td>79.0</td>
</tr>
<tr>
<td></td>
<td>5.66 x 10^-3</td>
<td>.371</td>
<td>.464</td>
<td>81.2</td>
</tr>
<tr>
<td></td>
<td>5.66 x 10^-3</td>
<td>.966</td>
<td>.474</td>
<td>90.9</td>
</tr>
<tr>
<td></td>
<td>6.54 x 10^-3</td>
<td>.0147</td>
<td>.178</td>
<td>47.1</td>
</tr>
<tr>
<td></td>
<td>6.54 x 10^-3</td>
<td>.102</td>
<td>.365</td>
<td>50.0</td>
</tr>
<tr>
<td></td>
<td>6.54 x 10^-3</td>
<td>.217</td>
<td>.397</td>
<td>46.2</td>
</tr>
<tr>
<td></td>
<td>6.54 x 10^-3</td>
<td>.371</td>
<td>.412</td>
<td>45.3</td>
</tr>
<tr>
<td></td>
<td>4.75 x 10^-3</td>
<td>.0144</td>
<td>.078</td>
<td>33.6</td>
</tr>
<tr>
<td></td>
<td>4.75 x 10^-3</td>
<td>.0456</td>
<td>.144</td>
<td>33.0</td>
</tr>
<tr>
<td></td>
<td>4.75 x 10^-3</td>
<td>.0993</td>
<td>.188</td>
<td>36.4</td>
</tr>
<tr>
<td></td>
<td>4.75 x 10^-3</td>
<td>.212</td>
<td>.211</td>
<td>34.4</td>
</tr>
<tr>
<td></td>
<td>4.75 x 10^-3</td>
<td>.363</td>
<td>.222</td>
<td>34.3</td>
</tr>
<tr>
<td></td>
<td>4.75 x 10^-3</td>
<td>.946</td>
<td>.231</td>
<td>27.6</td>
</tr>
<tr>
<td></td>
<td>5.14 x 10^-3</td>
<td>.0142</td>
<td>.058</td>
<td>18.5</td>
</tr>
<tr>
<td></td>
<td>5.14 x 10^-3</td>
<td>.0986</td>
<td>.195</td>
<td>23.8</td>
</tr>
<tr>
<td></td>
<td>5.14 x 10^-3</td>
<td>.210</td>
<td>.229</td>
<td>22.2</td>
</tr>
<tr>
<td></td>
<td>5.14 x 10^-3</td>
<td>.359</td>
<td>.245</td>
<td>20.6</td>
</tr>
<tr>
<td></td>
<td>5.14 x 10^-3</td>
<td>.932</td>
<td>.262</td>
<td>17.5</td>
</tr>
<tr>
<td></td>
<td>5.04 x 10^-3</td>
<td>.0136</td>
<td>.030</td>
<td>12.1</td>
</tr>
<tr>
<td></td>
<td>5.04 x 10^-3</td>
<td>.0946</td>
<td>.113</td>
<td>12.1</td>
</tr>
<tr>
<td></td>
<td>5.04 x 10^-3</td>
<td>.202</td>
<td>.159</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>5.04 x 10^-3</td>
<td>.344</td>
<td>.180</td>
<td>16.5</td>
</tr>
<tr>
<td></td>
<td>5.04 x 10^-3</td>
<td>.898</td>
<td>.189</td>
<td>9.3</td>
</tr>
<tr>
<td></td>
<td>5.98 x 10^-3</td>
<td>.0131</td>
<td>.018</td>
<td>2.69</td>
</tr>
<tr>
<td></td>
<td>5.98 x 10^-3</td>
<td>.0912</td>
<td>.190</td>
<td>6.18</td>
</tr>
<tr>
<td></td>
<td>5.98 x 10^-3</td>
<td>.194</td>
<td>.283</td>
<td>5.95</td>
</tr>
<tr>
<td></td>
<td>5.98 x 10^-3</td>
<td>.331</td>
<td>.350</td>
<td>5.93</td>
</tr>
<tr>
<td></td>
<td>5.98 x 10^-3</td>
<td>.864</td>
<td>.440</td>
<td>5.80</td>
</tr>
</tbody>
</table>

^a Best fit K and (Eo-E). ^b CSD is conditional standard deviation and MSD is marginal standard deviation for best fit K. ^c Equilibrium constant for each absorbance change after best fit (Eo-E) was determined and held constant.
Figure 2-7. Van't Hoff plot for the P(p-tolyl)$_3$ system.
\textbf{Ln K vs. }1/T\textbf{ }

\begin{center}
\begin{tikzpicture}
\begin{axis}[
    width=\textwidth,
    height=\textwidth,
    xlabel={$1/T \times 10^{-3}$},
    ylabel={Ln K},
    xmin=3.0, xmax=3.7,
    ymin=1.0, ymax=6.0,
    xtick={3.0,3.1,3.2,3.3,3.4,3.5,3.6,3.7},
    ytick={1.0,2.0,3.0,4.0,5.0,6.0},
    legend pos=south east
\]
\addplot +[only marks,mark options={scale=0.5}] table {
3.0 4.0
3.1 4.5
3.2 5.0
3.3 5.5
3.4 6.0
3.5 6.5
3.6 7.0
3.7 7.5
};
\addlegendentry{$P(p\text{-}toly)_3$}
\end{axis}
\end{tikzpicture}
\end{center}
Figure 2-8. Van't Hoff plot for the THTP system.
Ln $K$ vs. $1/T$

**Legend**
- $\bullet$ = THTP

Axis:
- $\text{Ln } K$
- $\frac{1}{T} \times 10^{-3}$
Table 2-4. Average M-H Bond Energies.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H$ (av. M-H) Kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh(P(p-toly1)$_3$)$_3$Cl(H)$_2$</td>
<td>57.6 ± 0.3</td>
</tr>
<tr>
<td>Rh(P(p-toly1)$_3$)$_2$(THTP)Cl(H)$_2$</td>
<td>57.9 ± 0.5</td>
</tr>
<tr>
<td>Ir(CO)XL$_2$H$_2$</td>
<td>57-61</td>
</tr>
<tr>
<td>Co-H</td>
<td>39 ± 6</td>
</tr>
</tbody>
</table>

a L. Vaska and Werneke.\textsuperscript{34}  b J. Beauchamp and Armentrout.\textsuperscript{35}
Comparing the values obtained for the two base systems, it is immediately apparent that within experimental error the average metal-hydrogen dissociation energies are identical. Thus the rhodium-hydrogen bond strength was found to be insensitive to varying one ligand around the rhodium center.

Based on the observation that two vastly different bases \((P(p\text{-tolyl})_3\) and THTP) had little or no effect on the Rh-H bond strength, it is probably safe to assume that other donor bases, such as pyridine, would also have little effect on the Rh-H bond dissociation energy. Thus the adverse effects the addition of pyridine (mentioned in the introduction) has on hydrogenation by Wilkinson's catalyst is probably due to factors other than those affecting the catalyst's metal hydrogen bond strength.

A variable temperature \(^1\text{H}\text{NMR}\) study reported by Hoselton et al.\(^{22}\) showed that the following kinetic process was taking place in the presence of excess pyridine:

\[
\begin{align*}
\text{P} & \begin{array}{c} \text{H} \\
\text{Rh} & \text{H} \\
\text{Cl} & \text{P}
\end{array} \\
\text{B} & = \text{Py}
\end{align*}
\]

The pyridine which is trans to a hydride was shown to exchange with free pyridine in solution. A proposed intermediate in the reaction was a trigonal bipyramid
"Rh(P(p-tolyl)$_3$)$_2$Cl(H)$_2$" species. The incoming pyridine could attack a position trans to either hydride which would account for the observed averaging of the two inequivalent hydride resonances with increasing temperature.

A similar kinetic process was reported for an analogous Wilkinson's catalyst system, Rh(P(C$_6$H$_5$)$_3$)$_2$Cl(H)$_2$, by Tolman et al. The first order rate constants observed for exchange of pyridine and P(C$_6$H$_5$)$_3$ for the similar intermediate were 50 sec$^{-1}$ and 1000 sec$^{-1}$ respectively at 25°C. This ligand exchange process serves a very important role in the proposed mechanism of Wilkinson's catalyst in that it provides an important open coordination site for the binding of an olefin. The fact that the rate of ligand exchange involving pyridine is an order of magnitude smaller than that observed for P(C$_6$H$_5$)$_3$ may account for added pyridine having adverse effects on catalytic activity due to efficient competition for the olefin binding site by pyridine.

The metal hydrogen bond energies determined can be compared to others reported in the literature (Table 2-4). In a study of the influence of ligand variation in the system Ir(CO)XL$_2$ (where L is a series of phosphines and X is Cl$^-$, Br$^-$, and I$^-$), enthalpies of hydrogenation of 2.7 to 18.1 kcal mole$^{-1}$ were measured corresponding to average metal hydrogen bond energy variations of 53 to 61 kcal mole$^{-1}$. The gas phase neutral
Co-H bond dissociation energy, determined by ion beam techniques,\textsuperscript{35} was reported as 39$\pm$6 kcal mole$^{-1}$.

**Conclusion**

The main purpose of this study was to investigate the process of hydrogen activation by transition metals and to understand what effect ligand environment has on the metal hydrogen bond dissociation energy.

The enthalpy of hydrogen activation by $\text{Rh(P(p-tolyl)}_3\text{Cl}_2$ was obtained for $B = \text{P(p-tolyl)}_3$ and THTP. Attempts to determine enthalpies for pyridine and $N$-methylimidazole systems were unsuccessful. The enthalpies that were obtained were used to determine average metal hydrogen bond dissociation energies. This provided a good estimate of the hydrogen bond energies associated with a good hydrogenation catalyst (Wilkinson's catalyst) and with one of its derivatives. It also greatly increased the amount of available data presently in the literature.

The two bases THTP and $\text{P(p-tolyl)}_3$ fortunately were substantially different so that the effect of ligand variation could be observed. The equilibrium constants obtained for Equation 1 parallel the basicities of the two bases toward the rhodium (I) center. However, the enthalpies obtained for the two systems were remarkably independent of the donor strength.\textsuperscript{37} Thus the average
metal-hydrogen bond energy was found to be insensitive to differences in the two ligands. Assuming this result could be extended to the pyridine system, the adverse effects of adding pyridine to the catalytic system are probably not due to pyridine's effect on the catalyst's metal hydrogen bond strength but more likely due to pyridine blocking important coordination sites on the catalyst.

A final outcome of this study was that a convenient method was developed for the determination of enthalpies of hydrogen activation.
III. IMMOBILIZED HOMOGENEOUS CARBON MONOXIDE REDUCTION CATALYSTS

Introduction

Immobilization of homogeneous transition metal catalysts on various organic or inorganic supports, often termed "hybrid" or "HETMETCO" (heterogenized transition metal complex) catalysts, is presently a very exciting and active field of catalysis research. The overriding goal in this area of research is to combine the advantages of heterogeneous and homogeneous catalysts, while minimizing their inherent deficiencies. A fair number of articles have been published reviewing the growing volume of reported studies involving synthesis, characterization and catalytic properties of supported homogeneous catalysts.

A list showing the major advantages of heterogeneous vs. homogeneous catalysts is given in Table 3-1. Heterogeneous catalysts, viewed by many as being first generation catalysts, have been widely used in industry for many years. One of the major advantages of these catalysts is their ease of separation from reaction products. Other advantages are that heterogeneous systems are generally more thermally stable and less corrosive than homogeneous systems. A major drawback that has hindered the development of heterogeneous catalysts has been the limited number of...
physical techniques available to characterize these systems. Although numerous studies over the years have revealed, little information about the actual active catalyst species, recent advancements in surface techniques such as SEM, ESCA, XPS, Auger etc. have provided a better understanding of the nature of these catalysts.

Table 3-1. Advantages of a Homogeneous Versus Heterogeneous Catalysts.

<table>
<thead>
<tr>
<th>Homogeneous</th>
<th>vs.</th>
<th>Heterogeneous</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. more active</td>
<td>1. separation of catalyst from product</td>
<td></td>
</tr>
<tr>
<td>2. reproducible</td>
<td>2. minimizes reactor corrosion</td>
<td></td>
</tr>
<tr>
<td>3. milder operating</td>
<td>3. more thermally stable</td>
<td></td>
</tr>
<tr>
<td>conditions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. characterization</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. more selective</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Homogeneous catalysts, termed second generation catalysts, are in many ways superior to heterogeneous systems. These catalysts are generally more active, more selective, and because these catalysts are derived from discrete soluble transition metal complexes they lend themselves to study by a large number of physical methods. They have the advantage that their properties can be widely varied by changing the ligand environment around the metal
center and because the composition of the catalyst or catalyst precursor is known these systems are very reproducible.

Industrially, homogeneous catalyst systems are much harder to handle than heterogeneous catalyst systems. One major problem involves the separation of the often precious metal catalyst from the reaction products. Usually, unless the reaction products can be easily distilled from the reaction mixture, such as in the Monsanto process for the carbonylation of methanol to acetic acid, the catalyst-product separation can be a very costly process. Other disadvantages of homogeneous systems are that they are generally more corrosive than heterogeneous systems, and the reaction medium is limited to the solvents in which the catalyst is soluble.

Immobilization of homogeneous catalysts may not only combine the advantages of homogeneous and heterogeneous catalysts but has the potential for some new desirable features. One feature is site isolation of catalytic species. This would prevent catalyst site interactions which are often a mechanism for catalyst deactivation. There is also the potential for site interaction between similar or different catalytic sites placed in close proximity to one another. This could possibly mimic some of the chemistry demonstrated by enzyme systems.

In this study attention will be focused on the use of immobilized homogeneous catalysts in the area of carbon
monoxide reduction catalysts. Known homogeneous ruthenium and iridium CO reduction catalysts have been ionically or covalently attached to inorganic supports. The development of these catalysts was geared toward discovering catalysts capable of selectively producing chemicals from mixtures of CO and H₂ gases, referred to as "syngas," under very mild reaction conditions. The supports chosen were silica gel and alumina functionalized by various organosilanes.

In the course of this study a novel catalytic system for the selective conversion of syngas and HCl to chloromethane was discovered (Equation 1).

\[ \text{H}_2 + \text{CO} + \text{HCl} \xrightarrow{\text{catalyst}} \text{H}_2\text{O} + \text{CH}_3\text{Cl} \] (1)

This reaction occurs under extremely mild conditions, 25°C and 1 atmosphere pressure, and has the potential to be an industrially significant process.

Processes involving the conversion of syngas, such as the Fischer-Tropsch synthesis described in Equation 2, have been known and extensively studied and reviewed since the early 1900's. In the last decade concerns over dwindling petroleum supplies have sparked a renewed interest
in the utilization of syngas as a viable source of chemicals and motor fuels. The Fischer-Tropsch process, which operates at elevated temperatures and pressures, utilizes a heterogeneous catalyst usually consisting of one of the three metals Fe, Co and Ru. The major disadvantage of the Fischer-Tropsch synthesis which has plagued its development since its discovery is its inherent lack of selectivity. Early studies\textsuperscript{51,52} demonstrated that the product distribution produced by traditional Fischer-Tropsch catalysts obeys the simple polymerization model below (Schutz-Flory distribution), Equations 3 and 4. This model assumes chain growth occurs by incorporation of single carbon fragments and that the probability of chain growth is

\[ W_n = n (1 - \alpha)^2 \alpha^{n-1} \quad (3) \]

\[ = \frac{r_p}{r_p + r_t} \quad (4) \]

independent of chain length. The term \( W_n \) represents the weight fraction of a certain carbon number \( n \), is defined as the probability of chain growth and is equal to the rate of polymerization divided by the sum of the rate of polymerization and the rate of termination, and \((1 - \alpha)\) represents the probability of chain termination.

In order to improve selectivity one needs to deviate from this type of Schultz Flory kinetics. Recently, there have been a number of reports\textsuperscript{53} of product distributions deviating significantly from this polymerization model. Product distributions have been altered by using new metal
loading techniques,\textsuperscript{54} selective catalyst poisoning\textsuperscript{55} (i.e. partial sulfiding) and the use of shape selective supports such as zeolites.\textsuperscript{56-58} Although these reports look promising, further work needs to be done to establish whether these effects are experimental artifacts or are due to actual mechanistic effects.

Due to their potential for greater product selectivity, homogeneous carbon monoxide reduction catalysts have been a subject of active research in the last decade. A number of systems involving primarily cobalt\textsuperscript{59,60} rhodium\textsuperscript{61,62} or ruthenium\textsuperscript{63,64} have been developed for the production of mixtures of oxygenated products (i.e. methanol, methylformate, ethylene glycol) but most operate under extreme conditions, with pressures usually exceeding 1000 atmospheres.

More recently several homogeneous systems have been developed which operate under moderate conditions (below 1000 atmospheres). Knifton\textsuperscript{65} at Texaco reported an active catalyst for the direct synthesis of ethylene glycol from syngas at 430 atmospheres and 140-250\textdegree C. The catalyst consisted of a number of ruthenium precursors dissolved in a highly polar molten quaternary phosphonium salt. The active catalyst species based on IR and \textsuperscript{1}H NMR studies was believed to be the anion [HRu\textsubscript{3}(CO)\textsubscript{11}]\textsuperscript{-}.

Two ruthenium based systems were reported by Dombek\textsuperscript{66,67} at Union Carbide. The first involved the monomer Rh(CO)\textsubscript{5}, evidenced by high pressure IR and
believed to be the active catalytic species for the conversion of syngas to methanol at 230°C and 340 atmospheres pressure. The addition of carboxylic acids was found to promote the formation of glycol esters.

The second system involved a substantially more active ruthenium catalyst promoted by ionic iodide promoters and polar solvents. At 230°C and 850 atmospheres H₂ and CO, the primary product was free ethylene glycol. The catalyst precursor, Ru₃(CO)₁₂ was thought to be converted to the two anions [Ru(CO)₃I₃]⁻ and [HRu₃(CO)₁₁]⁻ by the reaction below (Equation 5) in a 2:1 ratio which was found to be the optimum ratio for maximum ethylene glycol production. The absence of either one of the anions results in an inactive system.

\[
\text{Ru}_3\text{(CO)}_{12} + 3\text{I}^- + \text{H}_2 \rightarrow 2[\text{HRu}_3\text{(CO)}_{11}]^- + [\text{Ru(CO)}_3\text{I}_3]^- + 3\text{CO}
\]  

(5)

In 1977 Muetterties and coworkers⁶⁸,⁶⁹ reported a novel homogeneous system which converted syngas to light saturated hydrocarbons under very mild reaction conditions, 180°C and 1-2 atmospheres pressure (Equation 6). The catalyst consisted of the cluster Ir₄(CO)₁₂ in a NaCl-AlCl₃ melt solvent and is the first reported homogeneous system capable of producing non-oxygenated products from syngas.

\[
\begin{align*}
\text{CO} + 3\text{H}_2 & \underset{\text{AlCl₃-NaCl melt}}{\xrightarrow{180°C, 1-2 \text{ atm}}} \text{C}_1 \text{ to C}_4 \text{ alkanes, (CH}_3\text{Cl)}
\end{align*}
\]  

(6)
This report was most significant in that it demonstrated the importance of Lewis acid interactions with metal bound CO, such as demonstrated below, allowing the CO to be reduced under mild conditions. Studies by Collman et al.\textsuperscript{70}

\[ M-\text{C}=\text{O}\ldots\text{Al Cl}_3 \]

further substantiated the above finding but also showed that methylchloride was a reaction product, indicating \text{AlCl}_3 was being consumed during the reaction.

A similar system reported by Muettterties and Choi\textsuperscript{71} showed that \text{Os}_3\text{(CO)}_{12} in a \text{BBr}_3 melt was also an active catalyst for the production of light alkanes under similar conditions and in this case methylbromide was detected as a reaction product.

Methylchloride is an important commodity chemical and its uses and corresponding consumptions in 1977 are listed in Table 3-2.

Table 3-2. Consumption of Methyl Chloride - 1977.

<table>
<thead>
<tr>
<th>Uses</th>
<th>Thousands of Metric Tons\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylchlorosilanes</td>
<td>175</td>
</tr>
<tr>
<td>Tetramethyl Lead</td>
<td>51</td>
</tr>
<tr>
<td>Butyl Rubbers</td>
<td>23</td>
</tr>
<tr>
<td>Other</td>
<td>28</td>
</tr>
<tr>
<td>Total</td>
<td>277</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Data obtained from "Chemical Economics Handbook".\textsuperscript{72}
The two principal commercial processes for producing chloromethane are the chlorination of methane and the methanol-hydrogen chloride process shown below (Equations 7 and 8). The chlorination of methane process

\[ \text{Cl}_2 + \text{CH}_4 \xrightarrow{> 400^\circ C} \text{CH}_3\text{Cl} + \text{HCl} \]  

\[ \text{CH}_3\text{OH} + \text{HCl} \xrightarrow{> 280^\circ C} \text{CH}_3\text{Cl} \]  

can be accomplished with or without a catalyst. Typical catalysts for the process are KCl, CuCl, and CuCl\(_2\) melts. Although the primary product of the process is chloromethane other multichlorinated methanes are produced as well. Presently, the preferred process is the methanol-HCl route, which is very selective for chloromethane, up to 97.8%. Typical catalysts for this process are gamma alumina or phosphoric acid on activated carbon.

An alternative synthesis reported in 1977 by Vannice\(^74\) at Exxon demonstrated that syngas plus a chloride source, such as Cl\(_2\) or HCl, could be used to produce chlorinated hydrocarbons at 200 to 1000\(^\circ\)C and 0.1 to 500 atmospheres pressure. The system consisted of a well dispersed supported catalyst containing Pt/Re, Pt/Ir, Pt, Ir, or Re on an acidic support such as alumina. The predominant product was methyl chloride but other products
such as multichlorinated methanes, ethene, propane and butyl halides were also produced.

Over the years a large number of supports, both organic and inorganic, have been utilized to heterogenize transition metal catalysts. A fairly complete list\textsuperscript{40} is shown in Table 3-3.

Table 3-3. Materials Used to Support Metal Complexes.

<table>
<thead>
<tr>
<th>Inorganic\textsuperscript{a}</th>
<th>Organic\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>silica</td>
<td>polystyrene</td>
</tr>
<tr>
<td>zeolites</td>
<td>polyamines</td>
</tr>
<tr>
<td>glass</td>
<td>silicates</td>
</tr>
<tr>
<td>clay</td>
<td>polyvinyls</td>
</tr>
<tr>
<td>metal oxide (i.e. Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, MgO)</td>
<td>polyallyls</td>
</tr>
<tr>
<td></td>
<td>polybutadiene</td>
</tr>
<tr>
<td></td>
<td>polyamino acids</td>
</tr>
<tr>
<td></td>
<td>urethanes</td>
</tr>
<tr>
<td></td>
<td>acrylic polymers</td>
</tr>
<tr>
<td></td>
<td>cellulose</td>
</tr>
<tr>
<td></td>
<td>cross-linked dextrans</td>
</tr>
<tr>
<td></td>
<td>agarose</td>
</tr>
</tbody>
</table>

\textsuperscript{a} List obtained from Hartley and Vezey.\textsuperscript{40}

In the work presented here both functionalized silica gel and alumina supports were used to ionically attach known
homogeneous CO hydrogenation catalysts. The choice of these supports over other available supports was based on their thermal stability, their intrinsic acidic nature, and the large variety of silanes (containing functional groups) that can be bond to the surface for metal attachment.

The surface of these supports consists of hydroxyl groups which can react with silanes of the formula $R_3\text{Si(CH}_2\text{)_x B (R=Cl, OEt, OMe)}$ by way of the simple condensation reaction shown in Equation 9. 

$$\begin{align*}
\text{OH} + (\text{OEt})_3\text{Si(CH}_2\text{)_x B} & \rightarrow \{\text{OH}\}^{3-y}_3 \quad \text{O-Si(CH}_2\text{)_x B} + 3 \text{ ETOH (9)}
\end{align*}$$

The symbol B represents any number of heteroatom groups (i.e. -P(Ph)$_2$, -NH$_2$, -SH) linked to the surface by a variable length organic chain. The letter Y represents the number of Si-O-Si bonds to the surface, which is dependent on the concentration of organosilane being used. These attached organosilanes can be used directly or modified to support transition metal complexes. The B groups used in the work presented here were -P(Ph)$_2$ and -N(CH$_3$)$_3$I$^-$.
Experimental

Reagents

All solvents and reagents were used as purchased unless otherwise stated. Triethoxypropylaminosilane and 2-(diphenylphosphino)ethyltriethoxysilane were purchased from Petrarch Chemical. Iridium trichloride $\cdot$ $3H_2O$, Ir$_4$(CO)$_{12}$ and Rh$_6$(CO)$_{16}$ were purchased from Strem. Triruthenium dodecacarbonyl, Ru$_3$ and [RhCl(CO)$_2$)$_2$ were purchased from Alfa. Sodium chloride was dried prior to use in an oven at 140°C.

Hydrogen was purchased from Air Products. Both carbon monoxide grade C.P. 99.5% and hydrogen chloride technical grade 99.0% gas were purchased from Matheson.

Silica gel was purchased from W.R. Grace and was Davison grade #62. Its wide pore diameter was 14 mm, pore volume was 1.1 cm$^3$/g and had a specific area of 340 m$^2$. Alumina used was Acid, Brockman Activity I, mesh 80-200. ZnO was purchased from Aldrich.

Instrumentation

All air sensitive manipulations were performed in a Vacuum Atmosphere Co. model HE-43-2 inert atmosphere box. Elemental analyses were performed by the Microanalytical Laboratory, (C,H and N) University of Florida, Gainesville,
Florida, and by Galbraith Laboratories Inc. (Ir and P by ICP) Knoxville, Tennessee.

GC analyses were performed on two different gas chromatographs. One was a model 3700 FID/TC Varian gas chromatograph equipped with a 1/16 inch x 1 meter stainless steel column packed with Chromosorb P supported diethylene glycol adipate (DEGA) and a 1/16 inch x 10 foot stainless steel Poropak Q column. The other was a model 940 FID Varian gas chromatograph equipped with a 1/16 inch x 8 foot stainless steel Poropak Q column.

Infrared spectra were recorded on a Perkin Elmer 283B spectrometer and also on a Nicolet 20DX using diffuse reflectance (spectra performed by Nicolet).

GC mass spectrometry was performed on a AEI MS30 mass spectrometer using a KOITOS DS55 data station and equipped with a PYE Unicam 104 GC containing a 1/4 inch x 5 foot Poropak Q column. Samples were run by Dr. R. King at the Microanalytical Laboratory, University of Florida, Gainesville, Florida.

**Fixed Bed Flow Reactor**

A specially designed gas flow system was assembled as shown in Figure 3-1. Hydrogen and carbon monoxide first enter a Matheson (model 7352) rotometer fitted with No. 610 tubes where the gasses were accurately mixed to the desired H₂CO ratio. When needed, HCl gas was passed through a Matheson #601 flow meter where it was combined with the
Figure 3-1. Fixed bed flow reactor.
already mixed syngas. The amount of HCl added was regulated by teflon needle valve #1. Problems were encountered with maintaining an even flow of HCl, and a pressure release bubbler (D) placed before the flow meter proved helpful. The gasses then were passed through the catalyst bed which consisted of a powder catalyst packed on top of a glass frit and held in place with a plug of glass wool. The gasses leaving the reactor tube were then passed through a CO2/acetone cold trap and exited finally through a mineral oil bubbler. The reactor contained two septa for syringing gas samples for analysis before and after the reactor. The flow of gasses through the catalyst was regulated by the teflon needle valve #2. As this valve was closed, a greater amount of the feed gas was forced through the reactor tube as opposed to exiting through the mineral oil bubbler (C). The reactor was designed so that the reactor could be assembled in an inert atmosphere box. The bypass arm B was designed for purging the system.

Surrounding the reactor tube was a Lindberg (model 123-8) thermostated tube furnace used to regulate the reactor temperature. The entire system was made of glass or teflon tubing due to the corrosive nature of HCl gas.

**Synthesis**

**Silica Gel Bound Propylaminosilane (silica gel)\(^\sim\)NH\(_2\)**

The functionalized support was prepared by a method reported by Leyden et al.\(^ {77} \) In a 125 ml Erlenmeyer flask,
10 g of silica gel was combined with 50 ml toluene. After stirring for 10 minutes, 5 ml of triethoxypropylaminosilane was added. The mixture was stirred for an additional 30 minutes, filtered and the solid was washed with copious amounts of toluene. The solid was air dried followed by heating in an oven at 80°C for 24 hours. Analysis: C, 3.74%; H, 1.08%; N, 1.40%. (Theoretically represents 1.0 mmole silane per gram silica gel.)

Trimethylammonium Iodide Salt of Silica Gel Bound Propylaminosilane (silica gel)~N(CH₃)₃I

The functionalized support was prepared by a method reported by Zombek. In an Erlenmeyer flask equipped with an addition funnel and blanketed with N₂, 10 g of propylaminosilane bound silica gel, 1.13 g 2,6-lutidine and 80 ml DMF were combined. A solution (30 ml) made up of 5.67 g MeI in DMF was added dropwise to the mixture while stirring. Stirring was continued for 15 hours at ambient temperature. The reaction mixture was filtered and the solid washed with acetone and benzene followed by vacuum drying (0.1 mm Hg) for 24 hours. Analysis, C, 4.52%; H, 1.30%; N, 1.22%; I, 8.37%. (Theoretically represents 0.68 mmole trimethylpropylammonium iodide groups per gram.)

Silica Gel Bound Phosphine Silane (silica gel)~P(Ph)₂

The synthetic method was patterned after a preparation reported by Schrader and Studer. Silica gel (5.0 g)
was dried under vacuum at 325°C for 4 hours. In a two neck 30 ml round bottom flask equipped with a reflux condenser and a rubber septum in a nitrogen filled glove bag, the silica gel and 100 ml of 3:1 benzene:p-dioxane (each distilled from CaH₂) were combined. The apparatus was flushed with N₂ for 1/2 hour while vigorously stirring. The stirring rate was reduced, 0.45 ml of 2-(diphenylphospho)ethyltriethoxysilane was syringed in and the mixture was refluxed for 12 hours. After cooling, the solid was filtered in a glove bag, washed with benzene and dried under vacuum for 24 hours at 25°C.

**Silica Gel Bound Phosphine Silane** (High Loading)

The same procedure was used as described above for (silica gel) P(Ph)₂ except the amounts of reagents used were 2 g silica gel, 100 ml 3:1 benzene:p-dioxane and 0.9 ml 2-(diphenylphospho)ethyltriethoxysilane.

**Alumina Bound Phosphine Silane** (alumina) → P(Ph)₂

Alumina (10 g Acid Brockman Activity I mesh 80-200) was washed with dilute HCl and dried in an oven at 90°C for 12 hours. In a 500 ml two neck round bottom flask equipped with a reflux condenser and a rubber septum, the alumina and 200 ml of xylene were combined. The mixture was degassed by bubbling N₂ through the suspension while stirring for 1.5 hours, followed by syringing in 1.5 ml 2-(diphenylphospho)ethyltriethoxysilane and refluxing for
12 hours under N₂. After cooling the solid was filtered, washed with xylenes, toluene, and absolute ethanol followed by drying at 100°C for 24 hours.

\([\text{NET}_4][\text{Ru}_3\text{H(CO)}_{11}]\)

A procedure was used similar to the synthesis reported by Lewis et al.80 All manipulations were performed in an inert atmosphere box, or with Schlenk-ware techniques. In a flask, 0.3291 g \(\text{Ru}_3(\text{CO})_{12}\), 0.1035 g \(\text{NaBH}_4\) and 50 ml tetrahydrofuran (degassed, distilled over \(\text{CaH}_2\)) were combined. After stirring for 30 minutes the solution turned deep red. The mixture was filtered through a frit and the THF was removed under vacuum. The reddish residue was then combined with 20 ml of degassed methanol followed by the addition of 0.132 g tetraethylammonium bromide dissolved in 5 ml methanol. The volume was reduced to 10 ml followed by cooling overnight in a \(\text{CO}_2/\text{acetone}\) bath. The precipitated solid was filtered, washed with a small amount of -78°C methanol and dried under vacuum for 24 hours. Analysis: C, 29.38%; H, 3.53%; N, 1.73%. Theoretical: C, 30.75%; H, 2.85%; N, 1.90%. (Problems were encountered during analysis due to \(\text{O}_2\) sensitivity.)
[Cs][Ru(CO)₃]₃

A procedure was used similar to that reported by Griffith and Cleare.³¹ In a 100 ml round bottom flask equipped with a reflux condenser, 1.1 g anhydrous RuI₃, 8.3 ml hydroiodic acid and 8.3 ml formic acid were combined. The mixture was refluxed and stirred for 12 hours. After cooling, the mixture was filtered and 0.83 g CsCl was added to the filtrate. The solvent was removed on a rotary evaporator, the residue was extracted with absolute ethanol and the solvent was then removed again. Analysis: C, 4.2%; I, 54.8%. Theoretical: C, 6.2%; I, 54.5%. The brownish-yellow residue was recrystallized in absolute ethanol.

Silica Gel Functionalized [RuI₃(CO)₃]⁻ and [HRu₃(CO)₁₁]⁻

In a 50 ml Erlenmeyer flask 0.1136 g of the ammonium iodide salt of silica gel bound propylaminosilane (8.37% I), 0.0222 g Cs[RuI₃(CO)₃] and 20 ml of tetrahydrofuran were combined. The purple mixture was heated while stirring and remained at reflux temperature for 10 minutes. After cooling, the light maroon solid was filtered and washed with THF. The resulting solid was brought into an inert atmosphere box and combined with an intensely maroon colored solution consisting of [NEt₄][HRu₃(CO)₁₁] dissolved in 5 ml of THF. After the mixture was stirred for 10 minutes,
the light maroon colored solid was filtered, washed with THF and dried under vacuum at 25°C.

\[ \text{Ir(CO)}_2\text{Cl(p-toluidine)} \]

A procedure reported by Klabunde\(^8\) was used. In a 100 ml round bottom flask equipped with a reflux condenser and a gas dispersion tube, 1.015 g IrCl\(_3\)-3H\(_2\)O, 0.290 g anhydrous LiCl, 40 ml 2-methoxyethanol and 4.5 ml H\(_2\)O were combined. The apparatus was purged with N\(_2\) through the gas dispersion tube for 15 minutes. The N\(_2\) was switched to CO and a slow bubble rate was maintained while refluxing and stirring for 10 hours. The mixture was cooled and while purging with N\(_2\), 0.377 g of p-toluidine was quickly added. The mixture was stirred for 15 minutes and added to 145 ml of H\(_2\)O. The purple precipitate was filtered in air, washed with 90 ml H\(_2\)O and dried under vacuum for 1 hour. The solution was filtered followed by removal of the solvent under vacuum. Analysis: C, 30.12%; H, 2.53%; N, 3.90%; Theoretical: C, 27.92%; H, 2.24%; N, 3.35%.

(Silica Gel)\(\text{P(Ph)}_2\text{Ir}_4\text{(CO)}_{11}\)

The method used was derived from a preparation reported by Schrader and Studer.\(^7\) In an inert atmosphere box in a 500 ml Parr pressure bottle set-up (described in the experimental section of Part Three) a degassed solution of 76.5 ml 2-methoxyethanol and 2.7 ml H\(_2\)O was combined with
0.055 g Ir(CO)$_2$Cl(p-toluidine), 18 g mossy zinc (acid washed and chopped into small chunks) and the entire yield of the resin resulting from the preparation of silica gel bound phosphine silane (5 g). The system was pressurized to 40 psi ten times with argon followed by ten times with CO. While stirring, the system was pressurized to 55 psi with CO and heated to 90°C. (Note: Good stirring was essential to obtain an active catalyst. A 1/2 inch star stir bar, purchased from Fisher Chemical Co., worked well.) After 24 hours the system was cooled and the slurry was decanted from the mossy zinc in air, followed by filtering. The yellowish support was washed with THF and dried under vacuum for 24 hours at 25°C. (Heating while drying may result in decomposition of the supported carbonyl cluster.) Analysis: Ir, 0.23% (obtained by ICP).

(Silica Gel)$\rightarrow$P(Ph)$_2$Ir$_4$(CO)$_{11}$ (High Loading)

The same procedure was used as above for (silica gel)$\rightarrow$P(Ph)$_2$Ir$_4$(CO)$_{11}$ except the pressure bottle set-up was loaded with 0.110 g Ir(CO)$_2$Cl(p-toluidine), 153 ml 2-methoxyethanol, 5.4 ml H$_2$O, 36 g mossy zinc and the entire yield from the preparation of high loading silica gel bound phosphine silane. Analysis: Ir, 0.69%.
(Alumina) \( \rightarrow \) \( P(\text{Ph})_2\text{Ir}_4(\text{CO})_{11} \)

The same procedure was used as above for

\( \text{(silica gel)} \rightarrow P(\text{Ph})_2\text{Ir}_4(\text{CO})_{11} \) except the reagents

loaded in the pressure bottle set-up were: 3 g alumina bound phosphine silane, 0.056 g \( \text{Ir}(\text{CO})_2\text{Cl}(\text{p-toluidine}) \), 76.5 ml

2-methoxyethanol, 2.7 ml \( \text{H}_2\text{O} \) and 18.0 g mossy zinc.

Analysis: \( \text{Ir} \), 0.75%: \( \text{P} \), 0.84%. (The theoretical \( \text{Ir}_4 : \text{P} \) ratio is 1:27.)

\( \text{Ir}_4(\text{CO})_{12} \) on Silica Gel (Physically adsorbed, 2.5% \( \text{Ir} \))

The method used was derived from a preparation reported

by Howe.\(^{83}\) In a 100 ml round bottom flask, 2.0 g silica
gel (untreated), 0.072 g \( \text{Ir}_4(\text{CO})_{12} \) and 50 ml cyclohexane
were combined. After stirring for 3 hours the solvent was
removed under vacuum and the resulting solid was dried for 6
hours at 25°C.

\( \text{Ir}_4(\text{CO})_{11}P(\text{Ph})_3 \)

The synthesis was derived from a preparation reported

by Shapley and Stuntz.\(^{84}\) In a 250 ml Parr pressure bottle
1 ml \( \text{H}_2\text{O} \) was combined with 30 ml 2-methoxyethanol. Carbon
monoxide was bubbled through the solution for 15 minutes by
way of a syringe needle. Quickly, 0.155 g (0.397 mmole) of
\( \text{Ir}(\text{CO})_2\text{Cl}(\text{p-toluidine}) \), 0.026 g (0.99 mmole) \( P(\text{Ph})_3 \),
3.0 g mossy zinc (acid washed) and a stir bar were added. A
pressure head was placed on the bottle and the system was
purged with 60 psi CO ten times. Under 60 psi CO, the mixture was heated while stirring to 90°C. After 30 minutes the mixture was cooled, the pressure released and the mixture filtered. The yellow filtrate was evaporated to dryness under vacuum.

The residue was dissolved in 50 ml of 5:1 hexanes:methylene chloride solution and added in portions to a 14" long, 1/2" diameter column packed with 230-400 mesh silica gel. The yellow solution separated into two yellow bands upon elution with 5:1 hexanes:methylene chloride. Each band was collected and the solvent was removed under vacuum. The first band off the column yielded a yellow crystalline solid, Ir₄(CO)₁₁P(Ph)₃, and the second band yielded a yellow oil Ir₄(CO)₁₀(P(Ph)₃)₂.

Infrared analysis of both compounds matched well with literature reported spectra.

(OEt)₃Si(CH₂)₂P(Ph)₂Ir₄(CO)₁₁ and

[(OEt)₃Si(CH₂)₂P(Ph)₂]₂Ir₄(CO)₁₀ Mixture

The preparation used was reported by Schrader and Studer. In an inert atmosphere box in a 500 ml Parr pressure bottle, a degassed solution consisting of 100 ml 2-methoxyethanol and 3.2 ml H₂O, 0.20 g IrCl(CO)₂(p-toluidine) and 4.5 g mossy zinc (acid washed) were combined. A pressure head was placed on the bottle and it was purged with 40 psi ten times with argon followed by ten times with CO. Under 55 psi of CO the
system was heated to 90°C while stirring. After 12 hours the mixture was cooled, brought into an inert atmosphere box and filtered. The solvent was removed from the filtrate under vacuum. The IR spectrum of the resulting yellow residue showed characteristic IR bands for both iridium silane complexes. No separation was attempted.

\[ \text{(Alumina)} \rightleftharpoons \text{P(Ph)}_2 \text{IrCl(CO)P(Ph)}_3 \]

The procedure used was derived from a preparation reported by Evans et al.\textsuperscript{85} In a 100 ml round bottom flask, 0.11 g of Ir(CO)Cl(P(Ph))\textsubscript{3} \text{P(Ph)}_2, 1.0 g alumina bound phosphine silane and 55 ml benzene (dried over CaH\textsubscript{2} and distilled) were combined. After the mixture was stirred at ambient temperature for 72 hours under N\textsubscript{2}, the support was filtered, washed with benzene and dried under vacuum.

\text{IrCl(CO)(P(Ph))_3}_2 \text{ on Alumina (Physically adsorbed)}

In a 100 ml round bottom flask, 0.11 g Ir(CO)Cl(P(Ph))\textsubscript{3}, 2.0 g alumina (acid washed) and 50 ml benzene were combined. After stirring at ambient temperature for 120 hours under N\textsubscript{2}, the solvent was removed by vacuum. The support was then dried under vacuum for 12 hours.
Pyrolyzed Rh₆(CO)₁₆ on ZnO (0.6% Rh)

The preparation used was reported by Ichikawa. In a 300 ml round bottom flask, 0.042 g Rh₆(CO)₁₆, 4.0 g ZnO and 200 ml acetone were combined. The mixture was stirred under N₂ for 24 hours and then the solvent was removed under vacuum. The resulting solid was placed in a glass tube and heated to 160°C under vacuum for 2.5 hours.

Results and Discussion

Polymer Supported [Ru(CO)₃I₃]⁻ and [HRu₃(CO)₁₁]⁻

Synthesis and characterization

The support used to attach the ruthenium anions [Ru(CO)₃I₃]⁻ and [HRu₃(CO)₁₁]⁻ was an aminopropylsilane functionalized silica gel that had been modified to a trimethylpropylammonium iodide form. The synthetic procedure for this support is shown in Figure 3-2.

Having a sufficient concentration of quaternary ammonium iodide groups on the silica gel surface was an important consideration. This would allow the ruthenium anions to interact with one another once ion exchanged onto the support. The ruthenium anion interactions are suspected to be important because in Dombek's homogeneous system both anions had to be present in solution for catalysis and neither anion was a good CO reduction catalyst.
Figure 3-2. Synthetic route for the preparation of trimethylpropylammonium iodide functionalized silica gel.
Step 1

\[ \text{OH} + (\text{OEt})_3\text{Si}^\text{NH}_2 \xrightarrow{\text{Toluene}} \text{O}^\text{Si}^\text{NH}_2 \]

Step 2

\[ \text{O}^\text{Si}^\text{NH}_2 + \text{CH}_3\text{I} \xrightarrow{\text{DMF}} \text{O}^\text{Si}^\text{N(CH}_3)_3\text{I} \]
Based on an infrared study, Nyberg and Drago\(^8\) reported that the concentration of organosulfide groups needed on a silica gel support to allow the formation of the rhodium carbonyl dimer shown below was 0.20 mmole S per gram of silica gel.

Elemental analysis of the quaternary ammonium iodide modified support showed that the support contained 8.37% iodine which translates theoretically to 0.63 mmole quaternary ammonium iodide groups per gram of silica gel. Thus the concentration of quaternary ammonium iodide sites should be more than sufficient to allow site interaction.

The anions \([\text{Ru(CO)}_3\text{I}_3]^-\) and \([\text{HRu}_3(\text{CO})_{11}]^-\) were first synthesized separately as shown by Equations 10 and 11, and isolated as the cesium and tetraethylammonium salts respectively.

\[
\begin{align*}
\text{RuI}_3 + \text{HI} + \text{HCOOH} & \xrightarrow{\text{reflux}} \text{CsCl} \xrightarrow{} \text{Cs[Ru(CO)}_3\text{I}_3] \quad (10) \\
\text{Ru}_3(\text{CO})_{12} + \text{Na[BH}_4] & \xrightarrow{\text{THF [NEt}_4]\text{Br}} \xrightarrow{25^\circ\text{C}} \text{[NEt}_4][\text{HRu}_3(\text{CO})_{11}] \quad (11)
\end{align*}
\]
A successful method for ion exchanging the two ruthenium anions onto the support utilized two separate ion exchange reactions in tetrahydrofuran. In the first ion exchange reaction, the modified silica gel support was stirred in a Cs[Ru(CO)₃I₃] THF solution which contained a quantity of [Ru(CO)₃I₃]⁻ ions equal to one half the number of theoretically available quaternary ammonium iodide sites. The infrared spectrum of the isolated support after stirring for 10 minutes at 25°C showed no evidence of [Ru(CO)₃I₃]⁻ being present (Figure 3-3b). Stirring the support for 15 minutes under reflux conditions resulted in an infrared spectrum (Figure 3-3c) containing two fairly intense bands at 2091 and 2021 cm⁻¹ (Table 3-4). These correspond well with the CO stretching bands observed at 2100 and 2027 cm⁻¹ for the KBr spectrum of Cs[Ru(CO)₃I₃] (Figure 3-4a). (The 2027 cm⁻¹ value is the average frequency of the two close bands at 2033 and 2021 cm⁻¹).

The resulting [Ru(CO)₃I₃]⁻ exchanged support was then contacted with degassed, intensely maroon colored THF solution containing the dissolved salt [NEt₄][HRu₃(CO)₁₁]. After 10 minutes of stirring at 25°C the isolated support contained three main infrared bands (Figure 3-4c) in the CO stretching frequency; 2099, 2036 and 1987 cm⁻¹. These infrared bands correspond well with what would result from adding together the two spectra of the separate anions. The infrared result fairly conclusively shows that the modified silica gel support contains both the anions [Ru(CO)₃I₃]⁻
Figure 3-3. Infrared spectra in the range 2500-2600 cm$^{-1}$ of a) (silica gel)$\aggle\ N(CH_3)_3$I, (nujol mull); b) [RuI$_3$(CO)$_3$]$^-$ exchanged at 25°C, (nujol mull); c) [RuI$_3$(CO)$_3$]$^-$ exchanged at reflux temperature, (nujol mull).
Table 3-4. Comparison of Infrared Carbonyl Stretching Frequencies of Supported and Non-Supported Ruthenium Complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Environment</th>
<th>$\nu C=O$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Cs[RuI$_3$(CO)$_3$]</td>
<td>KBr</td>
<td>2100(s), 2033(s) 2021(s)</td>
</tr>
<tr>
<td>2) [NEt$<em>4$][HRu(CO)$</em>{11}$]</td>
<td>CH$_3$CN</td>
<td>2070(w), 2010(s), 1998(s), 1440(m)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[2075(vw), 2018(vs), 1985(s), 1945(m)]$^a$</td>
</tr>
<tr>
<td>3) [RuI$_3$(CO)$_3$]$^-$ on</td>
<td>nujol</td>
<td>2091(vs), 2021(s)</td>
</tr>
<tr>
<td>(Silica Ge1)(\wedge)N(CH$_3$)$_3^+$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4) [RuI$_3$(CO)$_3$]$^-$[HRu$<em>3$(CO)$</em>{11}$]$^-$ on</td>
<td>nujol</td>
<td>2099(s), 2036(Br), 1987(Br)</td>
</tr>
<tr>
<td>(Silica Ge1)(\wedge)N(CH$_3$)$_3^+$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Johnson et al. 80
Figure 3-4. Infrared spectra in the range 2500-1800 cm$^{-1}$ of a) Cs[Ru$_3$(CO)$_3$]$, (KBr); b) [NEt$_4$][HRu$_3$(CO)$_{11}$], (in CH$_3$CN); c) [RuI$_3$(CO)$_3$]$^-$ and [HRu$_3$(CO)$_{11}$]$^-$ on (silica gel) N(CH$_3$)$_3^+$, (nujol mull).
and $[\text{HRu}_3(\text{CO})_{11}]^-$ but the relative concentration of each is unknown.

**Catalysis**

Approximately 0.5 grams of the ruthenium substituted support was placed in a reactor tube in an inert atmosphere box, and the tube was then placed in the flow reactor system described in the experimental section. On passing a 3:1 $\text{H}_2:\text{CO}$ mixture through the catalyst at atmospheric pressure and a flow rate of 10 cm$^3$/minute no products were observed at temperatures below 150°C. At 150°C a small amount of methane was detected along with some $\text{CO}_2$, which is often produced as a byproduct of methanation or Fischer-Tropsch by way of the water gas shift reaction. On raising the temperature to 175°C there was little or no increase in methane production.

**Covalently Supported Ir$_4$(CO)$_{11}$**

**Synthesis**

The method used to attach Ir$_4$(CO)$_x$ (where $x = 10$ or 11) clusters onto the surface of silica gel or alumina involved covalently bonding them to surface bound phosphine silane groups. The synthetic procedure used was derived from work published by Schrader and Studer$^{79}$ and is shown in Figure 3-5. The silane, 2-(diphenylphosphino)ethyltriethoxysilane was first bound to the surface of the support by reaction of the ethoxy groups on the silane with the hydroxyl groups on the support
Figure 3-5. Synthetic route for the preparation of (silica gel or alumina) \( \text{P(Ph)}_2 \text{Ir}_4(\text{CO})_{11} \).
**Step 1**

\[
\text{Step 1}
\]

\[
\begin{align*}
\text{Benzene Dioxane} & \quad \xrightarrow{\text{Reflux}} \\
\text{I} & \quad + \quad \text{(OEt)}_3\text{Si-P(Ph)}_2 \quad \xrightarrow{\text{Benzene Dioxane}} \\
\text{O-Si-P(Ph)}_2 + 3 \text{ETOH}
\end{align*}
\]

**Step 2**

\[
\text{Step 2}
\]

\[
\begin{align*}
\text{I} & \quad + \quad \text{Ir(CO)}_2\text{Cl}(p\text{-toluidine}) \quad \xrightarrow{\text{CO}} \\ & \quad \text{Zn} \quad \xrightarrow{\text{H}_2\text{O}} \\
\text{O-Si-P(Ph)Ir}_2\text{(CO)}_{11}
\end{align*}
\]

2-methoxyethanol
surface. The next step involved assembling the tetrairidium clusters from the monomer Ir(CO)$_2$Cl(p-toluidine) during covalent attachment to the surface bound phosphine groups. Through a fairly extensive FTIR study of the metal loaded silica gel Studer and Schrader demonstrated that the primary species functionalized on the surface was a mixture of the following two clusters, $\text{---P}\text{Ir}_4(\text{CO})_{11}$ and $\text{P}_2\text{Ir}_4(\text{CO})_{10}$.

It was found that complete mixing in the cluster supporting step was an important factor in obtaining an active catalyst. Attempts to double the synthesis procedure (using 10 g of support) resulted in severe stirring problems and thus an inactive catalyst.

The three primary catalyst formulations investigated in this study are shown in Table 3-5 along with their elemental analyses.

Infrared characterization

A fairly extensive Fourier transform infrared study was conducted by Studer and Schrader on tetrairidium clusters bound by 2-(diphenylphospho)ethyltriethoxysilane functionalized silica gel. The characteristic carbonyl stretching bands reported for both the mono-phosphine substituted (silica gel) $\sqrt{\text{P(Ph)}_2}\text{Ir}_4(\text{CO})_{11}$ and the diphosphine substituted (silica gel) $\vee\text{P(Ph)}_2\text{Ir}_4(\text{CO})_{10}$ are listed in Table 3-6. Also included is a summary of
Table 3-5. Elemental Analysis of the Primary Catalyst Formulations.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Wt%</th>
<th>Ir</th>
<th>P</th>
<th>H</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (Silica Gel) V P(Ph)₂Ir₄(CO)₁₁</td>
<td>.23</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2. (Silica Gel) V P(Ph)₂Ir₄(CO)₁₁</td>
<td>.69</td>
<td>-</td>
<td>6.40</td>
<td>1.34</td>
<td>-</td>
</tr>
<tr>
<td>3. (Alumina) V P(Ph)₂Ir₄(CO)₁₁</td>
<td>.75</td>
<td>.84</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 3-6. Infrared Spectra of Silica Gel or Alumina Bound Tetrairidium Clusters and Molecular Analogs.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Environment</th>
<th>ν_CO (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir₄(CO)₁₁P(Ph)₃</td>
<td>Cyclohexane</td>
<td>2082w, 2048s, 2013m, 1869vw, 1853m, 1829m</td>
</tr>
<tr>
<td>Ir₄(CO)₁₁P(Ph)₃ a</td>
<td>CH₂Cl₂</td>
<td>2088m, 2056vs, 2020s, 1887vw, 1847m, 1825m</td>
</tr>
<tr>
<td>Ir₄(CO)₁₁P(Ph)₃ on Alumina</td>
<td>Nujol</td>
<td>2083w, 2051s, 2019m</td>
</tr>
<tr>
<td>(Silica) (√ P(Ph)₂)Ir₄(CO)₁₁ a</td>
<td>Wafer</td>
<td>2090m, 2061m, 2023m, 1890vw, 1825m, 1835m</td>
</tr>
<tr>
<td>(Silica) (√ P(Ph)₂)₂Ir₄(CO)₁₀ a</td>
<td>Wafer</td>
<td>2074s, 2050vs, 2017m</td>
</tr>
<tr>
<td>(Alumina) (√ P(Ph)₂)₁,(2)Ir₄(CO)₁₁,(10)</td>
<td>Diffuse Reflectance</td>
<td>2114m, 2060m, 2004s</td>
</tr>
<tr>
<td>(Silica) (√ P(Ph)₂)₁,(2)Ir₄(CO)₁₁,(10)</td>
<td>Nujol</td>
<td>2092sh, 2070sh, 2041s, 2005m</td>
</tr>
</tbody>
</table>

a Schrader and Studer.⁷⁹
spectra taken of the polymer bound tetrairidium clusters and molecular analogs used in this study.

The majority of the spectra were taken on a Perkin Elmer 283B grating spectrometer except for the spectra of \( \text{Ir}_4(\text{C}0)_x \) \((x=10 \text{ or } 11)\) bound to phosphine functionalized alumina. These spectra were done by Nicolet on a Nicolet 20DX FT infrared spectrometer, using the diffuse reflectance technique.

Spectra obtained for silica gel bound tetrairidium clusters at two different iridium concentrations, 0.23% and 0.69%, are shown in Figure 3-6. At the low iridium concentration (0.23%) the carbonyl stretching frequencies due to the tetrairidium cluster were almost indistinguishable from the background. The infrared spectrum of the 0.69% Ir support showed more pronounced carbonyl stretching bands. However accurate measurement of these bands was difficult due to the limitations of the IR spectrometer. Therefore it was difficult to determine if the tetrairidium cluster was mono or diphosphine substituted.

The spectra taken on the analogous alumina system \((\text{Ir} = 0.75\%)\) were more conclusive. Figure 3-7 (a,b) shows the FTIR spectra of the phosphine silane supported alumina and metal supported phosphine silane functionalized alumina. The spectrum resulting from the subtraction of spectrum (a) from (b) is shown in (c). The remaining three bands, 2114, 2060 and 2004 cm\(^{-1}\) of the tetrairidium
Figure 3-6. Infrared spectra (nujol mulls) in the range 2500-1600 cm⁻¹ of (silica gel)\(^{\wedge}\)P(Ph)\(_2\)Ir\(_4\)(CO)\(_{11}\) a) 0.23% Ir; b) 0.69% Ir.
Figure 3-7. Fourier transform infrared spectra in the range 4000-400 cm\(^{-1}\) (diffuse reflectance) of a) (Alumina)\(~\wedge\) P(Ph)\(_2\), b) (Alumina)\(~\wedge\) P(Ph)\(_2\)Ir\(_4\)(CO)\(_{11}\), c) b-a.
cluster correspond more closely to the spectrum reported for the monophosphine supported cluster,
(silica gel)\(\wedge\) P(Ph)\(_2\)Ir\(_4\)(CO)\(_{11}\)\.

Figure 3-8 shows the infrared spectrum of
Ir\(_4\)(CO)\(_{11}\)P(Ph)\(_3\) before and after physical adsorption (spectrum a and b respectively) onto the surface of alumina. The spectrum of the cluster in cyclohexane and the nujol spectrum of the cluster on alumina correspond well with the spectrum of the cluster in CH\(_2\)Cl\(_2\) reported in the literature\(^7^9\) (Table 3-6).

Catalysis

A summary of the products produced by the following catalyst studies are shown in Table 3-7. The polymer supported tetrairidium cluster catalyst was first tested under conditions similar to those reported by Collman et al.\(^7^0\) and Muetterties et al.\(^6^9\) for the Ir\(_4\)(CO)\(_{12}\)/AlCl\(_3\)-NaCl system. In the gas flow system described in the experimental section the reactor tube was loaded with a physical mixture of 0.7 g of
(silica gel)\(\wedge\) P(Ph)\(_2\)Ir\(_4\)(CO)\(_{11}\) (0.23% Ir), 8 g AlCl\(_3\) and 1.8 g NaCl. Syngas containing a 3:1 H\(_2\):CO mixture was passed through the catalyst bed at slightly above atmospheric pressure.

On heating the catalyst mixture to 145°C the polymer became suspended in the now liquid 2:1 AlCl\(_3\)-NaCl melt. A GC trace of the effluent gas is shown in Figure 3-9. The
Figure 3-8. Infrared spectra in the range 2500-1800 cm$^{-1}$ of a) Ir$_4$(CO)$_{11}$P(Ph)$_3$, (in cyclohexane); b) Ir$_4$(CO)$_{11}$P(Ph)$_3$, physically adsorbed on alumina, (nujol mull).
Table 3-7. Product Produced on Exposure to 1:3 CO:H₂.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Products 25°C</th>
<th>Products 145°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (SG)(\wedge)P(Ph)(_2)Ir(<em>4)(CO)(</em>{11}) / AlCl(_3)-NaCl(^b)</td>
<td>CH(_3)Cl</td>
<td>CH(_4), C(_2)H(_6), CH(_3)Cl</td>
</tr>
<tr>
<td>2. Ir(<em>4)(CO)(</em>{12}) / AlCl(_3)-NaCl</td>
<td>N.A.</td>
<td>CH(_4), C(_2)H(_6), CH(_3)Cl</td>
</tr>
<tr>
<td>3. (SG)(\wedge)P(Ph)(_2)Ir(<em>4)(CO)(</em>{11}) / P(but)(_4)Br</td>
<td>N.A.</td>
<td>CH(_4), C(_2)H(_6)</td>
</tr>
<tr>
<td>4. (SG) / AlCl(_3)-NaCl</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>5. (SG)(\wedge)P(Ph)(_2) / AlCl(_3)-NaCl</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
</tbody>
</table>

\(^a\) N.A. = no activity.  \(^b\) SG = silica gel.
Figure 3-9. GC traces of the products produced from CO and H₂ by (Silica Gel)\(\sqrt{P(Ph)_{2}Ir_{4}(CO)_{11}}\) and AlCl₃-NaCl at 25°C (attenuation = 1, 500 l sample, Poropak Q). a) After 0.25 hr. b) After 1.75 hr.
identified products observed were methane, ethane, and chloromethane which are some of the same products observed in the homogeneous Ir₄(CO)₁₂/AlCl₃-NaCl system.

While still hot and under O₂ free conditions the molten AlCl₃-NaCl was filtered through the frit in the reactor tube leaving the silica gel support behind. The resulting AlCl₃-NaCl melt, which solidified at room temperature, was transferred to another reactor tube and tested for its CO reduction activity. The melt showed similar activity and product selectivity. As a check, a mixture of unsubstituted silica gel and AlCl₃-NaCl was tested and showed no catalytic activity.

Based on the above evidence, it appears that the polymer supported tetrairidium cluster in an AlCl₃-NaCl melt solvent undergoes the phosphine exchange reaction with CO shown in Equation 12 generating a homogeneous system consisting of unsupported Ir₄(CO)₁₂ in molten AlCl₃-NaCl.

\[
\text{CO} \\
\text{(Silica Gel)} \uparrow \text{P(Ph)}₂ \text{Ir₄(CO)₁₁} \rightarrow \text{(Silica Gel)} \uparrow \text{P(Ph)}₂ + \text{AlCl₃-NaCl} \quad \text{Ir₄(CO)₁₂ (12)} \\
145°C
\]

Thus at melt temperatures there is no benefit in covalently supporting the tetrairidium cluster as it quickly leached off of the support.
However, below melting temperatures in this system an interesting new observation was made. At $25^\circ$C, on passing 3:1 $H_2:CO$ syngas through the physical mixture, CO reduction was observed to produce a single product. This product has been identified using two GC columns (Poropak Q and DEGA) and GC mass spectrometry (discussed later) as chloromethane.

The production of $CH_3Cl$ decreased steadily with time as shown in Figure 3-10 where the intensity of the GC peak had greatly decreased after 1.75 hours on stream. The unsupported cluster $Ir_4(CO)_{12}$ was tested under conditions similar to those used for the polymer supported cluster. A physical mixture of 0.05 g $Ir_4(CO)_{12}$ with $AlCl_3-NaCl$ was tested. No activity was observed below melting temperature ($75^\circ$C). At $75^\circ$C partial melting occurred and intense GC peaks were observed for methane, ethane, $CH_3Cl$ and some larger products at retention times above 10 minutes.

The phosphine substituted support (no Ir present) combined with $AlCl_3$ was tested and found to also be inactive for $CH_3Cl$ production. Thus the polymer supported iridium cluster species is important in the chemistry observed at $25^\circ$C.

(Silica gel)$\wedge P(Ph)_{2}Ir_{4}(CO)_{11}$ (0.23% Ir) was tested in another polar melt salt, tetrabutylphosphonium bromide (melting point 100-103°C). Passing syngas through
Figure 3-10. GC traces of the products produced from CO and H₂ by (Silica Gel)\(^{\text{P(Ph)}_2\text{Ir}_(CO)_1}\) and AlCl₃-NaCl at 145°C (attenuation = 2, 500₁ sample, Poropak Q).
a physical mixture of 0.7 g supported \( \text{Ir}_4(\text{CO})_{11} \) and 4 g tetrabutylphosphonium bromide resulted in no activity below 175°C. Above 175°C a small amount of methane and ethane was observed along with some unidentified peaks at retention times greater than 10 minutes.

**CH₃Cl catalyst development**

The novel chemistry observed for the selective production of CH₃Cl by silica gel supported \( \text{Ir}_4(\text{CO})_{11} \cdot \text{AlCl}_3 \) under mild conditions warranted testing its potential use as a CH₃Cl catalyst.

At 25°C a catalyst consisting of a physical mixture of 0.7 g (silica gel)\( \checkmark \) P(Ph)₂Ir₄(CO)₁₁ (0.23% Ir) and 0.1 g AlCl₃ was exposed to 3:1 H₂:CO gas. Methylchloride activity was observed but it dropped off rapidly with time.

The addition of anhydrous HCl to the feed gas, the feed now approximately 3:1:0.8 H₂:CO:HCl, resulted in restoration of the initial CH₃Cl activity. This cycle of loss and gain of activity corresponding to the presence and absence of HCl in the feed could be repeated numerous times. The loss of chlorine (the source being AlCl₃) from the catalyst mixture, which leads to rapid loss in activity, can thus be counteracted by addition of HCl gas to the feed. Temporary exposure of the catalyst to O₂ after previous exposure to the syngas-HCl feed resulted in permanent deactivation of the catalyst.
The proposed role of AlCl$_3$ in Muetterties' et al. homogeneous system was to aid in the activation of metal bound carbonyls to allow reduction by hydrogen under milder conditions (shown below). Also, the AlCl$_3$ provides a chloride source for the minor production of CH$_3$Cl.

\[ M-\text{C}=\text{O} \cdots \text{AlCl}_3 \]

It is believed that AlCl$_3$ plays a similar beneficial role in the polymer supported phosphine tetrairidium cluster system. However, the presence of AlCl$_3$ in the catalyst formulation was detrimental to use of the catalyst at elevated temperatures due to the low melting point of AlCl$_3$. As demonstrated previously upon melting the AlCl$_3$, the attached cluster leached off the support generating the non CH$_3$Cl selective homogeneous system. (Table 3-7, catalyst 1).

Both the silica gel functionalized and a similar alumina functionalized phosphine tetrairidium cluster were tested for their ability to convert syngas and HCl(g) to CH$_3$Cl in the absence of AlCl$_3$. In both cases after an initial 15-20 minute induction period, CH$_3$Cl was observed as the primary product at 25°C. Increasing reaction temperature from 25°C up to 100°C greatly increased catalyst activity while maintaining its selectivity for CH$_3$Cl. Figures 3-11 and 3-12 show the GC traces at
Figure 3-11. GC traces (Poropak Q) of the products produced from syngas and HCl by (Alumina)\( \flows \)P\( \text{Ir}_4\text{CO})_{11} \) at a) 50°C and b) 100°C.
Figure 3-12. GC traces (Poropak Q) of the products produced from syngas and HCl by (silica gel)\(^{\wedge}\)P\(_{4}\)Ir\(_{4}(CO)_{11}\) a) .23% Ir, 25°C; b) .23% Ir, 100°C; c) .69% Ir, 100°C.
select temperatures for the alumina and silica gel based systems respectively.

In the two figures, the initial three peaks labeled 1, 2 and 3 observed for the majority of the reported GC traces correspond to CH\textsubscript{4}, CH\textsubscript{2}CH\textsubscript{2}, and HCl respectively. The methane observed results from an impurity in the CO gas source. The ethylene observed is an impurity found in the HCl source. The HCl source also contains a slight CH\textsubscript{3}CH\textsubscript{2}Cl impurity. As can be seen qualitatively, CH\textsubscript{3}Cl (peak 4) is the principle product observed in both the silica and alumina systems. The positively identified secondary products designated by the numbers 5, 6 and 7 correspond to acetylaldehyde, methylformate and ethylchloride respectively and are present in both systems although the relative amounts vary. (Products were positively identified by GC mass spectrometry, discussed later). The alumina catalyst seemed to produce more ethylchloride relative to the other minor products than the silica gel catalysts. Also, the unidentified impurity between peaks 6 and 7 is slightly more prominent in the alumina case. Comparison of a 0.23% Ir and a 0.69% Ir silica gel supported catalyst shows no significant difference in product selectivity as evidenced by the almost identical GC traces at 100\textdegree{}C (Figure 3-12, b and c).

The induction period observed before the appearance of CH\textsubscript{3}Cl was probably due to the formation of surface chloride species, resulting from the reaction of surface
hydroxyls with HCl as shown in Equation 13. These surface

\[
\begin{align*}
\text{OH} & \quad \text{OH} \quad \text{OH} \rightarrow \quad \text{Cl} \\
\text{Alumina or silica} & \\
\end{align*}
\]

Si-Cl or Al-Cl species could then act in a manner similar to that previously proposed for AlCl₃ in aiding the reduction of carbon monoxide.

The activities of various silica gel and alumina catalysts at various temperatures for the production of CH₃Cl are listed in Table 3-8. The activities are based on the rate of CH₃Cl leaving the reactor and do not take into account any deactivation which might have occurred over the time the catalysts were tested. Comparison of the two silica gel based catalysts containing 0.23% and 0.69% Ir shows that increasing the metal loading on the support results in an increase in the production of CH₃Cl per gram of catalyst. This increase in activity appears to be more substantial at the higher reaction temperatures. The alumina based catalyst which has the highest percent iridium of the three catalysts listed, 0.75%, showed the highest activity per gram of catalyst.

Table 3-9 illustrates the data in terms of the turnover numbers of these same catalysts. The turnover number is defined as the moles of CH₃Cl produced per tetrairidium
### Table 3-8. Chloromethane Activities Per Gram Catalyst.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CH$_3$Cl Activity$^a$ (mole/sec • g catalyst)</th>
<th>25°C</th>
<th>50°C</th>
<th>75°C</th>
<th>100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (Silica Gel) $\checkmark$ P(Ph)$_2$Ir$<em>4$(C0)$</em>{11}$</td>
<td>3.4X10$^{-11}$</td>
<td>2.5X10$^{-10}$</td>
<td>4.6X10$^{-10}$</td>
<td>1.5X10$^{-9}$</td>
<td></td>
</tr>
<tr>
<td>(Ir = .23%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. (Silica Gel) $\checkmark$ P(Ph)$_2$Ir$<em>4$(C0)$</em>{11}$</td>
<td>8.6X10$^{-11}$</td>
<td>4.6X10$^{-10}$</td>
<td>1.6X10$^{-9}$</td>
<td>7.7X10$^{-9}$</td>
<td></td>
</tr>
<tr>
<td>(Ir = .69%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. (Alumina) $\checkmark$ P(Ph)$_2$Ir$<em>4$(C0)$</em>{11}$</td>
<td>-</td>
<td>6.4X10$^{-10}$</td>
<td>2.6X10$^{-9}$</td>
<td>1.1X10$^{-8}$</td>
<td></td>
</tr>
<tr>
<td>(Ir = .75%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Exit gas flow rate .02 - .04 ml/sec.
### Table 3-9. Turnover Rates of CH$_3$Cl Per Tetrairidium Cluster.

<table>
<thead>
<tr>
<th></th>
<th>Turnover # (molecules CH$_3$Cl/Ir$_4$·Sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25°C</td>
</tr>
<tr>
<td>1. (Silica Gel)$\Leftrightarrow$P(Ph)$_2$Ir$_4$(CO)$_n$</td>
<td>1.13X10$^{-5}$</td>
</tr>
<tr>
<td>(Ir = 0.23%)</td>
<td></td>
</tr>
<tr>
<td>2. (Silica Gel)$\Leftrightarrow$P(Ph)$_2$Ir$_4$(CO)$_n$</td>
<td>9.58X10$^{-6}$</td>
</tr>
<tr>
<td>(Ir = 0.69%)</td>
<td></td>
</tr>
<tr>
<td>3. (Alumina)$\Leftrightarrow$P(Ph)$_2$Ir$_4$(CO)$_n$</td>
<td>-</td>
</tr>
<tr>
<td>(Ir = 0.75%)</td>
<td></td>
</tr>
</tbody>
</table>
cluster per second. A plot of turnovers vs. temperature for the catalysts is shown in Figure 3-13.

Comparison of the 0.23% and 0.69% silica gel catalysts showed that at 25°C and 50°C the 0.23% Ir was more active per metal cluster. At higher temperatures, 75°C and 100°C, the 0.69% Ir catalyst becomes more active than the 0.23% Ir catalyst. The alumina catalyst, which had an even higher iridium concentration (0.75%), had a turnover number at 50°C between the two silica gel catalyst values. However, at 75°C and more so at 100°C this catalyst was the most active per tetrairidium cluster.

It is difficult to place a high level of confidence in the differences observed in the activities of these catalysts. This is due to the substantial error introduced in the activity measurements especially at lower temperatures. But if the differences can be believed at higher temperatures it appears that in the concentration range studied the activity for the production per metal cluster increases with metal loading.

The differences observed may be due to many factors other than metal loading, such as support interactions, concentration of phosphine on the surface, and deactivation processes all of which need to be explored further.

Based on the results to date, chloromethane appears to be the primary product of this catalytic reaction, though total confidence cannot be placed in this statement without
Figure 3-13. Plot of turnover number versus temperature for both silica gel and alumina supported tetrairidium cluster catalysts.
TURNOVER # vs. TEMP.

LEGEND
- □ = Silica Ir=.23%
- ○ = Silica Ir=.69%
- △ = Alumina Ir=.75%
a proper material balance which was not possible with the current experimental setup.

The rate of CH$_3$CH$_2$Cl production by the alumina supported catalyst at 100°C was estimated to be on the order of 4 x 10$^{-11}$ mole/sec·g of catalyst. Based on the assumption that the production of the other impurities observed was similar to CH$_3$CH$_2$Cl, the selectivity toward the production of CH$_3$Cl was calculated to be greater than 99%.

A byproduct observed condensing at the top of the reactor tube for both the silica gel and the alumina catalysts was H$_2$O. No detectable quantity of CO$_2$ was observed being produced indicating that all of the carbon monoxide oxygen (except for the small amount of oxygen contained in the minor products) was going into the production of H$_2$O. GC analysis of a H$_2$O sample using a TC detector and a DEGA column showed the presence of two unknown high molecular weight and/or polar compounds at retention times 4.16 and 6.07 minutes (Figure 3-14). No such compounds were observed with the alumina catalyst.

Qualitatively, the rate of production of CH$_3$Cl appeared stable at temperatures less than or equal to 75°C for these tetrairidium supported catalysts for weeks. At 100°C there was some catalyst deactivation with time. One factor that was observed to affect catalyst stability was the concentration of unreacted HCl gas leaving the reactor. If the HCl gas in the feed was adjusted to minimize HCl in
Figure 3-14. GC traces of the products present in the water produced from syngas and HCl by (Silica Gel)\(\wedge\)P(Ph)\(_2\)Ir\(_4\)(CO)\(_{11}\) (.23% Ir) at 80°C (attenuation = 1, DEGA column).
the exit gas, the catalyst qualitatively appeared more stable. The amount of HCl in the exit gas was monitored by GC.

Prior to exposure to HCl, the catalysts are stable to air at room temperature. Once exposed to HCl-syngas, subsequent exposure to oxygen renders the catalyst inactive. This indicates the active catalyst species, or an intermediate species in the catalytic cycle, is oxygen sensitive unlike the catalytic precursor.

Table 3-10 lists the experimental results for a number of different systems tested for catalytic activity. These were designed to help understand what property(s) are most important to the catalytic activity of the silica gel and alumina covalently supported tetrairidium cluster catalyst.

A catalyst of physically adsorbed \( \text{Ir}_4(\text{CO})_{12} \) (2.5% Ir) on silica gel was found to be inactive for the production of \( \text{CH}_3\text{Cl} \) from syngas and HCl up to 100°C. Based on the GC retention time a small amount of what was believed to be \( \text{CH}_3\text{CH}_2\text{Cl} \) was observed being produced at 80°C. On heating to 150°C the light yellow catalyst turned grey (indicating decomposition to iridium metal) followed by production of a small amount of \( \text{CH}_4 \), \( \text{CH}_3\text{Cl} \) and other higher molecular weight hydrocarbons. This result, along with the observation discussed earlier that \( \text{Ir}_4(\text{CO})_{12} + \text{AlCl}_3 \) does not produce \( \text{CH}_3\text{Cl} \) at low temperatures, illustrates the importance of the substituted
Table 3-10. Qualitative Activities Observed for the Production of CH₃Cl from Syngas and HCl.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Activity</th>
<th>100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir₄(CO)₁₂ on Alumina (2.5% Ir)</td>
<td>inactive</td>
<td></td>
</tr>
<tr>
<td>(OEt)₃Si[P(Ph)₂]Ir₄(CO)₁₁ and [(OEt)₃Si[P(Ph)₂]₂]Ir₄(CO)₁₀</td>
<td>slight activity</td>
<td></td>
</tr>
<tr>
<td>Ir₄(CO)₁₁P(Ph)₃ + AlCl₃</td>
<td>inactive</td>
<td></td>
</tr>
<tr>
<td>Ir₄(CO)₁₁P(Ph)₃ on Alumina</td>
<td>inactive</td>
<td></td>
</tr>
<tr>
<td>Ir(CO)Cl(P(Ph)₃)₂ on Alumina</td>
<td>inactive</td>
<td></td>
</tr>
<tr>
<td>(Alumina)(\text{P(Ph)}₂)Ir(CO)ClP(Ph)₃</td>
<td>slight activity</td>
<td></td>
</tr>
<tr>
<td>Rh₆(CO)₁₆ on ZnO (pyrolyzed)</td>
<td>inactive</td>
<td></td>
</tr>
</tbody>
</table>
phosphine and/or the phosphine silane linkage to the clusters catalytic activity.

The compounds \((\text{OEt})_3\text{Si}\bigwedge\text{P(Ph)}_2\text{Ir}_4(\text{CO})_{11}\) and \([(\text{OEt})_3\text{Si}\bigwedge\text{P(Ph)}_2]_2\text{Ir}_4(\text{CO})_{10}\) which are believed to be the molecular analogs of the supported clusters, were synthesized\(^7\) and tested for \(\text{CH}_3\text{Cl}\) activity. The material isolated from the preparation consisted of a mixture of the two complexes and 0.1 g of this material was mixed with 4.0 g AlCl\(_3\) in an inert atmosphere. On exposure to syngas and HCl at 25\(^\circ\)C, this solid catalyst showed slight activity for \(\text{CH}_3\text{Cl}\).

A similar molecular analog was tested, \(\text{Ir}_4(\text{CO})_{11}\text{P(Ph)}_3\), which contained \(\text{P(Ph)}_3\) instead of a phosphine silane group. This was mixed with AlCl\(_3\) (0.01 g \(\text{Ir}_4(\text{CO})_{11}\text{P(Ph)}_3\), 3.5 g AlCl\(_3\)) and showed no production of \(\text{CH}_3\text{Cl}\) at 25\(^\circ\)C. When the temperature was increased, the production of \(\text{CH}_3\text{Cl}\) was observed along with production of \(\text{CH}_4\) indicating that partial melting of the AlCl\(_3\) may have occurred.

The monophosphine complex \(\text{Ir}_4(\text{CO})_{11}\text{P(Ph)}_3\) physically adsorbed onto alumina was also tested for its \(\text{CH}_3\text{Cl}\) activity. As seen in the previous test (\(\text{Ir}_4(\text{CO})_{11}\text{P(Ph)}_3\) mixed with AlCl\(_3\)) no \(\text{CH}_3\text{Cl}\) production was detected on exposure to syngas and HCl at 25\(^\circ\)C. No products were observed up to 100\(^\circ\)C. At 100\(^\circ\)C, a small amount of \(\text{CH}_3\text{Cl}\) was observed along with
CH₄. Problems with isolating Ir₄(CO)₁₀(P(Ph)₃)₂ during synthesis prevented testing it for catalytic activity.

The results of the molecular analog tests illustrated that the role of the covalent linkage to the phosphine silane may be important to the low temperature production of CH₃Cl. The inactivity of the monophosphine cluster P(Ph)₃Ir₄(CO)₁₁ for production of CH₃Cl at 25°C could be explained in a number of ways: 1) as well as supplying a phosphine ligand, the phosphine silane may be playing an additional role in the chemistry, 2) the diphosphine substituted cluster might be the active species and 3) there may be enough of a difference in the electronic properties of the silane phosphine and P(Ph)₃ to alter the chemistry.

In an attempt to illustrate that an iridium cluster is needed to facilitate the low temperature reduction of CO to CH₃Cl, a supported iridium monomer was tested. The monomer chosen was Ir(CO)Cl(P(Ph)₃), Vaska's complex. The choice was based on the fact that its ligand environment about the iridium atom is similar to what might be expected for an iridium atom in the active supported cluster catalyst. Also the Vaska complex is well known for its ability to oxidatively add H₂ and HCl.

Ir(CO)Cl(P(Ph)₃)₂ was supported on alumina by two methods. The first method involved physical adsorption onto unfunctionalized alumina. The second made use of covalent linkage to a phosphine silane functionalized alumina, taking
advantage of the phosphine exchange reaction shown below (Equation 14).

\[
\text{O-Si} \bigvee \text{P(Ph)}_2 + \text{Ir(CO)Cl(P(Ph)}_3 \rightarrow \text{O-Si} \bigvee \text{P(Ph)}_2 \text{Ir(CO)ClP(Ph)}_3 + \text{P(Ph)}_3
\]

(14)

On exposure to syngas and HCl the physically adsorbed \(\text{Ir(CO)Cl(P(Ph)}_3\) showed no activity at 25°C. After increasing the temperature to 50°C, the only product observed was \(\text{CH}_3\text{CH}_2\text{Cl}\). It was not until 100°C had been reached that any \(\text{CH}_3\text{Cl}\) production was observed (see GC traces in Figure 3-15).

GC traces of the products observed for the covalently attached \(\text{Ir(CO)ClP(Ph)}_3\) are shown in Figure 3-16. Unlike the physically adsorbed catalyst slight \(\text{CH}_3\text{Cl}\) activity was observed at 25°C. Increasing the temperature to 75°C greatly increased \(\text{CH}_3\text{Cl}\) production. However this production level was very low compared to that observed for the \(\text{Ir}_4(\text{CO})_{11}\text{P(Ph)}_2\) supported cluster catalyst.

Again it appears that the covalent phosphine linkage is important for \(\text{CH}_3\text{Cl}\) activity. The iridium monomer did show \(\text{CH}_3\text{Cl}\) activity at 25°C but in no way compared with the activity of the iridium cluster catalysts. This
Figure 3-15. GC traces (Poropak Q) of the products produced from syngas and HCl by IR(CO)Cl(P(Ph)₃)₂ physically adsorbed on alumina at a) 50°C b) 100°C.
Figure 3-16. GC traces (Poropak Q) of the products produced from syngas and HCl by (Alumina)\(\wedge\) P(Ph)\(_2\)Ir(CO)ClP(Ph)\(_3\) at a) 25°C  b) 75°C.
illustrates the importance of the role of a multimetal cluster in this type of chemistry.

To help demonstrate the uniqueness of the chemistry shown by these covalently supported tetrairidium clusters, a methanol catalyst reported by Ichikawa\textsuperscript{86} was tested for its ability to convert syngas and HCl to CH\textsubscript{3}Cl. The catalyst was composed of pyrolyzed Rh\textsubscript{6}(CO)\textsubscript{16} on ZnO, and is known to produce methanol from syngas under mild conditions (220\textdegree C, 45 cm Hg). On exposure to syngas and HCl, the catalyst showed no CH\textsubscript{3}Cl production activity up to 80\textdegree C. At 80\textdegree C a small amount of CH\textsubscript{3}Cl and CH\textsubscript{3}OH was observed. Increasing the temperature further only slightly improved the CH\textsubscript{3}Cl activity but other products such as CH\textsubscript{4} were also produced.

**Halogen sources**

Other halogen sources besides HCl tested in conjunction with syngas with these tetrairidium supported catalysts were HBr, aqueous HCl and Cl\textsubscript{2} gas.

At 100\textdegree C while passing syngas and HCl(g) through a silica gel supported catalyst (0.23\% Ir) the HCl was replaced in the feed by HBr(g). Before HBr was introduced into the feed, HCl free syngas was passed through the catalyst until almost no CH\textsubscript{3}Cl product was observed in the exit gas. Figure 3-17 contains GC traces which illustrate the progression of products as a function of the time that the HBr was present in the feed. After 1\%2/\% hour, the
Figure 3-17. GC traces (Poropak Q) of the products produced from syngas and HCl by (silica gel)\(^\text{\wedge}\) P(Ph)\(_2\)Ir\(_4\)(CO)\(_{11}\) (.23% Ir) at 100°C on introducing HBr for a) 0.0 hrs b) 0.5 hrs c) 1.5 hrs d) greater than 10 hrs.
HBr Present

0.0 hr.

0.5 hr

1.5 hrs

>10.0 hrs
primary product observed was CH₃Cl and the beginning of CH₃Br production was observed. (CH₃Br was identified by GC-mass spectroscopy discussed later). A small peak at the retention time of ethylchloride was also observed. After 1.5 hours, the production of CH₃Br appeared greater than CH₃Cl, and the appearance of unknown minor products above the retention time of CH₃CH₂Cl were detected. Finally after a period greater than 10 hours the sole primary product was CH₃Br and there was almost no trace of CH₃Cl. However a minor product at a retention time of about 13 minutes was still present which could be ethylbromide though there has been no positive identification.

On changing the HBr in the feed back to HCl, it was observed that the catalyst was nearly inactive as it produced only very small amounts of CH₃Cl. Thus this catalyst can produce CH₃X selectively using at least two different hydrogen halide sources, HCl and HBr. These results also demonstrate that the catalyst can be converted from a CH₃Cl to CH₃Br producing catalyst but not in the reverse order. The production of CH₃Cl a short time after introducing HBr into the feed demonstrated that a significant amount of Cl⁻ remained inactive on the catalyst, probably in the form of Si-Cl groups which became active in the presence of HBr.

An experiment similar to that described above was performed using an alumina supported iridium cluster
catalyst at 100°C, except in this case anhydrous HCl was replaced by aqueous HCl as opposed to HBr. The catalyst was first made active using anhydrous HCl. Then the HCl was removed until almost no CH$_3$Cl production was observed. To introduce the aqueous HCl a stream of argon gas, passed through a gas dispersion tube submerged in concentrated hydrochloric acid, was used. The resulting argon-HCl(aq) gas was then mixed with 3:1 H$_2$:CO syngas and passed through the catalyst. After 15 minutes the catalyst showed good activity for producing CH$_3$Cl. After 1 hour the activity was at a maximum and proceeded to decrease with time. This indicated that the catalyst may not be stable to a feed gas with a high water vapor content, and/or the decrease in activity results from the decrease in the concentration of HCl in the aqueous solution. The concentration of HCl in concentrated hydrochloric acid starts at 38% HCl. As the argon gas is passed through, this concentration will eventually drop to 20% which is the HCl H$_2$O constant boiling azeotrope. Further study is needed to determine if the CH$_3$Cl activity levels out with time.

Preliminary results were obtained on a parallel experiment using Cl$_2$ as the chlorine source. When Cl$_2$ was introduced to an alumina catalyst under the same conditions as described above, activity for CH$_3$Cl was observed but at levels lower than for either HCl(g) or
HCl(aq). Further studies with Cl$_2$ were hindered due to lack of time.

**GC-Mass spectrometry**

Volatile products obtained from the reaction of syngas and HX (X=Cl, Br) over the catalyst (silica gel)$\small\wedge$ P(Ph)$_2$Ir$_4$(CO)$_{11}$, where Ir= 0.23%, were analyzed by GC mass spectrometry. The products were collected over a 24 hour period in a CO$_2$/acetone trap at the exit of the reactor tube.

For the HCl case the GC trace obtained is shown in Figure 3-18. The mass spectra of peaks A, B, and C are shown in Figures 3-19, 3-20, and 3-21 and are compared to literature reported spectra. Peak A, the major component, was CH$_3$Cl. The peaks B and C correspond to acetylaldehyde and methylformate respectively. The peak labeled D has the same retention time as ethylchloride but was not identifiable by mass spectrometry. Subsequent investigations have positively identified peak D as ethylchloride.

When HCl was replaced by HBr in the feed gas the volatile products that were trapped are shown in the GC trace in Figure 3-22. The mass spectrum of peak E, which represents the major component, CH$_3$Br, is shown in Figure 3-23 compared to its literature reported spectrum. Peak F was unidentifiable, but because it has a retention
Figure 3-18. GC traces (Poropak Q) of the products produced from syngas and HCl by (silica gel) $\textsc{P(Ph)}_2\text{Ir}_4\text{CO}_{11}$ ($\text{Ir} = .23\%$) at 75° and analyzed by GC mass spectrometry.
Figure 3-19. Mass spectrum of CH$_3$Cl, peak A (Figure 3-18), a) observed spectrum b) literature reported spectrum.
CH$_3$Cl
Figure 3-20. Mass spectrum of acetylaldehyde, peak B (Figure 3-18), a) observed spectrum b) literature reported spectrum.
Acetaldehyde
Figure 3-21. Mass spectrum of methylformate, peak C (Figure 3-18), a) observed spectrum b) literature reported spectrum.
Figure 3-22. GC traces (Poropak Q) of the products produced from syngas and HBr by (Silica Gel)\(\times\)P(Ph)\(_2\)Ir\(_4\)CO\(_{11}\) (Ir = .23\%) at 100°C and analyzed by GC mass spectrometry.
Figure 3-23. Mass spectrum of CH₃Br, peak E (Figure 3-22), a) observed spectrum b) literature reported spectrum.
time similar to that of ethylchloride, it is believed to be ethylbromide.

**Mechanism**

The mechanism for the novel chemistry demonstrated by these covalently supported tetrairidium clusters may only be speculated about at this point. Figure 3-24 shows one possible reaction pathway based on some already established organometallic chemistry.

One of the first steps toward the production of CH₃Cl that might be envisioned is the oxidative addition of H₂ generating a dihydride (1). Because the covalent attachment of the phosphine silane to the cluster appears to be necessary for catalytic activity, it may be that the iridium atom directly bound to the phosphine is involved in the H₂ activation. This is because the iridium bound directly to the phosphine is predicted to be more electron rich than the other iridium atoms in the cluster.

Interaction of the dihydride with the support surface consisting of A-Cl groups (A = Al or Si) could induce rapid hydride migration forming the formyl type intermediate (2). This reaction step is modeled after the reaction reported by Shriver et al.⁹⁰ (Equation 15). The rate of CO insertion (alkyl migration) into a metal alkyl bond was shown to be increased by CO interacting with the Lewis acid AlBr₃ generating a stable metal acyl complex. Stable
Figure 3-24. Speculative mechanistic scheme for the production of CH₃Cl from syngas and HCl by polymer supported Ir₄(CO)₁₁.
Route 1:

1. \( \text{P-M-CO} \) + \( \text{H}_2 \) → 2.

2. \( \text{P-M-CO} \) + \( \text{H}_2 \) → 3.

3. \( \text{P-M-CO} \) + \( \text{P-M-CO} \) → 4.

4. \( \text{P-M-CO} \) + \( \text{P-M-CO} \) → 5.

5. \( \text{P-M-CO} \) + \( \text{P-M-CO} \) → 6.

6. \( \text{P-M-CO} \) + \( \text{P-M-CO} \) → 7.

7. \( \text{P-M-CO} \) + \( \text{P-M-CO} \) → 8.

Route 2:

1. \( \text{CH}_3\text{Cl} + \text{H}_2\text{O} + \text{A-Cl} \) → 2.

2. \( \text{CH}_3\text{Cl} + \text{H}_2\text{O} + \text{A-Cl} \) → 3.

3. \( \text{CH}_3\text{Cl} + \text{H}_2\text{O} + \text{A-Cl} \) → 4.

4. \( \text{CH}_3\text{Cl} + \text{H}_2\text{O} + \text{A-Cl} \) → 5.

5. \( \text{CH}_3\text{Cl} + \text{H}_2\text{O} + \text{A-Cl} \) → 6.

6. \( \text{CH}_3\text{Cl} + \text{H}_2\text{O} + \text{A-Cl} \) → 7.

7. \( \text{CH}_3\text{Cl} + \text{H}_2\text{O} + \text{A-Cl} \) → 8.

8. \( \text{CH}_3\text{Cl} + \text{H}_2\text{O} + \text{A-Cl} \) → 9.

9. \( \text{CH}_3\text{Cl} + \text{H}_2\text{O} + \text{A-Cl} \) → 10.
metal formyl formation was not achieved using the metal hydride.

\[
\text{(CO)}_4\text{Mn} \begin{array}{c} \text{CH}_3 \\ \text{CO} \end{array} + \text{AlBr}_3 \rightarrow \text{(CO)}_4\text{Mn} \begin{array}{c} \text{C} \\ \text{Br} \end{array} \begin{array}{c} \text{O} \\ \text{Al} \end{array} \begin{array}{c} \text{Br} \\ \text{Br} \end{array}
\] (15)

At this point in the catalytic cycle, the second hydride transfer can be envisioned to occur by one of two routes. In the first route, the second hydride is transferred to the formyl carbon along with the concerted formation of a A-O and a M-Cl bond, generating intermediate (3). This intermediate activates H\textsubscript{2} generating the dihydride (4) which on hydride transfer to the metal bound methoxy-A generates CH\textsubscript{3}OA and intermediate (5). The methoxy-A group then can react with HCl producing CH\textsubscript{3}Cl and A-OH which on reaction with another molecule of HCl would be converted back to A-Cl. The hydride intermediate (5) can react with H\textsubscript{2} giving a metal dihydride (6) which upon bonding a CO results in the formation of intermediate (1) again.

The other route (route 2) forms a bound formaldehyde type intermediate (7) on transfer of the second metal hydride to the formyl intermediate (2). Similar reduction eliminations of a formyl group to form a bound formaldehyde have been proposed in the past.\textsuperscript{66,91} On addition and
transfer of another $\text{H}_2$ molecule a Lewis acid bound methanol molecule and intermediate (8) are formed. The bound methanol can then react with a molecule of $\text{HCl}$ generating $\text{CH}_3\text{Cl}$ and $\text{H}_2\text{O}$. Intermediate (8) can then bind a CO molecule closing the catalytic cycle.

The formation of the minor products, acetylaldehyde and $\text{CH}_3\text{CH}_2\text{Cl}$ which contain C-C bonds probably proceeds through a CO insertion step involving one of the intermediates in the catalytic cycle. Another potential source of ethyl chloride could be from a metal catalyzed reaction of ethylene with $\text{HCl}$, the source of ethylene being an impurity in the $\text{HCl}$ gas source.

**Conclusion**

The main goal of this study was to immobilize known homogeneous CO reduction catalysts geared toward developing catalysts capable of selectively producing chemicals from syngas under very mild reaction conditions.

Two catalyst systems were studied. The first involved the ionic attachment of two ruthenium anions $[\text{Ru(CO)}_3\text{I}_3]^-$ and $[\text{HRu}_3\text{(CO)}_{11}]^-$ simultaneously on ammonium iodide functionalized silica gel. The ions were successfully attached to the support as evidenced by infrared spectroscopy but showed little or no syngas conversion up to $175^\circ\text{C}$.
The second system involved the covalent attachment of $\text{Ir}_4(\text{CO})_{11}$ to both phosphine silane functionalized silica gel and alumina. This catalyst, in conjunction with AlCl$_3$-NaCl under melt conditions (140°C), demonstrated no significant benefits over Meutterties' homogeneous Ir$_4$(CO)$_{12}$/AlCl$_3$-NaCl system. The polymer supported P(Ph)$_2$Ir$_4$(CO)$_{11}$ underwent an exchange reaction with CO generating what was believed to be a homogeneous Ir$_4$(CO)$_{12}$/AlCl$_3$-NaCl system.

At 25°C in the presence of AlCl$_3$ under non-melt conditions the supported tetrairidium catalysts were found to produce CH$_3$Cl selectively from syngas. The AlCl$_3$ was successfully replaced in both the alumina and silica gel system by the addition of HCl to the syngas feed. This allowed the operation of the catalyst at a higher temperature, up to 100°C, while still maintaining a greater than 99% selectivity for CH$_3$Cl.

The presence of a Lewis acid, either AlCl$_3$ or the Lewis acid sites on the support surface, as well as the phosphine silane linkage to the surface appear to be important to the catalysts' activity. Although a phosphine silane iridium monomer catalyst precursor, Ir(CO)ClP(Ph)$_3$, showed slight CH$_3$Cl activity, the bound tetrairidium cluster was superior.

The chemistry was also demonstrated using other halogen sources, aqueous HCl, HBr, and Cl$_2$. In the case of HBr the primary product was CH$_3$Br.
The polymer supported tetrairidium cluster system has demonstrated novel, selective chemistry for the production of methyl chloride under very mild conditions. This system not only demonstrates some of the potential advantages of "hybrid" type catalyst systems but has the potential for being an industrially important process for the production of CH\textsubscript{3}Cl from syngas and HCl.
IV. IMIDAZOLE FUNCTIONALIZED SILICA GEL

Introduction

The ligand imidazole or the deprotonated form, imidazolate are of interest because of their role in the active sites of many biological systems\textsuperscript{93-98} as well as their involvement in homogeneous catalysis.\textsuperscript{2,3}

\[ \text{Imidazole (ImH)} \quad \text{Imidazolate (Im)} \]

The metalloenzymes carbonic anhydrase,\textsuperscript{99} carbonyl peptidase,\textsuperscript{100} thermolysin,\textsuperscript{101} and bovine erythrocyte superoxide dismutase,\textsuperscript{102} all have been found to contain imidazole in some form in their transition metal binding sites. In the case of carbonic anhydrase, which catalyzes the reaction of \( \text{CO}_2 \) to \( \text{HCO}_3^- \), \( \text{Zn(II)} \) is believed to be bound in the active site by three imidazole rings of the enzyme's histidine residues. Studies on an active form of bovine erythrocyte superoxide dismutase has revealed an imidazolate bridged copper (II) active site.\textsuperscript{93}
Imidazole's role in homogeneous catalysis was revealed by two Japanese patents$^2,^3$ in which a rhodium imidazolate trimer [Rh(Im)COD]$^3_3$ (COD = cyclo-octa-1,5-diene) was reported as an active catalyst for the hydroformylation of terminal olefins (Equation 1):

$$\text{R-C}=\text{C} + \text{CO} + \text{H}_2 \xrightarrow{\text{catalyst}} \text{R-CH}_2\text{CH}_2\text{C} = \text{H} \quad (1)$$

The proposed structure of the catalyst precursor is shown below. A study of similar polynuclear rhodium and iridium complexes of the formula $[\text{M(RIm)(diolefin)}]_x$ ($\text{R}=$H, 2-Me) reported by Tiripicchio and Uson.$^{103}$ Molecular weight measurements determined that $x$ was equal to a value between 2 and 3. A crystal structure of $[\text{Rh(2-MeIm)(CO}_2]_x$ which was easily obtained from the diolefin complex was found to have a structure similar to that shown above, but the complex was a tetramer ($x=4$).

Reported in this study is the synthesis of an imidazole functionalized silica gel support that has the potential to
form these rhodium imidazolate polynuclear complexes on the surface of silica gel. A heterogenized rhodium imidazolate catalyst will hopefully mimic the activity of the homogeneous system while maintaining some of the advantages of a heterogeneous system previously discussed in the introduction to chapter 3 (i.e. ease of catalyst separation from product, greater solvent variability).

The following considerations were taken into account when designing the imidazole support. First, there needs to be sufficient surface coverage of the imidazole groups to allow the polynuclear complexes to form. Second, the groups connecting the imidazole to the silica gel surface should be flexible and long enough to allow the imidazole to obtain the necessary orientations. Finally, the synthesis of the functionalized support should be relatively uncomplicated.

One of the most popular and flexible methods of functionalizing silica gel has been by using organosilanes. A method reported by Burwell for synthesizing an imidazole functionalized silica gel using organosilanes is shown in Equation 2. In this method the imidazole silane was synthesized on the silica gel surface by reacting imidazole with a chloropropylsilane functionalized support. The major problem with using this
imidazole support is that it lacks bridging capabilities due to the imidazole ring being attached to the organic chain through one of the ring nitrogens. Burwell reported attempting the synthesis of the 4(5) substituted imidazolylsilane below which would have the potential to act as a bridging ligand, but the synthesis was unsuccessful.

\[
\text{(C}_2\text{H}_5\text{O})_3\text{Si}
\]

Reported here is a convenient method for the synthesis of a 4(5) substituted imidazolylsilane functionalized silica gel utilizing a series of simple Schiff base reactions. This support was then reacted with Rh(COD)(acac) in an attempt to generate a functionalized rhodium imidazolate polynuclear catalyst. The catalyst was then screened for its hydroformylation activity.

The hydroformylation or OXO reaction (Equation 1) has been the subject of extensive study.\textsuperscript{110,111} The early commercial processes involved homogeneous cobalt carbonyl catalysts operating at 150\textdegree{}C and 180\textdegree{}C and pressures of 200 to 400 atm. The active catalytic species was believed to be HCo(CO)\textsubscript{4}. The traditional cobalt catalysts have been replaced by more selective and active rhodium systems. These operate at 100\textdegree{}C and pressure of 100 to 300 psi and
are generally of the form $L_2\text{Rh(CO)}_2\text{H}$ ($L=$trialkyl or triaryl phosphines).

Improved catalyst systems should demonstrate high activity under mild reaction conditions, low by-product production and show a high selectivity toward normal aldehydes vs. isooaldehydes, which have little commercial value. The commercial rhodium\textsuperscript{112} systems are $10^4$ times more active than the cobalt catalyst systems and demonstrate normal to isooaldehyde ratios of 8-16:1 vs. 3-4:1 for the cobalt case. Another important property should be easy product separation with minimal catalyst loss.

**Experimental**

**Materials**

All solvents and reagents were used as purchased unless otherwise stated. Triethoxypropyaminosilane was purchased from Petrarch Chemical. The complex $[\text{RhCl(CO)}_2]_2$ was purchased from Alfa. Silica gel was purchased from W. R. Grace and was Davison grade #62. The wide pore diameter was 14 mm, pore volume was 1.1 cm$^3$/g and had a specific area of 340 m$^2$/g.

**Instrumentation**

Elemental analyses were performed by the Microanalytical Laboratory, University of Florida,
Gainesville, Florida. Infrared spectra were recorded as Nujol mulls on a Perkin Elmer 283B spectrometer. GC analyses were performed on a model 3700 FID Varian gas chromatograph equipped with 1/16" X 1 m stainless steel column packed with Chromasorb P supported diethylene glycol adipate.

Hydroformylation reactions were performed in a 500 ml Parr pressure bottle containing a teflon coated magnetic stir bar. The bottle was sealed with a silicone rubber stopper fitted with a brass gas flow tube, pressure gauge, and gas inlet and exit control valves. The bottle was jacketed with a steel mesh sleeve and the entire set-up was submerged in a mineral oil temperature bath. After charging the reactor with catalyst and substrate the system was purged of the ambient atmosphere by filling-evacuating five times with 1:1 H$_2$:CO. The gases H$_2$ and CO were then added to the desired pressure followed by heating of the oil bath to the desired temperature.

Synthesis

Synthesis of silica bound propylaminosilane

The propylamine functionalized silica gel was prepared using a method similar to that reported by Howell et al. In a 500 ml round bottom flask equipped with a reflux condenser, 150 ml of xylenes was added to 10 g of silica gel (dried at 100°C under vacuum for 24 hours). While stirring, the flask was purged with N$_2$ and then 11.07 g
(11.6 ml) of triethoxypropylaminosilane was added. The mixture was then heated to reflux for 24 hours. After cooling, the mixture was filtered, washed with xylenes, and dried under vacuum at room temperature for 24 hours. Analysis: C, 6.42%; H, 1.5%; N, 2.08%. Theoretical: C, 6.5%; H, 1.5%; N, 2.4%.

To a solution containing 0.5 g (0.00373 mole) 1,4-dihydroxy 1-2,5-dibenzaldehyde in 200 ml absolute ethanol, 1 g of propylaminosilane bound silica gel (synthesized by method 2) was slowly added. After 2 hours of stirring the resulting orange resin was filtered, washed extensively with absolute ethanol (1 liter) until no color was observed in the filtrate, and dried under vacuum for 24 hours at 25°C. Analysis: C, 12.40%; H, 1.53%; N, 1.78%.

In a 125 ml Erlenmeyer flask equipped with a reflux condenser 0.75 g of histamine • 2HCl and 0.75 g sodium bicarbonate were added to 30 ml absolute ethanol. While
stirring, the mixture was refluxed for 30 minutes. After cooling, the solution was filtered, the solid washed with 50 ml of absolute ethanol, and the filtrate and washings were combined. The resulting free base histamine solution was added to a 300 ml round bottom flask containing 0.9 g of the silica gel bound benzaldehyde in 150 ml of absolute ethanol. The mixture was stirred under N₂ for 2 hours, filtered and washed with absolute ethanol extensively. The resulting orange resin was dried under vacuum for 14 hours at 25°C. Analysis: C, 11.17%; H, 1.60%; N, 2.21%.

The synthesis of this Schiff base complex was derived from a method reported by Folkers et al. In a 125 ml Erlenmeyer flask equipped with a reflux condenser, 1 g (0.0054 mole) histamine-2HCl, 3 ml absolute ethanol and 1 g sodium bicarbonate were mixed. While stirring, the mixture was refluxed for 30 minutes. After cooling, the solution was filtered, the solid washed with 50 ml absolute ethanol,
and the filtrate and washings combined. Under a $N_2$ atmosphere 0.250 g (0.0037 mole) 1,4-dihydroxyl-2,5-dibenzaldehyde was added to the histamine solution, and an orange precipitate immediately formed. After stirring for 3 hours, the mixture was filtered and the precipitate was washed with ethanol and dried under vacuum at 25°C for 30 minutes.

**Rh(acac)(CO)$_2$**

Dicarbonyl(pentane-2,4-dionato)rhodium(I) was synthesized by a procedure reported by Wilkinson and Bonati. In a 100 ml round bottom flask equipped with a reflux condenser 0.5 g of $[\text{RhCl(CO)}_2]_2$, 1.668 g BaCO$_3$, and 1.25 ml acetylacetone were added to 42 ml of hexanes. The mixture was refluxed with stirring for 1 week, cooled and filtered to remove the BaCO$_3$ precipitate. The volume of solvent was reduced to 3 ml under vacuum. The reddish green crystals were filtered, washed with a minimum amount of hexanes and dried under vacuum for 10 minutes at 25°C. Yield: 0.57 g.

**Rh(acac)(COD)**

Cyclo-octa-1,5-diene(pentane-2,4-dionato)rhodium(I) was synthesized by a procedure reported by Wilkinson and Bonati. In a 100 ml round bottom flask 0.2 g Rh(CO)$_2$(acac) and 4 ml cyclo-octa-1,5-diene was dissolved
in 20 ml (20-40°C) petroleum ether. The mixture was stirred for 30 minutes at room temperature, the solvent removed by vacuum, and the solid extracted with (40-60°C) petroleum ether. After concentration of the solution, the yellow solid which crystallized was filtered and air dried.

\[ \text{[Rh(Im)(COD)]}_x \text{ functionalized silica gel} \]

In a round bottom flask 0.62 g histamine substituted silica gel and 0.76 g Rh(acac)(COD) was added to 25 ml of acetone. The mixture was stirred for 4 hours under \( \text{N}_2 \). The volume was reduced to 12 ml and the orange support was filtered, washed with methanol and dried under vacuum for 24 hours at 25°C.

**Results and Discussion**

**Synthesis - Imidazole Support**

The synthetic route for the preparation of the 4(5) substituted imidazole functionalized support is shown in Figure 4-1. The method shown avoids the difficulties that have been encountered when synthesizing a 4(5) substituted imidazole silane. This is done by linking two readily available reagents, the silane triethoxypropylaminosilane and the 4(5) substituted imidazole histamine using hydroxy substituted dibenzaldehyde as the linking agent.
Figure 4-1. Synthetic route for the preparation of $4(5)$ substituted imidazole functionalized silica gel.
\[
\text{I} + \text{excess II} \rightarrow \text{III}
\]
Infrared spectroscopy proved to be an excellent probe for following the sequence of reactions. Figure 4-2 shows the IR spectra of intermediates in the region 1800-1400 cm\(^{-1}\) at various stages in the synthesis.

The first step in the synthesis involves a condensation reaction of triethoxypropylaminosilane, with the silanol groups on the surface of the silica gel generating the amino functionalized support I. Support I was then contacted with an ethanol solution containing 1,4-dihydroxy-2,5-dibenzaldehyde in a seven fold excess (based on the theoretical concentration of amine groups present) yielding the Schiff base functionalized support II. Utilizing an excess of the dibenzaldehyde hopefully minimized any cross linking of the type shown below.

![Chemical Structure](image)

The infrared spectrum of II (Figure 4-2b) shows two characteristic bands at 1629 cm\(^{-1}\) and 1670 cm\(^{-1}\) which are assigned to the carbon nitrogen stretching mode of the imine group (-N═C-) and the carbonyl stretching mode of the aldehyde group respectively. The peak at 1670 cm\(^{-1}\) corresponds well with the carbonyl peak observed for the infrared spectrum of 1,4-dihydroxy-2,5-dibenzaldehyde.
Figure 4-2. Infrared spectra in the range 1800-1400 cm$^{-1}$ of functionalized silica gel and molecular analogs.
The presence of both an imine and an aldehyde carbonyl band provide evidence for the proposed structure of II and that one aldehyde group is still available on the benzene ring for further reaction.

The reaction of free base histamine in a nine fold excess with a solution of the benzaldehyde support II resulted in the isolation of support III. This final step in the synthesis is based on a Schiff base reaction shown in Equation 3 reported by Heyl et al. In this reaction, pyridoxal was reacted with histamine in an alcohol solution generating a stable imine linked compound.

\[
\begin{align*}
\text{CH}_3\text{OH} & \quad \text{H}_2\text{N} \quad \text{H} \quad \text{H} \\
\text{HO} & \quad \text{CH}_2\text{OH} \\
\text{N} & \quad \text{O} \\
\text{C} & \quad \text{C} \\
\end{align*}
\]

The infrared spectrum of III (Figure 4-2C) contains only the band at 1626 cm\(^{-1}\) assigned to the stretching frequency of the imine groups. The absence of the carbonyl stretch of the aldehyde group observed for II indicates
Table 4-1. Infrared Stretching Frequencies Observed in the Range 1800-1500 cm\(^{-1}\).

<table>
<thead>
<tr>
<th>Compound(^a)</th>
<th>(\nu(C=0))</th>
<th>(\nu(C=N))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{SG})</td>
<td>-</td>
<td>1626</td>
</tr>
<tr>
<td>(\text{SG})</td>
<td>1670</td>
<td>1629</td>
</tr>
<tr>
<td></td>
<td>1673</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1631</td>
</tr>
</tbody>
</table>

\(^a\) Nujol mulls.
that the remaining benzaldehyde groups of II successfully reacted with histamine forming the second imine link.

The model compound shown below was synthesized and its infrared spectrum shown in Figure 4-2d.

\[
\text{\begin{tikzpicture}
    \node (a) at (0,0) {\text{imidazole}};
    \node (b) at (2,0) {\text{imidazole}};
    \node (c) at (0,-2) {\text{imidazole}};
    \node (d) at (2,-2) {\text{imidazole}};
    \node (e) at (0,-3) {\text{COD}};
    \node (f) at (2,-3) {\text{COD}};
    \node (g) at (0,-4) {\text{COD}};
    \node (h) at (2,-4) {\text{COD}};
    \draw (a) -- (b);
    \draw (a) -- (c);
    \draw (a) -- (d);
    \draw (a) -- (e);
    \draw (a) -- (f);
    \draw (a) -- (g);
    \draw (a) -- (h);
    \node (i) at (0,-5) {\text{Silica Gel}};
\end{tikzpicture}}
\]

The single band observed at 1631 cm\(^{-1}\) corresponds well with the imine stretching band observed for the imidazole functionalized support III (Table 4-1).

An important consideration in synthesizing the imidazole support III was the degree of surface coverage of the imidazole groups that would be needed in order to allow formation of the rhodium imidazolate trimer as shown below.
Based on an infrared study, Drago and Nyberg\textsuperscript{107} reported that the concentration of organosulfide needed on the surface of silica gel for the formation of predominantly rhodium carbonyl dimer species shown below was 0.20 mmole S per gram of silica gel. Based on the N analysis of III (\%N = 2.21\%) theoretically 0.395 mmoles of substituted imidazole per gram of silica gel is present. This concentration should be more than sufficient to allow trimer formation.

\[
\text{Hydroformylation}
\]

Metalation of the imidazole polymer was attempted by the method\textsuperscript{103} shown below (Equation 4) which was derived from a reported synthesis of \([\text{Rh}(\text{RIm})(\text{COD})]_x\) (R=CH\textsubscript{3}, H and refers to the 2 position of the imidazole ring) complexes.

\[
\text{Rh(COD)(acac)} + \text{III} \rightarrow [\text{Rh(Im)(COD)}]_x
\]  

(4)

Only preliminary results were obtained on the hydroformylation activity of the functionalized rhodium
imidazolate catalyst. This system was tested for the hydroformylation of 1-hexene. The pressure reactor described in the experimental section was charged with 0.25 g of the rhodium catalyst, 0.77 g of the promoter PPh₃, 10 ml 1-hexene and 80 psig with 1:1 H₂:CO. At 25°C no reaction was observed. On heating to 75°C a pressure drop was observed at a rate of 80 psi/hr which continued upon repeated pressurization to 80 psig with 1:1 H₂:CO.

During the course of the reaction, an aliquot of the liquid was syringed from the reactor and analyzed by gas chromatography. Two predominant products being formed were n-heptanal and 2-methylhexanal. Assuming equal GC sensitivity of the two products the ratio of normal to branched was 3.9:1.

The degree of leaching of the catalyst into solution, which is often a problem with immobilized catalysts, was tested by filtering off the support and recharging the filtrate with 80 psi of H₂:CO gas. The filtrate was much less active, a 60 psi pressure drop was observed after 48 hours. Recharging the filtered support also showed diminished activity. Due to these preliminary results the supported rhodium imidazole catalyst appears to be a very active hydroformylation catalyst for 1-hexene but there appears to be a fair amount of catalyst leaching taking place.
One possible solution to the apparent leaching problem is to utilize the catalyst in a fixed bed reactor (similar to the system used in chapter 3) for the hydroformylation of a more volatile alkene such as 1-butene. A preliminary test was performed but problems were encountered due to plugging of the reactor caused by melting of the $P(\text{Ph})_3$ at reaction temperature. These results were inconclusive.

**Conclusion**

The objective of this study was to develop an imidazole functionalized support that could be used to heterogenize a homogeneous hydroformylation catalyst. A convenient method for the synthesis of a 4(5) substituted imidazole functionalized silica gel was developed. To this authors knowledge, this is the first successful synthesis of an imidazole functionalized support in which the imidazole ring is attached through the 4(5) position. Previous reports have shown the imidazole ring attached through one of the ring nitrogens. Back substitution on the imidazole ring frees both nitrogens allowing the imidazole to act as a bridging ligand.

The synthetic method involved linking the 4(5) aminoethyl substituted imidazole histamine to an aminosilane functionalized silica gel by way of Schiff base reactions with 1,4-dihydroxy-2,5-dibenzaldehyde. Infrared
spectroscopy proved to be an extremely useful tool for following the course of the synthesis. The length and flexibility of the organic chain connecting the imidazole ring to the supported silane, along with a sufficient coverage of the groups on the silica gel surface, should allow the imidazole groups to obtain the desired orientation for generating $[\text{Rh(Im)(COD)}]_x$ on the surface.

Preliminary results after metalation of the resultant imidazole support with Rh(acac)(COD) showed this support, in conjunction with a triphenylphosphine promoter, to be an active catalyst for the hydroformylation of 1-hexene. Problems with leaching of the metal catalyst into solution were encountered using a slurry bed type system. An attempt at using this catalyst in a fixed bed type reactor for the hydroformylation of 1-butene was inconclusive due to experimental difficulties.

The synthesis and potential use of a 4(5) substituted imidazole support to attach homogeneous catalysts has been demonstrated. Further work in the future should be undertaken to illustrate the full potential of this hydroformylation catalyst. Other uses of this type of imidazole support need to be explored. These include the potential use in other catalytic systems or possibly in the modeling of metaloenzymes like carbonic anhydrase.
V. SOLUBLE BIMETALLIC COMPLEXES

Introduction

In Chapter Three of this thesis, synergistic interactions between two separate metal centers aiding the reduction of carbon monoxide by hydrogen were illustrated. The synthesis and characterization of macromolecules capable of binding two metal centers in close proximity within the same molecule is a natural extension of this work. The synergistic interactions between metal centers in the same molecule not only has relevance to the area of catalysis but also to metallobiomolecules and electron transfer processes. Many metalloenzymes contain multimetal centers. Hemocyanin, laccase and tyrosinase contain coupled binuclear copper sites and superoxide dismutase may involve a Cu-Zn active center.

A large number of complexes have been synthesized utilizing ligands capable of binding two metals in close proximity that lack solubility in all but strong donor solvents. Recently, Drago et al. have reported a series of bimetallic complexes based on the ligand shown below which are soluble in non-polar solvents such as \( \text{CH}_2\text{Cl}_2 \). This prevented the system from being limited to only solid state measurements or solution studies in donor solvents.
In this study a number of bimetallic complexes having the proposed structure shown below have been synthesized and characterized, and have the potential for the activation of small molecules such as H₂, CO, C₂H₄, O₂ etc. These complexes are based on the ligand

\[
[M(DIOX)BF₂]_2
\]

bis-4-tert-butyl-2,6-diformyl-phenol dioxime, derived from a precursor of the ligand reported by Drago et al. When reacted with BF₃·Et₂O these complexes demonstrate solubility in poor donor solvents such as acetone.
Experimental

Materials

All reagents and solvents were used as purchased unless otherwise stated. The reagent 4-tert-butyl-6-formylsa1icyl-aldehyde was supplied by Mike Desmond and was synthesized by the procedure reported by Drago et al.\(^\text{123}\) Acetone used was dried by a literature reported method.\(^\text{124}\) Reagent grade acetone was saturated with dry NaI and frozen at -15° C. The unfrozen liquid was decanted and the frozen solid distilled. N,N-Dimethylformamide (DMF) was refluxed over BaO for 48 hours, then distilled under nitrogen.

Instrumentation

Elemental analyses were performed by the Microanalytical Laboratory, University of Florida, Gainesville, Florida. Infrared spectra were recorded as Nujol mulls on a Perkin Elmer 283B spectrometer.

Cyclic voltammetry was carried out in DMF and acetone electrolyte solutions. All voltammograms were recorded by sweeping from the most positive potential to the most negative and back (100 mV/s). Cyclic voltammetry was conducted using a PARC model 175 Universal Programmer and a PAR 173 Potentiostat/Galvanostat.
Voltammograms were recorded on a Houston Instrument X-Y Omnigraphic 2000 Recorder.

The electrochemical cell used was a modified version of a cell reported by Desmond\textsuperscript{125} (Figure 5-1) and consisted of a three electrode arrangement. The auxiliary electrode was a course grade frit with a coiled Pt wire inside. The working electrode (constant area) was made by sealing a Pt wire in the end of a glass tube. There were two types of reference electrodes used in this study. Ag/AgI was used when acetone was the solvent. The electrode was made by attaching a "Vycor" tip to the end of the glass tube. The tube was then filled with equal amounts of 0.05M Bu\textsubscript{4}NI and 0.1M Bu\textsubscript{2}NCIO\textsubscript{4}. The added solution was then saturated with AgI and a Ag wire was inserted down the tube just lightly making contact with the tip. The electrode was allowed to equilibrate in a storage container that was also filled with equal amounts of 0.05M Bu\textsubscript{4}NI and 0.1M Bu\textsubscript{2}NCIO\textsubscript{4} for one week. A Ag/AgCl electrode was used when DMF was the solvent and was made as described by Drago et al.\textsuperscript{123} The electrolyte solutions used in these experiments were 0.10M Bu\textsubscript{4}NCIO\textsubscript{4} in acetone and 0.1M Bu\textsubscript{4}NCIO\textsubscript{4} in DMF.

The reduction potentials reported were referenced to the ferrocene/ferrocinium couple. The ferrocene/ferrocinium couple occurs at 0.160 V relative to aqueous SCE and 0.40 V relative to NHE\textsuperscript{126} and are assumed to occur at the same redox potential in both solvents.\textsuperscript{127}
Figure 5-1. Cyclic voltammetry cell.

A. Reference electrode with "VYCOR" tip (Ag/AgCl and Ag/AgI).
B. Counter electrode, platinum wire coil enclosed in coarse grade frit.
C. Working electrode with platinum button at the tip.
D, E, F. Openings for reference, counter, and working electrodes.
G. Gas outlet attached to bubbler.
H, I. Teflon valves.
J. 50/50 ground glass male joint.
K. 50/50 ground glass female joint.
Synthesis

(DIOX)

Bis-4-tert-butyl-2,6-diformyl-phenol dioxime, was prepared by a method patterned after a procedure reported by Baucom and Drago.\textsuperscript{128} In a 250 ml round bottom flask equipped with a reflux condenser, 6.30 g of freshly recrystallized 4-tert-butyl-6-formylsalicylaldehyde from hexanes was combined with 2.6 g NaOH, 4.5 g NH\textsubscript{2}OH • HCl and 30 ml 50% aqueous methanol. The 4-tert-butyl-6-formylsalicylaldehyde was synthesized by and obtained from M.J. Desmond.\textsuperscript{125} The mixture was heated while stirring on a steam bath for 1.5 hours. After cooling, the brown precipitate was filtered and washed with H\textsubscript{2}O. The light brown solid was then dried under vacuum for 4 hours at 50\textdegree C. Analysis: C, 61.31%; H, 6.86; N, 11.68%. Theoretical: C, 61.0%; H, 6.8%; N, 11.9%.

[Cu(DIOX)OH\textsubscript{2}]

In a 100 ml beaker, 0.755 g DIOX (3.07 mmole) was combined with 0.748 g Cu(NO\textsubscript{3})\textsubscript{2} • 3H\textsubscript{2}O (3.07 mmole) and 60 ml MeOH. The solution was heated while stirring and was maintained at reflux temperature for 15 minutes. After cooling, the dark green precipitate was filtered, washed with methanol and dried under vacuum for 24 hours at 60\textdegree C. Analysis: C, 48.14%; H, 4.71%; N, 9.13%. Theoretical: C, 48.4%; H, 4.8%; N, 9.4%.
[Zn(DIOX)OHO]$_2$

In a 50 ml beaker, 0.5 g DIOX (2.03 mmole) was combined with 0.446 g Zn(acetate)$_2$·H$_2$O (2.03 mmole) and 30 ml of methanol. Immediately, a white-ish precipitate formed. The mixture was heated while stirring and maintained at reflux temperature for 15 minutes. After cooling the solid was filtered, washed with methanol and dried under vacuum over P$_2$O$_5$ for 6 hours at 25°C. Analysis: C, 47.46%; H, 4.89%; N, 8.98%. Theoretical: C, 48.09%; H, 4.72%; N, 9.35%.

[Pd(DIOX)OHO]$_2$

In a 50 ml beaker, 0.24 g DIOX (0.974 mmole) was combined with 0.228 g Pd(NO$_3$)$_2$·H$_2$O and 30 ml methanol. The mixture was heated while stirring and maintained at reflux temperature for 15 minutes. After cooling, the brown precipitate was filtered, washed with methanol and dried under vacuum at 60°C for 4 hours. Analysis: C, 43.39%; H, 4.42%; N, 8.73%. Theoretical: C, 42.30%; H, 4.15%; N, 8.22%.

[Ni(DIOX)OHO]$_2$

In a 50 ml beaker 0.5 g DIOX (2.03 mmole) was combined with 0.505 g Ni(acetate)$_2$·4H$_2$O (2.03 mmole) and 30 ml methanol. Immediately, a green precipitate formed. On heating and stirring the precipitate turned light brown. After stirring at reflux temperature for 15 minutes the
mixture was cooled, filtered and washed with methanol. On drying under vacuum over P₂O₅ at 25°C for 6 hours, the light brown solid turned green. Analysis: C, 48.20%; H, 4.77%; N, 8.85%. Theoretical: C, 49.2%; H, 4.85%; N, 9.56%.

\[ \text{[Cu(DIOX)BF}_2\text{]}_2 \cdot 2\text{H}_2\text{O} \]

The method used for this synthesis was patterned after the procedure reported by Schrauzer and Windgassen. In a 50 ml round bottom flask, 0.459 g [Cu(DIOX)OH0]₂ (0.77 mmole), 1.10 ml BF₃·Et₂O (9.69 mmole) and 12 ml Et₂O were combined. The mixture was stirred for 20 hours at 25°C under nitrogen. The solvent and excess BF₃·Et₂O were removed under vacuum and the resulting dull green solid was further dried under vacuum at 25°C for 2 hours. The solid was recrystallized in a minimum amount of CH₃CN. The resulting microcrystalline product was dried under vacuum at 60°C. Analysis: C, 39.55%; H, 4.05%; N, 7.62%. Theoretical: C, 39.63%; H, 4.17%; N, 7.71%.

\[ \text{[Zn(DIOX)BF}_2\text{]}_2 \cdot \text{MeOH} \]

In a 50 ml round bottom flask 0.5 g [Zn(DIOX)OH0]₂, 2 ml BF₃·Et₂O and 10.0 ml Et₂O were combined. After stirring for 24 hours at 25°C under nitrogen, the white solid was filtered and washed well with Et₂O. The solid was vacuum dried for 4 hours at 25°C. Recrystallization
in a minimum amount of methanol and drying under vacuum at 25°C yielded a white crystalline solid. Analysis:
C, 41.66%; H, 4.395; N, 7.75% Theoretical: C, 41.30%; H, 4.16%; N, 7.70%.

\[\text{[Pd(DIOX)BF}_2\]_2\]

In a 50 ml round bottom flask, 0.21 g [Pd(DIOX)OH], 1.80 ml BF₃·Et₂O and 10.0 ml Et₂O were combined. After stirring for 20 hours at 25°C under nitrogen, the brownish red precipitate was filtered, washed with Et₂O and dried under vacuum at 25°C. Analysis: C, 38.38%; H, 4.00%; N, 6.95%. Theoretical: C, 37.10%; H, 3.38%; N, 7.21%.

\[\text{[Ni(DIOX)BF}_2\]_2 \cdot 7\text{H}_2\text{O}\]

In a 50 ml round bottom flask, 0.18 g [Ni(DIOX)BF]₂, 1.5 ml BF₃·Et₂O and 10.0 Et₂O were combined. After 24 hours of stirring at 25°C under nitrogen, the greenish precipitate was washed with Et₂O. Upon air drying, the solid turned purplish white. Drying under vacuum at 68°C for 15 minutes caused the color of the complex to return to its original green color. The purplish white solid was analyzed. Analysis: C, 35.75%; H, 4.62%; N, 6.79%. Theoretical: C, 35.69%; H, 5.0%; N, 6.93%.
[Ni(DIOX)OH$_2$]$_2$(NO$_3$)$_2$ • 2H$_2$O

In a 100 ml beaker, 0.5 g DIOX (1.03 mmoles) was combined with 0.446 g Ni(NO$_3$)$_2$ • 6H$_2$O (2.03 mmole) and 60 ml methanol. The mixture was heated while stirring and maintained at reflux temperature until the volume was reduced to 30 ml. After cooling, addition of diethyl ether yielded a grey blue precipitate. The solid was filtered and dried under vacuum. Analysis: C, 38.60%; H, 4.55%; N, 11.10%. Theoretical: C, 38.5%; H, 4.6%; N, 11.2%.

Results and Discussion

Ligand Preparation

The synthetic route for the preparation of bis-4-tert-butyl-2,6-diformyl-phenol dioxime, DIOX, is shown below (Equation 1) and is based on a procedure reported by Baucom and Drago. Successful synthesis of DIOX was confirmed

![Chemical structure](image)
by elemental analysis, which showed excellent agreement between the predicted theoretical and experimental values for the percentage C, H, and N (Table 5-1).

The most difficult part of synthesizing the DIOX ligand was obtaining the dialdehyde reagent, 4-tert-butyl-6-formylsalicylaldehyde. Its synthesis entails a fairly lengthy procedure developed by Desmond et al.,\textsuperscript{123,125} whom graciously supplied the reagent for use during this study.

Metalomers, Synthesis and Characterization

Combining an equimolar amount of DIOX ligand with the acetate or nitrate salt of any of the divalent cations Cu, Zn, Pd, or Ni results in the formation of a bimetallic complex which is believed to have the structure shown below.

\[
\text{[M(DIOX)OH}_2]_2
\]
Table 5-1. Elemental Analysis of the DIOX Ligand and Metal DIOX Complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>C</th>
<th>Calcd. %</th>
<th>H</th>
<th>N</th>
<th>C</th>
<th>Found %</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIOX</td>
<td></td>
<td>61.0</td>
<td>6.8</td>
<td>11.9</td>
<td></td>
<td>61.31</td>
<td>6.86</td>
<td>11.68</td>
</tr>
<tr>
<td>[Cu(DIOX)OH]_2</td>
<td></td>
<td>48.4</td>
<td>4.8</td>
<td>9.4</td>
<td></td>
<td>48.14</td>
<td>4.71</td>
<td>9.13</td>
</tr>
<tr>
<td>[Zn(DIOX)OH]_2</td>
<td></td>
<td>48.1</td>
<td>4.7</td>
<td>9.4</td>
<td></td>
<td>47.46</td>
<td>4.89</td>
<td>8.98</td>
</tr>
<tr>
<td>[Pd(DIOX)OH]_2</td>
<td></td>
<td>42.3</td>
<td>4.2</td>
<td>8.2</td>
<td></td>
<td>43.39</td>
<td>4.42</td>
<td>8.73</td>
</tr>
<tr>
<td>[Ni(DIOX)OH]_2</td>
<td></td>
<td>49.2</td>
<td>4.8</td>
<td>9.6</td>
<td></td>
<td>48.20</td>
<td>4.77</td>
<td>8.85</td>
</tr>
<tr>
<td>[Ni(DIOX)(OH)=[NO_3]=_2 (NO_3)_2 * 2H_2O</td>
<td></td>
<td>38.5</td>
<td>4.6</td>
<td>11.2</td>
<td></td>
<td>38.60</td>
<td>4.35</td>
<td>11.10</td>
</tr>
<tr>
<td>[Cu(DIOX)BF_2]_2 • 2H_2O</td>
<td></td>
<td>39.6</td>
<td>4.2</td>
<td>7.7</td>
<td></td>
<td>39.55</td>
<td>4.05</td>
<td>7.62</td>
</tr>
<tr>
<td>[Zn(DIOX)BF_2]_2 • MeOH</td>
<td></td>
<td>41.3</td>
<td>4.2</td>
<td>7.7</td>
<td></td>
<td>41.66</td>
<td>4.39</td>
<td>7.75</td>
</tr>
<tr>
<td>[Pd(DIOX)BF_2]_2</td>
<td></td>
<td>37.1</td>
<td>3.4</td>
<td>7.2</td>
<td></td>
<td>38.38</td>
<td>4.00</td>
<td>6.95</td>
</tr>
<tr>
<td>[Ni(DIOX)BF_2]_2 • 7H_2O</td>
<td></td>
<td>35.7</td>
<td>5.0</td>
<td>6.9</td>
<td></td>
<td>35.75</td>
<td>4.62</td>
<td>6.79</td>
</tr>
</tbody>
</table>
The structure consists of two divalent cations bridged by two phenoxy groups and further bound through the nitrogens of the four oxime groups. Infrared analysis supports the existence of the capping 0-H⋯0 groups on each side of the molecule. A representative infrared spectrum for these complexes is shown in Figure 5-2 for the copper system.

In all four complexes a broad band around 1750 cm\(^{-1}\) was observed due to the presence of 0-H⋯0 bridging groups. These bands are in a range similar to that reported for the complex CH\(_3\)Co(DH)\(_2\)Py shown below (\(\nu_{\text{OH}} = 1740 \text{ cm}^{-1}\)).

![Infrared spectrum of CH\(_3\)Co(DH)\(_2\)Py](image)

Table 5-2 lists the 0-H⋯0 group frequencies observed for the various metal complexes along with the frequencies of the bands assigned to C=N stretches, which also occur in a range similar to complexes previously reported\(^\text{129,130}\).

Elemental analysis of the complexes shown in Table 5-1 also agree with the proposed structure. Thus these complexes of the formula [M(DIOX)OHO]\(_2\) are neutral with each DIOX ligand effectively having a formal negative two charge.
Figure 5-2. Infrared spectrum of [Cu(DIOX)OH]$_2$, Nujol mull.
Table 5-2. Infrared Bands Observed in the Frequency Range 1800-1500 cm\(^{-1}\).

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu(0-H\cdots0)) cm(^{-1})</th>
<th>(\nu(C=\text{N})) cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(DIOX)OH(_0)](_2)</td>
<td>1742 (Br)</td>
<td>1561</td>
</tr>
<tr>
<td>[Zn(DIOX)OH(_0)](_2)</td>
<td>1723 (Br)</td>
<td>1557</td>
</tr>
<tr>
<td>[Ni(DIOX)OH(_0)](_2)</td>
<td>1758 (Br)</td>
<td>1552</td>
</tr>
<tr>
<td>[Pd(DIOX)OH(_0)](_2)</td>
<td>1770 (vBr)</td>
<td>1550</td>
</tr>
<tr>
<td>[Ni(DIOX)(OH(_2)](_2)(\text{NO}_3)](_2) (\cdot) 2H(_2)O</td>
<td>1553</td>
<td></td>
</tr>
<tr>
<td>CH(_3)Co(DH)Py(^a)</td>
<td>1740 (Br)</td>
<td>1548</td>
</tr>
<tr>
<td>ClCo(DH)Py(^b)</td>
<td>1710</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Schrauzer and Windgassen\(^{129}\) DH = dimethylglyoxime anion.  
\(^b\) Gillard and Wilkinson\(^{130}\)
The metal salt used, either the acetate or nitrate, was found to have an effect on the bimetal complex produced in the nickel system. When Ni(acetate)$_2$ was used as the nickel source the usual O-H····O bridged complex was formed. If Ni(NO$_3$)$_2$ was used a cationic non O-H····O bridged complex was formed and is believed to have the structure shown below.

![Diagram of complex](image)

\[ [\text{Ni(DIOX)}(\text{OH})_2]_2 \]

This complex can be isolated as a nitrate salt by addition of ether to the reaction mixture. Infrared spectra of the products formed from Ni(acetate)$_2$ and Ni(NO$_3$)$_2$ are shown in Figures 5-3 and 5-4 respectively. It can be quickly seen that the spectrum of the complex formed from Ni(NO$_3$)$_2$ does not contain the broad O-H····O band at 1758 cm$^{-1}$ and contains bands above 3000 cm$^{-1}$ due to
Figure 5-3. Infrared spectrum of [Ni(DIOX)OH]$_2$, Nujol mull.
Figure 5-4. Infrared spectrum of $[\text{Ni(DIOX)(OH)}_2]_2(\text{NO}_3)_2$, Nujol mull.
0-H stretches of the oxime groups. Elemental analysis (Table 5-1) also agrees well with the above proposed structure. This behavior was not observed in the Cu system. Regardless of the Cu source, nitrate or acetate, the same 0-H⋯0 bridged complex was formed. Thus it appears that in the nickel case a stronger base such as acetate is needed to abstract a proton from one of the oxime 0-H groups to allow formation of a 0-H⋯0 cap.

The 0-H⋯0 bridged complexes showed very poor solubilities in non-polar solvents and only slight solubility in polar solvents such as DMSO and hot acetonitrile. In an attempt to improve the solubility the complexes were reacted with BF$_3$·Et$_2$O forming the BF$_2$ capped complexes as shown in Equation 2. This reaction was
patterned after work reported by Schrauzer and Windgassen.\textsuperscript{129}

Elemental analysis of the four metal complexes (Cu, Ni, Pd, Zn) indicated successful conversion of the \(0\cdot H\cdots O\) bridge to a BF\textsubscript{2} cap. Infrared spectra of the resulting complexes lacked the \(0\cdot H\cdots O\) band usually observed at about 1750 cm\(^{-1}\). A representative infrared spectrum for these complexes is shown in Figure 5-5 for the copper system. In addition a large, very broad absorbance at about 1050 cm\(^{-1}\) was observed which is difficult to assign but probably can be attributed to the bridging BF\textsubscript{2} groups. (B-F stretches have been found to occur in the range 750-1500 cm\(^{-1}\)).

The nickel BF\textsubscript{2} bridged complex demonstrates some interesting chemistry not observed for the other metal complexes. The infrared spectrum of the green, vacuum dried complex (68\textdegree C, 1.5 hours) is shown in Figure 5-6. On exposure to air the complex quickly turned to a purplish-white color, and its infrared spectrum is shown in Figure 5-7. The only major difference in the two spectra was in the 3000-4000 cm\(^{-1}\) region which indicates the color change was due to adsorbed H\textsubscript{2}O. The complex can be reversibly returned to the green color upon vacuum drying. Elemental analysis indicated the presence of about seven H\textsubscript{2}O per complex.

The four BF\textsubscript{2} capped complexes, unlike the \(0\cdot H\cdots O\) bridged complexes, were soluble in acetone, methanol, ethanol, CH\textsubscript{3}CN and DMF. These complexes were insoluble in
Figure 5-5. Infrared spectrum of \([\text{Cu(DIOX)}\text{BF}_2]_2 \cdot 2\text{H}_2\text{O}\), Nujol mull.
Figure 5-6. Infrared spectrum of [Ni(DIOX)BF₂]₂ xH₂O, Nujol mull.
Figure 5-7. Infrared spectrum of \([\text{Ni(DIOX)BF}_2]_2 \cdot 7\text{H}_2\text{O}\), Nujol mull.
toluene, Et₂O and H₂O. Recrystallization of [Cu(DIOX)BF₂]₂ by slow evaporation of a methanol solution yielded crystals that could be used for an X-ray structure analysis.

**Electrochemistry**

The reduction potentials of [Cu(DIOX)BF₂]₂ relative to ferrocene/ferrocinium couple were obtained in two solvent systems, acetone and DMF and are shown in Table 5-3. Cyclic voltammograms showed two redox couples in both acetone and DMF, and the voltammogram obtained in DMF is shown in Figure 5-8. Based on the fact that the difference between the peak potentials is greater than 60 mV, the theoretical value for a one electron transfer, the two redox couples appear to be quasireversible one electron transfers. These redox couples are assumed to represent the stepwise reduction of the two Cu(II)'s to Cu(I)'s then stepwise reoxidation back to Cu(II)'s.

The differences between redox couples, E₁ - E₂ can be used to estimate K_con, the equilibrium constant for the conproportionation reaction below. The value of the K_con indicates the stability of the Cu(I)Cu(II)L⁻ mixed valence state. If two metal centers are totally
Table 5-3. Electrochemistry of Cu₂ Complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>1 ( E_{1/2}, \text{V} )</th>
<th>V, mV</th>
<th>2 ( E_{1/2}, \text{V} )</th>
<th>V, mV</th>
<th>( E_{1} - E_{2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Cu(DIOX)BF}_2] \cdot 2\text{H}_2\text{O})</td>
<td>Acetone</td>
<td>-0.86</td>
<td>90</td>
<td>-1.34</td>
<td>73</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>-0.93</td>
<td>91</td>
<td>-1.40</td>
<td>156</td>
<td>0.47</td>
</tr>
<tr>
<td>(\text{Cu}_2\text{BB(0Et)}^c)</td>
<td>(\text{CH}_2\text{Cl}_2)</td>
<td>-1.06</td>
<td>222</td>
<td>-1.78</td>
<td>235</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>-1.10</td>
<td>151</td>
<td>-1.60</td>
<td>270</td>
<td>0.50</td>
</tr>
<tr>
<td>([\text{Cu}_2\text{L}]\text{[ClO}_4\text{]}_2 \cdot 2\text{H}_2\text{O})^d</td>
<td>DMF</td>
<td>-0.917^e</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Cyclic voltammetry under \(\text{N}_2\) atmosphere, scan rate 100 mV/s. \(^b\) Potentials relative to an internal standard, ferrocene/ferrocinium couple. \(^c\) Drago et al., 123 \(^d\) Gagne et al., 9 \(L = N\) and \(O\) donor macrocyclic ligand, obtained from polarography.
Figure 5-8. Cyclic voltammogram of \([\text{Cu(DIOX)BF}_2]_2\) in DMF electrolyte at a scan rate of 100mV/s under N\(_2\) (referenced to ferrocene/ferrocinium couple).
$[\text{Cu(DIOX)BF}_2]_2$

in DMF
non-interacting, $K_C = 4$. Values of $K_C$ greater than $1 \times 10^3$ have been found to be Class II and values greater than $1 \times 10^{10}$, Class III (the electron completely delocalized) mixed valence complexes.

The values of $K_C$ calculated for acetone and DMF are $1.3 \times 10^8$ and $1.1 \times 10^9$, respectively. These results indicate that the $[\text{Cu(II)Cu(I)}(\text{DIOX})\text{BF}_2]^{-}$ might be approaching Class III. The $K_C$ values reported\textsuperscript{123} for $\text{Cu(II)Cu(I)BB(OEt)}^{-}$ in both a non-coordinating and coordinating solvent, $\text{CH}_2\text{Cl}_2$ and DMF, showed a large solvent dependence resulting in $K_C$ values equal to $3 \times 10^8$ and $2 \times 10^{12}$. The solvent dependence observed in the $\text{Cu}_2\text{DIOX}$ system was much smaller than for $\text{Cu}_2\text{BB(OEt)}$ for reasons that are not fully understood but may result from the absence of a removable anionic bridge ($\text{OEt}^-$) which is present in $\text{Cu}_2\text{BB(OEt)}$.

Electrochemical studies of $[\text{Zn(DIOX)BF}_2]_2$ showed no redox activity in the range allowed by the solvent and electrolyte. The corresponding Ni and Pd complexes were not well behaved and showed complicated irreversible redox couples.

**Conclusion**

In this study a series of bimetallic complexes of the formula $[\text{M(II)(DIOX)OH}_2]^-$, where M=Cu, Ni, Zn or Pd, have
been synthesized using the ligand bis-4-tert-butyl-2,6-diformyl-phenol dioxime. The insoluble $0\text{-H}\cdots\text{O}$ bridged complexes on reaction with $\text{BF}_3\cdot\text{Et}_2\text{O}$ are transformed into $\text{BF}_2$ capped complexes which are soluble in poor donor solvents such as acetone. This solubility allows solution studies to be carried out. In the past, solution studies of reported bimetallic ligands has proven difficult due to their lack of solubility in all but strong donor solvents.

Preliminary electrochemical studies were performed on the Cu(II) dimer which demonstrated a strong interaction between the two Cu(II) centers. Further work is needed to pursue the chemical and the potential catalytic properties of these complexes.
VI. SUMMARY AND CONCLUSION

The results obtained from the four studies presented here provided a fundamental understanding and insight into future catalytic processes which involve the activation of carbon monoxide and/or hydrogen. In the first study enthalpies of hydrogen activation were obtained for a typical hydrogenation catalyst and its derivatives. The enthalpies obtained were found to be independent of the variations made in the ligand environment about the rhodium metal center.

The second study investigated immobilized homogeneous CO reduction catalysts as selective catalysts for producing chemicals from syngas. Ionic attachment of two ruthenium anions to an ammonium iodide functionalized silica gel was demonstrated but showed no syngas conversion activity. A covalently attached Ir$_4$(CO)$_{11}$ cluster in combination with a Lewis acid co-catalyst was found to show excellent selectively for the conversion of syngas and HCl to CH$_3$Cl under very mild conditions.

In the third study a new type of catalyst support was synthesized which was designed for potential use in supporting a known homogeneous rhodium imidazole hydroformylation catalyst. This study demonstrated the
first successful synthesis of a 4(5) substituted imidazole functionalized silica gel.

In the fourth and final study a series of soluble bimetallic complexes were synthesized and characterized which have potential for use as bifunctional catalysts. Electrochemical studies illustrated strong metal site interactions.
REFERENCES


5. R. L. Pruett, Advances in Organometallic Chemistry (1979), 17, 1.

6. C. Masters, Advances in Organometallic Chemistry (1979), 17, 1.


38. R. H. Grubbs, Chemtech (1977), 512.
72. "Chemical Economics Handbook" SRI, Menlo Park, California, 635.2030C.

75. B. Arkles, Chemtech (1977), 766.


In August 1979, he entered the graduate school of the University of Illinois at Urbana-Champaign and he began his graduate work in inorganic chemistry. In June 1982, he transferred to the graduate school at the University of Florida, Gainesville, Florida (following his graduate research advisor's transfer). He completed his graduate work in inorganic chemistry in 1985. During his graduate study, he held various teaching and research assistantships.

On June 20, 1981, he married the former Nancy M. Holcomb in Ithaca, New York. On May 7, 1984, the author began employment with Union Carbide Corporation, Tarrytown, New York, as a Staff Chemist in the Catalyst and Process Systems Division.

He is co-author of the following publications and patent:


I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Russell S. Drago
Professor of Chemistry

Harry H. Bisler
Distinguished Service Professor of Chemistry

David Richardson
Assistant Professor of Chemistry

Anna Brajtej-Toth
Assistant Professor of Chemistry
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Waldo R. Fisher, M.D.  
Professor of Biochemistry and Molecular Biology

This dissertation was submitted to the Graduate Faculty of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December, 1985  
Dean, Graduate School