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Entitled

Asymmetric Hydroformylation of Styrene in Supercritical Carbon Dioxide

By

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An Abstract of

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Hydroformylation reactions in supercritical carbon dioxide provide an environmentally conscious method of producing aldehydes for fine chemical and pharmaceutical products. Asymmetric ligands, such as (R)-BINAP, may be used to provide an enantioselective product. The benefits of producing a selective product include an overall reduction in costs, including those costs associated with separation and disposal of undesired and potentially harmful products. When these reactions are performed in environmentally benign solvents, such as supercritical carbon dioxide (scCO₂), additional environmental benefits are derived, such as ease of recycling of the solvent and unconverted reactants and elimination of the need for organic solvents.

In this study, rhodium based catalysts were prepared in supercritical carbon dioxide and evaluated for the hydroformylation of styrene to produce 2-phenylpropionaldehyde. Triphenylphosphine and (R)-BINAP were examined as ligands and their effects on the

reaction were examined. The experiments showed that a catalyst is produced that promotes hydroformylation of styrene in supercritical carbon dioxide and that enantiomeric selectivity could be obtained using (R)-BINAP ligands.

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Chapter One

Introduction

1.1 Pollution Prevention

The Pollution Prevention Act (PPA), codified as 42 USC 13101, was first passed by Congress in 1990, and “focused industry, government, and public attention on reducing the amount of pollution through cost-effective changes in production, operation, and raw materials use” (EPA, 2005). The Environmental Protection Agency (EPA) notes that source reduction is more desirable than waste management and pollution control; however, source reduction is complicated for several reasons including existing regulations and industrial resources required for compliance (EPA, 2005). This sentiment is echoed by others in the field of green engineering who point out that the maximum opportunity to reduce environmental impact occurs as early in the process design as possible. The EPA also notes that pollution prevention includes practices that increase efficiency in the use of energy, water, and other natural resources, as well as protecting resources via conservation (EPA, 2005).

The concept of improving a process or designing a process to be more environmentally friendly and have minimal negative impacts is referred to as green engineering. This concept is broadened and referred to as sustainable engineering when looking at the holistic impact on the people, the environment, and the benefits received

over a span of time. Sustainable engineering focuses not only on the reactants being used and the products being created, but also on the origin or destination of these resources, the energy expenditures associated with the processes, and the well-being of the people impacted by the process (Abraham, 2004). While there are few, if any, truly sustainable processes; sustainability is meant as an improvement to the current situation.

1.2 The Reaction

Hydroformylation reactions were first discovered by Otto Roelen in 1938 (van Leeuwen, 2000). During the reactions, an olefin reacts in the presence of a catalyst, carbon monoxide, and hydrogen, to produce an aldehyde, as shown in Figure 1.1. In the 1960s, Wilkinson began investigating phosphorus modified rhodium catalysts (van Leeuwen, 2000); these catalysts were to improve the regioselectivity of the hydroformylation reaction towards the formation of the linear product. Wilkinson's research showed that rhodium provided selective hydroformylation under mild conditions in the presence of arylphosphines as a ligand; this led to further research on hydroformylation and ligand effects (van Leeuwen, 2000).

Figure 1-1. Hydroformylation Reaction.

Providing selectivity to reactions has many benefits for industrial applications. For example, by producing a desired product in excess of an undesired product, separation processes can be reduced and possibly eliminated. In addition to reducing costs associated with separations, this would also reduce costs incurred through disposal of unwanted products. Furthermore, by increasing the yield of the desired product, the ability to produce the end products is greatly enhanced. This ultimately can increase the availability of the finished product.

1.3 Reactions in supercritical carbon dioxide

Supercritical carbon dioxide has been extensively studied in efforts to replace organic solvents that have traditionally been used in the hydroformylation reaction (Tack, 2003). Carbon dioxide is naturally abundant; it is non-toxic, readily available in large quantities, and relatively inexpensive. Supercritical carbon dioxide possesses favorable properties of both a liquid and a gas; it has high miscibility with reactant gases, no liquid/gas phase boundary, very low viscosity, very high diffusivity, and high compressibility (Koch & Leitner, 1998; Tack, 2003). These solvent properties provide a suitable environment for hydroformylation reactions that minimizes their environmental implications, and allows for a more sustainable process to produce aldehydes. Additionally, aldehyde formation is often slower in traditional solvents, such as toluene, than in scCO_2 (Koch & Leitner, 1998). Since carbon dioxide is not consumed by the reaction, it can be recycled and reused for future applications.

1.4 Motivation

Hydroformylation is widely used for large-scale processes, but it has not yet been applied extensively to fine chemical production (van Leeuwen, 2000). Aldehydes are often used in medicinal chemistry as intermediates between the starting components and the end product or pharmaceutical; thus, many benefits can be reaped if hydroformylation can be used to produce the aldehydes needed for fine chemical and pharmaceutical production (Hudson, 2004).

Applying asymmetric hydroformylation processes to fine chemical production can be greatly beneficial. To bring a new pharmaceutical to market, drug companies must provide evidence to the Food and Drug Administration (FDA) that their drug is both safe and effective. If a pharmaceutical is made with racemic mixtures of compounds, the drug company must show that both components of the racemic mixture are non-toxic. The process to ensure a product's safety can be very time consuming and costly, thereby delaying the product's market entry and delaying its benefits to patients. This process can be greatly simplified if the processes used to produce the pharmaceuticals synthesize only the desired enantiomeric aldehyde rather than producing a racemic mixture (Hudson, 2004).

Homogenous asymmetric catalysis is used to produce fine chemicals often used in pharmaceuticals, agrochemicals, flavors, and fragrances (Ojima, 2000). Chiral aldehydes with high enantiomeric purities obtained via asymmetric hydroformylation serve as useful intermediates for pharmaceutical drugs (Ojima, 2000). In particular, the branched aldehydes obtained from the hydroformylation of styrene can be converted to various non-steroidal anti-inflammatory agents (Ojima, 2000). Although the hydroformylation

reaction used in this research focused on producing products with one chiral center, hydroformylation can also be used to produce products with more than one chiral center. The more complex chemistry using multiple chiral centers can be further enhanced by using specific ligands which target a specific chiral center (Hudson, 2004).

More cost-effective and safer large scale production of aldehydes for pharmaceutical use could provide great economic and health impacts. Asymmetric hydroformylation reactions can be used as a tool for the preparation of a large number of chiral products that can be used as precursors to organic compounds with therapeutic benefits (Castellanos-Paez, *et al.*, 1997).

By synthesizing pharmaceuticals through new pathways, the availability of pharmaceuticals can be greatly increased and the cost can be greatly decreased. By increasing the availability of pharmaceuticals, the standard of living and general health can be greatly improved, especially among people in low and middle income countries. Life expectancies have increased over the years, with the greatest increases being in areas where antibiotics, other medicines, and immunizations are available (The World Bank Group, 2004). Although pharmaceuticals are available to help treat flu, pneumonia, diarrhea, cholera, and malaria, many third world childhood deaths are still attributed to these diseases; additionally, many children in third world countries are not immunized against many deadly, infectious diseases such as diphtheria, measles, polio, tetanus, typhoid, tuberculosis, and whooping cough (The World Bank Group, 2004).

Benefits of enhancing a pharmaceutical's availability are not limited to what improvements can be made in third-world countries; many benefits also exist in developed countries. Medicines play an important role in not only treatment, but also

prevention. A study at Columbia University found that it is less costly overall to use newer medicines than it is to provide non-drug related health care (Lichtenberg, 2002). By using newer drugs, the need for costly hospitalization, institutionalization, or surgery is reduced (Lichtenberg, 2002).

1.5 Research Focus

The current study examines the enantiomeric hydroformylation of styrene to produce 2-phenylpropionaldehyde; the significance of aldehyde production is that aldehydes are used in many fine chemical and pharmaceutical syntheses, as previously discussed. By performing the reaction using supercritical carbon dioxide and an enantioselective catalyst, a hydroformylation reaction can occur in such a way that minimizes negative environmental impacts and optimizes pharmaceutical benefits.

Chapter Two

Literature Review

2.1 Hydroformylation

A German by the name Otto Roelen first described hydroformylation or ‘oxo reactions’ in a patent filed in 1938; for these reactions, Roelen used a cobalt-catalyzed process (van Leeuwen, 2000). Hydroformylation reactions add one molecule of carbon monoxide and one molecule of hydrogen to an olefin, thereby producing an aldehyde.

While the first generation of hydroformylation catalysts were based on cobalt carbonyls, the second generation of catalysts used rhodium and phosphorus ligands, particularly triphenylphosphine (van Leeuwen, 2000). The major advantage of rhodium catalysts is that the reactions could be carried out in low pressure; cobalt-catalyzed reactions required high pressures to stabilize the catalyst (van Leeuwen, 2000). Additionally, the rhodium catalysts provided better utilization of feed stocks and much faster reactions, which directly correlated to milder conditions noted above (van Leeuwen, 2000). The first rhodium precursors used were simple compounds such as RhCl_3 and $\text{Rh}/\text{Al}_2\text{O}_3$. The rhodium catalysts provided greater aldehyde formation than the cobalt catalysts and reduced the undesired hydrogenation reaction, hence the cobalt catalysts were replaced with rhodium catalysts in the mid 1970s (van Leeuwen, 2000).

Wilkinson and his colleagues have made significant contributions to rhodium catalyzed hydroformylation (van Leeuwen, 2000). Using $\text{RhCl}(\text{PPh}_3)_3$, Wilkinson, *et al.* found that substitution at the aromatic ring affected the reaction rate (van Leeuwen, 2000). Wilkinson's group also determined that phosphine ligand variations had a minimal affect on rate and selectivity at the conditions used, 70 °C and 100 bar (about 1470 psig) (van Leeuwen, 2000). A generally accepted mechanism for rhodium-catalyzed hydroformylation is summarized in Figure 2.1.

Figure 2-1. Generally accepted mechanism for the rhodium-catalyzed hydroformylation. (Van Leeuwen, 2000)

2.1.1 Homogeneous Catalysis

Homogeneous catalysis is defined as a catalytic reaction in which the catalyst and the reactants are in the same phase. Since the catalyst is dissolved in the medium, each molecule of a particular structure acts like any other molecule (Satterfield, 1991); therefore, not only do homogeneous reactions in supercritical fluids dissolve the organic substrates, they can lead to longer catalyst lifetimes relative to gas-phase heterogeneous catalysis (DeSimone & Tumas, 2003).

Homogeneous reactions require the reclamation of highly expensive and often specialized catalysts (Aresta, 2003). Extensive research has enabled researchers to control the stereoelectronic environment around the transition-metal center via ligand design; this has led to significant developments in homogeneously catalyzed reactions over the past 30 years (DeSimone & Tumas, 2003).

Phosphorus ligands are the only ligands used in hydroformylation in addition to carbon monoxide (van Leeuwen, 2000). The performance of the hydroformylation catalyst can be greatly affected by the phosphorus ligands present in the reaction (Bunten, *et al.*, 2002). Modified phosphorus ligands sometimes form very selective catalysts (van der Slot, *et al.*, 2002).

Triphenylphosphine is one of the most commonly used ligands in industry. Dickson (1985) reported that co-oxidation of triphenylphosphine and terminal alkenes produces rhodium catalysts, among which, $\text{RhCl}(\text{PPh}_3)_3$ was observed to be the most effective catalyst. During the 1970s, Celanese, Union Carbide Corporation, and Mitsubishi Chemical Corporation used triphenylphosphine for ligand-modified processes (van Leeuwen, 2000).

Under hydroformylation conditions, a rhodium carbonyl hydride, $[\text{HRh}(\text{CO})_3]_2$, is produced (van Leeuwen, 2000). This rhodium carbonyl hydride is the active catalytic species of the reaction (van Leeuwen, 2000). Additionally, Bensaid reported that free phosphines play an important role in transformation of catalyst precursors into the presumed catalytically active complexes, the rhodium carbonyl hydrides (2002). Bensaid also notes that systems in which the excess quantity of free phosphine is greater than ten-fold, the hydroformylation reactions are inhibited (2002).

Hydroformylation research has focused on developing new ligands to obtain highly active and selective catalysts (van der Slot, *et al.*, 2002). Ligand modifications are the most effective way to influence the selectivity of rhodium-catalyzed reactions (Reinius & Krause, 2000). For this reason, it is important to understand the structure-activity relationships so that a ligand can be designed specifically to favor the desired products. The influence of the ligands is primarily due to the electronic and the steric effects (van Leeuwen, 2000); however, the dominant effect is believed to vary depending on the stability of the catalyst complex.

Reinius and Krause observed regiocontrol during the hydroformylation of styrene with an *in situ* formed rhodium-phosphorus complex (2000); they also state that the factors that most greatly affected regioselectivity were the substrate and the modifying ligand. Ali, *et al.* (2005) noted that high catalytic activity occurred during a reaction in which $\text{Rh}_6(\text{CO})_{16}$ was used as a rhodium complex. The activity was likely due to protonation of the rhodium carbonyl intermediates and stabilization of an active catalytic intermediate (Ali, *et al.*, 2005). Advanced knowledge of the correlation between central atoms and ligands has greatly improved the activity and selectivity (Ali, *et al.*, 2005).

Although the ligand sometimes provides much desired selectivity, it can often slow the rate of reaction (van der Slot, *et al.*, 2002). The general trend is that the greater the phosphorus loading, the greater the inhibition of the reaction. Ideally, a ligand would provide selectivity and not affect the activity of the reaction.

Phosphite ligands were examined in the 1960s, but triphenylphosphine (TPP) continued to be the catalyst of choice; the interest in phosphite ligands arose again in the 1980s because Bryant *et al.* made bulky monophosphites with better stability and they

were found to give very high rates (van Leeuwen, 2000). Eastman's BISBI is an example of a diphosphine ligand that became very popular for rhodium hydroformylation (van Leeuwen, 2000).

The regioselectivity of the reaction, which is the ratio of linear to branched products, depends on the substrate being used. When styrene, a vinyl substrate, is used, the branched aldehyde should be produced in abundance (van Leeuwen, 2000). In a system in which the unmodified rhodium-based precursors were used between 20 °C and 100 °C, van Leeuwen states that the formation of the linear aldehyde during styrene hydroformylation increased as temperature increased (2000). Van Leeuwen did not note selectivity changes for a phosphorus modified rhodium-based system (2000). Additional research by Matsuda *et al.* (2001) reports that enantioselectivity can be increased by decreasing the pressure while maintaining a constant temperature. Balsells and Walsh (2000) note that enantioselectivity can also be controlled by the use of diastereomers.

The partial pressures of carbon monoxide and hydrogen during the reaction also affect regioselectivity, but only when the reaction is carried out at high temperatures (100°C) (van Leeuwen, 2000). Van Leeuwen notes that for styrene hydroformylation at 100 °C, an equimolar mixture of CO and H₂ at 170 bar (~2500 psig) would give a branched to linear ratio of 80 to 20 (2000).

2.1.2 Asymmetric Hydroformylation

Many hydroformylation reactions on pro-chiral alkenes provide two enantiomeric products that are generally equimolar. Asymmetric hydroformylation, however, provides an enantiomeric excess of one enantiomer relative to the production of the other

enantiomer. Asymmetric hydroformylation has historically been done using transition-metal complexes, primarily those using rhodium and platinum (Castellanos-Paez, *et al.*, 1997). Additionally Wilkinson's catalyst was used for asymmetric hydrosilylation of ketones; since this catalyst provided asymmetric products, research grew in the area of using rhodium complexes with chiral phosphine ligands (Ojima, 2000). During the 1970s, several chiral phosphine-rhodium catalysts were used that provided low-to-moderate enantioselectivity (Ojima, 2000).

Asymmetric hydroformylation used to transform substrates into aldehydes can be used on substrates with one or more chiral center (Ojima, 2000). Styrene is extensively studied for asymmetric hydroformylation reactions because it has a high reactivity and high selectivity for yielding branched aldehydes (Ojima, 2000).

Rhodium-BINAP complexes are often studied for their enantioselective hydrogenation abilities (Bunten, *et al.*, 2002); although other ligands have been used to successfully perform asymmetric hydroformylation reactions. Chiral diphosphite ligands have been used in asymmetric hydroformylation of styrene; a regioselectivity of branched:linear = 98:2 was observed using this ligand (Ojima, 2000). A Rh-BINAPHOS complex supported on a highly cross-linked polymer was found to also provide high regioselectivity and enantioselectivity when styrene is used as the substrate (Ojima, 2000).

Figure 2-2. (R)-BINAP and (R,S)-BINAPHOS. (R)-BINAP ligand is shown on the left and (R,S)-BINAPHOS is shown on the right.

2.1.3 NMR and IR Spectroscopy

Various ^{31}P NMR data can be found for rhodium phosphine complexes. Quin and Verkade (1994) reported doublets at 61.6 and 46.1 ppm, with $J_{\text{RhP1}}=189$ and $J_{\text{RhP2}}=205$ Hz for $[\text{CIRh}(\text{P}\sim\text{O})(\text{PO})]$. Quin and Verkade (1994) also reported $\delta\text{P-Rh}$ with the following values: 26.5, 29.3, 25.3, and 25.5 ppm; thereby giving $\delta\text{P-Rh}$ a range in the mid-to high twenties (ppm). Quin and Verkade (1994) also reported values for $^1J_{\text{RhP1}}$ equal to 104, 100, 134, and 111 Hz; thereby giving an acceptable range of 100 to 134 Hz for values of $^1J_{\text{RhP1}}$.

Bunten, *et al.* (2002) reported doublets found in Rhodium-BINAP complexes at 50, 46.1, 24.9, and 48.6 ppm; singlets were found in oxidized Rhodium-BINAP complexes at 28.1 and 29.3 ppm. Values of J_{RhP} were also reported at 195, 163, 128, and 175 Hz for compounds using BINAP as a ligand (Bunten, *et al.*, 2002).

Various IR frequencies of carbonyl groups can be found throughout the literature. Van der Slot, *et al.* (2002) reported a value for ν_{CO} (cm^{-1}) of 1978 for triphenylphosphine when used with $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$. Bunten, *et al.* reported values for similar active catalysts at ν_{CO} of 1978 and 2018 cm^{-1} (2002). Van Leeuwen reports rhodium hydride signals for similar active catalysts ranging from 1996 to 2093 cm^{-1} (2000).

2.2 Supercritical Carbon Dioxide as a reaction solvent

The interest in supercritical fluids is justified on several bases; supercritical fluids (Akgerman, 1997):

- (1) reduce environmental problems associated with commonly used organic solvents,
- (2) provide a less expensive means of separation with respect to energy costs, and
- (3) provide a means of achieving necessary separations that can adapt to emerging industrial needs.

Supercritical carbon dioxide has many advantages over traditionally used solvents. According to Koch and Leitner (1998), “Supercritical carbon dioxide is an environmentally benign reaction medium for highly efficient rhodium-catalyzed hydroformylation reactions.” Many advantages are associated with using scCO_2 for metal-catalyzed chemical synthesis because of its “gas-like” properties: high miscibility with reactant gases, no liquid/gas phase boundary, very low viscosity, very high diffusivity, and high compressibility (Koch & Leitner, 1998; Tack, 2003). Another advantage of scCO_2 is that it is nonflammable, which is an advantage that it has when compared to conventional organic solvents used in hydroformylation reactions (Liu, *et al.*, 2003). Additionally, carbon dioxide can be separated from product gases and reused;

absorption, cryogenic distillation, adsorption, and membranes provide means of separating CO₂ from other gases used in the synthesis (Liu, *et al.*, 2003).

Homogeneous catalysis in scCO₂ has been extensively studied; these reactions provide equal, if not better regioselectivity in hydroformylation reactions (Aresta, 2003). Higher reaction rates are obtained when using scCO₂ as a reaction medium for rhodium-catalyzed hydroformylation, with a reaction rate increase at least 5 times that obtained when using toluene as a reaction medium (Koch & Leitner, 1998). Additionally, phosphorus donor ligands have been used for hydroformylation in scCO₂ when the ligands are soluble in the supercritical fluid (Koch & Leitner, 1998).

Palo and Erkey (2000) reported that the electron withdrawing effect of fluoroalkyl moieties increases the activity of the rhodium hydroformylation catalysts when the form of the catalysts is HRh(CO)L₃, with L being the ligand; Palo and Erkey's research focused on evaluating the effect of ligand modifications for rhodium-catalyzed homogeneous hydroformylation in scCO₂ (2000).

Akgerman has made many contributions in the area of supercritical fluids. Akgerman (1997) reported that using supercritical fluids yields better selectivity to desired compounds, which eliminates costly separations of products and minimizes waste accumulation due to undesired product formation. Akgerman (1993) also reported that advantages of using scCO₂ in catalytic reactions also include "ease of solvent recovery, elimination of residual solvent in the extracted medium, lower pressure drops, and enhanced mass transfer rates." Akgerman and associates have also conducted research in areas of supercritical fluids, including supported rhodium catalysis (Kani, *et al.*, 2004; Kani, *et al.*, 2002).

Chapter Three

Experimental

3.1 Reactor

Hydroformylation of styrene in supercritical carbon dioxide was used to evaluate various methods of *in situ* catalyst preparation with variations in rhodium to phosphorus ratios. The 300 mL reactor (Figure 3.1) was manufactured by Autoclave Engineers; it is operable to 5400 psig (37.2 MPa) at 344 °C, as described in previous works (Tadd 2001, Tack 2003). To ensure safety, the reactor was equipped with a 5000 psig rupture disc and was operated with a Lexan shield surrounding the reactor. The reactor used an Omega Type K thermocouple and a Sensotech pressure transducer for temperature and pressure indication, respectively.

The reactor was heated using a clamp-on ceramic heating jacket supplied by Industrial Heater Corporation. Temperature control was provided by a Partlow 1160+ PID controller in conjunction with a type K thermocouple placed in the reactor.

1. From main CO ₂ cylinder	7. Stirrer shaft
2. High pressure CO ₂ pump –Applied Separations Spe-ed SFE	8. Thermocouple – Type K
3. Detachable cylinder for addition of CO/H ₂	9. Pressure transducer – Sensotech
4. Bypass for addition of styrene & n-heptane	10. Syringe for rinsing of sample loop
5. Reactor with catalyst basket	11. Sample loop – 1 mL
6. Rupture Disc	12. Sample vial
	13. Vent to laboratory hood

Figure 3-1. High pressure batch reactor system.

3.2 Catalyst Loading

The catalysts used in all experiments were solids in the form of flakes or powder. A 5 μ m nylon mesh material (Spectrum Labs) was created by cutting two small rectangles of mesh; three of the rectangle's edges were fused together using a variable wattage soldering iron. A measured amount of catalyst or catalyst precursors was added to the pouch through the open end; the remaining edge was then soldered to secure the catalyst inside the pouch and prevent disbursement throughout the reactor.

The catalyst envelope was then clamped between two heavy gauge screens mounted on discs located on the stirring shaft. The screens and discs were configured so that two catalyst envelopes could be used during reactions, however only one catalyst envelope was used during any reaction.

3.3 Reactant Loading

An equimolar mixture of carbon monoxide and hydrogen was added to a sample cylinder (Whitey) from a gas cylinder (AirGas); the sample cylinder was pressurized to 1400 psig. The sample cylinder was then weighed and its contents brought into equilibrium with the sealed reaction vessel. The sample cylinder was then weighed to determine the weight of the carbon monoxide and hydrogen added to the reactor. The reactor was then heated to the desired temperature.

Experimental variances occurred after the desired temperature was obtained; these variances are noted in the results and discussion section of this work. The first variance is that the reactor was maintained at the pressure obtained by adding only carbon monoxide and hydrogen to the vessel; the contents of the reactor were held at this

pressure and temperature for 24 hours to allow *in situ* catalyst formation to occur. The second variance is that carbon dioxide was added to the reactor using a high pressure liquid pump (Applied Separations Spe-ed SFE). This increased the pressure inside the vessel to obtain supercritical conditions; the contents of the reactor were then held at this elevated pressure and temperature for 24 hours to allow *in situ* catalyst formation to occur.

Prior to the experiment, a known amount of styrene and n-heptane was added to the bypass section (item 4 in Figure 3-1). After the 24 hour *in situ* catalyst preparation period, the high pressure liquid pump was used to push CO₂ through the bypass line, thereby forcing the styrene and n-heptane from the bypass line into the reaction vessel. The pump was turned off when the reaction pressure was achieved.

3.4 Experimental Procedure

In preparation for an experimental run, the reaction vessel was disassembled and thoroughly cleaned using acetone and ethyl acetate. After cleaning, the reaction vessel was reassembled. The sample loop was flushed with ethyl acetate to remove any remaining reactants or products. The pressure transducer was also rinsed using acetone and allowed to air dry.

After sealing the reactor with the catalyst envelope attached to the stir column as previously described, the system was then powered on so that the system pressure and temperature could be observed. The heating jacket was set to provide a temperature slightly greater than room temperature, so as to minimize temperature fluctuation affects during pressurization. The reaction vessel was flushed using CO₂ with a maximum

pressure no greater than 500 psig. The CO₂ was purged from the reaction vessel via the sample loop and discharged into the hood; the purging allowed the pressure inside the reactor to drop to atmospheric pressure.

The sample cylinder containing an equimolar mixture of carbon monoxide and hydrogen was connected to the system and its contents brought into equilibrium with the contents of the reaction vessel. The temperature of the heating jacket was then incrementally increased until the desired temperature was obtained; this process was carefully observed so as to minimize overshoot, with a maximum overshoot no greater than 10 °C above the desired temperature.

After heating to the desired temperature, carbon dioxide was added in select experiments so that the reaction vessel was brought to an elevated pressure. To allow for *in situ* catalyst preparation, the contents of the reactor were maintained at the given temperature and pressure with mixing for 24 hours. At the conclusion of the 24 hour period, the reactor was pressurized using liquid CO₂ to obtain a pressure approximately 500 psig lower than the desired reaction pressure. The reaction system was then allowed to stabilize, normally requiring no greater than ½ hour to achieve stability. After achieving stability, the styrene and n-heptane present in the bypass were pushed into the reactor using liquid CO₂; this process continued until the desired reaction pressure was achieved, usually requiring no greater than 3 minutes to obtain desired pressure. The start of the experiment is marked from the time the contents of the bypass line began being flushed into the reactor.

Sampling began at 15 minutes; additional samples were taken generally at 30, 45, 60, 75, 90, and 120 minutes with hourly samplings occurring for the next 4 hours of the

experiment. If additional samples were needed, they were taken at the 9 hour mark and then every 6 or 12 hours thereafter.

Following the reaction, the contents were purged into the ventilation hood and the power to the system terminated. The system was allowed to cool to ambient temperature before disassembling. The catalyst pouch was removed and placed in a sample vial; the contents collected on the bottom of the reactor were removed via pipette and put into sample vials for later analysis using GC/MS. The cleaning procedure described previously was used to prepare the reactor for the next experimental run.

3.5 Analytical Methods

The reaction's progress, the utilization of styrene and the production of products, was monitored by taking samples for analysis by gas chromatography. Products were identified using a Hewlett-Packard 6980 gas chromatograph and a 5973 mass selective detector. A chiral Supelco Beta Dex™ 225 column (30 m x 0.25 mm x 0.25 µm film, column number 16651-018) was used to achieve separation of the styrene reactant and the enantiomeric products. A temperature ramp was used, with an initial temperature 40°C for 5 minutes, then increasing 10 °C per minute until a temperature of 85 °C was reached; the total time needed to complete a sample's analysis was 39.5 minutes. Samples were collected from the reactor by expansion through 1 mL of ethyl acetate in a 5 mL screw cap vial. The sample was bubbled through the solvent. The organic components were trapped in the liquid solvent while the CO, H₂, and CO₂ escaped; therefore, these components were not quantified.

The contents of the sample were quantitatively measured; this was accomplished by using known mixtures of the reactants and products and comparing the samples' contents to the internal standard, n-heptane. Mass spectrometry was used to identify the components. Gas chromatography was used to obtain absorbance measurements of the components in the reaction sample; the absorbance measurements were compared to the calibrations to quantify the amount of each component in the sample. Most reactions were terminated when full conversion of styrene was obtained, and the time required to achieve full conversion varied. Calibration curves were constructed in which the areas observed were converted to mole ratios. The standardization curves exhibited a linear fit. The slopes were assumed to be response factors, R_f , which would allow the concentrations in the reactor to be quantified by using the observed area ratios of the samples.

$$\frac{A_A}{A_S} = R_f \left(\frac{N_A}{N_S} \right) \quad (3.1)$$

$$N_A = \frac{1}{R_f} \left(\frac{A_A}{A_S} \right) N_S \quad (3.2)$$

The internal standard, n-heptane, was used because it would not react with either the reactants or the products of the reaction.

The known samples used in producing the calibrations were prepared using purchased materials of high purity. The products from the reaction, 2-phenylpropionaldehyde, shown in Figure 3-2, are enantiomers and were purchased in a mixture, which is believed to be racemic. Both enantiomeric products were obtained from the analysis; however, no effort was made to identify the individual enantiomers because the separate enantiomers were not found to be commercially available.

Figure 3-2. 2-Phenylpropionaldehyde. 2-Phenylpropionaldehyde is the enantiomeric product produced by the hydroformylation reaction.

3.6 Catalysts

Most of the catalysts used were produced in the reaction vessel. These catalysts were made during a pretreatment process in which the $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$ and the phosphorus component, either (R)-BINAP or triphenylphosphine, were placed in a mesh envelope, the envelope sealed and affixed to the stir bar, and put into the reactor with mixing at a specified temperature, pressure, and mixture of CO , and H_2 , or CO , H_2 , and CO_2 . $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$ was prepared in the Department of Chemistry at The University of Toledo; the procedure for synthesis can be found in *Inorganic Syntheses* (Giordano & Crabtree, 1990). The (R)-BINAP, was purchased from Strem Chemicals; its purity is 98%. The triphenylphosphine was purchased from Aldrich Chemical Company, Inc.; its purity is 99%. Figure 3-3 shows the chemical structure of each ligand used in the experiments.

Figure 3-3. (R)-BINAP and TPP. (R)-(+)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl is shown on the left and triphenylphosphine on the right.

Other catalysts used were prepared by Nick Kingsley of the Department of Chemistry at The University of Toledo. These catalysts included: Wilkinson's Catalyst, a solid catalyst with a Rh:P ratio of 1:3, a solid catalyst with a Rh:P ratio of 2:1, and a solid rhodium-BINAP complex. The catalysts that were prepared by Nick Kingsley were characterized by ^{31}P solid state NMR spectroscopy. The preparation and characterization of the solid catalysts with Rh:P ratios of 1:3 and 2:1 can be found in the dissertation by Marteel (2003). The preparation method for the solid rhodium-BINAP complex, $\text{C}_{96}\text{H}_{80}\text{Cl}_2\text{P}_4\text{Rh}_2$, can be found in the supplemental materials of an article by Bunten, *et al.* (2002). The preparation of Wilkinson's catalyst can be found in *The Journal of the American Chemical Society* (Gassman, *et al.*, 1985).

After the reaction was completed, the mesh envelope was opened and the catalyst was removed. The catalysts were analyzed using solid state phosphorus (^{31}P) NMR, liquid state phosphorus (^{31}P) NMR, liquid state proton (^1H) NMR, and IR spectroscopy, all of which occurred with the assistance and supervision of Dr. Yong-Wah Kim from the

Department of Chemistry at The University of Toledo. Working with the constraint of having very small amounts of catalyst, some of the catalysts were not able to be analyzed after the reaction. All obtained spectroscopy outputs can be found in Appendix A.

Chapter 4

Results and Discussion

4.1 Experiments Conducted

Table 4-1 shows the experiments that were conducted over the course of my research. The components used include the following compounds: $[\text{RhCl}(\text{C}_6\text{H}_5)_3]_2$, triphenylphosphine (TPP), and (R)-(+)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl (BINAP). The atomic ratio of rhodium to phosphorus is noted, as it was varied for experiments to determine its effects on selectivity.

The catalysts were placed in the reactor for a 24 hour period prior to injecting styrene and n-heptane into the reactor. The purpose of this pretreatment period was to allow the catalyst time to undergo an *in situ* reaction in which the two components of the catalyst would react to make a homogeneous soluble catalyst; although several experiments noted in Table 4-1 show that only one catalyst component was used, the *in situ* preparation period was used in all experiments to maintain uniformity throughout the experiments. Additionally, for the pretreatments in which the pressure was 650 psig, only carbon monoxide and hydrogen were present in the reactor; whereas, for the pretreatments in which the pressure was 2000 psig, carbon dioxide was present in the reactor in addition to carbon monoxide and hydrogen. When the reactions were performed, carbon monoxide, hydrogen, and carbon dioxide were present in the reactor.

Table 4-1. Reaction specifications.

Rxn. Code	Components	Rh:P Ratio	Pretreatment Conditions		Reaction Conditions	
			Temp. (°C)	Pressure (psig)	Temp. (°C)	Pressure (psig)
1F	[RhCl(C ₈ H ₁₂)] ₂ & TPP	1:8	90	650	90	2500
2G	[RhCl(C ₈ H ₁₂)] ₂ & BINAP	1:4	90	650	90	2500
3H	[RhCl(C ₈ H ₁₂)] ₂	N/A	90	650	90	2500
4J	Wilkinson's Catalyst	1:3	90	650	90	2500
5K	Solid Catalyst – TPP	1:3	90	650	90	2500
6L	[RhCl(C ₈ H ₁₂)] ₂ & TPP	1:34	50	2000	75	3000
7M	[RhCl(C ₈ H ₁₂)] ₂ & TPP	1:8	50	2000	90	2500
8N	[RhCl(C ₈ H ₁₂)] ₂ & TPP	1:34	50	2000	90	2500
9P	[RhCl(C ₈ H ₁₂)] ₂ & TPP	1:8	50	2000	75	3000
10Q	[RhCl(C ₈ H ₁₂)] ₂ & TPP	1:8	90	2000	90	2500
11R	[RhCl(C ₈ H ₁₂)] ₂ & TPP	1:2	90	650	90	2500
12S	[RhCl(C ₈ H ₁₂)] ₂ & BINAP	1:4	90	650	90	2500
13T	C ₉₆ H ₈₀ Cl ₂ P ₄ Rh ₂ (BINAP)	1:2	90	650	90	2500
14U	[RhCl(C ₈ H ₁₂)] ₂ & TPP	1:8	90	2000	75	3000

Throughout the course of the reactions, the yields of styrene and products were monitored. Figure 4-1 shows the decrease in styrene and the formation of two enantiomeric products with time.

Figure 4-1. General Reaction Profile. The experiment shown in the graph above is experiment 8N.

The yield was calculated using the calibration obtained from direct injection of standards into the GC. The styrene yield is the amount of reactant remaining in the reactor relative to the initial amount of styrene injected into the reactor. The yields obtained through the calibrations did not provide a justified mass balance, most likely due to the method used for sample calibration. The calibrations were obtained by mixing known quantities in a vial and running these known samples through the GC/MS. Unlike the reaction samples, the known samples were not sampled through the reactor. Since the known samples did not go through the sampling procedure, the error is believed to be associated with differences in the way n-heptane, styrene, and products were removed from the reactor and dissolved into the ethyl acetate solvent.

In order to provide consistent data for comparison purpose, a normalized yield was used for the data analysis. The normalized yield was calculated using the following equation:

$$y_{n,i} = \frac{y_i}{y_s + y_{p1} + y_{p2}}, \quad (4.1)$$

where $y_{n,i}$ is the normalized yield of component i , y_i is the yield of component i , and y_s is the yield of styrene, and y_{p1} and y_{p2} are the yields of the 2-phenylpropionaldehyde enantiomers.. The data shown in Figure 4-1 is reproduced in terms of the normalized yield in Figure 4-2, which demonstrates that the normalization process was simply a scaling factor.

Figure 4-2. General Reaction Profile, Normalized. The experiment shown in the graph above is experiment 8N.

For the purposes of easily displaying data, the graphs displaying product peak data show the first product peak and do not show the second product peak. Since the reactions did not show large enantioselectivity towards either product, the first product peak was arbitrarily chosen to simplify comparisons among reactions.

Replicate experiments (2G and 12S) were performed to examine the reproducibility of the experiments. The experiments were conducted with the following conditions:

Rh:P ratio of 1:4, pretreatment conditions of 90 °C and 650 psig, and reaction conditions of 90 °C and 2500 psig. Figures 4-3 and 4-4 show the reproducibility of the experiments for both reactant conversion and product formation.

Figure 4-3. Loss of Styrene – Reproducibility. The yield profiles of styrene appear to be very similar, indicating that the reaction is repeatable.

Figure 4-4. Yield of Products – Reproducibility. The yield profiles of the first product peak appear to be very similar, again indicating that the reaction is repeatable.

By confirming that this reaction is reproducible, we demonstrate validity of the results obtained from each individual experiment.

4.2 NMR & IR Spectroscopy and Catalyst Evaluation

Since *in situ* preparation of catalysts in supercritical fluids is a developing technology, there was a concern that the pretreatment conditions used in the reactions would not synthesize the catalysts. Therefore, NMR and IR spectroscopy were used to analyze the catalysts remaining in the envelopes after the reactions were completed; all NMR and IR evaluations were conducted in the analytical laboratories of the Department of Chemistry at The University of Toledo. Solid state phosphorus (^{31}P) NMR, liquid state phosphorus (^{31}P) NMR, liquid state proton (^1H) NMR, and IR were used to examine the catalysts. Two rhodium hydride peaks should be present on the (^{31}P) NMR data and one carbonyl peak should be present on the IR data if an active catalyst was formed and catalysts remaining in the pouch.

4.2.1 NMR and (R)-BINAP Catalysts

Figure 4-5 and Figure 4-6 show the NMR spectra of pure (R)-BINAP and the catalyst remaining in the envelope after reaction 2G, in which $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$ and (R)-BINAP were used to make a catalyst *in situ*. The catalysts prepared from (R)-BINAP do not show either a rhodium hydride or a carbonyl peak; the ^{31}P NMR spectrum of pure (R)-BINAP shows peaks at the same locations as the catalyst that was attempted to be made *in situ*. This suggests that the catalyst from experiment 2G does not vary from the (R)-BINAP, and that no rhodium-phosphine catalyst was formed during the *in situ*

preparation. However, since the analytical methods were conducted on the catalyst remaining in the pouch, we cannot conclude that catalyst was not made *in situ* because the reaction profiles discussed later in this chapter indicate that a catalyst was present. Bunten, *et al.* (2002) reported that a J_{RhP} equal to 163 Hz and doublets at 46 ppm were found for the Rhodium-BINAP complex that should have been formed in experiments 2G and 12S. The J_{RhP} shown in Figure 4-5 is 146 Hz with the doublet occurring near -12.8 ppm; these would indicate that the Rhodium-BINAP complex was not formed inside the reactor. A possible explanation for this is that the catalyst was solubilized during either pretreatment or reaction and was transported outside of the catalyst envelope; this explanation is supported by the fact that no catalyst visibly remained in the catalyst envelope at the end of experiment 13T, which used a solid catalyst made with BINAP.

Figure 4-5. Solid State ^{31}P MAS NMR spectrum of (R)-BINAP. Peaks are shown at -11.9 and -13.7 ppm.

Figure 4-6. Solid State ^{31}P MAS NMR spectrum of remaining catalyst residues from experiment 2G. Peaks are shown at -11.8 and -13.6 ppm.

4.2.2 NMR and Triphenylphosphine Catalysts

Figure 4-7 and Figure 4-8 show the NMR spectra of pure triphenylphosphine and the catalyst remaining in the envelope after reaction 1F, in which $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$ and TPP were used to make a catalyst *in situ*. With the peaks of TPP and the catalyst formed *in situ* being at different locations, it is believed that catalyst was formed from triphenylphosphine and $[\text{RhCl}(\text{cod})]_2$ during the *in situ* pretreatment conditions. However, for the catalysts in which a Rh:P ratio of 1:34 was used, no catalyst remained in the envelopes to analyze. With triphenylphosphine's melting point of 79-81 °C at atmospheric pressure, it is believed that the triphenylphosphine melted during the pretreatment and became uniformly dispersed throughout the reaction vessel. Additionally, the J_{RhP} value for the data in Figure 4-7 is 107.4 Hz; this is within the range

reported to have rhodium-phosphorus coupling. Therefore, it can be concluded that the catalysts using TPP for ligands were able to be made during *in situ* pretreatment.

Figure 4-7. Solid State ^{31}P MAS NMR spectrum of pure triphenylphosphine. A peak is shown at -7.1 ppm.

Figure 4-8. Solid State ^{31}P MAS NMR spectrum of remaining catalyst residues from experiment 1F. Peaks are shown at 34.0 and 32.7 ppm.

4.2.3 Infrared Spectroscopy

IR literature reports that a peak between 1978 and 2093 cm^{-1} may indicate rhodium-hydride presence; therefore, peaks found in the following IR graphs within or near that range are believed to be rhodium-hydride peaks. The findings of the NMR showed that the catalysts using TPP as a ligand formed a catalyst; the IR data reflects these findings.

Experiments 10Q and 7M used triphenylphosphine as a ligand and experiment 2G used BINAP as a ligand. Catalyst recovered from experiment 10Q following reaction showed a peak at 1965 cm^{-1} , catalyst recovered from experiment 7M showed a peak at 1965 cm^{-1} , whereas catalyst recovered from experiment 2G showed no peak within or near the given range.

Figure 4-9. IR spectrum of remaining catalyst residues from experiment 10Q. A rhodium-hydride peak is shown at 1965 cm^{-1} .

Figure 4-10. IR spectrum of remaining catalyst residues from experiment 7M. A rhodium-hydride peak is shown at 1965 cm^{-1} .

Figure 4-11. IR spectrum of remaining catalyst residues from experiment 2G. A rhodium-hydride peak is not shown within the expected range.

4.3 Effect of Pretreatment Conditions

Figures 4-12 and 4-13 describe yields over a range of catalyst pretreatment variables. Experiments 1F (90 °C & 650 psig), 7M (50 °C & 2000 psig), and 10Q (90 °C & 2000 psig) were conducted using $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$ and TPP, a Rh:P ratio of 1:8, reaction conditions of 90 °C and 2500 psig, and variable *in situ* preparation conditions. These graphs show that the experiment using a higher pretreatment pressure provided a faster rate of reaction when comparing experiments with 90 °C pretreatment temperatures. Additionally, among the reactions with the pretreatments at higher pressures, the reaction with the catalyst prepared at the lower temperature provided a faster rate of reaction. The reactions had similar yields, but the rate of reaction varied. The fastest reaction resulted in a maximum yield of products in less than 5 hours. As the catalyst pretreatment conditions moved away from the critical conditions of CO_2 , a successively poorer catalyst was formed. The presence of CO_2 during pretreatment may have provided a solvent environment in which the catalyst precursors effectively interacted, thereby creating a good catalyst. However, in the absence of CO_2 , the catalyst formation reaction is slow and a poor quality catalyst is produced.

Figure 4-12. Loss of Styrene at Different Pretreatment Conditions. Conditions: $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$ & TPP, Rh:P ratio = 1:8, reaction conditions = 90 °C & 2500 psig; Variable: *in situ* pretreatment conditions.

Figure 4-13. Yield of Products. Conditions: $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$ & TPP, Rh:P ratio = 1:8, reaction conditions = 90 °C & 2500 psig; Variable: *in situ* pretreatment conditions.

By comparing experiments 9P (50 °C) and 14U (90 °C) the effects of pretreatment temperature can be observed. Both reactions used $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$ and TPP, a Rh:P = 1:8, pretreatment pressure of 2000 psig, and reaction conditions of 75 °C and 3000 psig. The reaction in which the catalyst was prepared at the lower *in situ* temperature had a much lower yield than the catalyst prepared at the higher temperature, consistent with the results shown in Figure 4-13. Additionally, the pretreatment temperature for the slower reaction was greater than the reaction temperature; however it is not clear why this influenced the catalyst performance.

Figure 4-14. *In situ* temperature effects. Conditions: $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$ & TPP, Rh:P = 1:8, pretreatment pressure = 2000 psig, reaction conditions = 75 °C & 3000 psig; Variable: *in situ* temperature.

4.4 Effects of Temperature and Pressure during Reaction

Figure 4-15 compares experiments 10Q (90 °C & 2500 psig) and 14U (75 °C & 3000 psig) which use $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$ and TPP, a Rh:P = 1:8, and pretreatment conditions of

90°C and 2000 psig; the variables being examined are the reaction temperature and pressure. The reaction with the lower reaction temperature and higher reaction pressure has a much lower yield than the reaction conducted at the higher temperature, as would be expected.

Figure 4-15. Reaction temperature and pressure effects. Conditions: $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$ & TPP, Rh:P = 1:8, pretreatment conditions of 90 °C & 2000 psig; Variables: reaction temperature and pressure.

The effect of reaction temperature and pressure are again seen in Figures 4-16 and 4-17; experiments 6L (75 °C & 3000 psig) and 8N (90 °C & 2500 psig) use $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$ and TPP, a Rh:P = 1:34, and pretreatment conditions of 50 °C and 2000 psig. The reaction at 90 °C goes to completion and has a much faster rate of reaction than the reaction at the lower temperature. The reaction at 90 °C also shows a product yield near 0.5 in less than 15 hours whereas the reaction at 75 °C shows a product yield less than 0.1 at more than 80 hours. Since styrene is still present in the reaction at 75 °C, it is

unknown what the maximum product yield may be when full conversion of styrene is obtained.

Figure 4-16. Loss of Styrene. Conditions: $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$ and TPP, Rh:P = 1:34, pretreatment conditions of 50 °C & 2000 psig; Variables: reaction temperature and pressure.

Figure 4-17. Yield of Products. Conditions: $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$ and TPP, Rh:P = 1:34, pretreatment conditions of 50 °C & 2000 psig; Variables: reaction temperature and pressure.

Figures 4-18 and 4-19 compare the effect of reaction temperature and pressure on the yield of styrene and products; experiments 7M (90 °C & 2500 psig) and 9P (75 °C & 3000 psig) use $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$ and TPP, a Rh:P=1:8, and pretreatment conditions of 50°C and 2000 psig. The reaction at 90 °C goes to completion much faster than the reaction at the lower temperature. The reaction at 90 °C obtained a yield near 0.5 in less than 10 hours, whereas the reaction at the lower temperature required more time to obtain a similar yield.

Figure 4-18. Loss of Styrene. Conditions: $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$ & TPP, Rh:P=1:8, pretreatment conditions of 50 °C & 2000 psig; Variables: reaction temperature and pressure.

Figure 4-19. Yield of Product Peak 1. The reaction at 90 °C obtained a yield near 0.5 in less than 10 hours, whereas the reaction at the lower temperature required more time to obtain a similar yield.

4.5 Effects of Rhodium to Phosphorus Ratios

The presence of phosphines during hydroformylation reactions is believed to slow the rate at which products are produced (Bensaid, 2002); however, selectivity increases as the amount of phosphorus per rhodium increases. In order to understand these effects during reaction in supercritical CO₂, a series of experiments were performed in which the Rh:P ratio was varied under otherwise identical conditions.

The experiments shown, Experiments 1F (1:8), 11R (1:2), and 3H ([RhCl(C₈H₁₂)]₂ only) compare the Rh:P ratios among catalysts using [RhCl(C₈H₁₂)]₂ and TPP, *in situ* preparation conditions of 90 °C and 650 psig, and reaction conditions of 90 °C and 2500 psig. The reaction with the greatest phosphorus loading had the slowest reaction rate. Additionally, in the experiment using only [RhCl(C₈H₁₂)]₂, a time lag is observed before

the aldehyde product is initially observed, indicating the importance of the phosphorus ligand in the performance of the catalyst.

Figure 4-20. Yield of Styrene – TPP as a ligand. Conditions: [RhCl(C₈H₁₂)₂]₂ & TPP, *in situ* pretreatment = 90 °C & 650 psig, reaction conditions = 90 °C & 2500 psig; Variable: Rh:P ratio.

Figure 4-21. Yield of Product Peak 1 – TPP as a ligand. Conditions: [RhCl(C₈H₁₂)₂]₂ & TPP, *in situ* pretreatment = 90 °C & 650 psig, reaction conditions = 90 °C & 2500 psig; Variable: Rh:P ratio.

Additional comparisons using experiments 6L (1:34) and 9P (1:8) further illustrate the effects of Rh:P ratio variances. These experiments used $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$ and TPP, *in situ* preparation conditions of 50 °C and 2000 psig, and reaction conditions of 75 °C and 3000 psig. The results are shown in Figure 4-22 for conversion of styrene, and Figure 4-23 for the yield of product 1. The catalyst in which Rh:P=1:8 provided the faster rate of reaction; this reaction provided nearly complete conversion at 50 hours whereas the experiment in which Rh:P=1:34, was not near complete conversion, even after 80 hours.

Figure 4-22. Loss of Styrene – Rh:P ratio variances using TPP. Conditions: $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$ & TPP, *in situ* pretreatment = 50 °C & 2000 psig, reaction conditions = 75 °C & 3000 psig; Variable: Rh:P ratio.

Figure 4-23. Yield of Product Peak 1 – Rh:P ratio variances using TPP. Conditions: $[\text{RhCl}(\text{C}_8\text{H}_{12})_2]$ & TPP, *in situ* pretreatment = 50 °C & 2000 psig, reaction conditions = 75 °C & 3000 psig; Variable: Rh:P ratio.

Experiments 7M (1:8) and 8N (1:34) used $[\text{RhCl}(\text{C}_8\text{H}_{12})_2]$ and TPP, *in situ* preparation conditions of 50 °C and 2000 psig, and reaction conditions of 90 °C and 2500 psig, as shown in Figures 4-24 and 4-25. As seen, with these pretreatment conditions and at this range of Rh:P ratio, the additional phosphorus had no effect on either the conversion or product yield. Although it is not clear why this should occur, it is possible that the formation of catalyst during the 24-hour pretreatment period at 90 °C and without added solvent was rate-limiting, and thus, the additional phosphorus ligands were not incorporated into the active catalyst. These experiments appear to provide similar yields of both styrene and products.

Figure 4-24. Loss of Styrene – Rh:P ratio variances using TPP. Conditions: $[\text{RhCl}(\text{C}_8\text{H}_{12})_2]_2$ & TPP, *in situ* pretreatment = 50 °C & 2000 psig, reaction conditions = 90 °C & 2500 psig; Variable: Rh:P ratio.

Figure 4-25. Yield of Products – Rh:P ratio variances using TPP. Conditions: $[\text{RhCl}(\text{C}_8\text{H}_{12})_2]_2$ & TPP, *in situ* pretreatment = 50 °C & 2000 psig, reaction conditions = 90 °C & 2500 psig; Variable: Rh:P ratio.

4.6 Comparing Catalysts

Figures 4-26 and 4-27 compare experiments 1F (TPP), 2G (BINAP), and 3H (No Phosphorus), in order to evaluate the effects of ligand on catalyst performance. The reactions were conducted with pretreatment conditions of 90 °C and 650 psig, reaction conditions of 90 °C and 2500 psig, and Rh:P ratios of 1:8, 1:4, and 1:0, respectively. Despite the difference in Rh:P ratios, the reactions using the phosphine ligands have very similar reaction profiles.

Figure 4-26. Loss of Styrene – Comparison of Ligands. Conditions: $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$, pretreatment conditions = 90 °C & 650 psig, reaction conditions = 90 °C & 2500 psig; Variables: ligands & Rh:P ratios.

Figure 4-27. Product Yield – Comparison of Ligands. Conditions: $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$, pretreatment conditions = 90 °C & 650 psig, reaction conditions = 90 °C & 2500 psig; Variables: ligands & Rh:P ratios.

Figure 4-28 and Figure 4-29 compare the yields obtained from catalysts with the lowest atomic ratios, pretreatment conditions of 90 °C and 650 psig, and reaction conditions of 90 °C and 2500 psig; these graphs show results from experiments 4J (Wilkinson's catalyst produced in the laboratory), 5K (Wilkinson's catalyst immobilized on a silica support), and 11R ($[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$ & TPP). Wilkinson's catalysts and the immobilized catalyst have Rh:P ratios of 1:3; the experiment in which the catalyst was made *in situ* has a Rh:P ratio of 1:2. The catalyst made *in situ* performed somewhat better than the two catalysts produced in the laboratory, both of which performed similarly. The product yield data shows a similar trend.

Figure 4-28. Loss of Styrene – TPP as a ligand. Conditions: pretreatment = 90 °C & 650 psig, reaction conditions = 90 °C & 2500 psig; Variables: catalyst and Rh:P ratio.

Figure 4-29. Yield of Products – TPP as a ligand. Conditions: pretreatment = 90 °C & 650 psig, reaction conditions = 90 °C & 2500 psig; Variables: catalyst and Rh:P ratio.

Figures 4-30 and 4-31 compare experiments in which BINAP was used as a ligand; 2G and 12S (both *in situ* preparation), 3H ([RhCl(C₈H₁₂)]₂ only), and 13T (Rh-BINAP produced in the laboratory). All reactions have *in situ* conditions of 90 °C and 650 psig and reaction conditions of 90 °C and 2500 psig. The catalysts in which phosphorus ligands were used appear to have similar reaction profiles and the reaction in which no ligand was used had the largest rate of reaction; as previously discussed, the presence of phosphorus slows the reaction rate, but may enhance enantioselectivity. These graphs show that the laboratory-prepared catalyst performed similarly to the ones that are prepared *in situ*, indicating that the catalysts were made inside the reactor, despite the NMR spectroscopy findings.

Figure 4-30. Loss of Styrene – BINAP as a ligand. Conditions: pretreatment = 90 °C & 650 psig, reaction conditions = 90 °C & 2500 psig; Variable: catalyst.

Figure 4-31. Yield of Products – BINAP as a ligand. Conditions: pretreatment = 90 °C & 650 psig, reaction conditions = 90 °C & 2500 psig; Variable: catalyst.

4.7 Selectivity of Products

Since the products of the hydroformylation reaction are enantiomers, the ratio of the areas of the enantiomer peaks can be used to determine if the reaction is selective towards either the R or the S configuration of the product. The use of a chiral ligand with an R configuration should yield an enantiomeric excess of products with R configuration.

Figure 4-32 compares experiments 1F (TPP), 2G (BINAP), and 3H (No Phosphorus), in order to evaluate the effects of ligand on selectivity. The reactions were conducted with pretreatment conditions of 90 °C and 650 psig, reaction conditions of 90 °C and 2500 psig, and Rh:P ratios of 1:8, 1:4, and 1:0, respectively. The reaction in which (R)-BINAP was used as the ligand provided some enantiomeric selectivity with an enantiomeric excess (defined as the yield of the second peak product minus the yield of the first peak product) of 10 – 15% at short times.

Figure 4-32. Selectivity. Conditions: $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$, pretreatment conditions = 90 °C & 650 psig, reaction conditions = 90 °C & 2500 psig; Variables: ligands & Rh:P ratios.

Figure 4-33 shows the ratio of the peaks among reactions using laboratory-produced catalysts. These experiments had pretreatment conditions of 90 °C and 650 psig and reaction conditions at 90 °C and 2500 psig. The reactions being compared are 3H ($[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$ only), 4J (Wilkinson's Catalyst), 5K (Immobilized Wilkinson's catalyst), and 13T (Laboratory-produced Rh-BINAP). Except for the experiments at short reaction times, for which very low conversions were observed, the Rh-BINAP catalyst shows a tendency to favor the formation of the second product, suggesting possible enantioselectivity from this catalyst.

Figure 4-33. Selectivity Comparison – Solid Catalysts. Conditions: pretreatment = 90 °C & 650 psig, reaction conditions = 90 °C & 2500 psig; Variable: catalyst.

Figure 4-34 compiles the data into two groups: (1) those using BINAP as a ligand and (2) those using TPP as a ligand. Again, except for experiments at short reaction times (and thus very low conversion), the catalysts produced with BINAP ligand have a tendency to favor the second product.

Figure 4-34. Selectivity of Ligands. The data has been grouped based on the ligand being used.

Chapter Five

Conclusions and Recommendations

5.1 Conclusions

Nuclear magnetic resonance and infrared spectroscopy were used to evaluate the catalysts and catalyst precursors on a structural level. Comparison of current results with known data from published works demonstrate that catalysts were made *in situ* using $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$ and triphenylphosphine. The formation of reaction products and the variation in catalyst performance brought on by varying catalyst preparation conditions further confirms that active catalyst was prepared through the *in situ* reaction.

However, no residual catalyst was detected in the basket from experiments using $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$ and (R)-BINAP as catalyst precursors. On the other hand, experiments with $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$ and (R)-BINAP showed that a catalyst was likely produced in the reactor, despite the inability of NMR and IR to confirm this conclusion. Since the NMR and IR spectroscopy was only able to analyze the catalyst remaining in the envelope, it can be concluded that the catalyst made *in situ* did not remain in the catalyst pouch after the reaction; instead, it was likely solubilized and disbursed throughout the supercritical fluid in the reactor. This conclusion is supported by the fact that the solid rhodium-BINAP complex produced by the Department of Chemistry was also not present in the catalyst envelope after the reaction.

The most active catalyst was formed by pretreatment at 50 °C and 2000 psig pressure. Reaction conditions of 90 °C and 2500 psig, with a Rh:P=1:8, were found to be active for the hydroformylation reaction. Higher loadings of phosphorus led to slower reaction, as expected from literature data. Similarly, increasing reaction temperature gave better activity. The effect of reaction pressure could not be independently discerned from these experiments, since pressure and temperature were always varied simultaneously. The catalysts prepared *in situ* performed comparably to those prepared in the laboratory, and to catalysts that were immobilized on solid supports.

Based on previous work on asymmetric hydroformylation, the reactions in which BINAP ligands were used should have provided enantioselective products, while the reactions using triphenylphosphine ligands should not have produced enantioselectivity. Despite the appearance of mild enantioselectivity in most reactions, the reactions using BINAP were similar to those found in the literature. Hegedus, *et al.* (2004) reported enantiomeric excess of 13% for conditions most similar to those used in the current work; this is compatible to the 10-15% enantiomeric excess observed in the current work. Hegedus, *et al.* (2004) noted high enantioselectivity at fairly low reaction temperature, much lower than that used in the current work, and decreasing enantioselectivity as the temperature increased. Thus, it is concluded that the mild enantioselectivity observed herein is consistent with previous asymmetric hydroformylation results.

5.2 Recommendations

To determine if the rhodium-BINAP catalyst was made *in situ*, the *in situ* conditions should be used to produce the catalyst and the experiment terminated prior to injecting

the vessel with reactants. Since the reaction vessel would be free from reactants and products, the catalyst should be recoverable from the pouch and/or the walls of the reaction vessel. In doing so, the catalysts that have undergone pretreatment can be examined using IR and NMR to determine if catalysts were made *in situ*. Additionally, the IR and NMR spectroscopy of the catalysts using rhodium and TPP prior to reaction should be similar to those of rhodium-TPP catalysts after a reaction.

Because the temperature of the current experiments was higher than that which should yield high enantioselectivity, additional experiments should be performed at lower temperatures to determine if greater enantioselectivity can be achieved. Based on the current results from experiments with both TPP and BINAP ligands, it is expected that greater enantioselectivity would be demonstrated if catalyst were prepared *in situ* from $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$ and BINAP at 50 °C and 2000 psig, followed by reaction at 75 °C and 2500 psig. Further experimentation should focus on obtaining optimal parameters for providing the desired selectivity.

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Appendix A
IR & NMR Spectra

THE UNIVERSITY OF TOLEDO CMC200

CON: TPP 040605

NUC: ³¹P
NA: 10000
FOS: 80.75376
TLR: 0.000
SK: 247.57 PPM
AL: 1024
DL: 6192

Figure A-1. Solid State ³¹P NMR: Triphenylphosphine.

THE UNIVERSITY OF TOLEDO CMC200

CON: BINAP 040805
NUC: ³¹P
NA: 10000
FOS: 80.753376
TLR: 0.000
SK: 247.67 PPM
AL: 1024
OL: 6192

Figure A-2. Solid State ³¹P NMR: BINAP.

THE UNIVERSITY OF TOLEDO CMC200

CONC: F 032905

NJC: 31P

NA: 10000

FOBS: 80.753376

TLB: 0.000

SW: 247.67 PPM

AL: 512

DL: 8192

Figure A-3. Solid State ^{31}P NMR: Experiment 1F.

THE UNIVERSITY OF TOLEDO CMC200

CON: TRI-PHENYLPHOSPHINE REFERENCE TO -7.20PPM

NUC: ^{31}P
NA: 10000
PSS: 80.753376
TLR: 0.000
SM: 247.67 PPM
AL: 1024
DL: 8192

Figure A-4. Solid State ^{31}P NMR: Experiment 2G.

THE UNIVERSITY OF TOLEDO CMC200

CON: J032905

NUC: ^{31}P
NA: 10000
F0BS: 80.753376
TLB: 14.921
SW: 247.67 PPM
AL: 512
DL: 8192

Figure A-5. Solid State ^{31}P NMR: Experiment 4J.

Figure A-6. Solid State ^{31}P NMR: Experiment 5K.

THE UNIVERSITY OF TOLEDO CMC200

CON: TRI-PHENYLPHOSPHINE REFERENCE TO -7.20PPM

NUC: ^{31}P
NA: 10000
FORS: 80.753376
TLR: 0.000
SN: 247.67 PPM
AL: 512
DL: 8192

Figure A-7. Solid State ^{31}P NMR: Experiment 7M.

THE UNIVERSITY OF TOLEDO CMC200

CON: H-0R-K-032405 NO2 24HC

NUC: 31P
NA: 10000
F0BS: 80.753376
TLR: 0.000
SK: 247.67 PPM
AL: 512
DL: 8192

Figure A-8. Solid State ^{31}P NMR: Experiment 8N.

Figure A-9. Solid State ^{31}P NMR: Experiment 9P.

THE UNIVERSITY OF TOLEDO CMC200

CON: Q 032505

NUC: 31P
 NA: 10000
 F0BS: 80.753376
 TLR: 0.000
 SW: 247.67 PPM
 AL: 512
 DL: 8192

Figure A-10. Solid State ^{31}P NMR: Experiment 10Q.

THE UNIVERSITY OF TOLEDO CMC200

CON: S 040405
NUC: ^{31}P
NA: 10000
FOS: 80.753376
TLR: 0.000
SW: 247.67 PPM
AL: 1024
DL: 8192

Figure A-11. Solid State ^{31}P NMR: Experiment 11S.

Figure A-12. Liquid State ^{31}P NMR: BINAP Ligand.

Figure A-13. Liquid State ^{31}P NMR: Solid BINAP-Catalyst prior to being used in Experiment 13T.

Figure A-14. Liquid State ^{31}P NMR: Experiment 1F.

Figure A-15. Liquid State ³¹P NMR: Experiment 2G.

Figure A-16. Liquid State Proton NMR: Experiment 10Q.

Figure A-17. Liquid State Proton NMR: Experiment 1F.

Figure A-18. Liquid State Proton NMR: Experiment 2G.

Figure A-19. Liquid State Proton NMR: Experiment 2G, redefined axis for clarification.

Figure A-20. IR: Experiment 10Q.

Figure A-21. IR: Experiment 2G.

Figure A-22. IR: Experiment 7M.

Appendix B

Data

1F - [RhCl(C₈H₁₂)]₂ & TPP; Rh:P=1:8; Pre: 90°C & 650 psig; Rxn.: 90°C & 2500 psig

Raw Data					
time	Sample	Heptane	Styrene	1st Peak	2cd Peak
0.25	1	12842796	40197623	1390048	1393908
0.5	2	11767877	30311621	1252636	1214025
0.75	3	14890612	42712811	1995703	2188330
1	4	13559526	36234916	1845725	1878754
1.25	5	10354202	28768106	1665677	1720337
1.5	6	11609560	32656725	1924345	2105652
2	7	13831594	31860925	2210485	2234551
3	8	12717056	30514634	2865593	3019159
4	9	11713407	24877731	2691819	2830049
5	10	12882602	28526920	3753103	4077237
6	11	12141565	24016218	3812598	4124148
9	12	12014816	23907922	5504511	5690388
15	13	12652555	18661099	8158559	8369497
21	14	10858455	11072049	9336901	9782327
27	15	14879975	9168435	15398717	16271526

Yield, Normalized		
Styrene	1st Peak	2cd Peak
0.944288	0.025295	0.030416
0.935481	0.02986	0.034658
0.918511	0.035915	0.045574
0.915045	0.039248	0.045707
0.901185	0.045922	0.052894
0.896057	0.046789	0.057153
0.884823	0.054173	0.061003
0.841095	0.074575	0.08433
0.82063	0.084364	0.095006
0.783367	0.101075	0.115558
0.748545	0.117927	0.133528
0.672599	0.159013	0.168388
0.514352	0.238261	0.247386
0.345793	0.318607	0.3356
0.201829	0.38771	0.410461

Moles Styrene = 0.016863
Moles Heptane = 0.0076914

Wt. of [RhCl(C₈H₁₂)]₂ (g) 0.0110
Wt. of Ligand (g) 0.0937

2G - [RhCl(C₈H₁₂)₂]2 & BINAP; Rh:P=1:4; Pre: 90°C & 650 psig; Rxn.: 90°C & 2500 psig

Raw Data						Yield, Normalized		
time	Sample	Heptane	Styrene	1st Peak	2cd Peak	Styrene	1st Peak	2cd Peak
0.25	1	2265599	29515845	220543	270253	0.986238877	0.005372616	0.008388507
0.5	2	4265374	50427782	1035897	1197748	0.95867873	0.01845405	0.02286722
0.75	3	3554847	55795136	1836716	2239286	0.930477186	0.030921102	0.038601712
1	4	3806546	45036363	1860759	2249955	0.914723443	0.038056941	0.047219616
1.25	5	4624644	58577519	3105909	3776649	0.891713732	0.04848294	0.059803328
1.5	6	4932428	59514113	3410478	4344630	0.881123865	0.051861517	0.067014618
2	7	4769678	57007251	3950968	4868471	0.861377625	0.061801093	0.076821283
3	8	3577141	36923370	3074094	3682136	0.83990704	0.072547081	0.087545879
4	9	5060732	48743297	5343400	6576421	0.796129723	0.091218214	0.112652062
5	10	4552256	40015204	5169203	5935782	0.774561862	0.104864331	0.120573807
6	11	3186980	28630796	4041039	4931281	0.752227718	0.111585505	0.136186777
9	12	5010594	37782831	8664154	10137205	0.655336385	0.159202852	0.185460763
15	13	3727460	16575682	8020422	8751537	0.481322294	0.248935488	0.269742218
21	14	3537381	9980066	10789068	11303232	0.295641001	0.345680953	0.358678046
27	15	3048494	3232103	11471441	11848727	0.110483517	0.439962423	0.44955406
33	16	2824092	839011	10224302	10428816	0.030183454	0.482691191	0.487125354
39	17	2839377	281633	11168682	11494664	0.00500591	0.493078613	0.501915477
45	18	3433185	97573	11830754	12169120	0	0.495546668	0.504453332
51	19	2593666	0	10044404	10266640	0	0.497269633	0.502730367

Moles Styrene = 0.025235427
Moles Heptane = 0.002357205

Wt. of [RhCl(C₈H₁₂)₂]₂ (g) 0.0114
Wt. of Ligand (g) 0.1138

3H - [RhCl(C₈H₁₂)]₂ & no ligand; Pre: 90°C & 650 psig; Rxn.: 90°C & 2500 psig

Raw Data					
time	Sample	Heptane	Styrene	1st Peak	2cd Peak
0.25	1	7804057	61907168	1795783	1787800
0.5	2	6885560	53770727	1076931	1159737
0.75	3	6274314	45793222	1612632	1660294
1	4	6385493	43466595	2460211	2543908
1.25	5	5123277	32087292	2467614	2544769
1.5	6	6229510	34330729	3952434	3972016
2	7	7884077	37931922	7724675	8105179
3	8	4179574	20134180	8779881	9205961
4	9	4896629	6945415	6586655	6924839
5	10	5577353	2782943	8807056	9191064
6	11	4647413	779393	7783710	8300770
9	12	4812539	0	8254622	8502300
15	13	3928352	0	5877048	6226084
21	14	5000706	0	8052647	8445571
27	15	4750743	0	7477287	7853307
39	16	4554790	0	6859354	7130674
45	17	4327468	0	6918166	6962519

Yield, Normalized		
Styrene	1st Peak	2cd Peak
0.94721	0.025596	0.027193
0.963216	0.016637	0.020146
0.934784	0.031193	0.034023
0.895987	0.050305	0.053708
0.862369	0.067	0.070631
0.807202	0.09558	0.097218
0.695232	0.148509	0.156259
0.51279	0.238689	0.248521
0.320818	0.331467	0.347715
0.115706	0.433655	0.450639
0.029672	0.470712	0.499615
0	0.493925	0.506075
0	0.486453	0.513547
0	0.4892	0.5108
0	0.488777	0.511223
0	0.49124	0.50876
0	0.499584	0.500416

Moles Styrene = 0.02414855
Moles Heptane = 0.00387212

Wt. of [RhCl(C₈H₁₂)]₂ (g) 0.0134
Wt. of Ligand (g) 0

4J - Wilkinson's Catalyst; Rh:P=1:3; Pre: 90°C & 650 psig; Rxn.: 90°C & 2500 psig

Raw Data						Yield, Normalized		
time	Sample	Heptane	Styrene	1st Peak	2cd Peak	Styrene	1st Peak	2cd Peak
0.25	1	4043804	34138735	2070406	2245080	0.885465	0.054348	0.060187
0.5	2	5184881	42011516	1398533	1524511	0.936032	0.029696	0.034272
0.75	3	6108651	46980734	1846813	1907902	0.926676	0.035222	0.038102
1	4	5955761	42479710	2182202	2308911	0.903918	0.045833	0.050249
1.25	5	6193015	42570039	3022979	3090689	0.872085	0.062572	0.065344
1.5	6	5980398	43607984	3990774	4137389	0.83835	0.078909	0.082741
2	7	5650286	35808153	4707146	5114594	0.77748	0.106275	0.116245
3	8	6484937	29699504	7232773	7587004	0.65532	0.168175	0.176505
4	9	6272968	22324272	9952817	10487797	0.506441	0.240842	0.252717
5	10	5644455	12869993	11043831	11568675	0.345739	0.320585	0.333676
6	11	7386133	10102324	16830108	17544477	0.21122	0.387715	0.401065
9	12	5075729	1528008	12993437	13475310	0.042587	0.472048	0.485365
15	13	5347466	0	10860988	11117560	0	0.495888	0.504112
21	14	4466523	0	12399368	12859528	0	0.493172	0.506828
27	15	1705395	0	5169072	5552976	0	0.484469	0.515531
33	16	4623584	0	11892161	12452657	0	0.490631	0.509369
39	17	4741742	0	11327410	11691159	0	0.494132	0.505868
45	18	9933570	0	26011667	26860204	0	0.494168	0.505832

Moles Styrene = 0.02410534

Moles Heptane = 0.00405276

Wt. of Wilkonson's Catalyst (g) 0.026

5K - Solid Catalyst – TPP; Rh:P=1:3; Pre: 90°C & 650 psig; Rxn.: 90°C & 2500 psig

Raw Data					
time	Sample	Heptane	Styrene	1st Peak	2cd Peak
0.25	1	7846047	49659372	2256725	2441677
0.5	2	5279215	34473107	607169	633389
0.75	3	10103794	58668473	1433824	1568825
1	4	7177484	44481967	1517685	1505121
1.25	5	6972499	42802805	1864657	1984536
1.5	6	6515840	32220457	1790664	1863296
2	7	6705050	28887965	2345551	2472227
3	8	7069851	31154391	5559399	5718528
4	9	7591004	20903545	5692471	6034266
5	10	8150817	15945101	7141449	7479496
6	11	7559781	10249946	7439310	7862132
9	12	5907929	1666736	7019780	7419334
15	13	9661403	96778	11992181	12521341
21	14	2764942	0	24014328	24818390
27	15	4081076	301871	5765045	6165029

Yield, Normalized		
Styrene	1st Peak	2cd Peak
0.914409258	0.04000546	0.045585282
0.969937004	0.013422458	0.016640537
0.955679142	0.019676461	0.024644398
0.939057037	0.029491431	0.031451532
0.918805578	0.038189313	0.043005109
0.899393938	0.047967977	0.052638085
0.856149274	0.068670861	0.075179864
0.725484969	0.134839118	0.139675913
0.628783444	0.1793901	0.191826456
0.50567974	0.240833199	0.253487061
0.38203072	0.300013498	0.317955782
0.08126878	0.446741256	0.471989964
0	0.489499361	0.510500639
0	0.495116542	0.504883458
0.005596378	0.481199003	0.513204619

Moles Styrene = 0.024105
Moles Heptane = 0.004053

Wt. of Catalyst (g) 0.0992

6L - [RhCl(C₈H₁₂)₂]₂ & TPP; Rh:P=1:34; Pre: 50°C & 2000 psig; Rxn.: 75°C & 3000 psig

Raw Data						Yield, Normalized		
time	Sample	Heptane	Styrene	1st Peak	2cd Peak	Styrene	1st Peak	2cd Peak
0.25	1	3788814	33827905	0	0	1	0	0
0.5	2	2316110	23893576	0	0	1	0	0
0.75	3	3124945	30400071	0	0	1	0	0
1	4	3310523	30861397	0	0	1	0	0
1.25	5	3350063	31203662	0	0	1	0	0
1.5	6	3983788	40288694	0	0	1	0	0
2	7	287312	2043979	0	0	1	0	0
3	8	3370196	28970678	0	0	1	0	0
4	9	3044738	26603581	186553	165472	0.99156091	0.003658867	0.004780223
5	10	3122801	28003932	301076	298209	0.982913485	0.007684219	0.009402297
6	11	3625912	31800149	506157	447268	0.974226385	0.012958823	0.012814792
9	12	3765647	29024449	554828	594994	0.965260701	0.015669051	0.019070249
15	13	2796856	22306906	688618	714975	0.942381203	0.02737943	0.030239366
21	14	3318124	25654102	1160924	1150958	0.917358669	0.040768824	0.041872506
27	15	2367985	17972378	958678	887947	0.906181636	0.048111841	0.045706523
33	16	2786850	19055386	1170798	1206919	0.887736441	0.054500539	0.057763021
39	17	2564094	18130272	1373996	1466871	0.861456936	0.066351182	0.072191882
45	18	2399137	16033525	1300505	1384518	0.853215416	0.070418839	0.076365745
57	19	2477384	16762246	1770502	1795047	0.819247066	0.089345569	0.091407365
69	20	1635047	11241141	1192917	1257829	0.815417516	0.08941761	0.095164875
81	21	1878030	11936121	1256589	1325245	0.816928988	0.088569919	0.094501093

Moles Styrene = 0.024317531
Moles Heptane = 0.003612652

Wt. of [RhCl(C₈H₁₂)₂]₂ (g) 0.0105
Wt. of Ligand (g) 0.3695

7M - [RhCl(C₈H₁₂)]₂ & TPP; Rh:P=1:8; Pre: 50°C & 2000 psig; Rxn.: 90°C & 2500 psig

Raw Data						Yield, Normalized		
time	Sample	Heptane	Styrene	1st Peak	2cd Peak	Styrene	1st Peak	2cd Peak
0.25	1	2854588	22223229	947850	952196	0.921509	0.038393	0.0400977
0.5	2	4817704	30947492	1990712	2157056	0.880322	0.056536	0.0631416
0.75	3	4585559	24732241	2739071	2976529	0.807152	0.091663	0.1011852
1	4	4548180	19534506	3501611	3841779	0.717819	0.133943	0.1482382
1.25	5	5041434	17506601	5121103	5511760	0.60916	0.187999	0.2028411
1.5	6	4897187	13212402	5424671	5787340	0.525664	0.229395	0.2449404
2	7	5486574	6729433	7646248	8114647	0.28034	0.349601	0.3700589
3	8	5442609	1320788	10466236	11250950	0.042484	0.462907	0.4946083
4	9	5045346	399330	9787458	10494657	0.005274	0.481551	0.5131755
5	10	5115583	286251	9758478	10510379	0	0.482942	0.517058
6	11	5038512	240920	10096754	10706422	0	0.486979	0.5130211
9	12	5292298	564579	10734841	11384078	0.011239	0.48151	0.5072515
15	13	5555147	843132	11208549	11898941	0.021277	0.476351	0.5023718
21	14	4524933	388657	9363868	9930432	0.006458	0.483875	0.5096668
27	15	4336106	257898	8249036	8848673	0.000654	0.483639	0.5157067
33	16	5266358	129953	9793093	10368094	0	0.487201	0.5127987
39	17	4599848	79712	9052239	9647239	0	0.485673	0.5143274

Moles Styrene = 0.0247045

Moles Heptane = 0.0038192

Wt. of [RhCl(C₈H₁₂)]₂ (g) 0.0104

Wt. of Ligand (g) 0.0926

8N - [RhCl(C₈H₁₂)₂]₂ & TPP; Rh:P=1:34; Pre: 50°C & 2000 psig; Rxn.: 90°C & 2500 psig

Raw Data					
time	Sample	Heptane	Styrene	1st Peak	2cd Peak
0.25	1	4417753	50702663	0	0
0.5	2	2992259	17290849	1685408	1809592
0.75	3	4659516	21743771	4121760	4389493
1	4	5324892	19500620	5798030	6211497
1.25	5	5054786	14454369	6321532	6825489
1.5	6	5772382	12584875	8436862	9095323
2	7	4767089	6269331	7733355	8341830
3	8	6173788	2947613	11169604	12119247
4	9	4848106	773252	9391540	10135271
5	10	3827076	178576	7292763	7945425
6	11	3858650	89309	7804657	8217657
9	12	4130432	0	7842527	8404674
15	13	3709994	0	8329286	8960904
21	14	3213567	0	5724113	6210943
27	15	3922043	0	8492402	9057355

Yield, Normalized		
Styrene	1st Peak	2nd Peak
1	0	0
0.82761	0.08238	0.090004
0.70905	0.14054	0.150418
0.6057	0.19024	0.204052
0.50804	0.23666	0.255296
0.40057	0.28891	0.310517
0.26261	0.35552	0.381862
0.09607	0.43475	0.469179
0.02371	0.47104	0.50525
0	0.48005	0.519949
0	0.48878	0.511223
0	0.48419	0.515811
0	0.48358	0.516416
0	0.48091	0.519088
0	0.48569	0.514307

Moles Styrene = 0.023859

Moles Heptane = 0.002966

Wt. of [RhCl(C₈H₁₂)₂]₂ (g) 0.0101

Wt. of Ligand (g) 0.3689

9P - [RhCl(C₈H₁₂)₂]2 & TPP; Rh:P=1:8; Pre: 50°C & 2000 psig; Rxn.: 75°C & 3000 psig

Raw Data					
time	Sample	Heptane	Styrene	1st Peak	2cd Peak
0.25	1	406314	13945048	0	0
0.5	2	979804	18798057	0	0
0.75	3	984539	19977715	335343	705208
1	4	628621	14260677	637079	488077
1.25	5	1323138	23314281	1241519	1358587
1.5	6	1084919	17744225	1204582	1186737
2	7	885139	14676668	1453383	1485885
3	8	780434	16079819	2632016	2499375
4	9	853352	14345687	3504391	3539238
5	10	1153546	11128341	3609589	3658183
6	11	989979	12085565	5350087	5834972
9	12	945997	7741637	5983132	5914544
15	13	738100	4163809	6110158	6314934
21	14	502442	2932555	7648117	7760229
27	15	650146	1851914	8367690	8078348
33	16	934100	1334872	7751900	7768384
39	17	923432	639319	7919301	7823276
45	18	1042782	571700	9322482	9149738
51	19	848597	455577	7484214	7475811
57	20	1031207	432152	10976293	11111606
69	21	935057	361819	8246930	8338224
75	22	890719	283889	10809109	11086871
81	23	833817	199754	7849820	7723914
93	24	639703	419822	7213070	7232839

Yield, Normalized		
Styrene	1st Peak	2cd Peak
1	0	0
1	0	0
0.97023	0.007081	0.02269
0.948435	0.029445	0.022119
0.926518	0.033755	0.039728
0.910885	0.043661	0.045454
0.865856	0.063878	0.070265
0.792948	0.102141	0.104911
0.710789	0.137825	0.151386
0.652308	0.165584	0.182108
0.562705	0.199539	0.237756
0.436642	0.271204	0.292154
0.283922	0.33636	0.379718
0.182388	0.387567	0.430045
0.117519	0.429517	0.452964
0.093743	0.432821	0.473437
0.047519	0.458351	0.49413
0.036987	0.464979	0.498035
0.036443	0.460931	0.502627
0.023972	0.463428	0.5126
0.026891	0.462489	0.51062
0.016304	0.463718	0.519979
0.016671	0.474103	0.509226
0.034362	0.460789	0.50485

Moles Styrene = 0.02710386
Moles Heptane = 0.00282525

Wt. of [RhCl(C₈H₁₂)₂]2 (g) 0.0108
Wt. of Ligand (g) 0.0912

10Q - [RhCl(C₈H₁₂)]₂ & TPP; Rh:P=1:8; Pre: 90°C & 2000 psig; Rxn.: 90°C & 2500 psig

Raw Data					
time	Sample	Heptane	Styrene	1st Peak	2cd Peak
0.25	1	6674921	41125891	0	0
0.5	2	5104691	33724554	0	0
0.75	3	7969270	49262407	0	0
1	4	7013585	42261857	1118437	1110170
1.25	5	5035865	28443574	935244	940579
1.5	6	6560946	52955726	2339473	2207670
2	7	5720615	31884417	1614738	1677817
3	8	6990963	32449123	3148156	3145057
4	9	5208272	20191529	3522761	3457869
5	10	4832866	15043679	3971228	3849857
6	11	4608391	9955885	5162533	5306707
9	12	5890138	3151852	10160035	9992940
15	13	4606392	0	8822938	8244811
21	14	5469007	0	10838907	11089091

Yield, Normalized		
Styrene	1st Peak	2cd Peak
1	0	0
1	0	0
1	0	0
1	0	0
0.996473396	0.003526604	0
0.965172076	0.019243274	0.01558465
0.966928527	0.017258068	0.015813405
0.908099249	0.046482442	0.04541831
0.820615765	0.089532549	0.089851686
0.74166811	0.128983592	0.129348298
0.568320738	0.205937893	0.225741369
0.175246769	0.401506468	0.423246763
0	0.500507631	0.499492369
0	0.475148676	0.524851324

Moles Styrene = 0.023909
Moles Heptane = 0.005606

Wt. of [RhCl(C₈H₁₂)]₂ (g) 0.0100
Wt. of Ligand (g) 0.0925

11R - [RhCl(C₈H₁₂)₂]₂ & TPP; Rh:P=1:2; Pre: 90°C & 650 psig; Rxn.: 90°C & 2500 psig

Raw Data					
time	Sample	Heptane	Styrene	1st Peak	2cd Peak
0.25	1	1005775	7905558	0	0
0.5	2	2725074	17921973	4247723	3938643
0.75	3	2222510	11540850	3782006	3726783
1	4	2629067	9883885	6049307	7004257
1.25	5	2363234	5775272	7737359	6432185
1.5	6	2745668	3746932	7955130	7700523
2	7	2147908	1227389	6766556	6421528
3	8	2437024	370976	7960742	7892819
4	9	2101504	0	5764211	6509410
5	10	2316145	0	4958222	6171815
6	11	2010816	0	4823569	5341176
9	12	2046932	0	5306922	5269800

Yield, Normalized		
Styrene	1st Peak	2cd Peak
1	0	0
0.742348	0.129962	0.127691
0.66582	0.162537	0.171643
0.485686	0.226986	0.287328
0.33682	0.35082	0.31236
0.231323	0.375671	0.393005
0.107124	0.440831	0.452045
0.032996	0.466047	0.500958
0	0.447821	0.552179
0	0.42219	0.57781
0	0.45319	0.54681
0	0.482263	0.517737

Moles Styrene = 0.025935
Moles Heptane = 0.004158

Wt. of [RhCl(C₈H₁₂)₂]₂ (g) 0.0107
Wt. of Ligand (g) 0.0223

12S - [RhCl(C₈H₁₂)₂]₂ & BINAP; Rh:P=1:4; Pre: 90°C & 650 psig; Rxn.: 90°C & 2500 psig

Raw Data					
time	Sample	Heptane	Styrene	1st Peak	2cd Peak
0.25	1	4854678	14697285	0	0
0.5	2	6974416	21161853	0	0
0.75	3	10199961	31216609	1736882	2067423
1	4	7883567	22351765	1362986	1482068
1.25	5	7182070	19216233	1313429	1452484
1.5	6	8723846	22919356	1936547	2061646
1.75	7	8324376	20480017	1946709	2333181
2	8	6061737	15329032	1757404	1993818
3	9	7345428	15155850	2016430	2045591
4	10	6784175	14218798	2611313	3258034
5	11	6991427	12039903	3064947	3434911
6	12	7019232	9847589	3133469	3454020
9	13	6648512	7067721	3987340	4525158
15	14	8179096	3445816	6659593	6212242
21	15	6187830	1212548	6641613	6399747
27	16	6864437	673904	7519891	7673017
33	17	5868761	308684	6579754	6683382
39	18	5866153	0	5869626	6353335
45	19	7219192	0	7648457	7447517

Yield, Normalized		
Styrene	1st Peak	2cd Peak
1	0	0
1	0	0
0.994595	0.002356	0.003049
0.996703	0.003297	0
0.990188	0.006494	0.003318
0.967205	0.018243	0.014552
0.946847	0.022793	0.03036
0.917425	0.038132	0.044443
0.924143	0.041325	0.034532
0.826522	0.071924	0.101554
0.777808	0.101778	0.120414
0.738319	0.121556	0.140125
0.575618	0.191092	0.23329
0.299533	0.358824	0.341642
0.129409	0.432777	0.437814
0.073498	0.444228	0.482274
0.047454	0.457822	0.494724
0.019411	0.453336	0.527253
0.019384	0.484477	0.496139

Moles Styrene = 0.01771847
Moles Heptane = 0.00535311

Wt. of [RhCl(C₈H₁₂)₂]₂ (g) 0.0098
Wt. of Ligand (g) 0.1058

13T - C96H80Cl2P4Rh2 (BINAP); Rh:P=1:2; Pre: 90°C & 650 psig; Rxn.: 90°C & 2500 psig

Raw Data						Yield, Normalized		
time	Sample	Heptane	Styrene	1st Peak	2cd Peak	Styrene	1st Peak	2cd Peak
0.25	1	6066938	35278514	0	0	1	0	0
0.5	2	5767107	29671128	0	0	1	0	0
0.75	3	6227815	31112429	0	0	1	0	0
1	4	6365370	33165187	0	0	1	0	0
1.25	5	7367490	37334014	0	0	1	0	0
1.5	6	7176382	36735571	431529	391660	1	0	0
2	7	7177532	34982501	636005	742898	1	0	0
3	8	8207622	41692451	1280829	1206513	1	0	0
4	9	7877832	37590264	1458587	1465304	0.995929	0.004071	0
5	10	5937687	26056482	1689578	1743697	0.957962	0.022095	0.019943
6	11	7522395	30829255	2788282	2587658	0.929983	0.039014	0.031003
9	12	7938498	27803598	3602922	3811404	0.875324	0.059981	0.064695
15	13	6992849	13770908	6995680	6647154	0.591229	0.205382	0.203389
21	14	5721862	5468937	6482792	6566758	0.371043	0.302758	0.326199
27	15	6110539	2104404	6656376	6998221	0.186467	0.382786	0.430747
33	16	5000306	618793	5319334	5919954	0.085288	0.415014	0.499699
40	17	5180493	403332	6820177	7125307	0.050358	0.447467	0.502175
45	18	4723602	0	6672519	6784473	0.013558	0.472119	0.514323
51	19	3786645	0	6094264	5916786	0.012036	0.485047	0.502917
57	20	4281344	0	6258164	5988273	0.013518	0.489195	0.497287
63	21	4209365	0	6258794	6318566	0.012854	0.474159	0.512987

Moles Styrene = 0.02107071
Moles Heptane = 0.00443298

Wt. of catalyst could not be measured; catalyst is air sensitive and complicates quantification.

14U - [RhCl(C₈H₁₂)]₂ & TPP; Rh:P=1:8; Pre: 90°C & 2000 psig; Rxn.: 75°C & 3000 psig

Raw Data						Yield, Normalized		
time	Sample	Heptane	Styrene	1st Peak	2cd Peak	Styrene	1st Peak	2cd Peak
0.25	1	4859176	22260064	0	0	1	0	0
0.5	2	5105566	23057198	0	0	1	0	0
0.75	3	5851802	27506135	0	0	1	0	0
1	4	4620525	21596184	0	0	1	0	0
1.25	5	4535804	21456363	0	0	1	0	0
1.5	6	4242289	20119867	0	0	1	0	0
2	7	4333144	20007712	0	0	1	0	0
3	8	4298710	20313502	0	0	1	0	0
4	9	4447023	20192326	0	0	1	0	0
5	10	4457989	21122882	0	0	1	0	0
6	11	4153121	19730807	0	0	1	0	0
9	12	4433523	19711954	0	0	1	0	0
24	13	3991692	18437953	0	0	1	0	0
41.25	14	4290853	18102311	610817	540052	1	0	0
48	15	3967036	16003522	949030	816145	0.981495	0.015551	0.002955
53	16	4261643	17370204	1065284	945599	0.976185	0.017423	0.006392
59	17	3862849	14633767	942219	784041	0.979981	0.017522	0.002497
72	18	3861851	15437684	846428	874016	0.980834	0.011639	0.007527
79.75	19	3923611	14233707	1022163	1148067	0.95483	0.021409	0.023761

Moles Styrene = 0.02112026
Moles Heptane = 0.00538105

Wt. of [RhCl(C₈H₁₂)]₂ (g) 0.0110
Wt. of Ligand (g) 0.0908