IN PURSUIT OF A TRANS-CHELATING DIPHOSPHINE LIGAND
Jacqueline Dragon; Samuel Flanzman; Johann Frias; Michael Gao; JinOh Jeong; Angela Jin; Meeki Lad; Kevin Lin; Yuzki Oey; Jessica Teipel; Mathini Vaikunthan; Evan Zou

Advisor: Dr. Mary-Ann Pearsall
Assistant: Nicholas Chiappini

ABSTRACT
Organometallic complexes have proven useful as both industrial catalysts and models to expand understanding of metal-ligand bonding in coordination complexes (4). This experiment analyzed the transformation of a molybdenum complex from a cis to trans isomer through the addition of bidentate diphenylphosphine ligands bound by varying hydrocarbon chains via an intermediary reaction with piperidine to replace two adjacent carbonyls. The resulting cis complexes were heated under reflux to produce the trans complexes (11). IR and NMR spectroscopy analyses revealed that diphenylphosphine ligands with at least six carbons and triphenylphosphine produced significant amounts of the trans chelating isomer and those amounts increased with longer carbon chains. However, ligands with four or five carbons only successfully produced the cis isomer and did not convert to the trans isomer even after the isomerization reaction. This novel synthesis presents future applications in science and industry.

INTRODUCTION
Organometallic Complexes
Organometallic chemistry is a vast and complex area of study that leads to tremendous real-world application. Coordination complexes, its foundation, were first scientifically recorded in blue dye and paint in the 17th and 18th century. The chemistry of these substances, however, was not developed until French chemist B.M. Tassert formed \([\text{Co(NH}_3\text{)}_6\text{]Cl}_3\), in which six ammonia molecules were associated with \(\text{Co}^{3+}\) and 3 \(\text{Cl}^-\) anions balanced the charge in an ionic interaction. By the 19th century, more complexes had been discovered and several theories were proposed. In 1893, Swiss chemist Alfred Werner’s coordination theory took the first steps in explaining the bonding seen in these compounds (1).

According to this coordination theory, coordination complexes are compounds formed when a central atom or ion is bound by ligand molecules via a coordinate covalent bond: a specialized interaction in which one member of the bond contributes both of the shared electrons. In these complexes, the ligand generally contributes both electrons, as it, by definition, has an available pair of electrons to share. In this experiment, the complex of interest is molybdenum hexacarbonyl \(\text{Mo(CO)}_6\), an organometallic complex—that is, a compound that contains at least one bond between a metal and the carbon of an organic compound. In the case of \(\text{Mo(CO)}_6\), the central ion, molybdenum, is bound to six carbonyl (CO) groups (Figure 1).
In general, organometallic complexes are prized for their catalytic abilities, unique modes of bonding, and accessible changes in oxidation state. Scientists search for ways to replace existing ligands on these complexes with other ligands and manufacture new compounds with improved efficiency as catalysts; these compounds can then improve energy and electron transfer reactions, which are significant in artificial photosynthesis mimics, molecular wires, and directional charge-transfer processes (2). An example of such a compound is Wilkinson’s catalyst, an organometallic complex that consists of rhodium surrounded by chlorine and three phosphine ligands \([\text{Rh}(\text{PPh}_3)_3\text{Cl}]\). It is able to catalyze the hydrogenation of alkenes to alkanes, which is useful in industries such as petroleum and food (3).

**Chelating Diphosphine Ligands and Catalytic Complexes**

Catalytic organometallic complexes rely on an effective match between the central atom and ligand. Though the central atom can vary greatly, strong catalytic ligands are limited primarily to halides \((\text{X}^-)\), amines \((\text{NR}_3)\), carbynols \((\text{CO})\), and phosphines \((\text{PR}_3)\) (4). Thus, methods for expanding the scope of ligand interactions are often sought. For instance, researchers have been investigating the unique chemistry of diphosphine ligands, compounds that are characterized by the presence of two phosphine groups linked by a backbone, often an organic chain of varying complexity (Figure 2). When used as a ligand in organometallic chemistry, diphosphines often chelate, meaning that they bond to a complex at multiple sites. These ligands are thus bidentate; they have two bonding sites, and in a manner analogous to two incisors biting down, the two bonding sites interact with the original compound (5).

**Figure 1:** The general structure of \(\text{Mo(CO)}_6\) with the coordinate complexes between the Mo atom and the CO ligands.

**Figure 2:** Structure of generic diphosphine ligand connected by a hydrocarbon chain.
Throughout the late 20th century, research of these compounds was driven by their potential as industrial catalysts. In the 1970s, researchers attempted to chelate diphosphines to square-planar transition metal compounds (6). They faced difficulty in attaining the sought-after trans isomer, defined by a 180 degree angle between the two coordination sites, due to the tendencies of the ligands to form oligomers, or multiple connected complexes, and different coordination modes. Instead, they focused on the cis, or 90 degree coordination, due to its application in industry (Figure 3). The focus on the cis isomer set a precedent for future research, and trans-chelating diphosphine organometallic complexes have yet to be fleshed out as a research field, with remarkably few publications on the topic.

![Cis (90°) vs. Trans (180°)](image)

**Figure 3:** Cis vs. trans chelation of bidentate ligand in octahedral complex.

Diphosphine ligands are often associated with transition metal organometallic chemistry, a subgroup that involves a transition metal as the central atom. This lends to a host of unique chemical properties. For example, these complexes can form multiple bonds with an order of 4 (a quadruple bond). Molybdenum is no exception to this property and has been found to form a quadruple Mo-Mo bond (7).

In this experiment, the starting organometallic complex, molybdenum hexacarbonyl, is of interest because after binding to diphosphine ligands, it can form an interactive and consequently catalytic complex. The derived complex could thus further knowledge of the interesting properties of transition metal organometallic chemistry.

**Synthesizing a trans isomer of Molybdenum Hexacarbonyl via Diphosphine Chelation**

The objective of this experiment was to chelate a bidentate diphenylphosphine ligand to molybdenum hexacarbonyl in the trans formation by first synthesizing and then heating the cis isomer. To synthesize the trans isomer, two carbonyl groups must be replaced by the two phosphine groups of the bidentate ligands. However, directly reacting Mo(CO)₆ with the diphosphines would result in at least three different products, due to mono-, di-, and tri-substitutions of carbonyl groups with the desired phosphine groups. Mono- and tri- substitutions
of the ligand leave an unpaired phosphine group, which binds with another adjacent complex and forms a dimer, which is not ideal for this experiment. Thus, a method must be utilized to ensure that only the di-substitution of the ligand occurred.

However, even within Mo(CO)$_4$L$_2$ where L is any ligand, a problem arises: in order to ensure that individual (non-dimer) complexes with diphosphine ligands form, the cis isomeric form must be obtained. Any alternate form, such as the trans, would result in dimerization via the bonding of the bidentate diphosphine to parallel binding sites of different complex molecules (8). Thus, an experimental solution which guaranteed the displacement of strictly two carbonyl groups in a cis configuration was required to eventually reach the trans isomer.

**Activated Precursor Complexes**

This solution was obtained by adopting a method used by previous researchers, in which an activated precursor complex with the cyclic amine piperidine as its preliminary ligand was used prior to the attachment of the actual desired ligand (9) (Figure 4). As a labile, or easily replaceable, ligand, piperidine binds weakly to the central atom of a coordination complex and can thus be easily replaced by the ligand of interest. Using an activator precursor complex is also advantageous because the labile ligand can “lock” the molecule in a desired conformation. In this particular reaction, the nature of the ligand ensured that two piperidine molecules would always attach to the molybdenum hexacarbonyl in the cis formation, because that configuration is more stable. However, once the piperidine was replaced by the linked diphosphines, as long as the trans isomer was thermodynamically favorable, heating the resulting product would allow for the conversion of the cis form to the final, desired trans configuration (10).

![Figure 4: Use of an activated complex to ensure formation of the cis isomer. Mo(CO)$_4$(pip)$_2$ + Ph$_2$P(CH$_2$)$_n$PPh$_2$ → Mo(CO)$_4$(Ph$_2$P(CH$_2$)$_n$PPh$_2$) + 2(pip)](image)

**Variability among Diphosphine Ligands in Hydrocarbon Backbone Length**

The basis of this experiment revolved around creating a trans--chelating molybdenum complex bound to a diphosphine ligand that could potentially find use in industry as a catalyst. In
creating this *trans* compound, the length of the hydrocarbon backbone in the diphosphine ligand was tested to observe: 1) the minimum length of the hydrocarbon chain necessary to form the *trans* isomer; and 2) which hydrocarbon length proved most effective in creating the *trans* isomer.

Several different bis-diphenylphosphine ligands were used, each with 2 phosphine groups that could bind to the organometallic complex and that had varying hydrocarbon lengths ranging from 4 carbons to 12. The ligands of interest were: the control, phosphine (PPh₃); 1,4-bis (diphenylphosphino) butane; 1,5-bis (diphenylphosphino) pentane; 1,6-bis (diphenylphosphino) hexane; 1,8-bis (diphenylphosphino) octane; and 1,12-bis (diphenylphosphino) dodecane (Figure 5).

![Structures of ligands](image)

**Figure 5:** All of the ligands used in this experiment.

**Hypothesis**

As the length of the carbon chain in the diphosphine ligand increased from 1,4-bis(diphenylphosphino)butane to 1,12-bis(diphenylphosphino)dodecane, it was hypothesized that the *trans* isomer would become more favorable because longer hydrocarbon chains allowed for less interference between bulky phenyl rings and strain on the carbon-carbon bonds (Figure 6).
By using the possible structures of ball-and-stick models rather than those of more laborious computational chemistry models, it was hypothesized that the minimum length of hydrocarbon chain needed for the \textit{trans} isomer to be favorable was six carbons. However, past a certain number of carbons, it was hypothesized that the long hydrocarbon chains would result in unintended bonding patterns across molecules, such as dimerization, reducing the favorableness of the \textit{trans} configuration.

\textbf{Procedure Summary}

Different ligands were used, with hydrocarbon backbone length being the independent variable of interest and overall conversion from \textit{cis} to \textit{trans} being the major dependent variable. Initially, independent samples of \(\text{Mo(CO)}_4\text{(pip)}_2\) were prepared by heating molybdenum hexacarbonyl in toluene (methylbenzene) under reflux and allowing piperidine to replace the carbonyls. The resulting \textit{cis}- configuration compounds were then heated in CH\(_2\)Cl\(_2\), each with a different bis-diphenylphosphine ligand. As a result of the favorable entropy state of the product, the complex was chelated by the ligand so that two coordinate bond locations were occupied (Figure 6). Once the chelation was complete, the new complex was heated in toluene at 110\(^\circ\)C and allowed to isomerize into the desired \textit{trans} configuration (11).

\textbf{Quantifying Observations}

In attempting to create the \textit{trans} configuration of the molybdenum-diphosphine complex, infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy were used to detect whether or not the \textit{trans} product was synthesized, and if so, the yield of the reaction.

\begin{equation}
\text{Mo(CO)}_4\text{(pip)}_2 \xrightarrow{\text{Reflux CH}_2\text{Cl}_2} \text{Mo(CO)}_4\text{(Ph}_2\text{P(CH}_2)_n\text{PPh}_2) \end{equation}
Infrared Spectroscopy

When infrared light interacts with covalent bonds, the bonds absorb some of the light and then vibrate with a specific frequency based on the bonds’ atoms and their arrangement in the bond. The frequency depends on the masses of the component atoms and the strength of the bonds between them (a double bond would vibrate with a higher frequency than a single bond would). Infrared spectroscopy can consequently be used to determine the bonds and the structure of a complex, as it gives data on the frequencies of infrared light that were absorbed. Frequency is normally recorded in cm\(^{-1}\), or wavenumbers, to promote ease of use, as opposed to hertz.

In order for infrared light to be absorbed by a vibration, a dipole moment must occur. Therefore, the orientation of the bonds in a complex can affect the absorption spectrum measured, since symmetry (or the lack thereof) in a molecule can affect the dipole moment. Symmetrical vibrations in a molecule can cancel each other out and result in no change in dipole moment and thus no absorption being measured.

The molecular symmetries of the complexes produced in this experiment were taken into account during the analysis of the spectroscopies, as they provided insight into the structures of the isomers produced. For Mo(CO)\(_6\), one peak in % transmittance was expected; for Mo(CO)\(_4\)(pip)\(_2\), three peaks were expected; for cis-Mo(CO)\(_4\)(Ph\(_2\)P(CH\(_2\))\(_n\)PPh\(_2\)), three peaks were expected; and for trans-Mo(CO)\(_4\)(Ph\(_2\)P(CH\(_2\))\(_n\)PPh\(_2\)) one peak was expected (Figure 7).

![Diagram](image)

**Figure 7:** Dipole shifts for *cis* and *trans*.

Due to various dipole shifts as shown in Figure 7’s pictures, the number of IR peaks change. This is explained in the description below each picture.
**Nuclear Magnetic Resonance Spectroscopy**

Designed originally to analyze hydrocarbons and other organic molecules, NMR spectroscopy is a powerful technique designed to analyze compounds using the intrinsic magnetic properties of their component atoms, in this case the phosphorus atoms found in the diphosphine ligands. A superconducting magnet introduces a powerful magnetic field which causes these phosphorus atoms to align with or against the field. Once excited by radio waves, they fall back to their ground energy level and release energy that the NMR spectrometer can detect and measure; it can also utilize a reference molecule with a very different frequency such as deuterium oxide or d$_1$-chloroform to compare and contrast the emitted waves. Instead, a control group with triphenylphosphine was used. Because each compound has a unique NMR spectrum, the chemical shifts in the spectrum when various compounds are analyzed can be used to determine whether they are present or not. This would mean, for instance, that the trans isomer would show a chemical shift in resonant frequency different from the cis isomer when tested under NMR (12).

**EXPERIMENTAL**

![Diagram of oxygen-free apparatus used for all syntheses.](image)

**Figure 8:** The oxygen-free apparatus used for all syntheses.
It was necessary for the refluxes in this experiment to happen under an atmosphere of N$_2$ because O$_2$ reacts with molybdenum to form unwanted crystalline product. To allow the entire system to be flushed of oxygen, N$_2$ was initially allowed to flow through the set up with the reaction flask stopcock and tube clamp open. Afterwards, the tube clamp was closed so that N$_2$ could flow through the reaction flask and condenser tube as well. Once the N$_2$ had flowed, the tube clamp was opened, and the stopcock on the reaction flask was closed (8) (Figure 8).

A small sample (~0.05 g) of molybdenum hexacarbonyl was extracted and dissolved in 1 mL dichloromethane; a small part of this sample was pipetted in a NaCl cell and analyzed using infrared spectroscopy with MIDAC and solution cells. A pure 1 mL sample of dichloromethane was also extracted for infrared spectroscopy to obtain a control spectra that could allow the subtraction of any dichloromethane peaks.

1.000 g of molybdenum hexacarbonyl (0.00378 mols, Acros Organics A015958301) was then collected and added to 40.00 mL of toluene (0.3763 mols, Fisher Scientific 126416) and 10.00 mL of piperidine (0.1012 mols, Sigma-Aldrich 53796MMV) in the reaction flask. Boiling chips were also added. The solution was heated at reflux for two hours under an N$_2$ atmosphere and then filtered hot into a Buchner flask under a vacuum. The remaining precipitate was then washed with a cooled solution of petroleum ether/ligroin (Sigma Aldrich) and massed to three decimal places. A small amount of the precipitate was then dissolved in 1 mL of dichloromethane (0.02 mols, Fisher Scientific 136753) and analyzed through infrared spectroscopy in NaCl cells (adapted from (11)). Dichloromethane spectra peaks were subtracted from the obtained IR spectra, and the number and location of absorbance peaks in the resulting absorbance chart were then compared with the IR analysis of molybdenum hexacarbonyl dissolved in dichloromethane.

0.500 g of the precipitate Mo(CO)$_4$(pip)$_2$ (0.500 g, 1.32 mmol) and 1.43 mmol of each respective ligand were then dissolved in 20.0 mL of dry dichloromethane (0.312 mols, Sigma Aldrich). 0.75 g of PPh$_3$ was added to one reaction flask as a control. Equal molar amounts of each ligand was then added to each reaction flask and dissolved in dichloromethane: 0.610 g of Ph$_3$P(CH$_2$)$_4$PPh$_2$; 0.630 g of Ph$_3$P(CH$_2$)$_8$PPh$_2$; 0.649 g of Ph$_3$P(CH$_2$)$_6$PPh$_2$; 0.689 g of Ph$_3$P(CH$_2$)$_8$PPh$_2$; and 0.770 g of Ph$_3$P(CH$_2$)$_12$PPh$_2$ respectively. Boiling chips were added, and the mixture was then heated at reflux for 15 minutes, after which it was cooled to room temperature and filtered in a Buchner flask. With a rotary evaporator, the filtrate was reduced to about 8 mL, allowing for the concentration of the product. 15.0 mL of methanol (0.370 mols, Fisher Scientific 083168) was added to the concentrated filtrate, and the mixtures cooled in a freezer for 48 hours to precipitate out a pale product ranging in color from yellow to brown. Upon crystallization of the precipitate, most of the liquid was decanted and then vacuum filtered through the Buchner flask/pump set up (adapted from (11)).
Several compounds filtered a colored viscous product. Keeping about 0.5 g of product in the original flask, the rest of the precipitate was fully dissolved in CH$_2$Cl$_2$. Enough of this solution was placed into an NaCl cell to completely fill it, and this cell was run through the IR spectrum. The remaining solution was transferred to a 30 mL vial and evaporated under N$_2$ gas to leave dried precipitate. An appropriate amount (0.5 - 1.5 mL) of d-chloroform (CDCl$_3$; Aldrich Chemistry MKBQ7918V) was added to this vial to completely dissolve the cis complexes and make a concentrated solution. After adding about 0.5 mL of this solution to an NMR tube, this CDCl$_3$ solution was run through the NMR.

Some compounds resulted in a perfectly dry precipitate after filtering the cooled suspension. The dried precipitate was transferred to a 30 mL vial. Approximately 0.05 g of this product was collected and dissolved in roughly of CH$_2$Cl$_2$, and this dilute solution was run through IR spectrum with an NaCl cell. 0.5 g of the precipitate was transferred to the round bottom flask for following steps. The remaining precipitate in the vial was fully dissolved in CDCl$_3$ to make a concentrated solution. 0.5 mL of this solution was transferred to an NMR tube and was run through the NMR.

All products in the round-bottom flask (i.e. those not used to make solutions for IR and NMR) were dissolved in 10.0mL of dry toluene and boiling chips were added. The mixture was heated at reflux for 30 minutes under N$_2$ after which it was cooled to room temperature. The resulting dark reddish-brown solution was then filtered in a Buchner flask/pump set up, and the filtrate was collected and put into a round-bottom flask. A rotary evaporator was used to completely evaporate the toluene in the mixture, leaving pale, brown residue on the bottom of the round bottom flask (adapted from (11)). Further purification of the compound was accomplished by dissolving the residue in 15 mL of dichloromethane. The solution was then filtered under a vacuum using a Buchner flask/pump set and the filtrate collected. A small sample of this filtrate was then pipetted into NaCl cells for IR spectroscopy. To the remaining filtrate, a steady stream of N$_2$ gas was introduced to evaporate out dichloromethane such that only the pure product remained. A slightly different procedure was used for groups in which there were not many impurities in the solution after rotary evaporation. The second filtration was foregone. Instead, one small sample of the product was obtained from the round bottom flask and dissolved in CH$_2$Cl$_2$ to form a dilute solution for IR spectroscopy. Around 0.5-1.5 mL of d-chloroform (CDCl$_3$, Aldrich Chemistry MKBQ7918V) was then added to dissolve the precipitate not used for IR analysis and prepare a solution for NMR analysis. 0.5 mL of this solution was subsequently transferred to an NMR tube for NMR spectroscopy analysis.
RESULTS AND DISCUSSION

Since it was impossible to completely purify every compound, almost every spectrum displayed unchanging overtones of unknown compounds that were suspected to be some oxidized metal carbon compound. These overtones were not crucial to the data analysis; they could be ignored when analyzing the spectra. The small peaks other than the major peaks could also be ignored, since they represent impurities. Washing with dichloromethane would produce a purer product, and this was done for the 1,6 compound.

![Figure 9](image.png)

**Figure 9:** a) IR spectrum of Mo(CO)$_6$; one distinct absorbance peak at 1982 cm$^{-1}$. b) IR of Mo(CO)$_4$(pip)$_2$; three peaks at 1934 cm$^{-1}$, 1888 cm$^{-1}$, and 1819 cm$^{-1}$.

Mo(CO)$_6$ can vibrate in only one way and therefore, as expected, had a single peak (Figure 9a). However, Mo(CO)$_4$(pip)$_2$ is asymmetric and can vibrate in three ways. Its spectrum thus had three peaks (Figure 9b).
The IR spectrum for Mo(CO)$_4$(PPh$_3$)$_2$, the control, showed three clear peaks in the transmittance graph, signifying the existence of the cis isomer in the solution (Figure 10a). After the isomerization of the cis complex, one very clear peak was identified, which signified the formation of the trans complex (Figure 10b). Upon further analysis, the NMR data of the cis product indicated a single product with little to no side compounds (Figure 10c); however, after reflux and isomerization of the cis compound, a new peak occurred at around 51 ppm, confirming the production of a trans compound (Figure 10d). The NMR data, therefore, revealed more precise information about the synthesis of the trans product that the IR data did not, indicating that isomerization was not incredibly efficient. This failure to effectively isomerize the cis compounds was caused by the insolubility of the trans product of triphenylphosphine.
The IR data for cis-Mo(CO)$_4$(Ph$_2$P(CH$_2$)$_4$PPh$_2$) showed three different peaks as expected (Figure 11a). The trans IR data also showed multiple peaks as predicted (Figure 11b), indicating that the conversion of a significant amount of cis to trans did not occur. As a result, the post-heated compound’s graph was almost identical to the cis graph. The lack of trans isomer formation was evident through the NMR data since the peaks present in the cis graph were about the same as the one in the post-heated graph, showing a large amount of very pure cis isomer and no trans isomer (Figures 11c and 11d, respectively). The lack of smaller peaks was attributed to the high purification of the compound.
The IR for cis-Mo(CO)$_4$(Ph$_2$P(CH$_2$)$_5$PPh$_2$) showed three distinct peaks as expected (Figure 12a). These peaks, however, did not change into one single peak for the post-heated compound, indicating no conversion of the cis product to a trans product. Although the peaks present in the post-heated compound’s spectrum appear smoother (Figure 12b), this cannot be attributed to formation of the trans isomer, but rather to the purification that the product underwent in the attempted cis to trans conversion. The lack of significant peaks besides the single cis peak in the cis isomer NMR demonstrates the purity of cis product (Figure 12c). In the attempted conversion from cis to trans, a relatively small peak was obtained downfield to the cis peaks, while a large peak remained at about 25 ppm, signifying a very low-efficiency conversion of cis to trans (Figure 12d). This was consistent with the IR, which failed to show the presence of the trans isomer.
Figure 13: a) IR of $\text{cis-Mo(CO)}_4(\text{Ph}_2\text{P(CH}_2\text{)PPh}_2)$; peaks at 1899 and 1843 cm$^{-1}$. b) IR of $\text{trans-Mo(CO)}_4(\text{Ph}_2\text{P(CH}_2\text{)PPh}_2)$; one clear peak at 1890 cm$^{-1}$. c) NMR of $\text{cis-Mo(CO)}_4(\text{Ph}_2\text{P(CH}_2\text{)PPh}_2)$; two main peaks at 25.47 and 29.63 ppm. d) NMR of $\text{trans-Mo(CO)}_4(\text{Ph}_2\text{P(CH}_2\text{)PPh}_2)$; peaks at 26.02 and 38.91 ppm.

The IR for $\text{cis-Mo(CO)}_4(\text{Ph}_2\text{P(CH}_2\text{)PPh}_2)$ isomer showed multiple peaks centered around 1900 cm$^{-1}$, as indicated by the asymmetry of the shouldered peak on the absorption spectrum (Figure 13a). This irregular shape was likely due to separate peaks that formed so closely to one another that they overlapped. For the IR spectrum after isomerization, a single absorption peak at 1890 cm$^{-1}$ was detected, showing that the desired $\text{trans}$ product had been obtained (Figure 13b). NMR spectroscopy of the $\text{cis}$ product indicated a peak at around 26 ppm while the main peak for the $\text{trans}$ product shifted downfield to around 39 ppm, indicating that a significant amount of $\text{trans}$ product was obtained after isomerization (Figure 13c and 13d). However, a smaller residual peak at 26 ppm did remain, showing that some $\text{cis}$ isomer remained.
Figure 14: a) IR of cis-Mo(CO)$_4$(Ph$_2$P(CH$_2$)$_8$PPh$_2$); three distinct peaks at 1916, 1904, and 1873 cm$^{-1}$. b) IR of cis-Mo(CO)$_4$(Ph$_2$P(CH$_2$)$_8$PPh$_2$); one narrow peak at 1890 cm$^{-1}$. c) NMR of cis-Mo(CO)$_4$(Ph$_2$P(CH$_2$)$_8$PPh$_2$); one peak at 25.98 ppm. d) NMR of trans-Mo(CO)$_4$(Ph$_2$P(CH$_2$)$_8$PPh$_2$); two peaks at 26.20 and 39.04 ppm.

The large double-shouldered peak of the cis-Mo(CO)$_4$(Ph$_2$P(CH$_2$)$_8$PPh$_2$) IR graph suggested that the cis compound was present, as the shouldered peak indicates overlapping peaks (Figure 14a). After heating the cis product, the trans IR showed one clean, symmetrical peak, which suggests a clean conversion to a new trans product (Figure 14b). The cis and trans NMR differed in that the major peak shifted downfield from the cis to the trans graph, which was expected. Additionally, a small peak in the trans graph in the location in which the large peak occurred in the cis graph indicated that a small amount of cis remained, perhaps due to imperfect purification (Figures 14c and 14d). More conversion to the trans did occur, however, than did occur for the 1,6 compound.
The IR for the \( \text{cis-Mo(CO)}_4(\text{Ph}_2\text{P(CH}_2)_2\text{PPh}_2) \) isomer spectrum showed three strong peaks, meaning the asymmetrical \( \text{cis} \) isomer was created; however, each peak had a weak secondary peak associated with it, indicating that impurities may have been formed due to the length of the hydrocarbon chain (Figure 15a). The long chain may have caused the formation of unwanted products because it could bind to another molecule instead of connecting to its own diphosphine group. Yet, the intended result of creating a \( \text{trans} \) isomer product was still achieved, as shown in the IR and NMR graphs. The IR graph after isomerization showed one strong peak, signaling the creation of the \( \text{trans} \) isomer (Figure 15b). The NMR data only supported this result by demonstrating a chemical shift (Figure 15c and 15d). The peak at around 26 ppm was the one major peak for the \( \text{cis} \) isomer, and it changed to a small peak in the \( \text{trans} \) isomer spectra, indicating that a small portion of the \( \text{cis} \) product did not convert into \( \text{trans} \). However, the major peak in the \( \text{cis} \) moved downfield to around 40 ppm, signifying a change from the \( \text{cis} \) to \( \text{trans} \) isomer.

Analysis

For the experimental 1,5, 1,6, 1,8 and 1,12 ligands, a viscous, semi-liquid yellow or brown precipitate was observed after the addition of the respective diphenyl hydrocarbon chains. By contrast, reaction with the triphenylphosphine and 1,4 ligands produced a solid, crystalline...
solid. This was most likely observed because larger, bulkier hydrocarbon chains interfered with proper solidification and crystallization.

Changes in the number of peaks and the direction in which the existing peaks shifted, rather than the exact frequencies at which the peaks occurred, were focused on because overtones consistently appeared and did so in approximately the same places. The overtones in the IR graphs were possibly a result of the Mo-C bond in all the compounds, and the overtones in the NMR at approximately -20 ppm may have occurred due to oxidation of the phosphorus in the complexes by oxygen, which can occur if the phosphorus ligand is left to sit for too long. The NMR graphs were more precise than the IR graphs, as the NMR graphs showed the relative amounts of cis and trans isomers in each complex (both were present for all complexes after the trans isomer was attempted, except for the complex with the four-carbon hydrocarbon chain), rather than just indicating the presence of large amounts of trans isomers. NMR spectroscopy was used to confirm the results obtained through IR spectroscopy.

According to NMR results, the cis forms of the 1,6, 1,8, and 1,12 had similar chemical shifts when converting to the trans. This is expected because the NMR was measuring how the phosphorus nuclei were affected by their nearby environments, therefore the number of carbons along the chain would have little impact. It is clear since there are two distinct chemical shift values (in ppm) on most of the “trans” graphs that a different compound was formed, even if in small quantities. There exists a general trend of increased yield of the trans compound, as demonstrated by the increase in trans peak size in the NMR.

A comparison of IR spectra demonstrates a general trend towards the disappearance of multiple peaks for compounds with a 6-carbon chain or longer. To identify compounds based on IR spectra, the direct correlation between number of absorption peaks and the shift in dipole moment of the complex as described in the introduction was taken into account. Thus, successful isomerization from the cis to trans compound is shown by the disappearance of all but one peak of interest in the trans absorption spectra, as shown in 1,6, 1,8, and 1,12 compounds. In contrast, multiple peaks in absorption remained in the final IR spectra for the 1, 4, 1,5 and control groups, indicating that isomerization failed to produce significant amounts of trans product. Moreover, because of the differences between the cis and trans isomers, a slight shift in the absorption peak should also be visible on the IR spectra, which is evident in the 1, 6, 1, 8, and 1, 12 compounds but not the other three.

In general, the initial hypotheses were corroborated. Data obtained through IR and NMR spectroscopy confirmed that reactions with 1,6, 1,8, and 1,12 ligands produced significant amounts of trans product, while those with 1,4, 1,5, and phosphine ligands produced negligible amounts of the trans product. As predicted, product yield for ligands containing shorter hydrocarbon chains was insignificant, while large amounts of the trans isomer were obtained for
the longer-chain ligands. However, contrary to the initial hypothesis, the longer the hydrocarbon chain, the more purified the *trans* product obtained. For instance, the highest product yield was seen for the 1,12 ligand, while the 1,6 ligand reaction resulted in significantly less *trans* isomer obtained.

**Comparison to Past Studies**

Although this paper’s experiment was the first to synthesize the *trans* isomer of an octahedral complex with a 1,ₙ- bis(diphenylphosphino) alkane ligand, similar experiments have achieved similar results with different ligands. One such experiment sought a similar isomerization of a molybdenum tetracarbonyl complex using a diphosphine ligand with a crown ether backbone. The focus of this experiment was carefully studying the x-ray diffraction studies of the complex, and analyzing the changes associated with temperature. The paper does cite several other octahedral complexes with *trans* chelating diphosphine ligands with complex backbones, but the experiment is only concerned with the crown ether ligand. This paper’s experiment differs from the past one in that this experiment focuses on finding which variations of ligands form the *trans* isomer, while the past one only focuses on the properties of its one ligand (13).

**Future Studies**

With the knowledge that the *trans* molybdenum tetracarbonyl 1,ₙ- bis (diphenylphosphino) alkanes form in significant abundance only when *n* > 5, an understanding of the spatial dimensions of the molybdenum complex is obtained and better models for the spatial geometries of similar chelating compounds can be constructed sans complex computations.

This experiment did not investigate the potential catalytic properties of the *trans* isomer, so future studies may attempt to do so. Considering the catalytic practicality of existing organometallic catalysts, there is great potential for the molybdenum complex to act in a similar way. For the *trans* isomer, the presence of the hydrocarbon chain allows for interactions with two equatorial carbonyl groups, while the other two do not interact, and the carbonyl groups may rotate around the central molybdenum, which may lead to catalytic properties.

Such catalytic potential for the complex may have significant implications in both science and industry. As such, one of the first tasks of these future researchers would be to further purify and crystallize the product and investigate its properties; one way to do this would be to conduct an x-ray crystal diffraction in order to gain the most insight into the structure of the complexes.

**REFERENCES**

(1) Kauffman G.B., Halpern J. Coordination compound [Internet]. Encyclopaedia Britannica Inc.; [cited 2014 Jul 28] Available from:


(4) Coordination Complexes and Ligands [Internet]. Purdue University; [cited 2014 Jul 30]. Available from: http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch12/complex.php


(8) Pearsall M. Research in Organometallic Chemistry: The Quest for a trans-Chelating Diphosphine Molybdenum Complex. In: Drew University; 2014 Jul 14; Madison, NJ.


