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Studies of homogeneous dirhodium catalyst system

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STUDIES OF HOMOGENEOUS DIRHODIUM CATALYST SYSTEM

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy
in

The Department of Chemistry

by
Catherine L. Thomas Alexander
B.S., Louisiana State University, 2004
May 2009

I have learned that success is to be measured not so much by the position that one has reached in life as by the obstacles which he has had to overcome while trying to succeed.

-Booker T. Washington

DEDICATION

This dissertation is dedicated to those that believed
in me from the beginning of this endeavor:

My parents, Diana and Arnold Thomas
My husband, Desmond Alexander
My brother, A.J. Thomas
My cousin, Keiona Murray
My grandmother, Catherine Minor

Thanks to you all for your continued and unwavering support.
I will love and cherish you all forever.

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I would first like to thank God for the strength that He has given me for this journey. Through His grace and mercy, I am still standing.

I would like to thank my family for their love, support, and prayers. To my mother, Diana Thomas, thank you for being the best friend that anyone could ever ask for. You will never know how many days that just hearing your voice got me through the day. To my father, Arnold Thomas, I greatly appreciate the countless words of wisdom and advice. I will always remember to take in the “big picture.” To my husband, Desmond Alexander, I love you for loving me through the goods days and the bad. Thank you for always making me laugh, even at times when I could cry. To my brother, A.J. Thomas, thank you for being my friend. You are wise beyond your years, and have provided words of encouragement when I least expected it. To my cousin, Keiona Murray, thank you for teaching me patience. To my grandmother, Catherine Minor, thank you for being a true example of a strong, hardworking woman. Your strength and determination have greatly influenced me.

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ABSTRACT

Hydroformylation studies were conducted to investigate the effects of various H₂/CO ratios on *rac*-[Rh₂H₂(μ-CO)₂(*et*,*ph*-P₄)]²⁺, a dirhodium tetrakisphosphine catalyst system. Similar experiments were also conducted with monometallic catalysts based on BISBI, NAPHOS, and Xantphos, some of the best bisphosphine ligands for hydroformylation catalysis. This was due to the lack of information in literature on the effects of variable ratios and pressures on activities and selectivities of catalysts that contain bisphosphine ligands, and these studies were also used as a basis of comparison for the dirhodium system. Results indicate that the dirhodium system is more efficient with higher H₂/CO ratios (2:1, 90 psig total pressure appears to be near optimum) with good turnover frequencies, high regioselectivities, and lower catalyst fragmentation reactions in comparison to standard 1:1 H₂/CO conditions. The dirhodium catalyst appears to be extremely sensitive to CO induced loss of Rh to deactivate the catalyst. The monometallic systems show that higher H₂/CO ratios increase catalytic activity and yield higher aldehyde regioselectivities, but also increase the percentage of olefin isomerization. The monometallic systems also demonstrate Rh-induced phosphine fragmentation reactions and catalyst decomposition due to the lower CO partial pressures.

Due to the increased activity and selectivity obtained when using a 2:1 H₂/CO ratio, *in situ* high pressure IR studies were conducted to determine if there were any structural differences between the dirhodium catalyst generated at a 1:1 H₂/CO ratio and a 2:1 H₂/CO ratio. Also due to the increased activity and selectivity in 30% water/acetone (by volume) in comparison to acetone, solvent effect studies were conducted to compare structural differences in acetone and 30% water/acetone. Preliminary IR studies suggest that there are not any structural differences

in the 2:1 H₂/CO ratio and 30% water/acetone studies in comparison to standard hydroformylation conditions.

CHAPTER 1: HISTORY OF HYDROFORMYLATION CATALYSIS

1.1 Introduction

Hydroformylation is a homogeneous reaction generally catalyzed by Rh or Co, where CO and H₂ are added to the double bond of an alkene converting the alkene to a linear (normal) or branched (iso) aldehyde. The aldehydes are generally hydrogenated to produce alcohols or oxidized to form carboxylic acids. The linear product is preferred due to its use in plasticizers, detergents, and surfactants where the branched product has poor properties. Unfavorable hydroformylation side products can be formed due to hydrogenation or isomerization of the alkene (Figure 1.1). The amount of side products produced in the reaction is determined by the selectivity of the catalyst used.

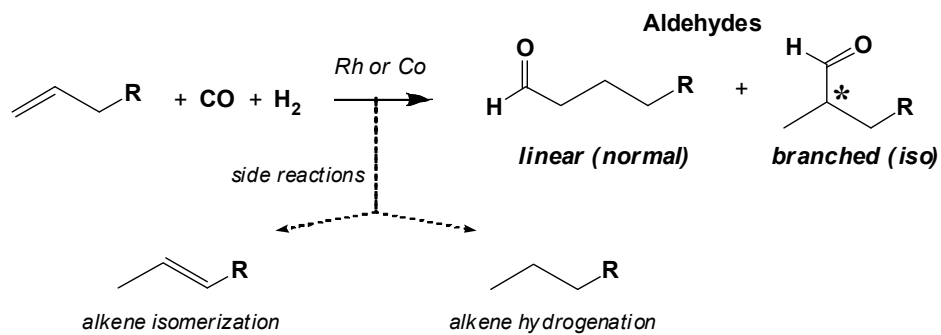


Figure 1.1. Hydroformylation Reaction.

Hydroformylation catalysis was accidentally discovered on July 26, 1938 by Otto Roelen of Ruhrchemie AG at Oberhausen Germany.¹ Roelen was investigating the presence of oxygenated compounds in the products of the Fischer-Tropsch synthesis, a heterogeneously catalyzed reaction that produces hydrocarbons from H₂ and CO.¹⁻³ One of his goals was to find a method to recycle the olefins generated by the Fischer-Tropsch reaction in order to increase the chain lengths of the hydrocarbons.¹ He attempted to repeat an experiment conducted by Smith by passing a mixture of syngas (H₂/CO) and ethylene over a fixed-bed-cobalt containing catalyst at

150 °C and 1 bar pressure.^{1,2} Propanal and some diethyl ketone, oxo-containing compounds, were produced as a result of the reaction so the reaction was called oxo synthesis or oxonation.¹ Adkins and Krsek later coined the term hydroformylation.⁴

The history of hydroformylation can generally be broken down into three periods, or generations, based on developments in research during that time. Cobalt catalysts represent first generation processes. Reaction conditions were harsh with pressures ranging from 200 to 350 bar to avoid catalyst decomposition and temperatures between 150 and 180 °C to achieve acceptable rates of reaction.¹ Development of first generation processes focused on improving the reaction by increasing selectivity to linear aldehydes, utilizing milder reaction conditions, and decreasing the amount of unwanted side products. Researchers also focused on separating the product from the catalyst in order to recycle the catalyst. Most consider the final development in this generation to be the discovery by Shell researchers that phosphines could be used as ligands for hydroformylation.⁵

Second generation processes are represented by phosphine-modified rhodium catalysts. These catalysts allow for far milder reaction conditions with a pressure range from 10-60 bar and temperatures from 60-130 °C.¹ These processes were referred to as low-pressure oxo (LPO) reactions. As seen in the first generation processes, second generation processes still faced the problem of separating the product and catalyst. This problem led to the development of third generation processes that utilize water soluble phosphines. This allows the hydroformylation to occur in an aqueous phase allowing easy separation of the product and catalyst.

2008 marked the 70th anniversary of hydroformylation. Since its fortuitous discovery, it has become one of the most important carbonylation reactions in the world. Today, more than 10 million tons of aldehyde are produced each year using this catalysis, an increase from an annual production of approximately 6 million tons in 1995.³ Continued growth of

hydroformylation catalysis can be attributed to two industrially important factors, the first being the growth of the petrochemical industry which generates a wide variety of pure olefins that are relatively inexpensive in comparison to the previous feedstock of natural or Fischer-Tropsch generated olefins. The second factor that contributes to continued growth are markets that utilize alcohols generated from the hydrogenation of the aldehydes, particularly the plastics and detergent industries. Although the majority of the aldehydes are converted to alcohols for these industries and others, several other compounds are accessible through hydroformylation (Figure 1.2).⁶

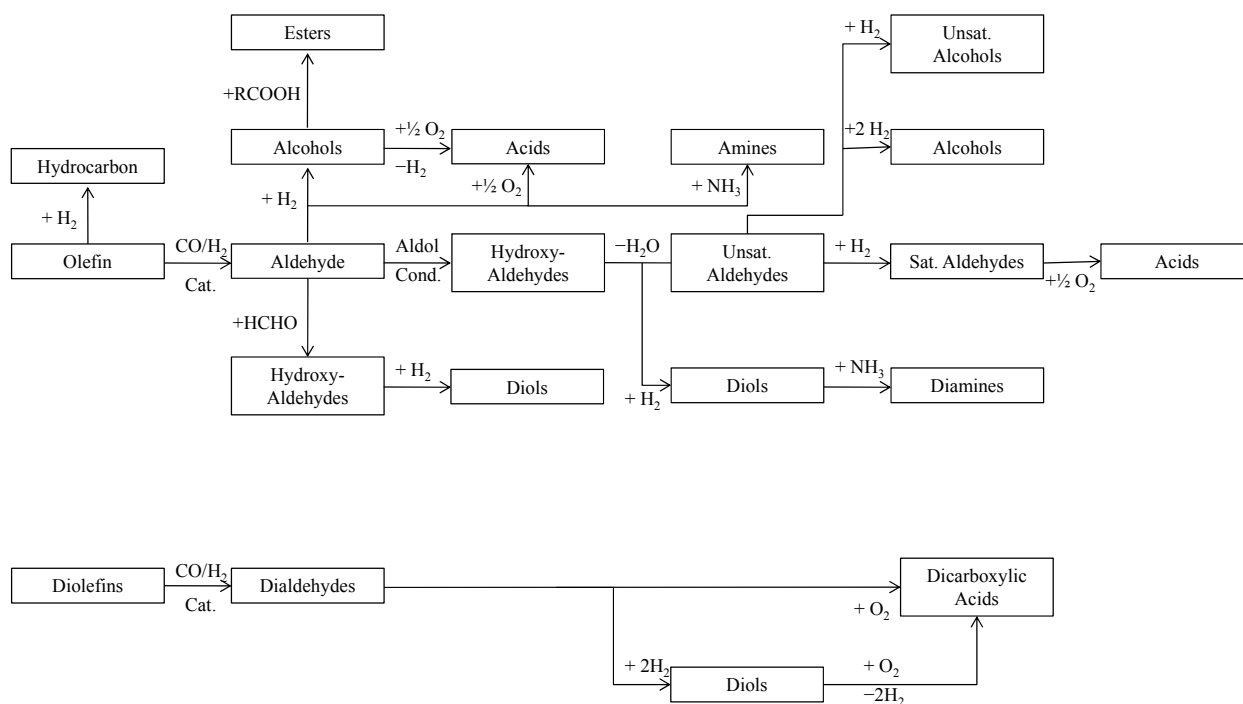


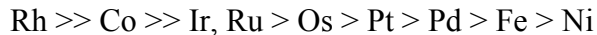
Figure 1.2. Compounds accessible through hydroformylation.⁶

1.2 Catalysts

1.2.1 Monometallic

Hydroformylation catalysts can generally be represented by the expression, $H_xM_y(CO)_zL_n$ where M is the transition metal and L represents ligands other than carbonyls. The catalyst is

considered to be unmodified for $n=0$.^{1,3} The original catalyst used by Roelen, $\text{HCo}(\text{CO})_4$, resulted from hydrogenation of dicobalt octacarbonyl, $\text{Co}_2(\text{CO})_8$, but since its initial discovery several metals have been investigated for use in hydroformylation catalysis. Metal carbonyls of groups 8-10 all catalyze the hydroformylation reaction. Molybdenum, chromium, manganese, and technetium, also form metal carbonyls and have all been claimed to be at least slightly active for hydroformylation catalysis, however, they are not nearly as active as metal carbonyl species from groups 8-10.¹ The generally accepted order of hydroformylation activity for groups 8-10 metals is shown below.⁷



Today, most research focuses on four of the most active transition metals, rhodium, cobalt, ruthenium, and platinum, however, industrial plants only run cobalt or rhodium systems so they will be the only metals discussed here.⁸

1.2.1.1 Unmodified Cobalt Catalysts

As mentioned previously, hydroformylation catalysis was discovered in 1938 and the first hydroformylation process went on line at the Ruhrchemie site in 1942. However, the currently accepted mechanism was not proposed until 1961 by Heck and Breslow (Figure 1.3).^{1,9} They proposed that the active catalytic species, $\text{HCo}(\text{CO})_4$ (**A**), is formed from the hydrogenation of $\text{Co}_2(\text{CO})_8$. A CO ligand dissociates from the $\text{HCo}(\text{CO})_4$ complex producing $\text{HCo}(\text{CO})_3$; a π -olefin complex is then formed when the olefin reacts with $\text{HCo}(\text{CO})_3$ forming species **B**. **B** then undergoes a migratory insertion, followed by the addition of CO, forming alkyl carbonyl complex **C**. A second migratory insertion occurs with the alkyl and a CO ligand, followed by the addition of a CO ligand forming an acyl species, **D**. Formation of **D**, is followed by loss of CO and the oxidative addition of H_2 forming **E**. The aldehyde is then reductively eliminated, regenerating the key catalytic species **A**. They also proposed a bimetallic pathway where a

possible intermolecular hydride transfer occurs between **A** and **D** to eliminate the aldehyde product.

High temperatures and CO partial pressures are required for reasonable catalytic activity. The high pressure increases catalyst stability by preventing the loss of the carbonyl ligands, which would otherwise result in the production of metallic cobalt. The increase in CO partial pressure decreases the rate of the hydroformylation reaction and alkene isomerization by minimizing unsaturated Co complexes, and increases linear to branched ratio of the aldehyde.¹⁰

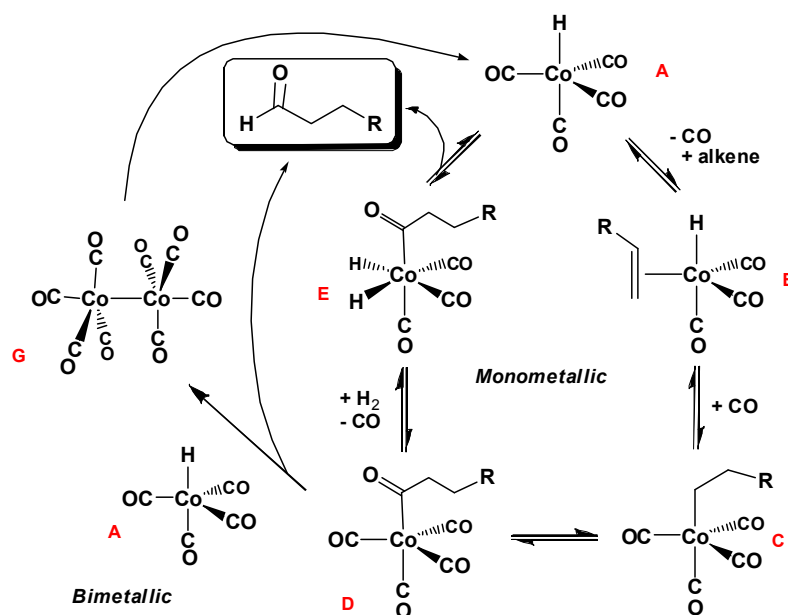


Figure 1.3. Cobalt catalyzed reaction proposed by Heck and Breslow.

1.2.1.2 Phosphine-Modified Cobalt Catalysts

Studies by Reppe *et al.* in 1941 represented some of the earliest work on phosphines as possible ligands in the synthesis of acrylic esters from alkynes, alcohols, and carbon monoxide.¹¹ Substituting one of the CO ligands with an electron donating alkyl phosphine ligand resulted in stronger Co-CO bonding, which resulted in a more stable catalyst system. The increased

stability, however, presents several advantages and disadvantages. Due to the increased stability, the catalysis is a hundred times slower than the unmodified cobalt catalyst.¹⁰ Also as a result of increased stability, the temperature at which the reaction is carried out must be increased from 140 °C to 170 °C to overcome the decrease in activity.¹ Another disadvantage was an increase in olefin hydrogenation activity.¹⁰ Some of the advantages of this modified catalyst were: lower H₂/CO pressures can be used (25-100 bar versus 200-300 bar), increased catalyst thermal stability, and considerably increased selectivity for the linear product.¹

Slaugh and Mullineaux of Shell first reported the use of phosphines in cobalt catalyzed hydroformylation processes in the 1960's.⁵ They tested several alkyl and arylphosphines for use in cobalt catalysis (195 °C, 36 bar). They found that the alkylphosphines led to increased stability, but slower catalysis with aldehyde linear:branched (L:B) ratios of 8:1 to 9:1. Arylphosphines, on the other hand, were not effective ligands for catalysis because they are weak electron donors compared to the alkylphosphines and do not produce stable catalysts. Arylphosphines also rapidly decompose at the higher temperatures required for the modified cobalt catalysts, and the effect is intensified as the electron withdrawing ability of the ligand increases.^{12,13} The alkylphosphine ligands were preferred over the arylphosphines for cobalt catalysis. The orders of activity (a) and selectivity (b) are shown below:¹⁰



The Shell hydroformylation process is believed to use a phosphabicyclononane such as 9-icosyl-9-phosphabicyclo[3.3.1] nonane.^{10,14} The ligand has a C-20 chain which increases the boiling point of the catalyst, allowing higher temperatures to be used to separate the product from the catalyst. Even though as much as 15% of the alkene feedstock can be hydrogenated, the increased hydrogenation activity is actually used as an advantage since most aldehyde products

are converted to alcohols - the desired product. The Shell process is the only industrial process that uses a phosphine-modified cobalt catalyst.

1.2.1.3 Unmodified Rhodium Catalysts

Rhodium catalysts were first reported in 1952 by Schiller as an alternative to cobalt for hydroformylation catalysis.³ Some of the first rhodium catalyst precursors used were RhCl_3 and $\text{Rh}/\text{Al}_2\text{O}_3$, and it was quickly evident that they were more active than unmodified cobalt catalysts. Other unmodified rhodium catalyst precursors such as $\text{Rh}_4(\text{CO})_{12}$, $\text{Rh}(\text{CO})_2(\text{acac})$, and $[\text{Rh}(\text{COD})(\text{OAc})]_2$ were of interest due to the fact that they were active under mild conditions in comparison to their cobalt counterparts.¹¹ Rhodium catalysts were found to be a thousand times more active than the cobalt catalysts, so only small amounts of catalyst were needed to achieve catalytic activity. This was an added benefit because one of the disadvantages of using rhodium is the cost of the metal with rhodium being a thousand times more expensive than cobalt.⁶ Some of the unmodified catalysts were even found to be active at room temperature.¹¹ Another advantage of the rhodium catalysts was that they were unaffected by the presence of functional groups on the olefins.⁶ It was also observed that rhodium catalysts reduced the number of side reactions that are typical in hydroformylation catalysis and were almost completely selective for the aldehyde product, but produced more branched products than cobalt catalysts.

1.2.1.4 Phosphine-Modified Rhodium Catalysts

As seen with cobalt catalysts, rhodium catalysts that are modified with strong electron donating ligands generate more stable and selective catalysts in comparison to their unmodified counterparts. Due to increased catalyst stability, lower CO pressures can be used, but a decrease in activity is observed. This can be overcome by using a larger reactor volume. Other advantages

of modified rhodium catalysts include increased linear to branched ratios and decreased olefin isomerization.^{1,10}

The most famous phosphorus-modified rhodium catalyst is $\text{RhH}(\text{PPh}_3)_3\text{CO}$. This compound was discovered by Vaska in 1963, but its catalytic activity was not reported until the late 1960's to early 1970's by Wilkinson and co-workers.¹⁵⁻¹⁸ $\text{RhH}(\text{PPh}_3)_3\text{CO}$ was found to be generally stable in air and easily prepared, but required excess phosphine ligand to remain active and stable (Figure 1.4). $\text{RhH}(\text{PPh}_3)_3\text{CO}$ yielded approximately 95% of the linear product and was catalytically active at room temperature. The mechanism for the Rh/ PPh_3 catalyst was proposed by Wilkinson (Figure 1.5).¹¹

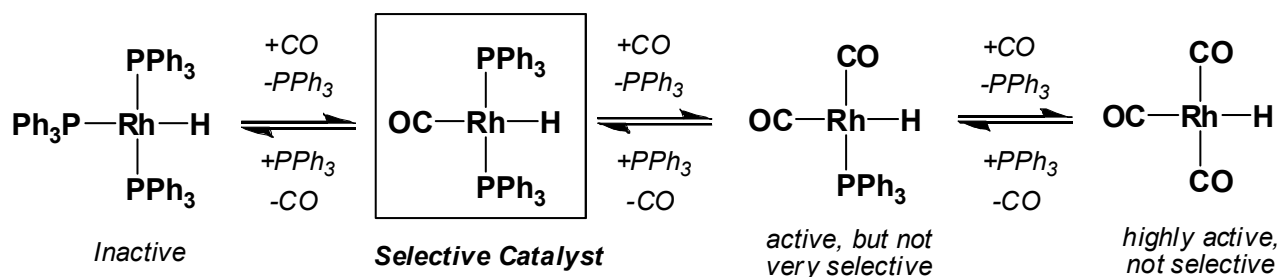


Figure 1.4. Deactivation pathway for phosphine modified rhodium catalysts.

The first industrial hydroformylation process using the triphenylphosphine modified rhodium catalyst went on line in 1974 by the Celanese Corporation (later the Hoechst Celanese Corporation). The Union Carbide Corporation soon followed when their process went on line in 1976, and the Mitsubishi Chemical Corporation in 1978.¹⁰ Overall, the phosphine-modified rhodium catalysts generally replaced cobalt catalysts since the benefits of the rhodium catalysts outweighed their cost. The Rh/ PPh_3 catalysts were faster, conditions were milder, and feedstock utilization was better than cobalt catalysts. However, rhodium catalysts never replaced cobalt catalysts for the hydroformylation of internal higher olefins for detergent alcohols used in motor oil.

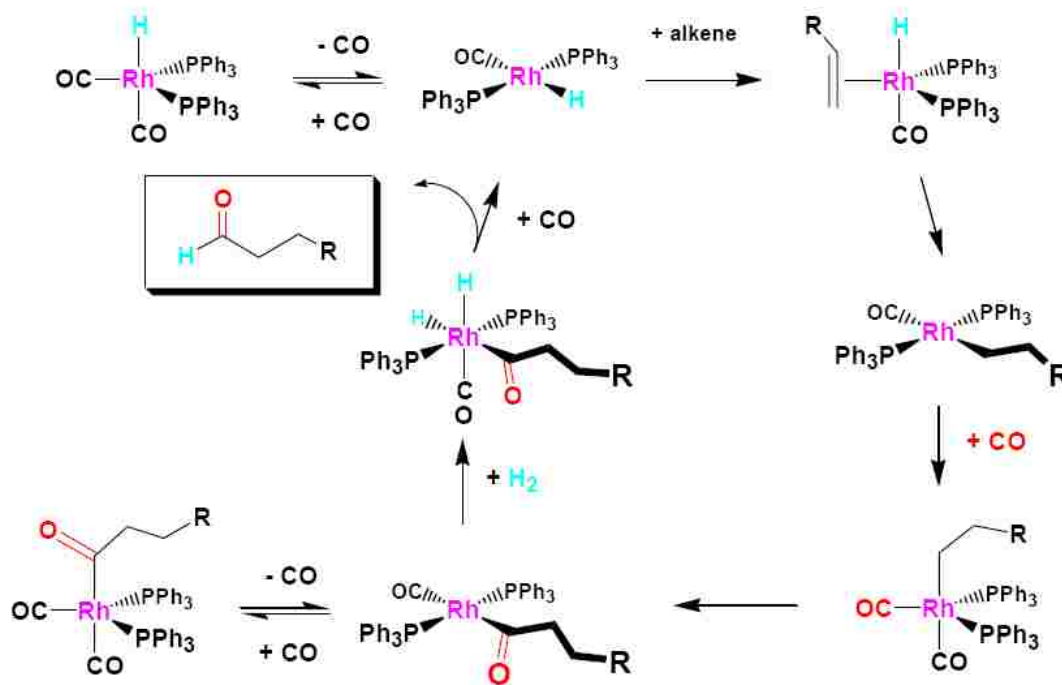


Figure 1.5. Hydroformylation mechanism proposed by Wilkinson.

1.2.2 Polymetallic Catalysts

Bimetallic catalysis was first introduced by Heck in 1961 in the proposed mechanism for cobalt catalyzed hydroformylation. Heck suggested, but did not favor, a bimetallic pathway in which an acyl cobalt complex and the hydrido cobalt tetracarbonyl species come together to reductively eliminate the aldehyde product thereby forming the bimetallic dicobalt octacarbonyl complex which could be hydrogenated to reform the key catalytic species to restart the catalytic cycle (Figure 1.6). The monometallic pathway dominated because the bimetallic pathway was limited by the concentrations of the hydride and acyl species in the solution as it was unlikely that they would frequently get close enough to each other to perform the reductive elimination for this to be an effective mechanism.

Since then, the majority of bi- and polymetallic research has focused on homo- and heterometallic cluster chemistry. Many researchers in this area of catalysis have reported

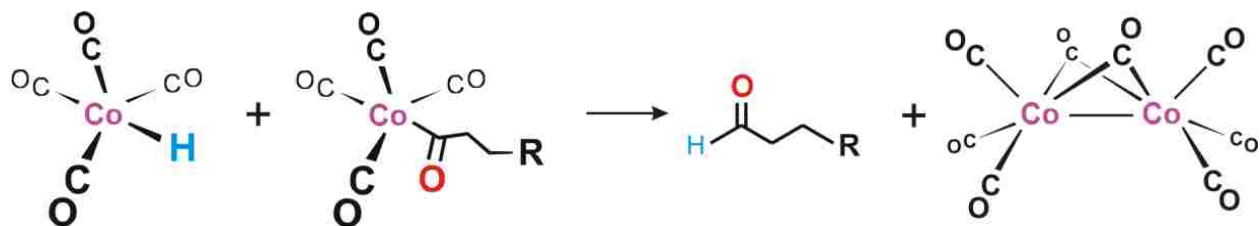


Figure 1.6. Bimetallic pathway proposed by Heck.

catalytic activity and synergistic effects when metal clusters are applied to hydroformylation catalysis. However, careful research by Garland showed that Rh clusters remain intact only at low temperatures and low pressures. Garland “proved” that the key catalytic species was actually the extremely active hydrido rhodium carbonyl species, $\text{HRh}(\text{CO})_3$, which was formed in small amounts from the metal clusters at the conditions used.¹⁹ The clusters that remained intact did not display any hydroformylation activity.¹

Work suggesting a bimetallic catalyst can be found in research conducted by Kalck.³ He used two bridging thiolate ligands to form the bimetallic complex, $\text{Rh}_2(\mu\text{-SR})_2(\text{CO})_2\text{L}_2$ ($\text{R} = \text{Bu}$, Ph and $\text{L} = \text{P}(\text{OMe})_3$, $\text{P}(\text{OPh})_3$, PPh_3). Kalck reported high catalytic activity in the hydroformylation of 1-hexene with exclusive formation of aldehydes and no alcohol or condensation products.^{20,21} As promising as the results seem, the activities and selectivities are very similar to those of the PPh_3 -modified monometallic Rh catalyst system, which suggests that the system may not be bimetallic after all. Kinetic and spectroscopic studies conducted separately by Southern and van Leewen further confirmed the monometallic nature of Kalck’s catalyst.^{22,23}

Work by Stanley and coworkers provide far more convincing evidence of bimetallic cooperativity in hydroformylation. Stanley reported that $(\text{Et}_2\text{PCH}_2\text{CH}_2)(\text{Ph})\text{PCH}_2\text{P}(\text{Ph})(\text{CH}_2\text{CH}_2\text{PEt}_2)$ can be used to chelate and bridge two rhodium metal centers, forming a catalyst that is highly active and selective in the hydroformylation of 1-

hexene. In order to provide strong evidence for the bimetallic cooperativity, Stanley tested the activity of catalysts that were structurally and electronically similar to the proposed bimetallic catalysts in order to determine whether or not the two metals were acting as independent monometallic catalysts. The rates using these modified catalysts were far lower than the bimetallic system, further confirming bimetallic cooperativity. The past and present work conducted by Stanley concerning this bimetallic catalyst will be further discussed in Chapter 2.

1.3 Ligands

1.3.1 Phosphine Ligands

In phosphorus modified catalysts, the steric and electronic properties, along with the number of the phosphorus-based ligands (P-ligands) used greatly influence the activity and selectivity of the catalyst. A bulky P-ligand can determine how many other P-ligands and CO ligands can bind to the metal center which will ultimately determine the electronic properties of the metal center (electron rich/poor). P-ligand effects vary depending on the parameters of the reaction in which they are used. In the early to mid 70's, Tolman published a method to classify P-ligands based on their steric size and electron donating ability.^{24,25} The steric profile, or cone angle θ , is defined as “the apex angle of a cylindrical cone centered at 2.28 Å from the center of the P atom which touches the outermost atoms of the model” (Figure 1.7a).¹¹ The electron donating and accepting abilities of a ligand are described by the electronic parameter χ . High χ values indicate strong π accepting properties whereas low χ values represent ligands that are strong σ donors (Figure 1.7b).

Phosphines (PR_3 , R = C_6H_5 , $n\text{-C}_4\text{H}_9$), triphenylphosphine, and phosphites (discussed below) are the only ligands used in industrial hydroformylation processes. Nitrogen-based ligands such as isonitriles, amines, and amides, cannot be utilized for hydroformylation catalysis.

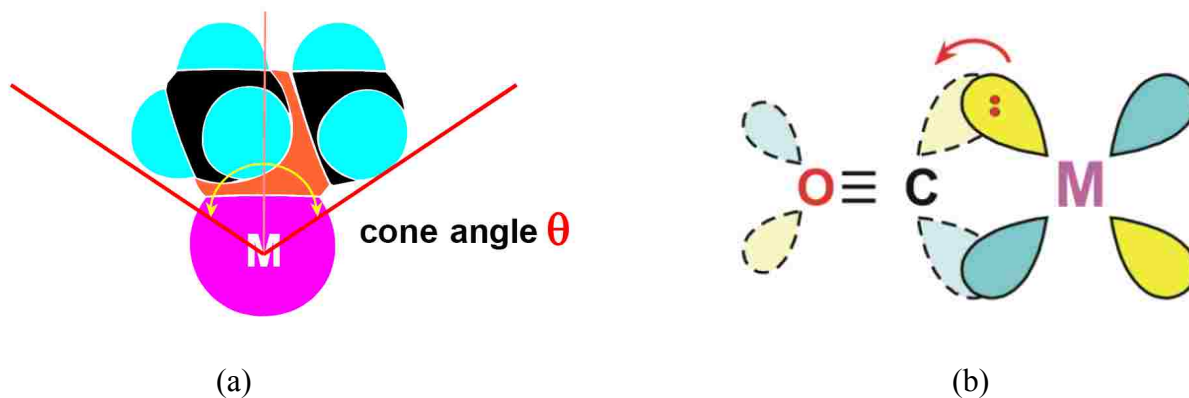
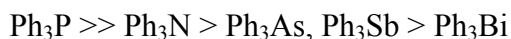


Figure 1.7. Tolman cone angle (a) and π -back donation to CO from the metal center (b).

Evidence to support the preferred use of phosphines over other comparable ligands was provided in a study by Carlock which compared the effects of aryl ligands based on Group V elements on the hydroformylation of 1-dodecene at 90 °C and 8 bar syngas. The order of reactivity is shown below:²⁶



Ligand effects vary based on the metal center. When applied to cobalt catalysts, alkylphosphines increase the stability of the catalyst, but decrease the activity of the catalyst. The reason is that alkylphosphines are strong electron donors which slows down the dissociation of the carbonyl ligand, and as a result reduces the rate of catalysis. Arylphosphines, on the other hand, are poorer σ -donors and better at π -backbonding and do not promote as much carbonyl ligand π -backbonding, thus promoting more facile CO dissociation. Wilkinson vividly demonstrated that arylphosphines produced very active rhodium catalysts that could even operate at ambient conditions.¹⁶ Arylphosphines are preferred over alkylphosphines for rhodium catalysis because alkylphosphines are too strong σ -donors resulting in decreased catalytic activity via too much Rh-CO π -backbonding.

The only known industrial use of a phosphine oxide is by Mitsubishi Kasei. In 1987, their process for the hydroformylation of octenes went on line producing 30,000 tons of the branched isononanol product per year. This rhodium catalyzed process uses triphenylphosphine oxide (TPPO) as a ligand. After the hydroformylation reaction occurs, the product is separated from the reaction mixture by distillation. Excess triphenylphosphine is added at this stage to prevent the loss of the catalyst. After the product is separated, the mixture containing the excess TPPO and triphenylphosphine is oxidized to regenerate the TPPO catalyst.

Water soluble phosphine ligands were discovered by researchers at Rhône-Poulenc and Ruhrchemie AG in 1982 when they sulphonated a triphenylphosphine ligand producing $P(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3$ (tppts) (Figure 1.8).^{1,10} When applied to rhodium catalysts, the catalyst becomes highly soluble in water. As mentioned above, water soluble ligands allow the catalysis to occur in the aqueous layer while the substrate and product remain in the organic layer which separates the aldehyde product from the catalyst. This method can only be used for the hydroformylation of lower alkenes such as propene and butene. It cannot be applied to higher olefins due to their low solubility in water (1-octene is 1000 times less soluble in water than propene). The Ruhrchemie Rhône-Poulenc-Process was commercialized in 1984 at Ruhrchemie (now Celanese) site for the hydroformylation of propene to form butanal. In 1995, the Hoechst (now Celanese) process went on line for the hydroformylation of 1-butene.¹⁰

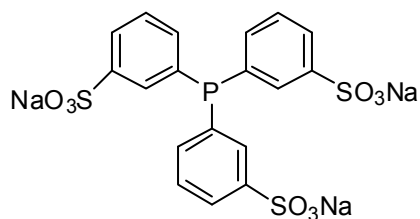


Figure 1.8. Sulphonated triphenylphosphine ligand.

1.3.2 Phosphite Ligands

In 1969, Pruett and Smith of Union Carbide reported the use of phosphite ligands for hydroformylation catalysis by successfully catalyzing the hydroformylation of methyl methacrylate and 1-octene.²⁷ They found that as the electron withdrawing properties of the ligand increased, the selectivity for the linear product increased. Van Leeuwen and Roobeek later reported success of applying bulky phosphites, particularly tris(2,2,2-trifluoroethyl) phosphite, in the hydroformylation of 1-alkenes and internal alkenes, which are generally unreactive. Rhodium catalysts using bulky phosphites produced 96% and 66% linear aldehyde product using 1-alkenes and internal alkenes respectively. There are some advantages to using phosphites over phosphines. Synthesis of phosphites is far easier than that of phosphines, and they are generally not as sensitive to sulfur compounds and oxidizing agents. Disadvantages of phosphites in comparison to phosphines are that they are more susceptible to hydrolysis and alcoholysis fragmentation side reactions.

Industrial chemists have been studying phosphite ligands for use in hydroformylation catalysis for approximately 25 years. Recently, there have been increasing concerns about exposure to and emissions of dioctyl phthalate (DOP), a plasticizer used in the production poly(vinyl chloride) (PVC). Exposure can easily occur from migration of plasticizers from plastic food packages and medicine containers to the food and medicine contained within them. Plasticizers can also be emitted from plastic containing building materials. 2-ethylhexanol (2-EH) is currently used to synthesize DOP. Higher chain alcohols are currently being investigated as alternatives for synthesizing less volatile plasticizers. 2-EH is synthesized by the hydroformylation of propene which is followed by aldol condensation and hydrogenation. The first step in the synthesis of higher chain alcohols, for the production of nonvolatile plasticizers,

is hydroformylation of higher chain olefins. The major problem is the separation of the Rh-phosphine (or phosphite) catalyst from the very high boiling point longer chain aldehyde or alcohol.

1.3.3 Diphosphine Ligands

New generation rhodium catalysts consist of chelating diphosphine and diphosphite ligands. The effects that these ligands have on the catalyst depend on the substituents on the phosphines, but the results, so far, seem very promising. In 1987, Devon of Eastman Kodak (now Eastman Chemical) developed a series of bidentate ligands based on NAPHOS, a highly active and selective bidentate ligand originally developed by Takaya (Figure 1.9). One of the first of these ligands was BISBI. The rhodium catalyst formed when using the BISBI ligand generated a highly active and selective catalyst ($3650 \text{ mol} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$, $1:b = 30$).¹¹

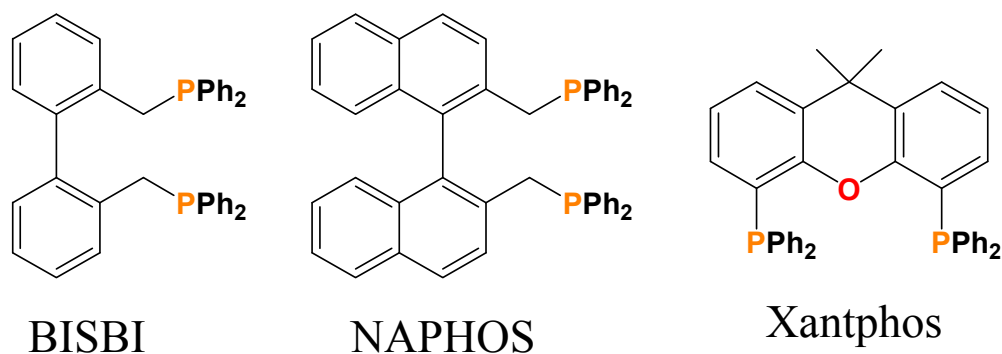


Figure 1.9. Structures of diphosphine ligands

It was suggested that the wide bite angle of the BISBI ligand was somehow responsible for the increased selectivity of the linear aldehyde product. The bite angle of the BISBI ligand was larger than the standard 90° bite angle seen in many other bidentate ligands. In order to determine if there was a possible link between selectivity and bite angle, Casey and Whiteker used molecular mechanics to calculate natural bite angles. It is defined as “the preferred

chelation angle of the bidentate ligand, as determined only by ligand backbone constraints and not by metal valence angles.”¹¹ Casey and Whiteker compared BISBI with *trans*-bis(diphenylphosphino)cyclopropane (*trans*-dppm-cyp). They synthesized complexes using both ligands and calculated the natural bite angle and the measured the bite angle from the crystal structure of each complex. The calculated natural bite angles for BISBI and *trans*-dppm-cyp were 112° and 126 ° respectively.^{11,28,29} The selectivity of the *trans*-dppm-cyp, however, was very low with a 2.6 ligand to branched ratio. The lower ratio was attributed to the fact that the ligand could not form stable chelates with the metal center due to strain. The studies also provided evidence of bis-equatorial coordination of the bidentate ligand to the metal center which leads to higher selectivity as opposed to an axial-equatorial binding which produces catalysts with lower selectivity.¹¹

The findings of Casey and Whiteker led to changes in work being done at the University of Amsterdam by van Leeuwen and coworkers. They were investigating the stabilizing effects of ligands with bite angles larger than the normal 75-99 ° on the metal center.¹¹ By using xanthene as a backbone, the ligand Xantphos was synthesized (Figure 1.9). Other compounds similar to xanthene were used to develop a complete series of ligands known as Xantphos ligands for the purposes of comparing the effects of the bite angle on the catalyst.^{11,30} The researchers found that for the most part, changing the bite angle generally has an advantageous effect on either the activity or the selectivity of the catalyst or both. Also, the ligand sulfonation mentioned above in monophosphine ligands can be applied to diphosphine ligands as well. Sulfonated diphosphine ligands retain their activity and selectivity in aqueous solutions, but have the added benefit of easy separation of the product and catalyst. The problem of hydroformylation of longer chain alkenes that are not soluble in water remains.

1.4 Reaction Conditions

Reaction conditions are equally as important to the success of a hydroformylation reaction as the metal center and ligands. Reaction conditions will vary for the metal center used and if the catalyst is phosphine-modified or not. It is important to optimize the reaction conditions so that the best activity and selectivity are achieved.

For unmodified catalysts, as the temperature of the reaction increases, the catalytic activity increases, but there is a slight decrease in the selectivity at higher temperatures. This is not the case, however, when functionalized α -olefins are used as the substrate. The linear to branched ratio actually increases at higher temperature for these substrates.¹ There is an increase in side product formation, particularly olefin hydrogenation and isomerization, and aldehyde hydrogenation. To maintain the highest activity and selectivity achieved with temperature optimization, higher total pressures are generally utilized (300-400 bar). At pressures lower than 300 bar and pressures higher than 400 bar there is a decrease in the selectivity of the catalyst.^{1,3}

As mentioned above, the use of phosphine ligands with rhodium and cobalt catalysts lead to an increase in selectivity, but catalytic activity decreases. The temperature of the reaction must be raised to compensate for the decrease in activity. However, raising the temperature decreases the selectivity and increases Rh-induced phosphine fragmentation reactions. Most industrial Rh/PPh₃ processes operate around 120 °C to maintain good activity and selectivity.¹¹ Even though these systems are not as active as unmodified catalysts, the benefits of the higher selectivity far outweigh the loss of activity.

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CHAPTER 2: HISTORY OF THE STANLEY BIMETALLIC CATALYST

2.1 Introduction

As mentioned previously, one of the earliest examples of bimetallic cooperativity in hydroformylation catalysis can be found in the mechanism proposed by Heck and Breslow in which they suggested, but did not favor, a bimetallic pathway to reductively eliminate the aldehyde product.¹ They concluded that this pathway was unlikely because the hydrido cobalt species and the acyl cobalt species would have to frequently interact in order for an intermolecular hydride transfer from the hydrido species to the acyl species to occur. This is then followed by a reductive elimination of the aldehyde product, forming $\text{Co}_2(\text{CO})_8$. Some of the subsequent polymeric complexes in literature were found to be active for hydroformylation catalysis. However, the activity can be attributed to the actual key catalytic species being a monometallic catalyst formed through decomposition of the clusters under hydroformylation conditions.

In order to address these problems, Stanley proposed a series of ligands that would chelate and bridge two metal centers so that they would remain in close proximity to cooperatively eliminate the aldehyde product. The ligands would also consist of electron donating phosphines to strongly coordinate to the metal center to prevent fragmentation of the catalyst under hydroformylation conditions. The first ligand synthesized using these guidelines was $(\text{Et}_2\text{PCH}_2\text{CH}_2)_2\text{PCH}_2\text{P}(\text{CH}_2\text{CH}_2\text{PEt}_2)_2$, or eHTP (ethyl substituted **H**exa**T**ertiary **P**hosphine).² The purpose of the four diethylphosphinoethyl arms was to form chelate rings, and the two internal phosphines would form a bridge between the two metal centers. The expected closed-mode geometry with a metal-metal bond was generally not observed. The open-mode structures, on the other hand, were prevalent and were not catalytically active for hydroformylation.³⁻⁶ This was believed to be due to the steric bulk of the ligand that would not

allow a closed structure or formation of a metal-metal bond. Also, the ligand takes up three coordination sites on the metal centers stabilizing 18e⁻ saturated complexes with low (or no) catalytic activity.

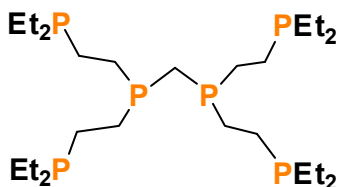


Figure 2.1. Ethyl substituted HexaTertiary Phosphine (eHTP) ligand.

These problems led to the design of another class of ligands that utilized the same properties of eHTP, but with less steric hindrance. Two of the diethylphosphinoethyl arms were removed from the internal phosphines, relieving the steric bulk, but maintain the donor ability of the ligand. These ligands were initially called Linear TetraTertiary Phosphines, or LTTPs, with a general formula of $R_2PCH_2CH_2(R')PCH_2P(R')CH_2CH_2PR_2$.⁷ Of the ligands synthesized, et,ph-P4 (P4), where R is an ethyl group and R' is a phenyl ring, produced the most effective bimetallic catalyst for hydroformylation.⁷⁻⁹ The bimetallic catalyst synthesized using the P4 ligand has been the basis of the Stanley research group in recent years, and the past and present work concerning this catalyst will be summarized here.

2.2 Ligand and Catalyst Precursor Synthesis

The first step in the synthesis of the P4 ligand was synthesizing bis(phenylphosphino) methane (bridge) as shown in Figure 2.2. A flask was charged with phenylphosphine ($PhPH_2$), dichloromethane (DCM), and dimethylformamide (DMF) as the solvent. A 56% aqueous solution of KOH was slowly added dropwise via cannula, and the bridge was extracted with pentane. Previously, the bridge was reacted with two equivalents of diethylvinylphosphine ($Et_2PCH=CH_2$) using AIBN and cyclohexane.⁸ Currently, a flask is charged with the bridge (1

equivalent) and diethylvinylphosphine (2.2 equivalents) without solvent, and allowed to stir under a UV light (xenon lamp) for 8 hours (Pyrex flask under N₂). Both methods yield two diastereomeric forms, *racemic* and *meso*. The diastereomers can be separated using 2 equivalents of NiCl₂·6H₂O in methanol. The *meso*-Ni₂Cl₄(et,ph-P4) forms a precipitate and the *rac*-Ni₂Cl₄(et,ph-P4) remains in solution. The et,ph-P4 ligand is released by reacting the nickel complexes with NaCN (250 equivalents) in H₂O/methanol.¹⁰ Separation can also be accomplished by adding hexane to the mixed ligands and placing the mixture in the freezer for at least 8 hours. The *meso* ligand will partially crystallize and the *racemic* will remain in solution. However, this must be repeated at least 3 times to remove approximately 80% of the *meso* ligand from the solution.

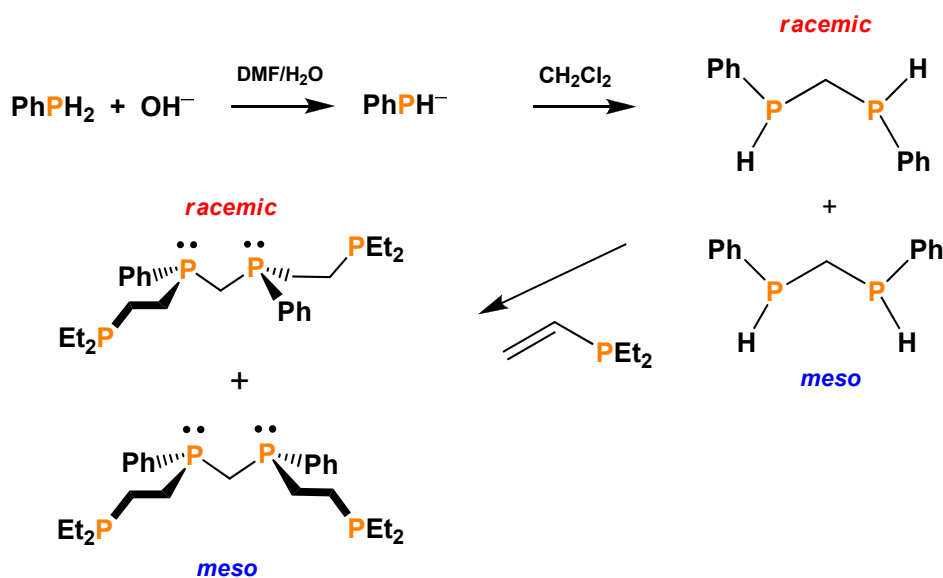


Figure 2.2 *Meso* and *racemic* et,ph-P4 ligand synthesis.

The catalyst precursor was synthesized by first separately dissolving [Rh(nbd₂)](BF₄) (2 equivalents) and 80% *meso* or *rac*-et,ph-P4 (1 equivalent) in DCM and placing them in separate flasks. The P4 solution was added dropwise via cannula to the flask containing the rhodium solution, forming the *meso* or *rac*-[Rh₂(nbd)₂(et,ph-P4)]²⁺ precursor.¹¹ The key catalytic species

is believed to be $rac\text{-}[\text{Rh}_2\text{H}_2(\mu\text{-CO})_2(\text{et,ph-P4})]^{2+}$ and is formed under hydroformylation conditions, 90 °C and 90 psig synthesis gas, H_2/CO (Figure 2.3).

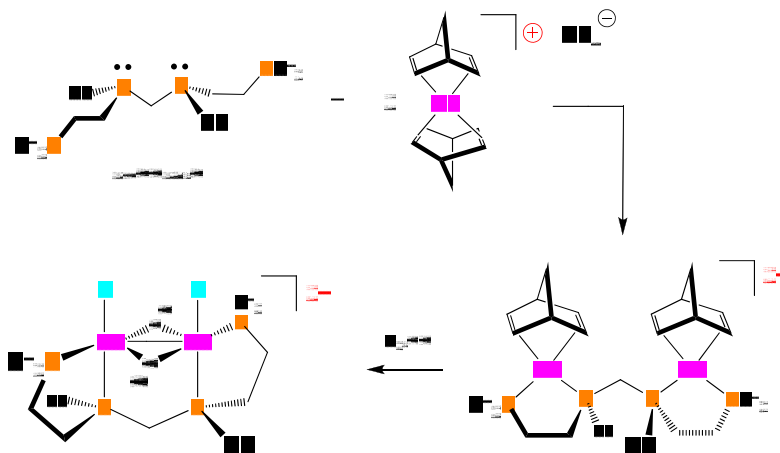


Figure 2.3. $rac\text{-}[\text{Rh}_2(\text{nbd})_2(\text{et,ph-P4})]^{2+}$ catalyst precursor synthesis.

2.3 Initial Results

The initial hydroformylation catalysis results were very promising for $rac\text{-}[\text{Rh}_2(\text{nbd})_2(\text{et,ph-P4})]$. In acetone, the racemic precursor was 120% faster (initial turnover frequency = 1200 hr^{-1}) than the commercial standard catalyst, Rh/PPh_3 (initial turnover frequency = 540 hr^{-1}), and produced similar conversion of the olefin to the linear aldehyde product ($\sim 94\%$). The regioselectivity for the linear aldehyde product (linear to branched ratio) was 28:1 for $rac\text{-}[\text{Rh}_2(\text{nbd})_2(\text{et,ph-P4})]^{2+}$ in comparison to 17:1 for Rh/PPh_3 . On the other hand, the *meso* precursor was not as active or selective as Rh/PPh_3 with an initial turnover frequency of 55 hr^{-1} , a linear to branched ratio of 14:1, but 34% alkene hydrogenation and isomerization side reactions.¹²

Rh/PPh_3 and all other monometallic rhodium catalysts generally require large amounts of excess ligand to maintain activity and selectivity. Phosphine and phosphite ligands are often displaced by carbonyl ligands during the reaction, so excess ligand is necessary to maintain the selective catalysts. This was not the case with the $rac\text{-}[\text{Rh}_2(\text{nbd})_2(\text{et,ph-P4})]^{2+}$ catalyst precursor.

The strong donor abilities of the P4 ligand allowed the ligand to chelate and remain strongly coordinated to the metal center, therefore hindering ligand dissociation.

The activity and selectivity of the *rac*-[Rh₂(nbd)₂(et,ph-P4)]²⁺ precursor was higher than any values previously seen in literature using polymetallic catalysts, so experiments were conducted to ensure that the catalyst was truly bimetallic. The purpose of the experiments was to investigate whether or not the two metal centers were acting as independent monometallic catalysts. The first series of studies used diphosphine ligands which would represent half of the P4 ligand: Et₂PCH₂CH₂P(Me)Ph (depmppe), which is electronically similar to P4; a ligand that is more electron rich in comparison to P4, Et₂PCH₂CH₂PEt₂ (depe); and ligands which were less electron rich, Et₂PCH₂CH₂PPh₂ (dedppe) and Ph₂PCH₂CH₂PPh₂ (dppe) (Figure 2.4). All of the monometallic analogs performed extremely poorly as hydroformylation catalysts with initial turnover frequencies of 1-3 hr⁻¹, 3:1 linear to branched aldehyde ratio, and 70% alkene side reactions.^{11,13} The second series of analogs used tetraphosphine ligands in which the methylene bridge was replaced with *p*-xylene or 1,3-propylene. These ligands yielded bimetallic catalysts that were electronically similar to the catalyst formed with the P4 ligand, but kept, to varying

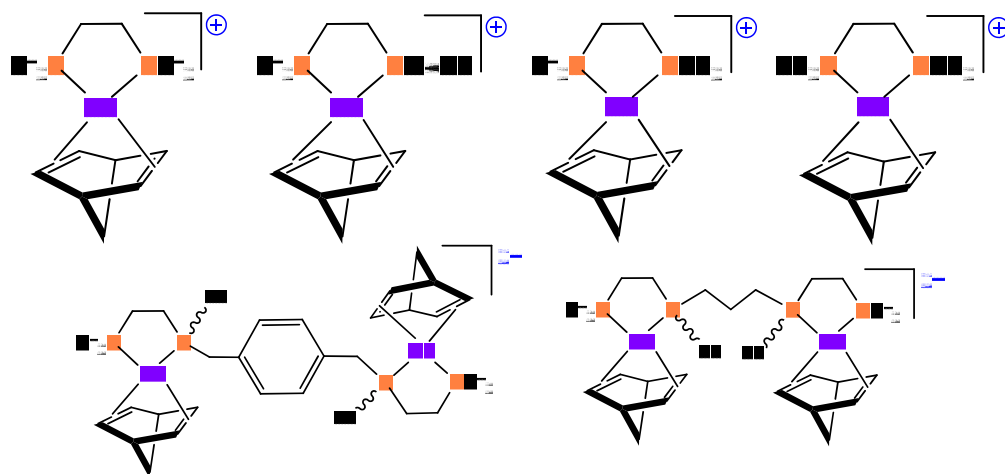


Figure 2.4. Monometallic and bimetallic catalyst analogs

degrees, the metal centers apart from each other. These “spaced” bimetallic analogs also performed poorly as hydroformylation catalysts with initial turnover frequencies of 0.5-6.0 hr⁻¹, 3:1 linear to branched ratios, and 70% alkene side reactions.^{11,13} These studies provided strong evidence to support the idea that the highly active and selective catalyst generated from the P4 ligand was truly bimetallic and utilized bimetallic cooperativity in the catalysis.

2.4 Proposed Mechanism

The bimetallic mechanism proposed by Stanley is shown below in Figure 2.5. The numbered structures in the mechanism have been characterized by IR, NMR or X-ray crystallography. The first steps are similar to the proposed Rh/PPh₃ mechanism. The mechanism begins with an open mode structure, **5**, which consists of a five-coordinate, 18 e⁻ Rh center and a four-coordinate 16 e⁻ Rh center. Structure **5** is considered the resting state of the catalytic cycle. The 16 e⁻ Rh center can then undergo an oxidative addition of H₂ followed by the loss of CO forming another open-mode species, **A**. The first proposed instance of bimetallic cooperativity



Figure 2.5. Proposed bimetallic mechanism

within the mechanism occurs when **A** undergoes a fast intramolecular hydride transfer via the **5** bridged species **2*** forming the metal-metal bonded complex **2**, which is the proposed key catalytic species. This is important because a metal center with more than one hydride ligand cannot effectively perform hydroformylation catalysis because it would have a higher tendency to perform olefin hydrogenation. **2**, can then undergo the loss of a CO, binding the alkene, forming species **B**. The alkyl species, **C**, is formed when the alkene inserts into the Rh-H bond to form a linear or branched alkyl (linear shown). A carbonyl ligand coordinates to **C** followed by another migratory insertion of CO into the Rh-alkyl bond yielding the acyl species, **D**. The reductive elimination of the aldehyde product via an intramolecular hydride transfer to yield **6** is proposed as the second occurrence of bimetallic cooperativity. **6** can react with CO to regenerate or possibly react directly with H₂ to reform **A/2***.

2.5 Solvent Effects

Initial hydroformylation studies using the bimetallic catalyst were carried out using acetone as a solvent. The rates and selectivities were impressive in comparison to Rh/PPh₃, but the catalysis was plagued by one of the main problems that persist in homogeneous catalysis - separation of the product from the catalyst. In order to address this problem, Novella Bridges and David Aubry attempted to create a simple polar phase solvent system by adding water to the acetone. They proposed that the non-polar aldehyde would easily separate from the catalyst which was dissolved in the polar solvent system.

They discovered that increasing the water content up to 30% in the solvent system had a dramatic effect on the activity, chemoselectivity, and regioselectivity of the catalyst. The initial turnover frequency increased from 20 min⁻¹ (linear to branched ratio = 25:1) in acetone to 30 min⁻¹ (linear to branched ratio = 33:1) in 30% water in acetone.^{12,14} The activity and selectivity

decrease when the water content is greater than 30% due to the decreased solubility of the olefin in the more polar solvent systems.

There was also an increase in the stability of the catalyst. Previously steady catalyst deactivation was observed at 90 °C and 45-70 psig H₂/CO with 80% deactivation after 50 minutes and complete deactivation at 80 minutes. With 30% water in acetone, only a 10% loss of activity was observed after 2 hours at 90 °C. Overall, the performance of the catalyst was improved using a polar solvent system, and 20% water in acetone or greater gave good product aldehyde phase separation. However the problem of separating the product from the catalyst was not solved. Unfortunately, the catalyst was more soluble in the product phase than the water-acetone phase as seen in the figure below. The dark red color of product phase is a result of the presence of the catalyst (Figure 2.6).¹⁴

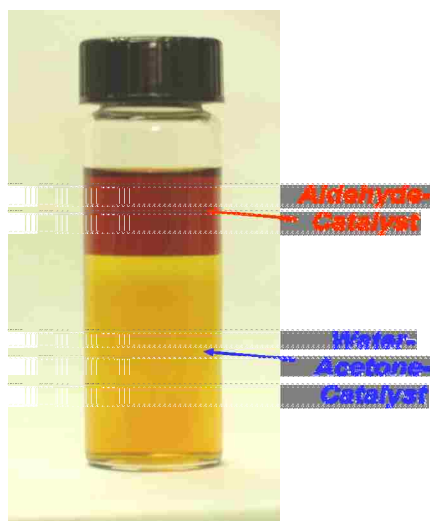


Figure 2.6. Product phase separation

2.6 Autoclave Redesign and Rebuild

Hydroformylation studies are carried out in 160 mL stainless steel Parr high pressure reactors (autoclaves). The previous design of the autoclave system is shown below in Figure 2.7.

Aside from the autoclave, the system featured stainless steel gas and olefin injection reservoirs. The reservoirs were connected to the autoclave with 1/8" stainless steel tubing. The main gas supply was connected to the gas reservoirs with copper tubing. Thermocouples and pressure transducers were attached to the autoclave and the gas reservoirs to monitor temperature and pressure. A packless, magnetic stirrer is used to stir the reaction up to 1100 revolutions per minute (RPM). Heating and stirring are controlled by a Parr 4871 process controller which is controlled by a computer. During the reaction, temperature and pressure data are automatically collected from the autoclave and the gas reservoirs and stored in a spreadsheet every 30 seconds. The data can then be used to calculate the number of turnovers and the turnover frequency of the reaction using the ideal gas law.

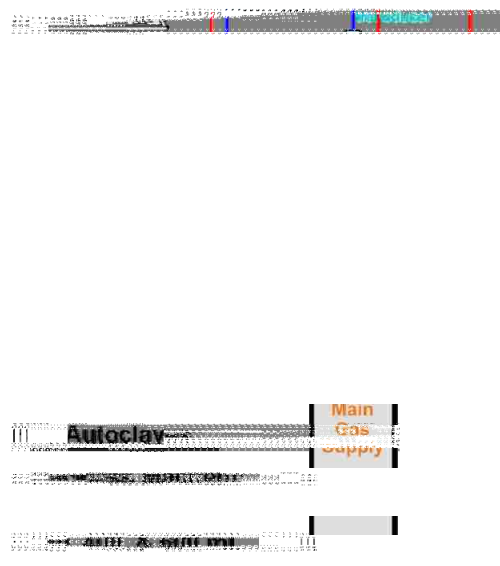


Figure 2.7. Photograph and schematic of previous autoclave design.

A standard reaction was carried out by first connecting the system to a vacuum line. The injection and gas reservoirs, and all tubing was evacuated for at least 15 minutes to remove any air that may have been present. The autoclave was placed unassembled in the glove box and

charged with an 80 mL, 1 mM catalyst solution and sealed. 1 mM of the olefin substrate was placed in a separate vial and sealed with a septum. Once the autoclave and the vial containing the olefin were removed from the glovebox, the autoclave was connected to the injection and gas reservoirs, and the olefin was then transferred to the injection reservoir via cannula. The injection reservoir featured a bypass loop that allowed gas to be delivered to the autoclave without passing through the injection reservoir in order to keep the olefin separate from the catalyst solution. The autoclave was then purged via the bypass loop using syngas to displace any air that may have been present. After purging, the autoclave was pressurized to 45 psig, half of the operating pressure, and heated to 90 °C with stirring (1000 rpm) for 20 minutes, this is referred to as the soaking period for the catalyst. After the soaking period, the pressure in the autoclave was reduced to 45 psig, and the olefin was pressure injected to the operating pressure of 90 psig. Samples were collected when the olefin was first injected, at 1 hour, and at the end of each run. The lengths of each run varied, but were a minimum of 2 hours. After each run, the autoclave was taken apart and cleaned with acetone. Acetone was also injected into the olefin injection reservoir and tubing to rinse any residue that may have condensed and collected there. Each week, the autoclaves were charged with 100 mL of acetone, sealed, and heated for a more thorough cleaning.

Over time, a steady decrease in activity and selectivity was noticed with each reaction. Initially, it was believed that catalyst precursor supply had decomposed into a less active and less selective hydroformylation catalysts due to the fact that the catalyst was completing turnovers but at an initial rate of 15-20 min⁻¹ instead of the usual initial turnover frequency of 30-35 min⁻¹. However, NMR analysis did not illustrate any evidence of decomposition in the catalyst precursor supply, so there was another source of contamination somewhere in the autoclave system or in the pre-run preparation of the catalyst and olefin. The stainless steel gas cylinders

were replaced with aluminum cylinders based on the possibility that over time, iron pentacarbonyl was building up in the cylinders and being delivered to autoclaves during a catalysis run, poisoning the reaction. Replacing the cylinders did not affect the catalysis results, so solvents and the olefin substrate were analyzed using GC/MS. The olefin is passed through an alumina column before it is used in a catalysis run to remove peroxides that can poison the reaction. The olefin was analyzed before and after it was passed through the column, and the water supply and acetone were analyzed. No known contaminants were observed. The contamination was obviously somewhere in the system, so acetone was heated in a warm water bath and injected into the injection reservoir, bypass loop, and tubing leading the autoclave. The acetone wash was allowed to flow out into a beaker and was a dark reddish/brown color signifying the presence of catalyst. The rinse was analyzed using GC/MS. Although the catalyst cannot be seen with the current GC/MS setup, there were several other compounds present in the rinse including 1-hexene and isomerized olefin, and linear and branched aldehyde (Figure 2.8). This was apparently the main source of contamination.

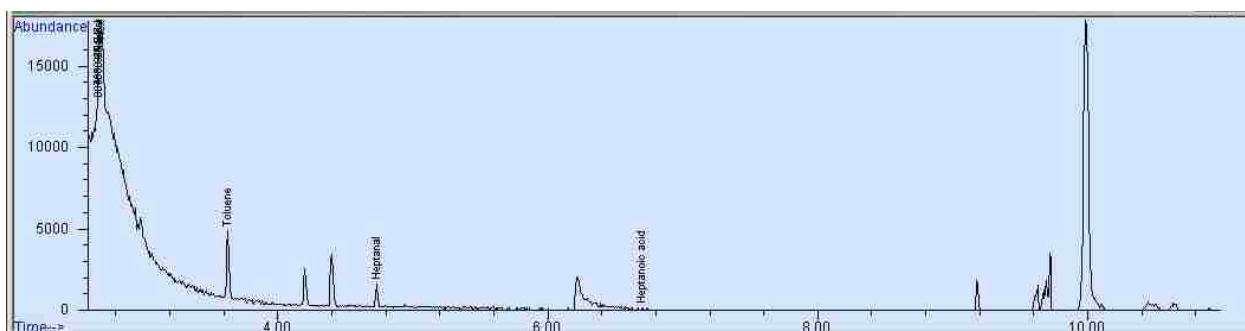
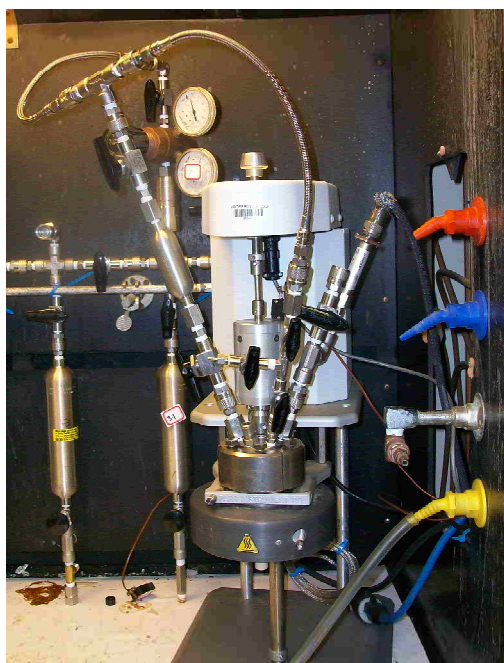


Figure 2.8. GC of acetone wash from old injection reservoir.

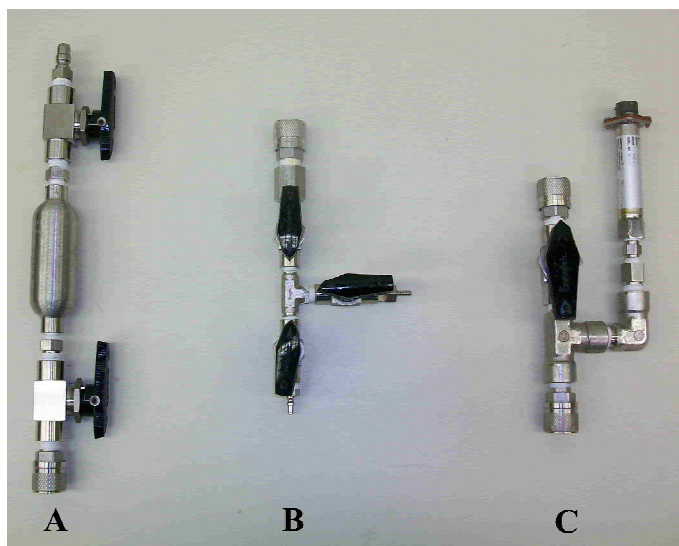
In order to eliminate the contamination, a better method of cleaning would have been required or a new autoclave design would have to be implemented. Due to the possibility that a new cleaning method may not always produce consistent results due to human error, it was decided that a new design was needed. The main goal of the new autoclaves was to improve the

previous olefin delivery method and eliminate the hard to clean stainless steel tubing leading from the injection reservoir to the autoclave. Another goal was to develop an autoclave that would be easy to disassemble for thorough cleaning after each run.

The new autoclaves were built from the old 160 mL Parr autoclaves that were previously used. The new autoclave features 3 “arms”, each serving a different purpose. The arms are all connected to the autoclave with Swagelok quick connect adapters, so they can be easily removed for cleaning. The olefin injection reservoir, arm **A**, provides a direct path for olefin delivery to the autoclave. Arm **B** allows samples to be taken from the autoclave during a reaction to monitor progress during the hydroformylation run using GC/MS analysis. Arm **C** contains a purge/release valve, and a pressure transducer. Gas is delivered to the autoclave through both arms **A** and **B** providing better gas mixing for fast reactions. A thermocouple is attached to the top of the autoclave to monitor the temperature of the reaction (Figure 2.9).



(a)



(b)

Figure 2.9. New autoclave, fully assembled (a), and arms (b): injection reservoir (A), sampling arm (B), and purge/release arm with pressure transducer (C).

A gas manifold was also designed to simplify delivery of the gas to the autoclaves and mixing of gases for H₂/CO ratio studies (chapter 3). Previously, one regulator was used to deliver gas from the cylinders to the autoclave gas reservoirs. The regulator was attached to a large quick connect adapter so that it could be switched from one cylinder to another when gases were mixed. With the current system, the manifold can house up to four gas cylinders at one time, with each cylinder having its own regulator and being completely isolated from the other cylinders (Figure 2.10). Stainless steel tubing delivers the gas from the manifold to the smaller reservoirs that are connected to the autoclaves. Each autoclave has a pressure regulator to control the delivery of gas from the smaller reservoirs to the autoclave. The autoclave is connected to the pressure regulator with a stainless steel hose fitted with quick connects, so it can be removed after each run to rinse out the reaction solution with acetone that can condense there during an experiment.



Figure 2.10. Current gas manifold design.

2.7 Optimizing Reaction Conditions

The previous method used for hydroformylation studies was initially applied to the new autoclave system. The bulk of the arms did not allow the autoclaves to be removed from the glovebox fully assembled, so a 100 mL round bottom flask was charged with the catalyst solution in the glovebox. The olefin was weighed out and placed in a separate vial. A vacuum pump was used to evacuate to remove any air that is present. A septum was placed on the olefin injection arm and the olefin was transferred from the vial via a cannula. A separate cannula was used to transfer the catalyst solution into the autoclave. The autoclave was purged with syngas to remove any trapped air, and the catalyst solution was allowed to heat and soak at 45 psig H₂/CO for 20 minutes. After the soaking period, some of the pressure was released from the autoclave via the release valve, and the olefin was pressure injected to the operating pressure of 90 psig. The results using the new autoclaves were comparable to the results from the old autoclave system. The average initial turnover frequencies for the preliminary studies were 25-30 min⁻¹ with a linear to branched ratio of 30:1. After a 2 hour reaction, on average 3% of the olefin remained unreacted, and 5% was isomerized to internal alkenes.

Since the results using a slightly modified version of the old method were consistent with previous results, the method was applied to current studies in which the activity and selectivity of the dirhodium catalyst are investigated under various H₂/CO ratios (results summarized in chapter 3). For example, for a 2:1 H₂:CO ratio study, the catalyst was allowed to soak under a 2:1 ratio of H₂ to CO gas for 20 minutes with heating. After the soaking period, the pressure in the autoclave was slightly reduced via the release valve, and the olefin was pressure injected to the operating pressure using the 2:1 gas mixture. The gas feed to the autoclave was then switched immediately from the 2:1 gas to a syngas feed to maintain the 2:1 gas ratio in the autoclave. This method produced varying results from one data set to next using the same reaction conditions.

The difference was probably partly due to the purge step before the olefin was injected. Purging the autoclave at 90 °C released both gas and vapor pressure from the solvent, so the amount of actual gas being released was unknown, and when the olefin was pressure injected the final ratio of gas in the autoclave was unknown and could easily vary from one run to the next which would lead to varying results. Due to the inconsistent results, the method was apparently not suitable for the H₂/CO ratio studies so a new method was required.

Several new methods were developed, but they were first applied to standard dirhodium runs (90 °C, 90 psig 1:1 H₂:CO, 1000 rpm stirring, 30% H₂O/acetone) . The goal was to develop a method that produced comparable results to previous standard runs, but with very little, if any, gas release during the soaking period of the reaction. For method CA-A, the catalyst, 1-hexene, and solvent were placed together in the autoclave. After purging, the autoclave was pressurized to 90 psig, and heated to 90 °C. The pressure in the autoclave had to be slightly reduced due to an increase in the overall pressure from the solvent vapor pressure. The catalyst and 1-hexene were dissolved in acetone and placed in the injection reservoir in method CA-B, and the remaining acetone, water and toluene were placed in the autoclave. The autoclave was pressurized to 90 psig and heated to 90 °C with stirring. After 20 minutes, the pressure in the autoclave was reduced to 80 psig, and the catalyst/olefin solution was pressure injected. Method CA-C was similar to CA-B, except the only the catalyst dissolved in acetone was placed in the injection reservoir. The 1-hexene was added to the remaining solvent in the autoclave. For method CA-D, the catalyst, olefin, and solvent were all placed together in the autoclave. After purging, the pressure in the autoclave was reduced to approximately 1-2 psig, and the autoclave was heated to 90 °C with no stirring. After 20 minutes of heating (the pressure in the autoclave was approximately 20-25 psig), the autoclave was pressurized to 90 psig.

The results using these methods are summarized in Table 2.1 below. The large amounts of olefin isomerization seen in some of the runs were further investigated, and it was found that as much as 9% of the olefin could be isomerized in a blank run (1 M 1-hexene in 30% water/acetone, 90 °C, 90 psig syngas). When a polytetrafluoroethylene (PTFE, Teflon) liner was placed in the autoclave, there was 0% olefin isomerization in a blank run. For method CA-E, a PTFE liner was placed in the autoclave, and the catalyst and solvent were placed in the autoclave, and the olefin was placed in the injection reservoir. Due to the insulating properties of the liner, the temperature of the autoclave was monitored with an internal thermocouple, but controlled with an external thermocouple that fits between the autoclave and the heating element.

Table 2.1. Summary of method development studies

Method	Reaction Time (hours)	% Conversion (By GC/MS)	% Unreacted Olefin	% Isomerized Olefin	Average Initial Turnover Frequency
CA-A	4	88	0	12	19 min ⁻¹
CA-B	6	84	6	10	19 min ⁻¹
CA-C	6.5	91	3	6	28 min ⁻¹
CA-D	6	84	11	5	28 min ⁻¹
CA-E	2	93	0	7	33 min ⁻¹

The autoclave was purged, and without stirring, the external temperature was set to 245 °C to heat the reaction mixture to 90 °C (approximately 30 minutes). When the catalyst solution reached 90 °C, the olefin was pressure injected to operating pressure of 90 psig which caused a decrease in the internal temperature to approximately 75 °C. The external temperature remained set at 245 °C, until the internal temperature reached 85 °C, after which the external temperature was set at 190 °C to maintain an internal temperature of 90 °C. At 85 °C the stirring speed was

set to 200 rpm and increased to 500 rpm at 88 °C, and 1000 rpm at 90 °C. Method CA-E was the method chosen for the next series of H₂/CO studies because it produced the fastest initial turnover frequencies, and one of the highest rates of completion in the shortest amount of time. This method also did not require any release of pressure during the soaking period to inject the olefin.

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CHAPTER 3: H₂/CO RATIO STUDIES

3.1 Introduction

A previous group member, Dr. Bobby Barker, began a series of studies to investigate the effects of increasing the H₂/CO gas ratio on the selectivity and activity of the *racemic* dirhodium catalyst. He then wanted to compare the results to monometallic catalysts based on some of the best bisphosphine ligands for hydroformylation catalysis, BISBI, NAPHOS, and Xantphos. Barker was curious about the effects on these catalysts due to the lack of information in literature on the effects of total and partial H₂ and CO pressure on catalysts that contain bisphosphine ligands.¹

Barker considered the solubility of CO and H₂ in solution when designing his experiments. The Henry's law constants for H₂ and CO in acetone are 3382 and 1312 respectively, with H₂ being approximately 2.5 times more soluble than CO in solution.^{2,3} The Henry's law constants for H₂ and CO vary for different solvents, but H₂ is generally always 2.3-2.6 times more soluble than CO in solution, so he assumed that this would be the case for the 30% water/acetone solvent system. The higher solubility of the H₂ gas essentially means that the 1:1 ratio of H₂/CO in syngas yields an approximate concentration ratio of 2.5:1 H₂/CO in solution. Even though H₂ was more soluble in solution than CO, Barker proposed to increase the partial pressure of H₂ (pH₂) in comparison to the partial pressure of CO (pCO) due to the fact that the dirhodium catalyst is susceptible to CO-induced fragmentation and deactivation.

3.2 Barker's Experiments and Results

All of the studies were carried out at 90 °C in 30% water acetone with 1000 rpm stirring, using 1 mM rhodium catalyst (5:1 ligand to Rh(CO)₂(acac) ratio for monometallic catalysts) and 1 M 1-hexene. For the first series of experiments, Barker decreased the overall operating

pressure of 90 psig to 45 psig yielding a partial pressure of 22.5 for both H₂ and CO. For the subsequent experiments, the partial pressure of CO remained at 22.5, and he increased the partial pressure of H₂. He also performed a series of experiments where the H₂ partial pressure remained at 22.5 psig and the partial pressure of CO was increased, however, these conditions did not produce active catalysts. The results of Barker's experiments are summarized in table 3.1.¹

Table 3.1 Barker's hydroformylation data from variable H₂/CO ratio and pressure studies. Conditions: 90 °C, 1 M 1-hexene (1000 equiv.), 1 mM Rh catalyst, solvent = 30% H₂O in acetone, constant pressure conditions, 1000 rpm stirring; pressures listed as psig, TOF = initial turnover frequency, TON = total turnover number, L:B = aldehyde linear to branched regioselectivity, Isom. = alkene isomerization. * ca. 5% *n*-heptanol produced

Rh Catalyst	H ₂ /CO	pH ₂	pCO	TOF	TON	L:B	% linear	Isom
Rh ₂	1:1	45.0	45.0	30(2)	1000	33:1	97.1	<1%
Rh ₂	1:1	22.5	22.5	20(1)	1000	55:1	98.2	<1%
Rh ₂	2:1	45.0	22.5	27(2)	1000	64:1	98.5	<1%
Rh ₂	3:1	67.5	22.5	30(2)	1000	75:1	98.7	<1%
Rh ₂	4:1	88.0	22.5	46(1)	1000	152:1	99.3	7.7%*
Rh ₂	1:4	22.5	82.5	-	0	-	-	-
Rh ₂	1:3	22.5	67.5	-	0	-	-	-
NAPHOS	1:1	45.0	45.0	35(1)	1000	120:1	99.2	2.2%
NAPHOS	1:1	22.5	22.5	27(2)	950	160:1	99.4	3%
NAPHOS	3:1	67.5	22.5	48(7)	700	360:1	99.7	4%
NAPHOS	4:1	88.0	22.5	87(7)	810	360:1	99.7	3%
BISBI	1:1	45.0	45.0	37(1)	1000	80:1	98.8	2%
BISBI	1:1	22.5	22.5	24(1)	975	90:1	98.9	3%
BISBI	3:1	67.5	22.5	61(7)	550	150:1	99.3	2%
BISBI	4:1	88.0	22.5	26(3)	530	162:1	99.4	3%
Xantphos	1:1	45.0	45.0	28(1)	1000	60:1	98.4	<1%
Xantphos	1:1	22.5	22.5	26(4)	900	55:1	98.2	1.5%
Xantphos	3:1	67.5	22.5	21(2)	750	49:1	98.0	2%
Xantphos	4:1	88.0	22.5	20(2)	845	40:1	97.6	5%

Barker observed that when the total pressure is decreased from 90 psig to 45 psig, the overall activity of all of the catalysts decreased, which is to be expected at lower pressures. There was, however, an increase in the percent linearity. For the dirhodium catalyst, increasing the H₂

partial pressure to 45 psig for a total operating pressure of 68 psig, caused an increase in the initial turnover frequency and the percent linearity in comparison to the 45 psig total pressure study. A 3:1 H₂/CO ratio (90 psig total pressure) seemed to be the optimal conditions for the dirhodium catalyst. At these conditions, the catalyst had the same activity seen using the standard 1:1 H₂/CO ratio, but the selectivity dramatically increased from a 33:1 linear to branched ratio (97.1% linear) to a 75:1 linear to branched ratio (98.7% linear). Increasing the ratio to 4:1 H₂/CO resulted in an increase in the linear to branched ratio (152:1, 99.3%) and the initial turnover frequency, however there was almost 8% olefin isomerization and 5% hydrogenation of heptaldehyde to produce heptanol. As mentioned above, increasing the CO partial pressure did not produce active catalysts. This was more than likely due to the fact that the dirhodium catalyst is susceptible to CO-induced fragmentation and deactivation.

Similar trends were seen with the monometallic catalysts as the H₂ partial pressure was increased, however, at higher H₂ partial pressures, they rapidly deactivated as indicated by their inability to convert the 1000 equivalents of 1-hexene to the aldehyde product. As the H₂ partial pressure increased, the monometallic catalysts were more susceptible to Rh-induced deactivation through phosphine ligand decomposition. Phosphine ligand decomposition in rhodium catalysts usually occurs via P-C bond cleavage or *ortho*-metallation (Figure 3.1).^{4,5} Rhodium catalyzed P-C bond cleavage can occur via oxidative addition of the phosphine to the metal complex or nucleophilic attack on coordinated phosphines. P-C bond cleavage can ultimately lead to the formation of stable Rh-phosphide cluster species which are not active for hydroformylation catalysis. Also, the phosphide group and an alkyl generated from the olefin can undergo a reductive elimination from the metal center, yielding a partially alkylated phosphine ligand. This ligand would generally not form a suitable catalyst for a hydroformylation reaction, yielding poor activity and selectivity. Although the exact deactivation pathway for the monometallic

catalysts was not known, it was obvious that at higher H₂ partial pressures they were rapidly deactivating to unfavorable species.

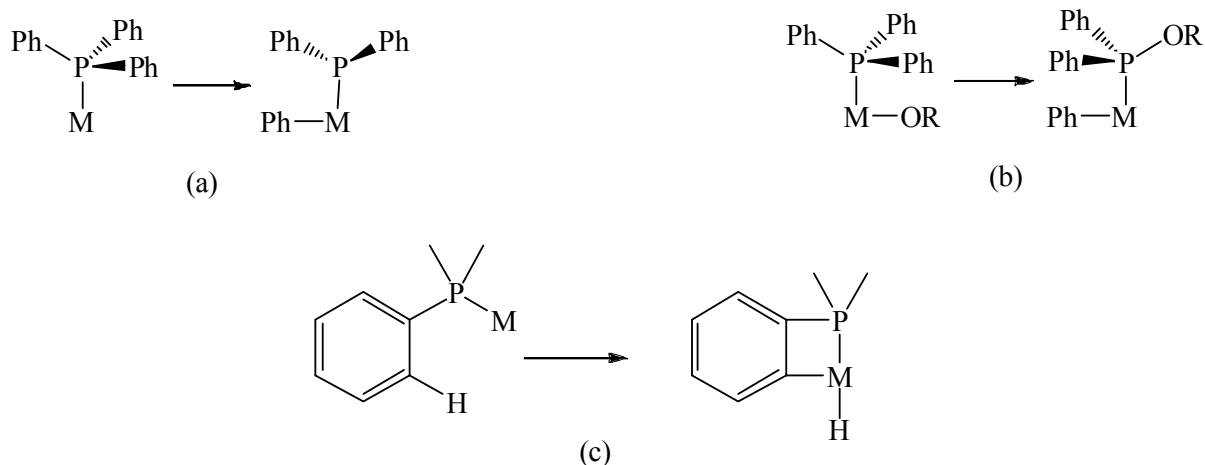


Figure 3.1 Oxidative addition (a) and nucleophilic attack (b) P-C bond cleavage and *ortho*-metallation (c) decomposition pathways.⁴

The P4 ligand used in the dirhodium catalyst is mainly alkylated, so it is generally not susceptible to the Rh-induced deactivation pathways seen with aryl phosphines. The proposed deactivation mechanism for the dirhodium catalyst is shown below in Figure 3.2. It is proposed that the deactivation of the dirhodium catalyst occurs via the loss of one of the Rh atoms. Loss of a Rh center leads to the formation of a monometallic species (**2**) or a bimetallic species (**3**), both of which are poor hydroformylation catalysts. In the proposed mechanism, the first step is dissociation of one of the P4 chelate arms yielding structure **A**. It was initially proposed by Prof. Stanley, that the increase in activity and selectivity of the dirhodium catalyst when the solvent system was switched from acetone to the more polar 30% water/acetone solvent system was due to a hydrophobic effect. He proposed that because the chelate arm of the P4 ligand was

nonpolar, when the polarity of the solvent was increased, dissociation of the arm would not be favored, thereby increasing the stability of **1**.

Due to the results of Barker's H₂/CO ratios, the effects of H₂ and CO on the deactivation pathway had to be reevaluated. Now, **1** and **A** are believed to be in rapid equilibrium, both being active catalysts for hydroformylation, with **1** being more selective and slightly less active than **A** which is less selective due to the dissociated arm, decreasing the amount of steric direction for olefins coordinating to the metal center. Higher CO partial pressures will favor the formation of **A** which will yield lower linear to branched ratios and can eventually lead to complete catalyst deactivation. The dissociation of the chelate arm in **A** yields a metal center that has less electron density, making it more susceptible to the formation of **B** via the reductive elimination of H₂. **B** can then undergo the loss of one of the Rh centers forming **C** which can lead to the formation of **2** when the P4 ligand fully coordinates to a single metal center. **C** can also dimerize to form the bimetallic species **3**.

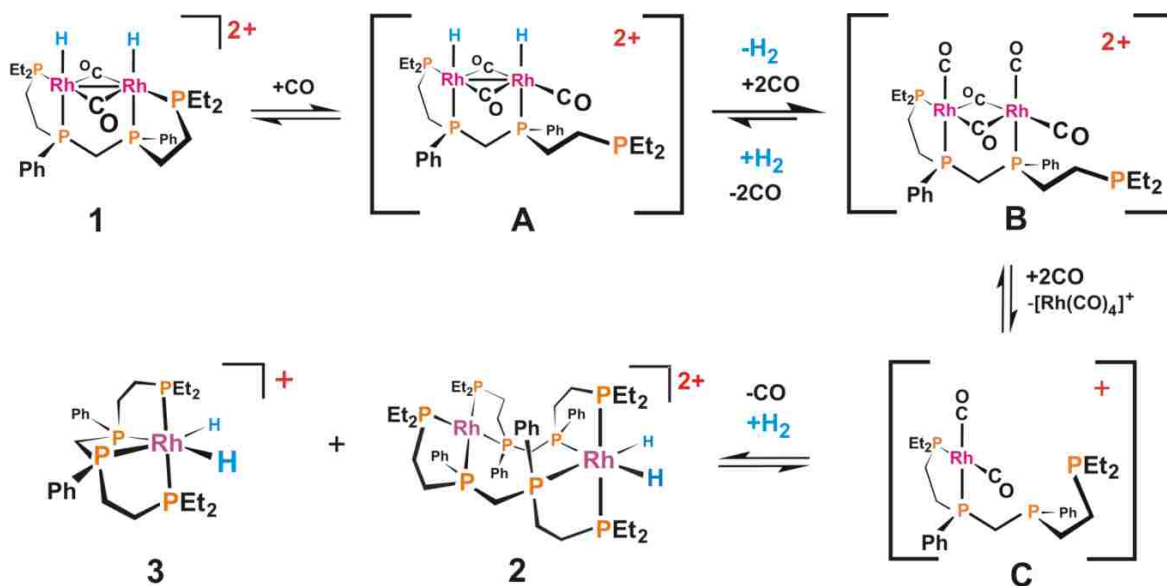


Figure 3.2 Proposed fragmentation pathway for the dirhodium catalyst.

On the other hand, at higher H₂ partial pressures the equilibrium between **A** and **B** is shifted towards **A**, which is in equilibrium with **1**. This explains the increase in selectivity seen in the higher H₂ partial pressure studies. Increasing the partial pressure of H₂ will lead to an increase in the concentration of **A**, increasing activity. However, an increase in the concentration of **A** will lead to an increase in the formation of **1**, the more selective catalyst, therefore increasing the linear to branched ratio.

3.3 10,000 Equivalent Studies

Current studies focused on continuing Barker's H₂/CO ratio studies. The goal was to repeat his experiments to ensure that his data was reproducible, and to investigate the lifetimes of the bimetallic and monometallic catalyst systems with various H₂/CO ratios. The lifetime experiments were designed to use 10,000 equivalents of 1-hexene instead of using 1000 equivalents. The percent conversion of the alkene to the aldehyde product would be indicative of the lifetime of the catalyst systems. These studies would have been necessary to accentuate the difference between the catalyst systems because many of the systems converted all or most of the 1000 equivalents of alkene to the aldehyde product.

Work immediately began on the lifetime experiments. Following Barker's method, the autoclaves were charged with a 0.1 mM catalyst solution (30% water/acetone) in the glovebox. 1 M 1-hexene was transferred from a separate vial prepared in the glovebox, to the injection reservoir via a cannula. After purging the autoclave with the gas mixture being tested, the autoclave was pressurized to 45 psig. The autoclave was heated to 90 °C with stirring for 20 minutes to allow the catalyst to soak. After the soaking period, the pressure in the autoclave was reduced to 45 psig, and the olefin was pressure injected to the operating pressure of 90 psig.

The preliminary results of these studies were not as expected. Results were highly inconsistent between runs of the same catalyst at the same conditions. For a given ratio, percent conversion of the 10,000 equivalents could be as high as 50% or as low as 2%. Similar inconsistencies were seen in the initial turnover frequencies and linear to branched ratios as well.

As mentioned in Chapter 2, we first assumed that the inconsistent data was a result of catalyst decomposition, contamination of stock chemicals, or contamination of the autoclave system. After catalyst decomposition was ruled out, isolation of the source of contamination became the primary focus. Presence of a contaminant in a standard run could cause small, but noticeable changes in activity and regioselectivity of a catalyst. However, only 10% (0.1 mM) of the normal amount of catalyst was used for the lifetime studies, so the effect of the contaminant on the catalyst was magnified by a factor of 10. Cleaning the injection reservoir with heated acetone, located the likely source of the contamination, but after repeatedly cleaning the consistency of the data still did not improve.

After taking a closer look at Barker's method, it was decided that using a constant feed of the gas mixture being tested, was not the correct way to perform experiments like these. In industry, these types of reactions are generally carried out in flow reactors, not in a closed system autoclave, or batch reactor. This is due to the fact that as a hydroformylation reaction proceeds, the gas is consumed at a 1:1 H₂/CO ratio. During the reaction, as gas is consumed, it is replaced with additional gas from the reservoir to maintain the operating pressure. The reaction using Barker's method was replacing the consumed gas with the mixed ratio gas feed. Over time this would eventually change the ratio of the mixture in the autoclave, eventually creating CO depleted conditions at higher H₂ partial pressure conditions (H₂ depleted at higher CO partial pressure). The final ratios of the H₂/CO gas in the autoclaves could easily vary from one run to the next, producing results that were inconsistent with one another.

The contamination combined with variable gas ratios during longer runs produced results that were inconsistent and not reproducible. We decided to redesign and build a new autoclave system (Chapter 2), but the method also had to be modified, or the same inconsistent results would be present in the new system. Also, it was assumed that Barker's results were not a true representation of the effects of variable H₂/CO ratios and pressures due to CO or H₂ depleted conditions at the end of the run, so all of his studies had to be repeated once the new method was developed in order to observe the true effects of variable H₂/CO ratios and pressures on the dirhodium and monometallic catalyst systems.

3.4 1,000 Equivalent Studies

The 10,000 equivalent studies ultimately led to the redesign and rebuild of the autoclave system, and the development of a new autoclave experimental method. The next set of experiments that were conducted focused on repeating Barker's experiments with the revised procedure. The goal was to create an environment in the autoclave that would maintain the gas ratio being tested. For instance, if the autoclave was pressurized to the operating pressure using a 3:1 H₂/CO mixture, the ratio would still be 3:1 H₂/CO at the end of the run. In order for this to occur, as gas is being consumed during the course of the reaction at a 1:1 H₂/CO ratio, it should be replaced with a 1:1 gas mixture.

The new method was loosely based on the procedure used with the old autoclave system. The method was first optimized under standard 1:1 H₂/CO conditions, before being applied to the H₂/CO ratio studies. After evacuating and purging the fully assembled autoclave, the catalyst was transferred to the autoclave with a cannula, and the 1-hexene was transferred to the injection reservoir. For a standard run it was found that heating the autoclave to 90 °C under 45 psig syngas with 1000 rpm stirring for 20 minutes, then reducing the pressure to 45 psig and pressure

injecting the olefin to the operating pressure of 90 psig yielded results that were consistent with the old autoclave system. The method was then slightly modified for the H₂/CO ratio studies. The autoclave was heated to 90 °C, and the catalyst soaked under 45 psig of the ratio being tested for 20 minutes with 1000 rpm stirring. After the soaking period, the pressure in the autoclave was reduced to 45 psig (25 psig for 45 psig total pressure studies), and the olefin was pressure injected to the operating pressure of the run with the gas mixture. Once the autoclave was pressurized, the gas feed was immediately switched from the test mixture to syngas. Ideally this should maintain the gas ratio mixture throughout the course of the run.

The results for the dirhodium catalyst using the modified standard method are shown below. There are some slight differences in the way in which the current data is reported in comparison to Barker's data. The average initial turnover frequency (AITOF) is the average of the initial turnover frequencies over the first 10 minutes of the run when the catalysis is the fastest. The percent linearity is calculated from the GC/MS data for the sample taken at 1 hour, instead of at the end of the run as previously done. Linear to branched ratios at the end of the run are actually lower due to back reactions of aldehyde with the catalyst, so calculating the ratio at the end of the run is not a good representation of the true regioselectivity capabilities of the catalyst.

When the total pressure is decreased from 90 psig to 45 psig, there is a significant decrease in the AITOF from 31 min⁻¹ to 9 min⁻¹. There is also a 1.5% decrease in the percent linearity and a 6% increase in olefin isomerization. Increasing the ratio to 2:1 H₂/CO for a total operating pressure of 68 psig, results in a decrease in the AITOF, but almost a 2% increase in the percent linearity of the aldehyde. However, the percentage of isomerized and unreacted olefin increased by 2% and 8% respectively. The total pressure for the 2:1 H₂/CO study was increased from 68 psig to 90 psig and the percentage of olefin isomerization and unreacted olefin

decreased to 1% and 2% respectively. Increasing the partial pressure to 3:1 and 4:1 at 90 psig increased the percent linearity, but there was a significant increase in the olefin isomerization with more than 20% of the olefin becoming isomerized by the end of the reaction. Increasing the CO partial did not have any beneficial effects on the activity or selectivity of the dirhodium catalyst. When the CO partial pressure was increased, the majority of the olefin remained unreacted.

Table 3.2 Hydroformylation data from Rh₂ variable H₂/CO ratio and pressure studies. Modified Standard Conditions: 90 °C, 1 M 1-hexene (1000 equiv.), 1 mM Rh₂ catalyst, solvent = 30% H₂O in acetone, constant pressure conditions, 1000 rpm stirring; pressures listed as psig, AITOF = average initial turnover frequency, TON = total turnover number, L:B = aldehyde linear to branched regioselectivity % Linear = percentage of linear product, % Isom. = percentage of alkene isomerization., % Unreact = percentage of unreacted olefin

Ratio	Total Pressure	pH ₂	pCO	AITOF	TON	L:B	% Linear	% Isom.	% Unreact.
1:1	90	45.0	45.0	31(6)	920	22:1	95.7(0.6)	6(2)	2(2)
1:1	45	22.5	22.5	9(6)	840	16:1	94.2(2.6)	12(7)	4(3)
2:1	68	45.3	22.7	22	840	39:1	97.5(0.3)	8(8)	10(5)
2:1	90	60	30	26	970	32:1	97.0(0.3)	1(2)	2(2)
3:1	90	67.5	22.5	8(4)	750	47:1	97.9(0.4)	22(4)	3(3)
4:1	90	72	18	13(4)	780	52:1	98.1(0.3)	22(5)	0
4:1	112	89.6	22.4	13(11)	930	58:1	98.3(0.2)	5(1)	3(4)
1:2	68	22.7	45.3	6(4)	320	9:1	90.3(2.0)	6(1)	62(15)
1:2	90	30	60	12(1)	740	12:1	92.3(0.8)	4(1)	22(6)
1:3	90	22.5	67.5	18(2)	930	18:1	94.6(0.2)	3(1)	7(1)
1:4	112	22.4	89.6	4(1)	380	8:1	89.4(0.8)	6(1)	56(7)

The results for the monometallic variable H₂/CO ratio studies using the modified standard method are summarized in the table 3.3 below. As seen in the dirhodium studies, decreasing the total pressure has an unfavorable effect on the percent conversion of the olefin to the aldehyde product for all of the monometallic catalysts. Increasing the H₂/CO ratio from 1:1 to 2:1 (68 psig total pressure) resulted in a decrease in the average initial turnover frequency and the number of turnovers. At 2:1 H₂/CO the percentage of olefin isomerization was almost 50% or greater for

each catalyst, and increased as the H₂ partial pressure was further increased in comparison to the 1:1, 90 psig study. There were small increases in the percent linearity as the H₂ partial pressure was increased, but the effect was not as great as in the dirhodium experiments.

Table 3.3 Hydroformylation data from monometallic variable H₂/CO ratio and pressure studies. Modified Standard Conditions: 90 °C, 1 M 1-hexene (1000 equiv.), 1 mM Rh catalyst, solvent = 30% H₂O in acetone, constant pressure conditions, 1000 rpm stirring; pressures listed as psig, AITOF = average initial turnover frequency, TON = total turnover number, L:B = aldehyde linear to branched regioselectivity % Linear = percentage of linear product, % Isom. = percentage of alkene isomerization., % Unreact = percentage of unreacted olefin

Catalyst	Ratio	Total Pressure	pH ₂	pCO	AITOF	TON	L:B	% Linear	% Isom	% Unreact
BISBI	1:1	90	45.0	45.0	68(1)	850	76:1	98.7(0.1)	14(3)	1
BISBI	1:1	45	22.5	22.5	19(21)	580	66:1	98.5(0.9)	41(21)	1(1)
BISBI	2:1	68	45.3	22.7	22(14)	470	249:1	99.6(1.0)	46(5)	0
BISBI	3:1	90	67.5	22.5	24(5)	390	166:1	99.4(0.2)	61(9)	0
BISBI	4:1	112	89.6	22.4	24(1)	420	249:1	99.6(0.2)	58(3)	0
NAPHOS	1:1	90	45.0	45.0	76(7)	820	110:1	99.1(0.3)	17(8)	1(1)
NAPHOS	1:1	45	22.5	22.5	19(19)	470	76:1	98.7(0.8)	39(18)	8(11)
NAPHOS	2:1	68	45.3	22.7	23(2)	320	199:1	99.5(0.2)	68(1)	0
NAPHOS	3:1	90	67.5	22.5	22(6)	400	166:1	99.4(0.2)	60(5)	0
NAPHOS	4:1	112	89.6	22.4	25(2)	530	199:1	99.5(0.1)	47(3)	0
Xantphos	1:1	90	45.0	45.0	38(10)	870	52:1	98.1(0)	10(1)	3(1)
Xantphos	1:1	45	22.5	22.5	7(5)	190	332:1	99.7(0.2)	78(10)	3(4)
Xantphos	2:1	68	45.3	22.7	21(5)	390	13:1	92.7(2.5)	58(6)	3(4)
Xantphos	3:1	90	67.5	22.5	22(6)	380	47:1	97.9(0.7)	54(19)	8(4)
Xantphos	4:1	112	89.6	22.4	6(1)	290	7:1	88.1(7)	71(3)	0

The percentages of linear aldehyde for the 1:1 studies were very high to begin with, so there was not much room for improvement. Increasing the CO partial pressure did not produce active catalysts for any of the monometallic systems. At H₂/CO ratios of 1:2 or higher, 90 % or more of the olefin remained unreacted or isomerized after at least 2 hours. These results initially suggest that there are no obvious benefits to altering the H₂/CO ratio for the monometallic systems.

There seemed to be some inconsistency with the data using the modified standard method, as evidenced by the large standard deviations, particularly for the monometallic studies. The difference in the data sets was attributed to the release of some of the pressure in the autoclave just before the injection of the olefin. This step occurs when the autoclave has reached 90 °C. At this temperature, the pressure in the autoclave has increased from 45 psig to approximately 70 psig, and the solution in the autoclave is boiling. The pressure that is being released is a combination of the gas mixture and vapor pressure from the solvent. The actual amount of gas being released during this step is unknown, and when the olefin is pressure injected with the gas mixture, the final concentration and ratio is slightly different than the starting ratio and is therefore not exactly known. This could easily lead to slightly varying results from one data set to next using the same reaction conditions.

Work began on the development of a new method for these studies. The results of the method development studies are summarized in chapter 2. Of the new methods, method CA-E, seemed to be the most promising for these studies because it allowed the olefin to remain separate from the catalyst solution during the soaking period. It also did not require the release of any pressure after the soaking period.

For method CA-E, a PTFE liner was used in the autoclave to reduce the amount of olefin isomerization. The autoclave was evacuated and purged fully assembled with the liner in place.

After the catalyst and olefin are transferred into the autoclave and the injection reservoir respectively, the external temperature is set to 245 °C with no stirring. Once an internal temperature of 90 °C is reached, the olefin is pressure injected to the operating pressure (pressure in autoclave before olefin is pressure injected = 23-25 psig). The external temperature remains set at 245 °C with no stirring, until an internal temperature of 85 °C is reached, at which point the solution is slowly stirred at 200 rpm and the external temperature is set to 190 °C to maintain an internal temperature of the 90 °C. The stirring speed is increased to 500 rpm when the internal temperature reaches 88 °C and is further increased to 1000 rpm at an internal temperature of 90 °C.

The results for the dirhodium and monometallic catalysts using method CA-E are summarized in table 3.4 below. In comparing the 1:1 H₂/CO studies from method CA-E to the modified standard method for all of the catalyst systems, there was a decrease in the AITOF. The decrease was very small for the dirhodium system (AITOF for standard method = 31 min⁻¹, AITOF for CA-E method = 30 min⁻¹), but for the monometallic systems, the decrease in rates was significant (25 - 47% decrease in AITOF). The overall olefin isomerization increased for all of the systems using method CA-E in comparison to the modified standard method. It was apparent that method CA-E was not at all suitable for these studies.

There are several factors that can contribute to the poor results using method CA-E. First, the PTFE liner acted as an insulator, making the actual heating of the solution difficult, and a time consuming process. When the external temperature was set to 245 °C, it took an average 45 minutes for the internal temperature to reach 90 °C. After the addition of the olefin, there was approximately an additional 5-10 minutes of heating before the temperature of the solution reached 90 °C again. The total time to heat the catalyst solution before data collection began was

approximately 1 hour. It is possible that the extended heating led to decomposition of the catalysts.

Another factor that could have contributed to the decrease in activity and selectivity was the fact that the catalysts were not truly operating at the set pressure of gas. For method CA-E, the autoclave is completely purged of all but 1 psig or less of gas, and heated. After the heating period, the olefin is pressure injected to the operating pressure, but at 90 °C, there is already 25 psig of vapor pressure from the solvent present in the autoclave, so the actual amount of gas injected is the set pressure minus 25 psig. For example, in a 90 psig, 1:1 H₂/CO study, after heating the autoclave and pressure injecting the olefin, the actual amount of syngas injected is only 65 psig. The effect was not as noticeable with the dirhodium catalyst, but was obvious with the monometallic catalysts which require higher total pressures (in comparison to the dirhodium catalyst) in order to maintain activity. This effect is more pronounced for all systems for the 45 psig, 1:1 H₂/CO study. After heating, only 25 psig of syngas was actually injected leading to the poor activities observed.

The final factor, and probably the most likely, is that the experiments are mass transfer limited. Hydroformylation reactions require good stirring (1000 – 2000 rpm) in order to achieve suitable distribution of gas throughout the reaction mixture. Initially not stirring the reactions after the olefin is injected proved to be disastrous for most if not all of the systems. This is supported by the higher than normal levels of isomerization for the dirhodium experiments, and decreased activity and selectivity for all experiments. GC/MS analysis of samples taken at 5 minutes after stirring reached 1000 rpm showed that on average, 75-90 % of the starting material was isomerized. For the monometallic catalysts, as the reaction proceeded, the percent of isomerized olefin product generally decreased over the length of the reaction, suggesting the

Table 3.4 Hydroformylation data from variable H₂/CO ratio and pressure studies (CA-E).
 Method CA-E Conditions: 90 °C, 1 M 1-hexene (1000 equiv.), 1 mM Rh catalyst, solvent =30% H₂O in acetone, constant pressure conditions, 1000 rpm stirring; pressures listed as psig, AITOF = average initial turnover frequency, TON = total turnover number, L:B = aldehyde linear to branched regioselectivity % Linear = percentage of linear product, % Isom. = percentage of alkene isomerization., % Unreac = percentage of unreacted olefin

Catalyst	Ratio	Total Pressure	pH ₂	pCO	AITOF	TON	L:B	% Linear	% Isom	% Unreac
Rh ₂	1:1	90	45.0	45.0	30(3)	930	22:1	95.6(0.1)	6(1)	1(1)
Rh ₂	1:1	45	22.5	22.5	3(1)	190	21:1	95.4(0.3)	67(16)	14(6)
Rh ₂	2:1	68	45.3	22.7	4(1)	170	52:1	98.1(0.3)	76(14)	7(10)
Rh ₂	3:1	90	67.5	22.5	7(1)	270	9:1	89.9(1.4)	6(0)	67(1)
Rh ₂	4:1	112	89.6	22.4	10	285	66:1	98.5(0.7)	72(9)	0
BISBI	1:1	90	45.0	45.0	45(6)	840	76:1	98.7(0.1)	15(3)	1(1)
BISBI	1:1	45	22.5	22.5	10(2)	580	41:1	97.6(1.3)	74(27)	0
BISBI	2:1	68	45.3	22.7	15(1)	290	76:1	98.7(0)	71(1)	0
BISBI	3:1	90	67.5	22.5	17(3)	190	110:1	99.1(0.2)	81(2)	0
BISBI	4:1	112	89.6	22.4	30(1)	500	249:1	99.6(0)	69(1)	0
NAPHOS	1:1	90	45.0	45.0	57(4)	790	142:1	99.3(0.5)	18(8)	3(3)
NAPHOS	1:1	45	22.5	22.5	13(8)	320	142:1	99.3(0.2)	68(3)	0
NAPHOS	2:1	68	45.3	22.7	18(1)	360	166:1	99.4(0)	64(6)	0
NAPHOS	3:1	90	67.5	22.5	26(6)	260	110:1	99.1(0.4)	74(13)	0
NAPHOS	4:1	112	89.6	22.4	35(2)	500	249:1	99.6(0)	50(1)	0
Xantphos	1:1	90	45.0	45.0	20(0)	870	52:1	98.1(0)	10(1)	3(1)
Xantphos	1:1	45	22.5	22.5	7(5)	190	332:1	99.7(0.2)	78(10)	3(4)
Xantphos	2:1	68	45.3	22.7	19(1)	250	2:1	66.7(0)	75(3)	0
Xantphos	3:1	90	67.5	22.5	25(4)	380	70:1	98.6(0.2)	67(6)	0
Xantphos	4:1	112	89.6	22.4	25(8)	230	2:1	70.8(5.9)	77(5)	0

presence of species in solution that are capable of performing hydroformylation on internal olefins, but are not very effective.

3.5 Conclusions

All conclusions made in this section will be based on the results by Barker, and the results using the modified standard method. Experimentation errors in method CA-E led to data that was inconclusive, but helped develop ideas for future variable H₂/CO ratio and pressure studies.

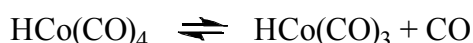
For the dirhodium catalyst using the modified standard method, a ratio of 2:1 H₂/CO, and a total operating pressure of 90 psig appears to be the optimum conditions. This slightly differs from Barker who found that optimum conditions for the dirhodium catalyst were a 3:1 H₂/CO ratio at 90 psig total pressure. The increase in selectivity and decrease in isomerization can still be explained with the deactivation pathway illustrated in Figure 3.2. The increase in the H₂ partial pressure prevents the reductive elimination of H₂ which would form complex **B** which can undergo the loss of a Rh center leading to the formation of inactive monometallic and bimetallic species, both of which are inactive for hydroformylation catalysis.

It is very likely that the results achieved with the 3:1 and 4:1 H₂/CO ratio studies are a result of mass transfer limitation problems. Several studies were conducted investigating the effects of total and variable H₂ and CO partial pressures on the activity and selectivity of Rh/PPh₃, the industrial standard for hydroformylation catalysis. If it is assumed that the dirhodium system behaves similar to the Rh/PPh₃, then the activity of the dirhodium system should increase with increasing H₂ partial pressure.

For unmodified catalysts (Co or Rh catalysts with only CO and H as ligands), at a ratio of 1:1 H₂/CO, the overall rate of the reaction is independent of the total pressure according to Natta's equation:^{6,7}

$$r = k \times [\text{substrate}] \times [\text{catalyst}] \times [p(\text{H}_2)]/[p(\text{CO})]$$

This holds true as long as a minimum pressure of carbon monoxide is maintained for stabilization of the metal carbonyl species. When the H₂ partial pressure is increased (lower CO partial pressure), the rate of the reaction increases initially, and the linear to branched ratio slightly increases. This effect can be described by the equilibrium expression below:⁷



The increased initial activity is a result of the unsaturated complex on the right side of the expression, and as the activity of the reaction decreases, it corresponds to a shift to the left. Increasing the H₂ partial pressure increases the amount of hydrogenation resulting in increased alkane and alcohol formation.⁷ This can be viewed as a positive or negative side since most aldehydes are converted to alcohols for plastics and detergent. However, the linear to branched ratio can be increased by using a 1:1 H₂/CO ratio, and increasing the overall total pressure. For industrial cobalt processes, the linear product increases by 0.5 kg/100 kg per 1 MPa increase in pressure, with optimum conditions ranging between 30-35 MPa. At pressures greater than 40 MPa, the linear to branched ratio begins to decrease.⁶

Similar effects are seen for phosphine modified rhodium catalyst, Rh/PPh₃. Increasing the H₂ partial pressure (lower pCO) resulted in an increase in the activity of the catalyst.⁸ Studies were conducted by Brown and Wilkinson to investigate the effects of variable H₂/CO ratios, total pressure, and temperature on the hydroformylation of 1-hexene (Table 3.5). An increase in the CO partial pressure, resulted in a decrease in heptanal production, but increasing the H₂ partial pressure resulted in an increase in the percentage of heptanal.^{8,9} The highest percentage of heptanal production occurred at a 2:1 H₂/CO ratio (40 °C, 1 atm). The results can be explained by the fragmentation pathway for Rh/PPh₃. A minimum CO partial pressure is

needed to push the equilibrium from **A** to **B**, to form and stabilize the formation of species **B**, the most selective catalyst in the pathway. Increasing the CO partial pressure pushes the equilibrium towards **C**, which is still active, but not as selective as **B**. The increased concentration of **C** leads to an increase in the concentration of **D** which is highly active but not selective. As seen in the unmodified catalyst, increasing the H₂ partial increases the amount of leads to higher hydrogenation.

Table 3.5 Results of Brown and Wilkinson's variable H₂/CO ratio, total pressure, and temperature studies. Conditions: Catalyst = HRh(CO)(PPh₃)₃, 30 mmol/L in experiments at 1 atm, 15 mmol/L in experiments at 27 atm. substrate = 1-hexene, solvent = benzene, *PPh₃/HRh(CO)(PPh₃)₃ molar ratio = 3

CO/H ₂	Temp (°C)	Total Pressure	% Heptanal
2	25	1	85
1	25	1	86
0.8	25	1	91
2	40	1	85
1	40	1	88
0.8	40	1	95
0.5	40	1	97
1	40	1	93*
0.5	40	1	98*
1	25	27	74
0.5	25	27	80

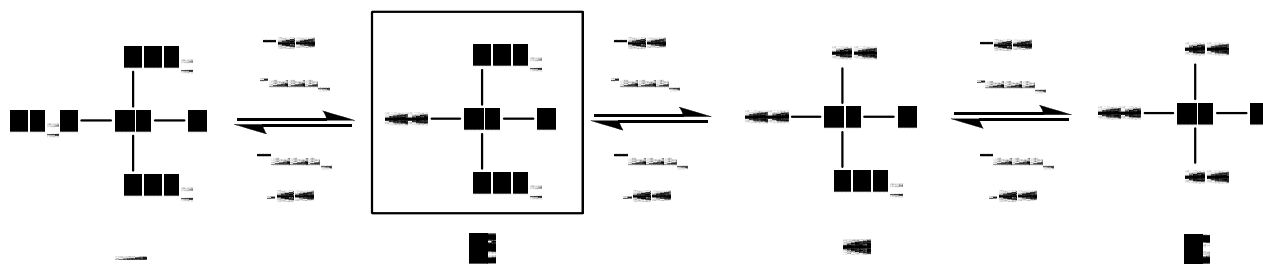


Figure 3.3. Fragmentation pathway for Rh/PPh₃.

In comparing the dirhodium catalyst to the monometallic R/PPh₃ system, it can be assumed that the significant decrease in the AITOF from the 2:1 H₂/CO study to the 3:1 study (26 min⁻¹ to 8 min⁻¹) may once again be due to mass transfer limitations. If increasing the partial pressure of H₂ increases the rate of the reaction, then it is possible that the initial rate of the reaction is too fast, and the distribution of the gas is not adequate enough to keep up with the rate of catalysis.

This is likely the explanation of the poor performance of the monometallic catalysts at ratios higher than 1:1 H₂/CO as well. If it is assumed that increasing the H₂ partial pressure will increase the rate of the reaction for the monometallic catalysts with bisphosphine ligands, then an increase in the rate should be observed. However, AITOFs for these catalysts were very fast to begin with, so an increase in the H₂/CO ratio from just 1:1 to 2:1 could yield a mass transfer limitation problem, as evidenced by the significant increase in olefin isomerization. In fact, mass transfer limitations may also be playing a role in fairly large percentages of olefin isomerization at 1:1 H₂/CO ratios.

3.6 Future Direction

This project is not complete by any means. Several other experiments need to be conducted to attempt to solve mass transfer limitations, including using faster stirring speeds, which our system is really not capable of doing. Also, since the 2:1 H₂/CO ratio appears to be the most optimal conditions from these studies for the dirhodium catalyst, more experiments can focus on this ratio, such as varying temperature and total pressure. Also, studies that investigate the effects of varying the ratio from 1-2:1 H₂/CO may help further optimize the ideal H₂/CO ratio for the dirhodium catalyst.

As mentioned previously, industrial reactions of this nature are generally carried out in a flow reactor instead of a batch reactor. The addition of a flow system in the Stanley research group may be beneficial to these studies, because at higher H₂/CO ratios, the hydroformylation reactions are probably too fast for an autoclave (batch reactor) to be effective. Until a flow process is designed, a new method is currently being developed for conducting these experiments in a batch reactor.

In a patent published by Peterson of E.I. Du Pont de Nemours and Company, he describes a hydroformylation processes for the preparation of predominantly linear aldehydes.¹⁰ This patent describes a method for continuously decreasing the partial pressure of CO throughout the reaction in order to achieve high percentages of the linear aldehyde. The invention states that the decrease in linear to branched ratio over the course of the reaction is due to an increase in aldehyde product which dilutes the olefin substrate in solution, therefore slowing down the reaction. As the reaction slows down, the rate at which the CO is consumed decreases, and as a result the concentration of CO in solution increases, displacing the phosphine ligands off the metal center (shifting equilibrium from **B** to **C** and eventually to **D**, Figure 3.3). The author states that this can be overcome simply by decreasing the CO partial pressure continuously or stepwise during the reaction.¹⁰

Decreasing the CO partial pressure can occur by one of three methods: reducing the total pressure of a 1:1 mixture of H₂ and CO during the course of the reaction, keeping the total pressure constant and increasing the H₂ partial pressure, or keeping the total pressure constant and decreasing the partial pressure of both H₂ and CO by diluting them with an inert gas such as nitrogen. The patent claims that all of the above methods can be carried out in a batch reactor or a flow reactor.¹⁰

This patent helps explain why Barker did not see higher levels of olefin isomerization. His constant feed of mixed gas automatically reduced the CO partial pressure in the autoclave, but it was not a controlled reduction. The method in which the total pressure is decreased over the course of the reaction seems the most feasible and the least “invasive.” The autoclave could be heated and pressurized, preferably without purging, but it may not be a factor if this method can be carried out as easily as described. Once pressurized to operating pressure, and the olefin is injected, then the total pressure can be reduced stepwise to reduce the CO partial pressure. This is not exactly like the studies that have been carried in the Stanley lab to date, but if it works it can provide insight into the true effects of reduced CO partial pressure on the selectivity of the catalyst systems. This method should be applicable to all of the catalysts because there weren't any major problems with the 1:1 H₂/CO studies which is essentially what this method starts as.

3.7 References

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CHAPTER 4: DEVELOPMENT OF METHODS FOR HYDROFORMYLATION STUDIES

4.1 Introduction

As mentioned previously, several methods have been developed in an attempt to optimize reaction conditions for the H₂/CO ratio studies using the new autoclave system. In order to apply a new method to the H₂/CO studies, it first had to be successful with a standard hydroformylation run. A method is considered to be successful if the average initial turnover frequency, percentage of olefin isomerization and hydrogenation, linear to branched ratio, and percent conversion of the olefin to the aldehyde product is as good as or better than the values obtained using the current method. The procedures and results of the developed methods are summarized here.

All hydroformylation runs and preparation of all blanks and catalyst solutions were carried out using air sensitive techniques. All solvents were used as received, and water was obtained from the Louisiana State University Chemistry Department's distilled water supply, and degassed with nitrogen. The 1-hexene was passed through an alumina column to remove any peroxides, which are known to contaminate hydroformylation reactions. Due to the actual technique of loading the catalyst and olefin varying for each method, all of the proposed methods were carried out several times as a blank reaction (without catalyst). This allowed the techniques to be learned before actually testing the catalyst using the different methods. This helped to keep down overall costs because most of the blank runs failed on the first try, which would have resulted in the loss of a large amount of catalyst if it had been used initially. Data for each method was collected to calculate average initial turnover frequencies. Samples were also taken at the end of each run to calculate percentages of isomerization and hydrogenation, and percent conversion (number of turnovers).

4.2 Modified Standard Method

This method was modified from the method used for a standard hydroformylation run using the old autoclave system. It is referred to as the modified standard method. In the glovebox, 90 mg (1 mM) of *rac*-[Rh₂(nbd)₂(et,ph-P4)](BF₄)₂ was weighed out in a 100 mL round bottom flask. 80 mL 30% water/acetone (including 5 mL of toluene as an internal standard) was added to the flask and it was sealed with a septum. 1 M 1-hexene was weighed out in a separate vial and it was also sealed with a septum. The autoclave was assembled and evacuated, and the catalyst solution and olefin were transferred to the autoclave with separate cannulas. The olefin and catalyst solution can also be transferred to the autoclave with a syringe. The autoclave was purged with a slow flow of syngas (~ 3 psig) to displace any trapped air, and it was pressurized to 45 psig. The autoclave was heated to 90 °C with stirring (1000 rpm), and the catalyst was allowed to soak (total heating and soaking period = 20 minutes). After the heating and soaking period was complete, the pressure in the autoclave was reduced to 45 psi, and the 1-hexene was pressure injected to the operating pressure of 90 psig. The average initial turnover frequency was 30 min⁻¹. From GC/MS analysis, 95% of the 1-hexene was converted to linear and branched aldehyde, and 5% was isomerized (Figure 4.1).

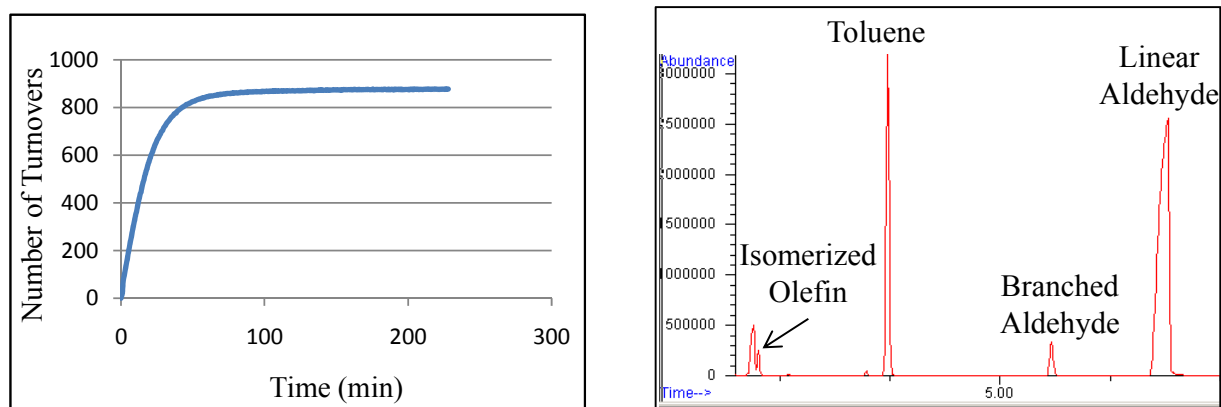


Figure 4.1 Aldehyde production curve and final GC spectrum for modified standard method.

4.3 Method CA-A

Method CA-A investigated the effects of pressurizing the autoclave to the full operating pressure of 90 psig before the heating and soaking period. After the soaking period was complete the pressure would be decreased just below the 90 psig operating pressure so that the olefin could be pressure injected to the operating pressure.

In the glovebox, 90 mg (1 mM) of *rac*-[Rh₂(nbd)₂(et,ph-P4)](BF₄)₂ was weighed out in a 100 mL round bottom flask. 80 mL of 30% water/acetone (including 5 mL of toluene as an internal standard) was added to the flask and it was sealed with a septum. 1 M 1-hexene was weighed out in a separate vial and it was also sealed with a septum. The autoclave was assembled and evacuated, and the catalyst solution and 1-hexene were transferred to the autoclave with separate cannulas. The autoclave was purged with a slow flow of syngas to displace any trapped air, and it was pressurized to 90 psig. The autoclave was heated to 90 °C with stirring (1000 rpm), and the catalyst was allowed to soak (total heating and soaking period = 20 minutes). After the heating and soaking period was complete, the pressure in the autoclave was reduced to approximately 75 psig (from approximately 115 psig), and the 1-hexene was pressure injected to the operating pressure of 90 psig. The aldehyde production curve and final GC spectrum are shown below in figure 4.2. The average initial turnover frequency was 19 min⁻¹. From GC/MS analysis, 88% of the 1-hexene was converted to linear and branched aldehyde, and the remaining 12% was isomerized. The aldehyde production curve and final GC/MS spectrum is shown below in figure 4.2. Although 88% conversion was achieved with this method, it was not considered as a viable method due to the high percentage of olefin isomerization.

4.4 Method CA-B

The purpose of method CA-B was to isolate the catalyst and 1-hexene from the syngas during the soaking period to see if the percentage of olefin isomerization could be reduced. Due

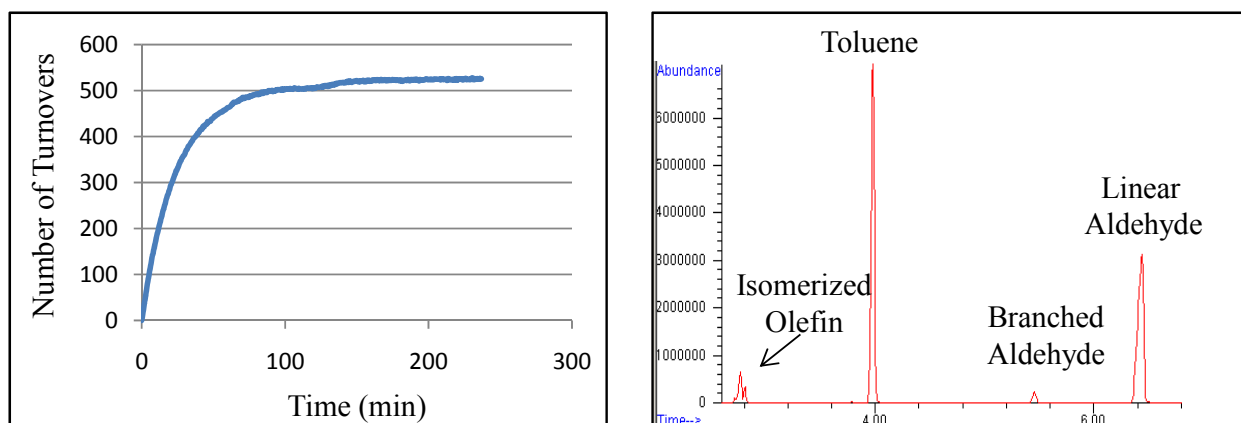


Figure 4.2. Aldehyde production curve and final GC spectrum for method CA-A.

to the increased olefin isomerization when method CA-A was used, it was possible that soaking the catalyst under syngas was converting some of the catalyst to a poor hydroformylation catalyst. A 50 mL round bottom flask was charged with 90 mg (1 mM) of *rac*-[Rh₂(nbd)₂(et,ph-P4)](BF₄)₂ and 1 M 1-hexene dissolved in 15 mL of acetone. The remaining acetone (36 mL), water (24 mL), and toluene (5 mL) were placed in a separate 100 mL round bottom flask. The autoclave was evacuated, and the catalyst was transferred into the injection reservoir, and the solvent mixture was transferred to autoclave. The autoclave was purged with syngas, and was pressurized to 90 psi. The solvent mixture was heated to 90 °C with stirring. When the temperature reached 90 °C, the pressure in the autoclave was reduced to approximately 75 psi, and the catalyst/1-hexene solution was pressure injected to the operating pressure of 90 psig. The average initial turnover frequency using this method was 19 min⁻¹. From GC/MS analysis, 84% of the 1-hexene was converted to linear and branched aldehyde. 6% of the 1-hexene remained unreacted after 6 hours (reactions are usually complete after 2 hours) and the remaining 10% was isomerized (Figure 4.3).

4.5 Method CA-C

Method CA-C was essentially a repeat of method CA-B, except that the catalyst and 1-

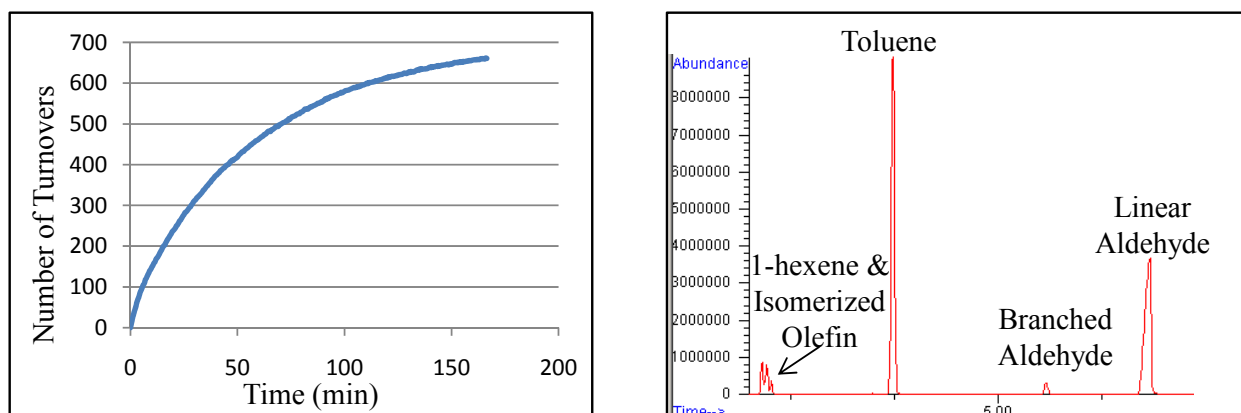


Figure 4.3. Aldehyde production curve and final GC spectrum for method CA-B.

hexene were separated. A 25 mL round bottom flask was charged with 90 mg (1 mM) of *rac*-[Rh₂(nbd)₂(et,ph-P4)](BF₄)₂ dissolved in 15 mL of acetone. A 100 mL flask was charged with 1 M 1-hexene and the remaining acetone (36 mL), water (24 mL), and toluene (5 mL). The autoclave was assembled and evacuated, and the catalyst was transferred to the injection reservoir, and the 1-hexene/solvent solution was transferred to the autoclave. The autoclave was purged with syngas and pressurized to 90 psig. The temperature was set to 90 °C, and the solution was stirred at 1000 rpm. Once 90 °C was reached, the pressure in the autoclave was reduced to 75 psig, and the catalyst was pressure injected to the operating pressure of 90 psig. The average initial turnover frequency using this method was 28 min⁻¹. From GC/MS analysis, 91% of the 1-hexene was converted to linear and branched aldehyde. 3% of the 1-hexene remained unreacted after 6.5 hours (reactions are usually complete after 2 hours) and the remaining 6% was isomerized (Figure 4.4). Separating, the 1-hexene and the catalyst slightly reduced the isomerization (10% to 6%), but it was still higher than the modified standard method, and 3% of the substrate remained unreacted, so it was not a suitable replacement for the modified standard method.

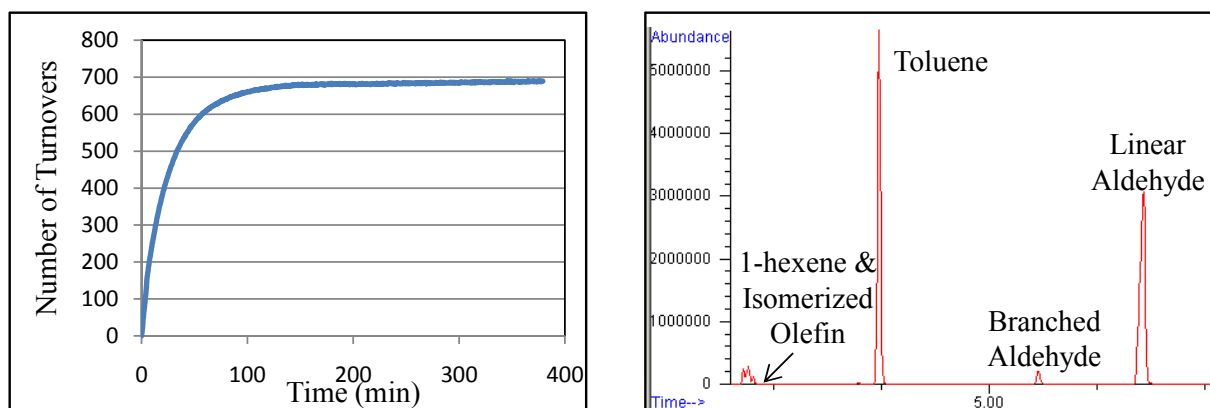


Figure 4.4. Aldehyde production curve and final GC spectrum for method CA-C.

4.6 Method CA-D

Method CA-D was set up as a true batch reaction. A 100 mL round bottom flask was charged with 90 mg (1 mM) of *rac*-[Rh₂(nbd)₂(*et*,*ph*-P₄)](BF₄)₂ and 1 M 1-hexene, dissolved in 80 mL 30% water acetone (including 5 mL toluene). The autoclave was assembled and purged with syngas. All but approximately 1 psig of gas was released. The autoclave was heated to 90 °C without stirring. When the temperature reached 90 °C, the autoclave was pressurized to 90 psig, and the stirring speed was set to 1000 rpm. The average initial turnover frequency using this method was 28 min⁻¹. From GC/MS analysis, 84% of the 1-hexene was converted to linear and branched aldehyde. 11% of the 1-hexene remained unreacted after 6 hours (reactions are usually complete after 2 hours) and the remaining 5% was isomerized (Figure 4.5).

4.7 Method CA-E

After conducting several blank runs, it was discovered that as much as 9% of the olefin could be isomerized in the absence of the catalyst. This could possibly be caused by rhodium plating on the inside of the autoclave. Polytetrafluoroethylene (PTFE, Teflon) liners were

ordered for each autoclave. Blank runs that were conducted with the PTFE liners did not result in any olefin isomerization.

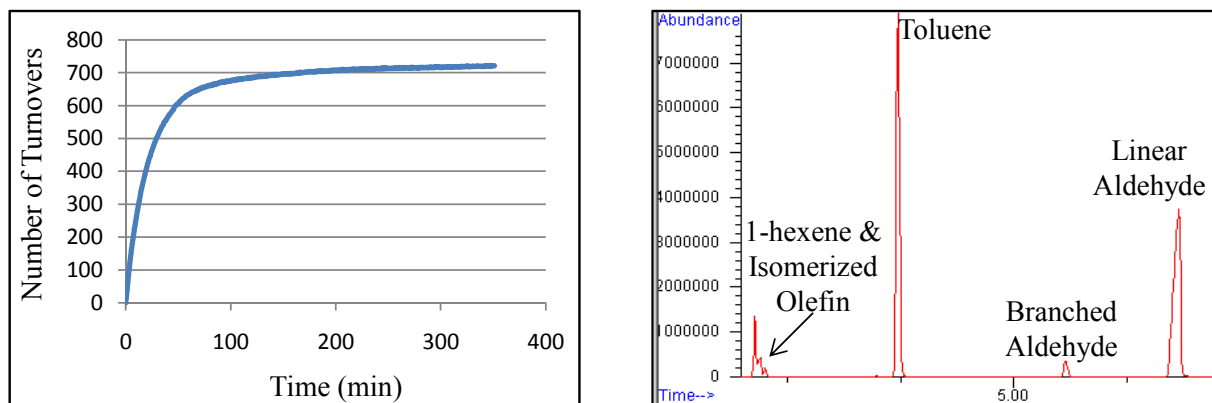


Figure 4.5. Aldehyde production curve and final GC spectrum for method CA-D.

Method CA-E was loosely based on method CA-D. A 100 mL round bottom flask was charged with 90 mg (1 mM) of *rac*-[Rh₂(nbd)₂(et,ph-P4)](BF₄)₂ dissolved in 80 mL 30% water acetone (including 5 mL toluene). 1 M 1-hexene was weighed out and placed in a separate vial. The autoclave was assembled with the PTFE liner and evacuated, and the catalyst solution and 1-hexene were transferred to the autoclave and the injection reservoir respectively. The autoclave was purged, and all but approximately 1 psig of the syngas was released. The temperature of the autoclave was monitored internally, but controlled externally due to the insulating properties of the liner. The external temperature was set to 245 °C to heat the reaction mixture to 90 °C (approximately 30 minutes) without stirring. When the catalyst solution reached 90 °C, the olefin was pressure injected to operating pressure of 90 psi which caused a decrease in the internal temperature to approximately 75 °C. The external temperature remained set at 245 °C, until the internal temperature reached 85 °C. When the internal temperature reached 85 °C, the external temperature was set at 190 °C to maintain an internal temperature of 90 °C, and the stirring speed was set to 200 rpm. At 88 °C, the stirring speed was increased to 500 rpm and 1000 rpm

at 90 °C. The average initial turnover frequency using this method was 33 min⁻¹. From GC/MS analysis, 93% of the 1-hexene was converted to linear and branched aldehyde and the remaining 7% was isomerized (Figure 4.6). Method CA-E produced the fastest initial turnover frequencies, and one of the highest rates of completion in the shortest amount of time so it is considered a suitable replacement for the modified standard method. This method also did not require any release of pressure during the soaking period to inject the olefin, which is believed to have a negative effect on the catalyst.

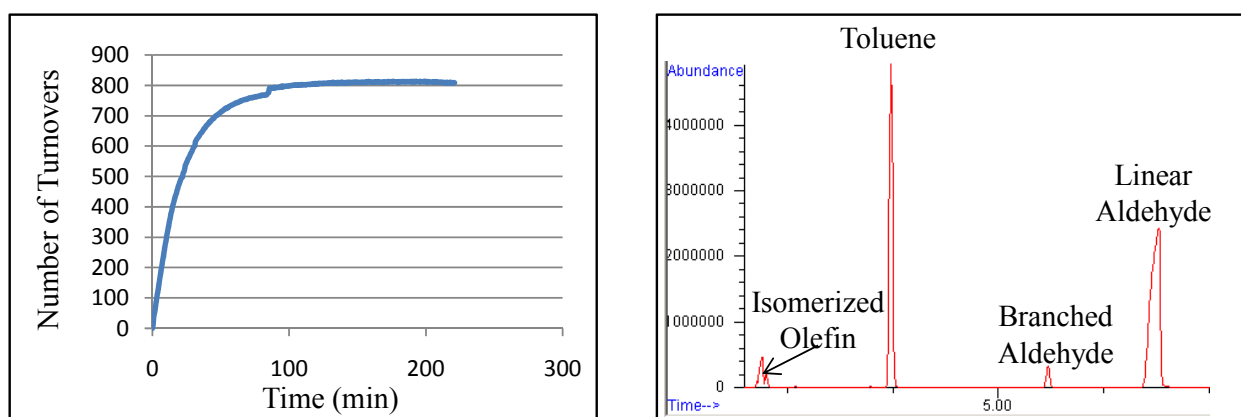


Figure 4.6. Aldehyde production curve and final GC spectrum for method CA-E.

CHAPTER 5: *IN SITU* FT-IR SPECTROSCOPY

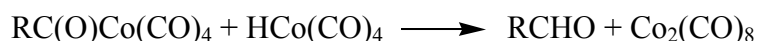
5.1 Introduction

The monometallic-based steps proposed by Heck and Breslow in 1961, were widely accepted as the mechanism for hydroformylation catalysis, but there were not any spectroscopic methods at the time to observe any of the proposed intermediates in the cycle under hydroformylation conditions.¹ However, high pressure IR cells developed in the late sixties and early seventies, allowed for the study of hydroformylation reactions at actual hydroformylation conditions ($>100\text{ }^{\circ}\text{C}$, $>100\text{ bar H}_2/\text{CO}$).^{2,3} Since the development of these cells, high pressure Fourier Transform Infrared Spectroscopy (FT-IR) has proven to be a valuable tool for mechanistic studies in hydroformylation catalysis.

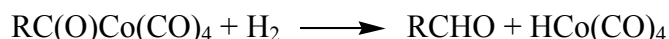
Whyman conducted some of the earliest high pressure IR hydroformylation studies by investigating the PBu_3 modified cobalt catalyst under hydroformylation conditions.^{4,5} These studies led to the identification of two key species, $\text{HCo}(\text{CO})_3(\text{PBu}_3)$ and $\text{Co}_2(\text{CO})_6(\text{PBu}_3)_2$. It was determined that Co_2CO_8 initially reacts with PBu_3 to form a salt, $[\text{Co}(\text{CO})_3(\text{PBu}_3)_2]^-$ $[\text{Co}(\text{CO})_4]^+$, and as the temperature is increased, it is converted to a dimer, $\text{Co}_2(\text{CO})_6(\text{PBu}_3)_2$. At higher temperatures, the dimer reacts with H_2 to form $\text{HCo}(\text{CO})_3(\text{PBu}_3)_2$, the active catalyst. Whyman also investigated the effects of using excess phosphine ligand with this catalyst system by using high pressure IR, and discovered that $\text{HCo}(\text{CO})_2(\text{PBu}_3)_2$ is formed when excess PBu_3 is used. However, when an excess of PBu_3 is not used, the formation of $\text{Co}_2(\text{CO})_7(\text{PBu}_3)$ was favored. As a result of these studies, Whyman proposed that substitution of CO by the alkene in the $\text{HCo}(\text{CO})_3(\text{PBu}_3)$ species was the rate limiting step in the reaction. He came to this conclusion because he was unable to observe an acyl species during the reaction, which he could see in reactions with unmodified cobalt catalysts. However, high pressure IR studies conducted

by Penninger did not provide support for the presence of an acyl species in hydroformylation using unmodified cobalt catalysts.⁶

High pressure IR studies also led to conflicting views on the formation of the aldehyde product. Using high pressure IR studies, Alemdaroğlu, determined that formation of the aldehyde occurred via a dominant bimetallic pathway.⁷



Due to the conflicting nature of Alemdaroğlu's results relative to that of other researchers and the proposed hydroformylation mechanism, Mirbach conducted a series of detailed high pressure IR studies using cyclohexene and 1-octene as substrates. Mirbach's studies supported the proposed hydroformylation mechanism in that the formation of the aldehyde product occurred via a monometallic pathway.⁷



He concluded that the bimetallic pathway was not favored, mainly due to the fact that reaction of $\text{Co}_2(\text{CO})_8$ with H_2 to form 2HCo(CO)_4 is the slowest step in the reaction.

High pressure IR has also been used extensively in the study of rhodium based catalysts. For unmodified rhodium catalysts, acyl intermediates are the only species that are detectable in the reaction by high pressure IR, but important kinetic and mechanism information was still able to be obtained. Garland was able to observe that the stable RC(O)Rh(CO)_4 complex was in equilibrium with the reactive RC(O)Rh(CO)_3 complex. RC(O)Rh(CO)_3 undergoes oxidative addition of H_2 to form the aldehyde product, which is the rate-limiting step.⁸ Claver and van Leeuwen investigated the Rh/PPH_3 system under hydroformylation conditions using high pressure IR, and observed four bands at 2042, 1992, 1981, and 1947 cm^{-1} corresponding to

carbonyl stretching frequencies. These bands were assigned to a mixture of two complexes that are considered the resting state of the catalyst, $\text{RhH}(\text{CO})_2(\text{PPh}_3)_2$ (PPh_3 ligand in equatorial-equatorial and axial-equatorial positions).⁹

5.2 Previous Studies

High pressure IR studies have also been conducted in the Stanley research group, providing valuable information in the identification of what are believed to be the key catalytic species in the proposed mechanism. The original proposed mechanism, based in part on the monometallic Rh/ PPh_3 system, started with the addition of H_2 and CO to the dicationic catalyst precursor, $\text{rac}[\text{Rh}_2(\text{nbd})_2(\text{et,ph-P4})](\text{BF}_4)_2$, to form the neutral Rh^{I} carbonyl hydrido bimetallic complex, $\text{rac}[\text{Rh}_2\text{H}_2(\text{CO})_2(\text{et,ph-P4})]$, which was proposed to be the key catalytic species (Figure 5.1).¹⁰

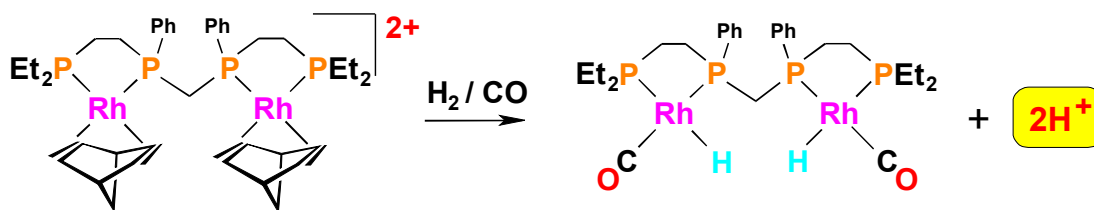


Figure 5.1. Originally proposed reaction of the dicationic species with H_2 and CO to generate the neutral key catalytic species.

This catalyst was highly active and regioselective (average initial turnover frequency $>600 \text{ hr}^{-1}$, 28:1 linear to branched ratio), but led to extensive olefin isomerization and hydrogenation, 8% and 3.4% respectively. It was initially believed that the two equivalents of HBF_4 , a strong acid, produced at the beginning of the cycle when the precursor reacts with H_2 and CO , somehow contributed to the isomerization and hydrogenation.¹¹

Hydroformylation studies were designed to determine whether or not the HBF_4 was contributing to the high percentages of side product formation. This was accomplished by

preparing a neutral, bimetallic catalyst precursor that would not produce an acid upon reacting with H₂ and CO. *Rac*-(Rh₂(η³-allyl)₂(et,ph-P4) was prepared by reacting allylmagnesium chloride with the dicationic precursor, resulting in a neutral catalyst precursor. Surprisingly, the neutral catalyst precursor generated a very poor hydroformylation catalyst with an initial turnover frequency of 35 h⁻¹ and a 2.4:1 linear to branched ratio. There was also 14% olefin isomerization and 5% olefin hydrogenation. However, upon addition of two equivalents of HBF₄, a highly active and selective catalyst was generated with rates and selectivities similar to those using the dicationic precursor.¹¹

These results suggested that the actual catalyst was not a neutral species as originally proposed, but a dicationic complex. High pressure IR studies were utilized, to determine the structural differences between the catalyst systems generated from the neutral and dicationic precursors. The spectra generated from the studies are shown below in Figure 5.2. The carbonyl stretching frequencies generated from the neutral precursor were approximately 100 cm⁻¹ lower in energy than the carbonyl bands produced from the dicationic species. The spectrum from the neutral complex correlates with IR spectra from neutral, dinuclear rhodium complexes in the +1 or 0 oxidation state, confirming that the key catalytic species is not neutral.

Addition of two equivalents of HBF₄ to the solution containing the neutral precursor generated spectrum **b**. This spectrum is identical to that produced using the dicationic precursor. This provided further evidence that the catalyst generated from the dicationic precursor generates a key catalyst that is dicationic instead of neutral, which was quite different from the monometallic Rh/PPh₃ and other monometallic catalysts that generate neutral catalysts, even when cationic precursors are used under the proper conditions.¹¹

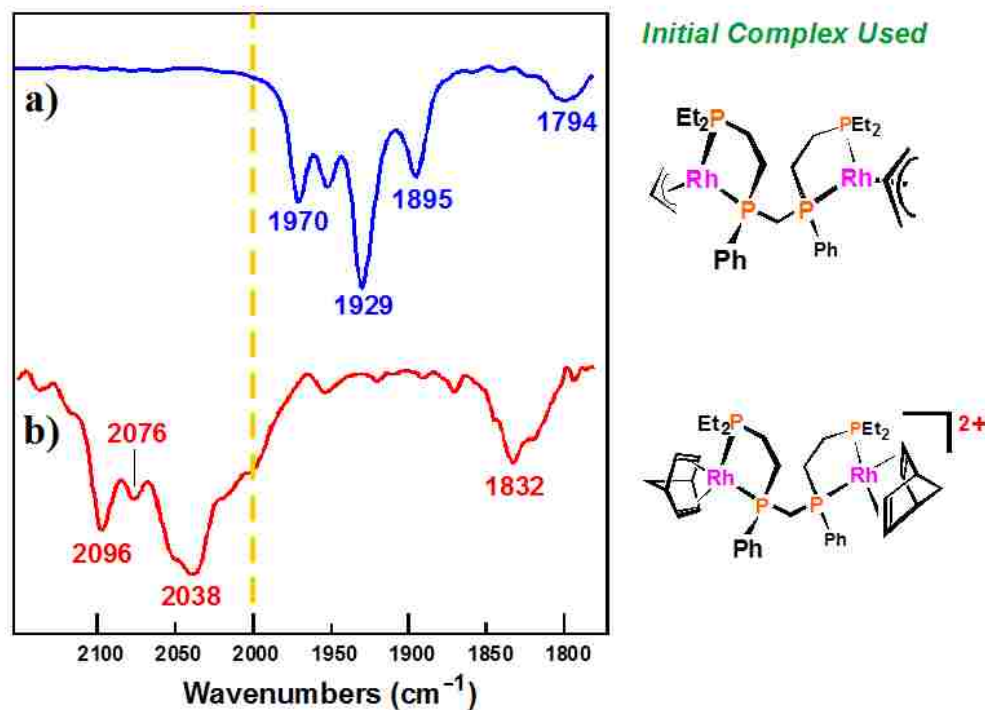


Figure 5.2. *In situ* FT-IR spectra of neutral (a) and dicationic (b) precursors at standard hydroformylation conditions (90 psig H₂/CO, 90 °C).¹¹

5.3 Current Experiments

Due to the increased activity and selectivity obtained when using a 2:1 H₂/CO ratio, high pressure IR studies were used to determine if there were any structural differences between the catalyst generated at a 1:1 H₂/CO ratio and a 2:1 H₂/CO ratio. Also due to the increased activity and selectivity in 30% water/acetone, solvent effect studies were attempted to compare structural differences in acetone and 30% water/acetone.

Similar to previous studies, all high pressure IR studies were carried out in a SpectraTech Circle Reaction high pressure IR cell which is essentially a Parr autoclave with a cylindrical zinc selenide crystal passing through it, slightly protruding from each side (Figure 5.3). It features a thermocouple and pressure transducer for monitoring temperature and pressure, and a packless

magnetic stirrer for stirring the reaction mixture throughout the experiment. The cell also contains a gas inlet for pressurizing the autoclave, and a release valve for purging and depressurizing the system at the end of a study. Sample solutions are loaded through the purge valve using a syringe.

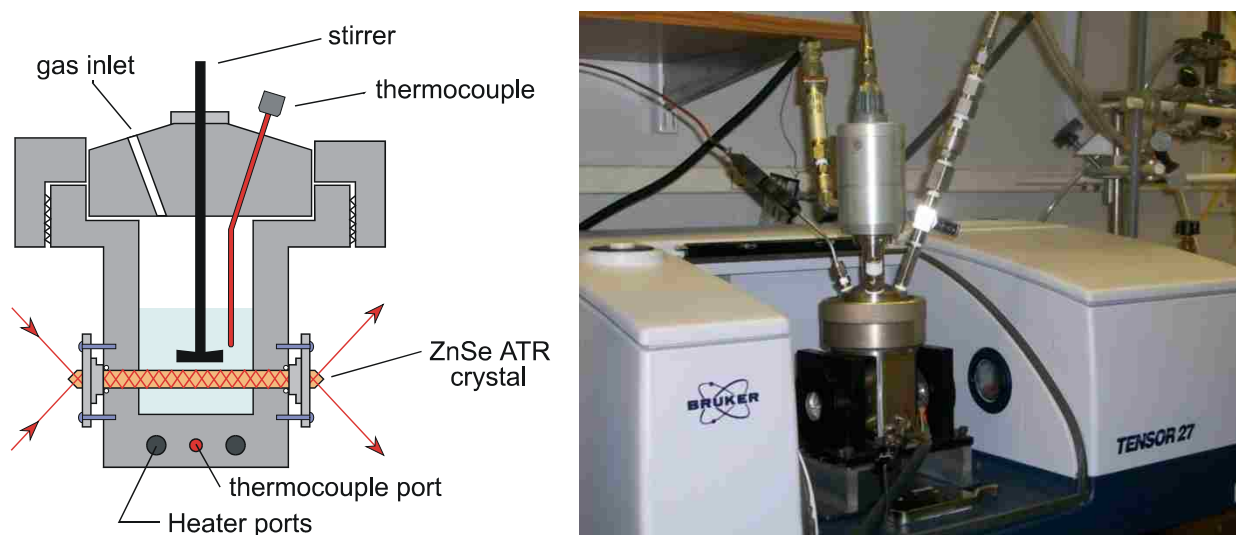


Figure 5.3. SpectraTech high pressure *in-situ* circle reaction FT-IR cell.

Since the reaction is carried out in a closed reaction vessel, the technique of Attenuated Total Reflectance (ATR) is used to acquire the data. In ATR spectroscopy, an IR beam is directed onto the ZnSe crystal, or another crystalline material with a high refractive index. The IR beam is internally reflected which creates an evanescent wave. The wave extends 0.5 to 5 microns beyond the surface of the crystal into the sample creating an IR “bubble.” When good contact between the solution and the crystal occurs, the evanescent wave is attenuated in the regions of the IR spectrum where the sample absorbs energy, and the attenuated energy is sent back to the IR beam. The IR beam exits the crystal, and the information is sent to a mercury cadmium telluride (MCT) detector which is cooled with liquid nitrogen to $-196\text{ }^{\circ}\text{C}$ to minimize

thermal noise. An IR spectrum is generated from the information collected from the detector (Figure 5.4).¹²

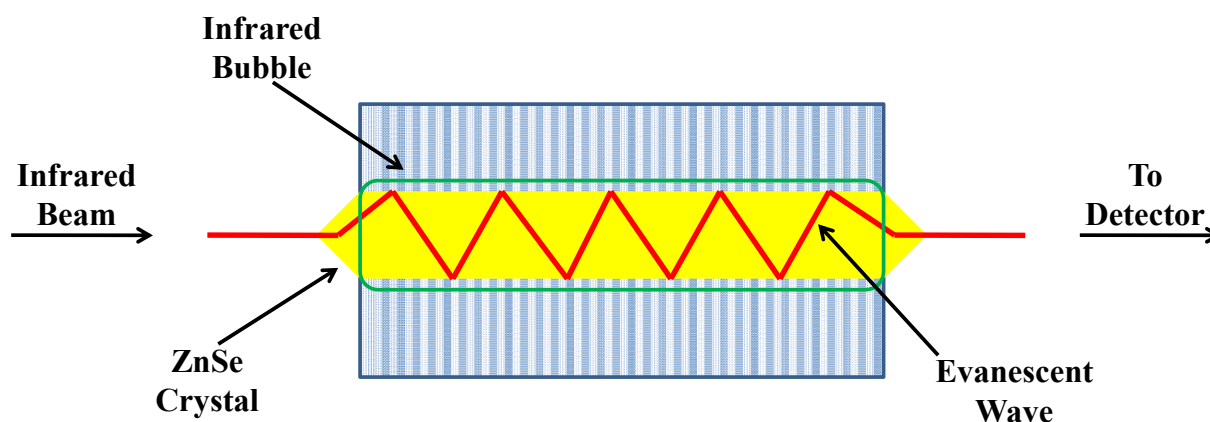


Figure 5.4. Illustration of ATR technique¹²

Backgrounds were taken of the crystal at room temperature, and the solvent from 20-90 °C at 10° increments. All of the samples were prepared in the glovebox, placed in vials and sealed with septa. The concentration of the samples in acetone was 25 mM, and 15 mM in 30% water/acetone. The reaction cell was purged with nitrogen to remove any air that was present, then purged with the reaction gas (1:1 or 2:1 H₂/CO). Under a slow purge of the reaction gas mixture, the catalyst solution was injected with a syringe. The samples were stirred at 400 rpm, and an initial room temperature scan was taken.

Preliminary IR studies conducted were essentially a repeat of previous studies of the dirhodium catalyst in acetone to ensure that the results were the same as before, and would therefore be a good basis of comparison for the 2:1 H₂/CO ratio and 30% water/acetone experiments. The goal of the first experiment was to observe the catalyst under CO gas only. This would aid in making structural assignments in the H₂/CO studies. The reactor was pressurized to approximately 3 psig with CO gas, and scans were taken at 23 °C in five minute increments for 20 minutes to observe structural changes. The temperature was then set to 60 °C,

and scans were taken at varying pressures at 60 °C (20, 40, and 60 psig). The IR spectra and proposed mechanism are shown below in Figure 5.5.

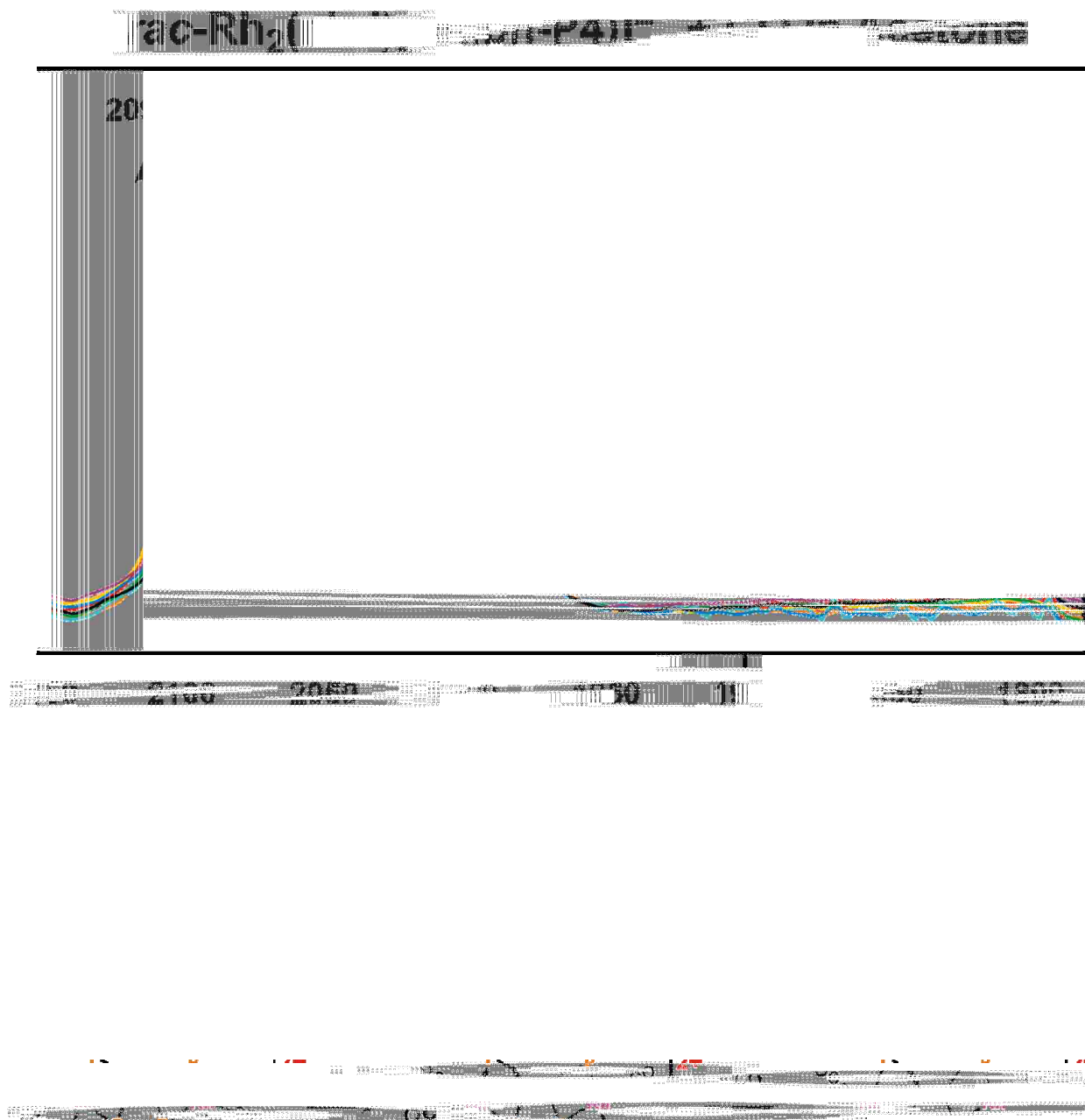


Figure 5.5. IR spectra and proposed mechanism for $rac-[Rh_2(nbd)_2(et,ph-P_4)](BF_4)_2$ under CO pressure.

This study resulted in three distinct carbonyl bands at 2095, 2043 and 2015 cm^{-1} . The band at 2015 cm^{-1} was assigned to the bis(norbornadiene)dicarbonyl species. The bands at 2095 and 2043 cm^{-1} were assigned to the hexacarbonyl and pentacarbonyl respectively which are in equilibrium. As the catalyst “soaked” under 3 psig of CO gas, and at higher temperatures and pressures the carbonyl bands at 2095 and 2043 cm^{-1} increased in intensity as the band at 2015 cm^{-1} decreased in intensity. During the soaking period, the CO displaces the norbornadiene off of the metal center which increases the concentration of the hexacarbonyl and pentacarbonyl species. As the temperature and pressure increase, the intensity of the band at 2015 cm^{-1} significantly decreases (almost nonexistent at 60 °C, 60 psig) representing a shift in the equilibrium to the bottom half of the mechanism.

After the CO studies were completed, the reactor was then cooled to 30 °C, and purged with 1:1 H_2/CO . The reactor was pressurized to 75 psig (1:1 H_2/CO), and the temperature was set to 90 °C to allow the catalyst to soak. When the temperature reached 90 °C, the reactor was pressurized to 90 psig (conditions for a standard hydroformylation run) and scans were taken. These experiments were used as a basis of comparison for the 2:1 H_2/CO and 30% water/acetone studies.

For the 1:1 H_2/CO and 30% water/acetone solvent study, the catalyst solution was loaded into the reaction cell as described above. After purging with syngas, the reactor was pressurized to 75 psig, and scans were taken at room temperature. In order to observe temperature effects, the reactor temperature was set to 90 °C, and scans were taken at varying temperatures until 90 °C was reached. When the set temperature was reached the reactor was pressurized to 90, then to 105 psig, to observe pressure effects. Scans were also taken at 105 psig as the reactor cooled down to monitor the stability of the catalyst (Figure 5.6)

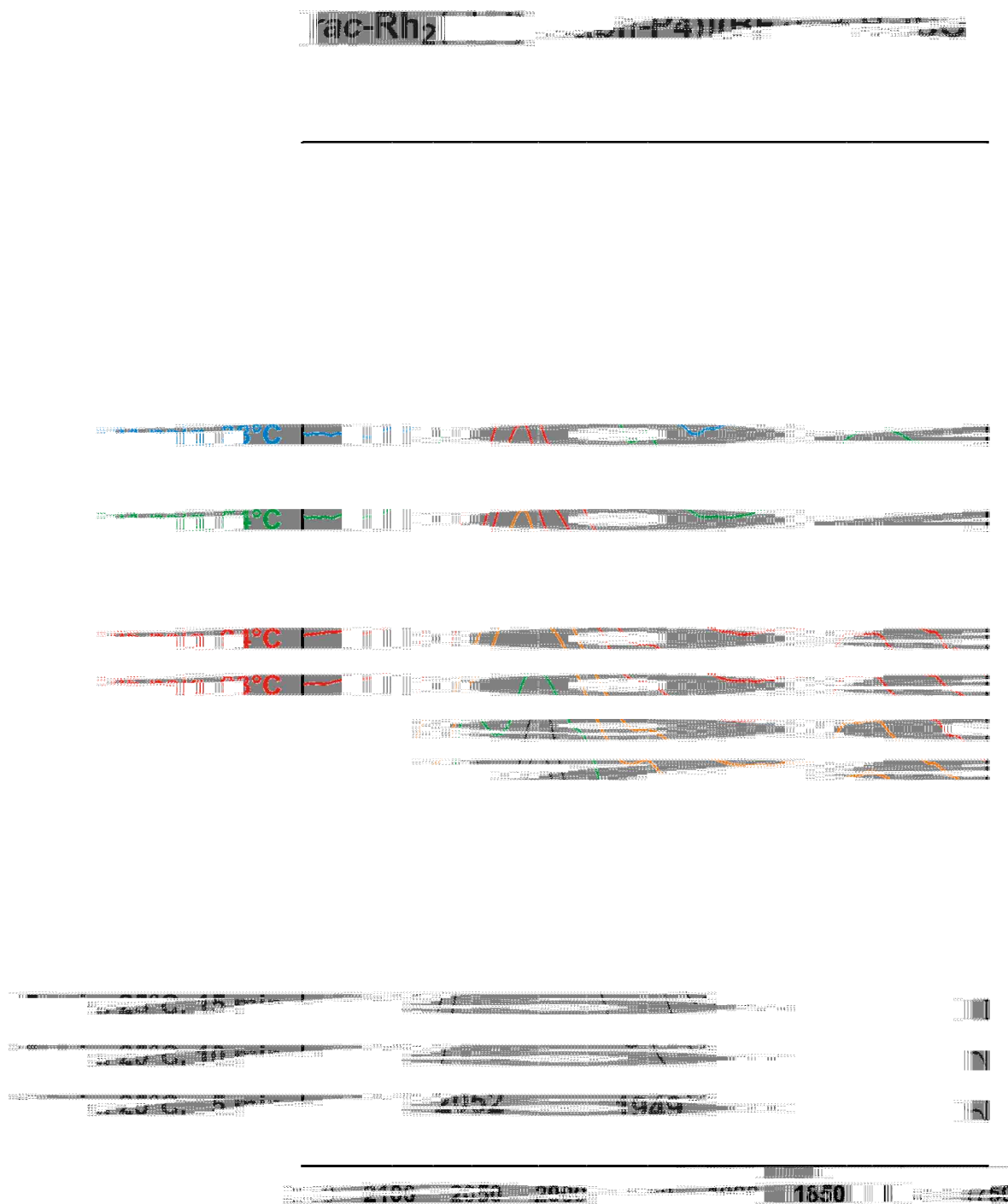


Figure 5.6. Effects of temperature and pressure on rac -[Rh₂(nbd)₂(et,ph-P4)](BF₄)₂ in 30% water/acetone (1:1 H₂/CO).

After 5 minutes of soaking under 75 psig syngas, there are several terminal carbonyl bands. The peak at 2096 cm^{-1} , which is very low in intensity, and at 2014 cm^{-1} can be assigned to the hexacarbonyl and the bisnorbornadiene species assigned in the CO experiments. As the temperature increases, the terminal bands at 2052 , 1983 , 1949 cm^{-1} decrease significantly in intensity as the structure appears to shift from the open mode structure to the closed mode structure in the proposed mechanism (Figure 5.7). This is determined by the increase in intensity of the bridging carbonyl peaks at 1832 and 1818 cm^{-1} . There is also a new terminal band at 2075 cm^{-1} at increased temperatures. As the reaction mixture cools the intensity of the terminal bands decrease and the bridging bands decrease as the structure is likely making a shift back to the open mode species.

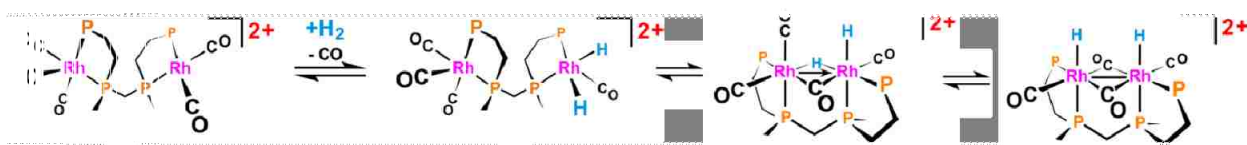


Figure 5.7. Shift from open to closed mode in the proposed hydroformylation mechanism.

For the 2:1 H_2/CO high pressure IR studies, after purging the reactor with a 2:1 H_2/CO mixture, the reactor was pressurized and scans were taken at 20, 40, 60, and 70 psig at room temperature to observe structural changes at varying total pressures. The temperature was then set to $90\text{ }^\circ\text{C}$, and scans were taken from room temperature to $90\text{ }^\circ\text{C}$ at varying temperatures to observe temperature effects at a set pressure. When the temperature reached $90\text{ }^\circ\text{C}$, the pressure in the autoclave was increased to 90 psig (temperature and pressure for a standard hydroformylation run) then increased to 105 psig to further observe pressure effects and catalyst stability. The IR spectra from the temperature and pressure effects studies using 2:1 H_2/CO are shown below in Figure 5.8.

rac-Rh₂(nbd)₂(et,ph-P4)](BF₄)₂
beratur



Figure 5.8. Effects of temperature and pressure on *rac*-[Rh₂(nbd)₂(et,ph-P4)](BF₄)₂ under 2:1 H₂/CO.

The first spectrum at 22 °C, 1 psig 2:1 H₂/CO, is almost identical to the room temperature spectrum under 3 psig CO, with terminal carbonyl bands at 2095, 2040, and 2017 cm⁻¹ although the peak at 2040 cm⁻¹ (pentacarbonyl species) is less intense. As seen with the 30% water/acetone studies, there are several terminal bands (2095, 2054, 2017/2010, and 1950 cm⁻¹) at varying pressures at room temperature, but as the temperature is increased, the intensity of these bands decrease, and the intensity of the bridging bands (1834 and 1818 cm⁻¹) and the terminal band at 2075 cm⁻¹ increase.

5.4 Conclusions

In Figure 5.9, the spectrum from the 1:1 H₂/CO (90 °C, 90 psig) study is compared to the 90 psig, 90 °C studies from the 2:1 H₂/CO and the 30% water/acetone studies. All of the spectra have terminal CO bands at 2094, 2075, and 2035 cm⁻¹ (slightly shifted to 2021 cm⁻¹ for the 30% water acetone study), and bridging CO bands at approximately 1834 and 1818 cm⁻¹. Preliminary results suggest that there are not any structural differences between the species formed under a 1:1 H₂/CO ratio (90 psig) at 90 °C, and the 2:1 H₂/CO and the 30% water/acetone studies. This provides further evidence for the proposed fragmentation pathway. The 30% water/acetone solvent system and the 2:1 H₂/CO gas mixture both contribute to stabilizing the key catalytic species during a hydroformylation reaction (90 °C, 90 psig).

Future studies will have to be conducted to observe structural changes over time. Studies will have to be conducted using the 1:1 H₂/CO (90 °C, 90 psig) for 2 hours, and compared to 30% water acetone and 2:1 H₂/CO at the same temperature and pressure, for the same amount of time to observe the true effects of gas ratio and solvent on the stability of the *rac*-[Rh₂(nbd)₂(et,ph-P4)](BF₄)₂ catalyst during a hydroformylation reaction.



Figure 5.9. Gas ratio (90 psig) and solvent effects on *rac*-[Rh₂(nbd)₂(et,ph-P4)](BF₄)₂ at 90 °C.

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CHAPTER 6: EXPERIMENTAL

6.1 General

All of the syntheses reported here have been previously published and are carried out with very slight or no modifications.¹⁻⁶ All reactions were performed under an inert atmosphere of nitrogen through the use of Schlenk and glovebox techniques. Most anhydrous solvents were purchased and used as received. 1-Hexene was passed through an alumina column before being used for hydroformylation experiments. Others were obtained from the chemistry department's dry solvent system. Water and other solutions prepared in the lab were degassed by sparging with nitrogen for at least 30 minutes before use. Nuclear magnetic resonance spectra were recorded on a Bruker DPX-250 (250 MHz) spectrometer ¹H and ³¹P analysis. Hydroformylation reactions were carried out in a stainless steel autoclave, equipped with a magnetic stirrer. GC-MS analysis was performed on an Agilent Technologies 6890N Network GC System. High pressure IR studies were carried out in a SpectraTech circle reaction cell attached to a SpectraTech external sample bench, using a Bruker Tensor 27 FT-IR instrument.

6.2 Synthesis of Phenylphosphine

In a 500 mL Schlenk flask, dichlorophenylphosphine (55.5 mL, 409 mmol) and 302 mL of tetra(ethylene glycol) dimethyl ether (t-glyme) were added to yield a colorless solution. To a second 1000 mL Schlenk Flask, lithium aluminum hydride (19.93 mL, 478 mmol) (LAH) and 517 mL of t-glyme were added to yield a gray solution. Both flasks were cooled to $-5\text{ }^{\circ}\text{C}$ and maintained at that temperature for at least 30 minutes. The dichlorophenylphosphine solution was then slowly added to the LAH mixture via a large bore cannula at a rate of about 1 drop per second with the temperature maintained below $0\text{ }^{\circ}\text{C}$ for the duration of the addition. Upon completion of the addition, the reaction mixture was allowed to warm to room temperature and

stir at least 1 hour. The phenylphosphine product was removed via a trap to trap distillation. Phenylphosphine can be obtained with yields as high as 83%. ^{31}P NMR: -121 ppm

6.3 Synthesis of Bis(phenylphosphino)methane (Bridge)

A 500 mL Schlenk flask with a stir bar is charged with phenylphosphine (15.00 g, 136 mmol), dichloromethane (5.79 g, 68.1 mmol), and DMF (100 mL) to give a colorless solution (solution A). The solution is placed in an ice bath and allowed to stir for at least 30 min. A potassium hydroxide solution (26.8 g, 477 mmol) (solution B) is then slowly added drop wise to solution A over at least a 30 min. period to give an orange/yellow solution with a ppt. The solution was allowed to stir under nitrogen at room temperature until it became colorless with a white ppt. Distilled water (~ 50 mL) was then added to the solution to dissolve any solid KCl. The product was extracted with pentane (3 x 150 mL) via cannula into a clean Schlenk flask. The pentane/product solution is heated to 80 °C in a water bath and pentane and impurities are removed under reduced pressure yielding a viscous, slightly yellow product. Isolated yield: 50%. ^{31}P NMR: -53 ppm (*racemic*), -54 ppm (*meso*)

6.4 Synthesis of Diethylchlorophosphine

A 250 mL Schlenk Flask with a stirbar was charged with phosphorus trichloride (30.0 g, 218 mmol) and t-glyme, double the volume of phosphorus trichloride, to give a colorless solution. A second 250 mL Schlenk flask was charged with diethylzinc (29.7 g, 240 mmol) and t-glyme, double the volume of diethylzinc, to give a colorless solution. Both flasks were then placed in ice baths for 30 min. With vigorous stirring, the diethyl zinc solution was slowly added drop wise via cannula to the PCl_3 solution. After the addition, the solution is allowed to stir room temperature for 30 min. to an hour. The product was collected using trap-to-trap distillation, with heating, into a clean pre-weighed Schlenk flask. Isolated yield: 70%. ^{31}P

NMR: 112 ppm (product), 66 ppm (Cl₂PEt, ok in small amounts)

6.5 Synthesis of Diethylvinylphosphine

A 250 mL Schlenk flask with a stir bar is charged with 100 mL 1 M vinyl magnesium bromide (12.99 g, 99 mmol) in THF and 100 mL t-glyme to give a brown solution with a white ppt (solution A). A second 250 mL Schlenk flask is charged with diethylchlorophosphine (11.21 g, 90 mmol) and 100 mL t-glyme to give a colorless solution (solution B). At least 95% of the THF is removed under reduced pressure with heating and stirring. Both flasks are then placed in an ice bath for at least 30 min. Solution B is then added drop wise via cannula to solution A with stirring. The reaction turns light yellow with a white ppt. The solution is heated to 90 °C, and the product is collected into a clean, pre-weighed Schlenk flask via trap-to-trap distillation

Isolated yield: 85%. ³¹P NMR: -18 ppm

6.6 Synthesis of et,ph-P₄ Ligand (Mixed *meso* and *racemic*)

A 25 mL pear shaped Schlenk flask with a stir bar was charged with bridge (4.7 g, 20.2 mmol) and vinyl-diethylphosphine (5.2 g, 44.5 mmol). The solution was then exposed to a UV light (xenon lamp) with stirring for at least 8 hours (generally overnight). The reaction becomes viscous as reaction proceeds. Excess vinyl-diethylphosphine was removed under reduced pressure with heating (90 °C water bath). Isolated yield (mixed product): > 85 %. ³¹P NMR: -17 ppm (arms), -25 ppm (racemic), -26 ppm (meso)

6.7 Hexane Separation of Ligand

The *racemic* form of the et,ph-P₄ ligand is the desired product and can be separated from the *meso* form by adding cold hexane to the mixture, and placing the solution in the freezer. The *meso* ligand crystallizes slightly, and the *racemic* ligand remains in solution. The *racemic*

solution was then transferred to a separate, clean Schlenk flask. Excess hexane was removed under reduced pressure and more hexane was added. The flask was placed in the freezer again to allow additional separation to occur. This process is repeated until the mixture is at least 85% racemic. ^{31}P NMR: -17 ppm (arms), -25 ppm (racemic), -26 ppm (meso)

6.8 Synthesis of Mixed $\text{Ni}_2\text{Cl}_4(\text{et,ph-P4})$

The ligand solution, in ethanol, was added dropwise to a rapidly stirring solution of NiCl_2 in ethanol and allowed to at least 12 hours or overnight. This mixture was then filtered to remove the orange precipitate, mainly *meso*- $\text{Ni}_2\text{Cl}_4(\text{et,ph-P4})$. This precipitate was then rinsed three times with ethanol (30 mL portions). The filtrate was then concentrated under vacuum to give a dark tarry amorphous solid, mainly *rac*- $\text{Ni}_2\text{Cl}_4(\text{et,ph-P4})$.

6.9 Cyanolysis of Filtrate Residue

A Schlenk flask containing *rac*- $\text{Ni}_2\text{Cl}_4(\text{et,ph-P4})$ (4.2 g, 6.26 mmol) was charged with 40.83 g NaCN (0.833 mol, 133 equiv.) in 250 mL of water and 100 mL MeOH. The solution was allowed to slowly stir for approximately three hours while the solution turned from orange to red. The solution was then charged with 46.1g (0.94 mol, 150 equiv.) of NaCN and then stirred slowly until all the NaCN dissolves (ca. 30 min). The free ligand was then extracted in three 100 mL portions of benzene as a light yellow solution. This solution was then passed through a neutral alumina column and the solvent removed to give 2.00 g of 70% pure *rac*-*et,ph-P4*. Yield not applicable due to 30% *meso*-*et,ph-P4* contamination.

6.10 Cyanolysis of *meso*- $\text{Ni}_2\text{Cl}_4(\text{et,ph-P4})$

6.9 g of *meso*- $\text{Ni}_2\text{Cl}_4(\text{et,ph-P4})$ was added to a Schlenk flask with 140 mL degassed deionized water and allowed to stir for 2 hours to give a dark red solution. A solution of 2.4 g

NaCN in 69 mL of water was then added drop wise very slowly (1 drop every 5 seconds) with very slow stirring. 138 mL of MeOH was then added followed by 24.2 g NaCN and allowed to stir rapidly giving a bright red solution. The free ligand was then extracted with four 100 mL aliquots of benzene, yielding a bright red solution. The red color is removed by passing the solution through two 12 inch columns (with fritted disks, 1 inch inner diameter) of neutral alumina, and the benzene is removed yielding 1.0 g of free ligand, in a ca 3:1 ratio of *racemic* to *meso*.

6.11 Synthesis of Rh(nbd)acac

A 250 mL Schlenk flask was charged with Rh(CO)₂(acac) (3.0 g, 11.6 mmol) and norbornadiene (nbd) (85 mL) forming a dark green solution. The solution was refluxed at 90 °C overnight forming a yellow solution. The solution was filtered, and excess nbd was removed under reduced pressure yielding a yellow solid. The product is then recrystallized by adding THF and hexane and placing the mixture in the freezer overnight. Isolated yield: 90%. ¹H NMR: 1.2-2.0 ppm (CH₂ of nbd, CH₃ of acac), 3.8-4.0 ppm (CH of nbd), 5.3 ppm (CO-CH-CO of acac), 6.2 and 6.7 ppm (olefinic CH of nbd).

6.12 Synthesis of [Rh(nbd)₂](BF₄)

Rh(nbd)acac (2.2 7.5 mmol) was dissolved in 30 mL THF forming a yellow solution, and cooled to -20 °C. HBF₄·OEt₂ (2.4 g, 15 mmol) was added dropwise with string producing a dark red solution. This addition was then followed by the dropwise addition of nbd (3.1 g, 33.7 mmol) which produces an orange precipitate. The flask was placed in the freezer for 2 hours and the precipitate was collected by filtration. Isolated yield: 90%. ¹H NMR: 1.7 ppm (CH₂ of nbd), 4.3 ppm (CH of nbd), 5.3 and 5.6 ppm (olefinic CH of nbd).

6.13 Synthesis of [*rac*-Rh₂(nbd)₂(et,ph-P4)](BF₄)₂

[Rh(nbd₂)](BF₄) (2 equiv) (solution A) and 80% *rac*-et,ph-P4 (1 equiv) (solution B) were dissolved separately in CH₂Cl₂ and placed in separate Schlenk flasks. Solution B was added dropwise to solution A with stirring. The CH₂Cl₂ was removed under reduced pressure. Acetone was then added to the solid allowing the pure *rac*-product to recrystallize. Any meso product present will not crystallize in acetone, and will remain in solution. Isolated Yield: 85% ³¹P NMR: 58.7 ppm and 46.9 ppm.

6.14 Hydroformylation of 1-hexene

Standard hydroformylation runs were performed in a stainless steel autoclave equipped with a packless magnetic stirrer, thermocouple for temperature monitoring, and an electronic pressure transducer for pressure monitoring. In the glovebox, 90 mg (1 mM) of *rac*-[Rh₂(nbd)₂(et,ph-P4)](BF₄)₂ was weighed out in a 100 mL round bottom flask. 80 mL 30% water/acetone (including 5 mL of toluene as an internal standard) was added to the flask and it was sealed with a septum. 1 M 1-hexene was weighed out in a separate vial and it was also sealed with a septum. The autoclave was assembled and evacuated, and the catalyst solution and olefin were transferred to the autoclave with separate cannulas. The olefin and catalyst solution can also be transferred to the autoclave with a syringe. The autoclave was purged with a slow flow of syngas to displace any trapped air, and it was pressurized to 45 psig. The autoclave was heated to 90 °C with stirring (1000 rpm), and the catalyst was allowed to soak (total heating and soaking period = 20 minutes). After the heating and soaking period was complete, the pressure in the autoclave was reduced to 45 psi, and the 1-hexene was pressure injected to the operating pressure of 90 psig.

6.15 *In Situ* FT-IR studies

A SpectraTech external sample bench, and circle reaction cell were attached to a Bruker Tensor 27 FT-IR instrument. The circle reaction cell contains a zinc selenide single crystal. The samples are analyzed using attenuated total reflectance. For samples in acetone instrument parameters were: 64 scans, resolution 4 cm^{-1} , scan speed 1.0 cm s^{-1} , scan range $4000\text{-}700\text{ cm}^{-1}$ (for data collection range narrowed to $2500\text{-}1400\text{ cm}^{-1}$). For samples in 30% water/ acetone instrument parameters were: 128 scans, resolution 4 cm^{-1} , scan speed 1.0 cm s^{-1} , scan range $4000\text{-}700\text{ cm}^{-1}$ (for data collection range narrowed to $2500\text{-}1400\text{ cm}^{-1}$). Backgrounds were taken of the crystal and the solvent. The reactor was assembled and purged with nitrogen, then charged with the sample solution under a slow nitrogen flow. The reactor was then purged with the reaction gas, and pressurized to the starting pressure of the experiment.

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