Synthesis and Hydrogenation of Iridium Complexes with Bidentate and Water-Soluble Phosphine Ligands: Developing Novel Water-Soluble Catalysts for Hydrogenation of Unsaturates

By

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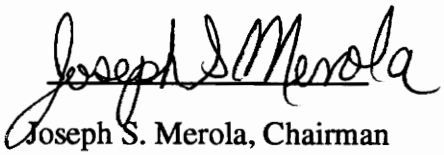

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(ABSTRACT)

The hydrogenation of unsaturated carbon-carbon bonds catalyzed by transition metal hydrido complexes has received considerable attention in the literature. Environmental interests have placed considerable emphasis on switching these processes into aqueous media. The dimeric complex $[Ir(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) has been found to undergo bridge-splitting reactions with bidentate phosphine ligands to produce coordinatively unsaturated, 16 electron complexes of the form [Ir(COD)(P-P)]Cl (P-P = bidentate phosphine). Two bidentate ligands were examined: 1,2-bis(dimethylphosphino)ethane [DMPE] and 1,2-bis(diethylphosphino)ethane [DEPE]. These compounds have been found to be both water soluble and reactive towards molecular hydrogen at room temperature, qualities that make them ideal for serving as catalysts for the aqueous hydrogenation of unsaturates.

Water-soluble ligands were also allowed to react with $[Ir(COD)Cl]_2$. In these cases, the product was analogous to the $[Ir(COD)(PMe_3)_3]Cl$ complex. Two water-soluble phosphines were examined: 1,3,5-triaza-7-phosphaadamantane [PTA] and tris(hydroxy-methyl)phosphine [THP]. When these complexes were hydrogenated in water, the PTA complex underwent an oxidative addition of molecular hydrogen with the loss of COD to form the facial isomer of $Ir(H)_2(PTA)_3Cl$. However, the THP made both

meridional and facial isomers of $Ir(H)_2(THP)_3Cl$ upon hydrogenation. The facial was determined to be the kinetically favored product while the meridional was the thermodynamically favored product.

The complexes Ir(COD)(DMPE)Cl, Ir(COD)(DEPE)Cl, and $Ir(H)_2(PTA)_3Cl$ were determined to be excellent aqueous hydrogenation catalysts. They catalyzed the reduction allyl alcohol to n-propanol under relative mild conditions.

To Mom and Dad

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Chapter 1: Literature Review

Section 1.1: Introduction

Hydrogenation, the addition of molecular hydrogen to carbon-carbon double and triple bonds, is one of the most extensively studied reactions. The process is a thermodynamically favorable reaction. However, this reaction is symmetry forbidden in the ground state via a concerted cis addition (Figure 1.1).[1] Since their is no net overlap, electrons are unable to flow from H_2 to the empty π^*-orbital. However, molecular hydrogen can react directly with transition metals since the *d*-orbitals have the correct symmetry, and electrons can flow from the filled *d*-orbital into the empty σ^*-orbital of H_2.[2] This dissociates the H-H bond and forms two metal-hydride bonds; theoretically, the hydrogen atoms can now be transferred in one step across a double bond (Figure 1.1).

Figure 1.1 H_2 addition to a double bond both symmetry-forbidden and allowed

Homogeneous hydrogenation catalysis can be defined as the addition of molecular hydrogen to an unsaturate in which the substrate and the catalyst are in the same phase.[2] Several advantages exist that make homogeneous catalysis more attractive than heterogeneous catalysis. First, kinetic and mechanistic studies are more easily performed in homogeneous conditions than under heterogeneous conditions. Another advantage is the product selectivity that homogeneous catalysis offers over heterogeneous catalysis.[3]

The earliest observation of homogeneous hydrogenation was reported by Calvin in 1938 and concerned the reduction of benzoquinone to hydroquinone.[4] The next year Inguchi discussed the hydrogenation of fumarate with rhodium complexes; however, the significance of this work was not recognized until many years later.[5] Perhaps the most influential article is that of Wilkinson and co-workers.[6] Wilkinson's elegant work enabled fundamental steps such as hydrogen activation and olefin coordination to be studied by his use of kinetic studies and physicochemical observations (especially NMR studies) of the interaction of small molecules with complexes.

Section 1.2: Wilkinson's Catalyst

The mechanism of olefin hydrogenation by Wilkinson's catalyst, $RhCl(PPh_3)_3$ is seen in Figure 1.2.[7] This mechanism is different from the original one proposed by Wilkinson. Omitted from the figure are side reactions in which binuclear species are formed for simplicity.

The complex $RhCl(PPh_3)_3$ dissociates one of its PPh_3 ligands L in solution to give complex [A], which has a coordinated solvent S. Oxidative addition of H_2 to [A] gives a dihydride complex [B]. The same dihydride can also be produced, though much less rapidly, by direct oxidative addition of H_2 to undissociated $RhCl(PPh_3)_3$, giving [E] and subsequent dissociation of triphenylphosphine. The octahedral complex [C] is formed by displacement of S from [B] by an olefin. Wilkinson originally proposed that in the next step the two hydride ligands attack the coordinated olefin in a concerted manner.[8] However, it is generally accepted that there is a two-step process in which the olefin inserts into the Rh-H bond to give the hydride-alkyl species [D], and the alkane is reductively eliminated to regenerate [A]. The coordinatively unsaturated complex [A] reacts further with H_2 to continue the catalytic cycle. It should be duly noted that both $RhCl(PPh_3)_3$ and [A] have a 16-electron configuration whereas the octahedral complexes have an 18-electron configuration. The catalytic cycle thus involves

coordinatively unsaturated d^8 square planar Rh(I) and coordinatively saturated d^6 octahedral Rh(III) species. In none of the intermediate species is the 18-electron configuration exceeded.

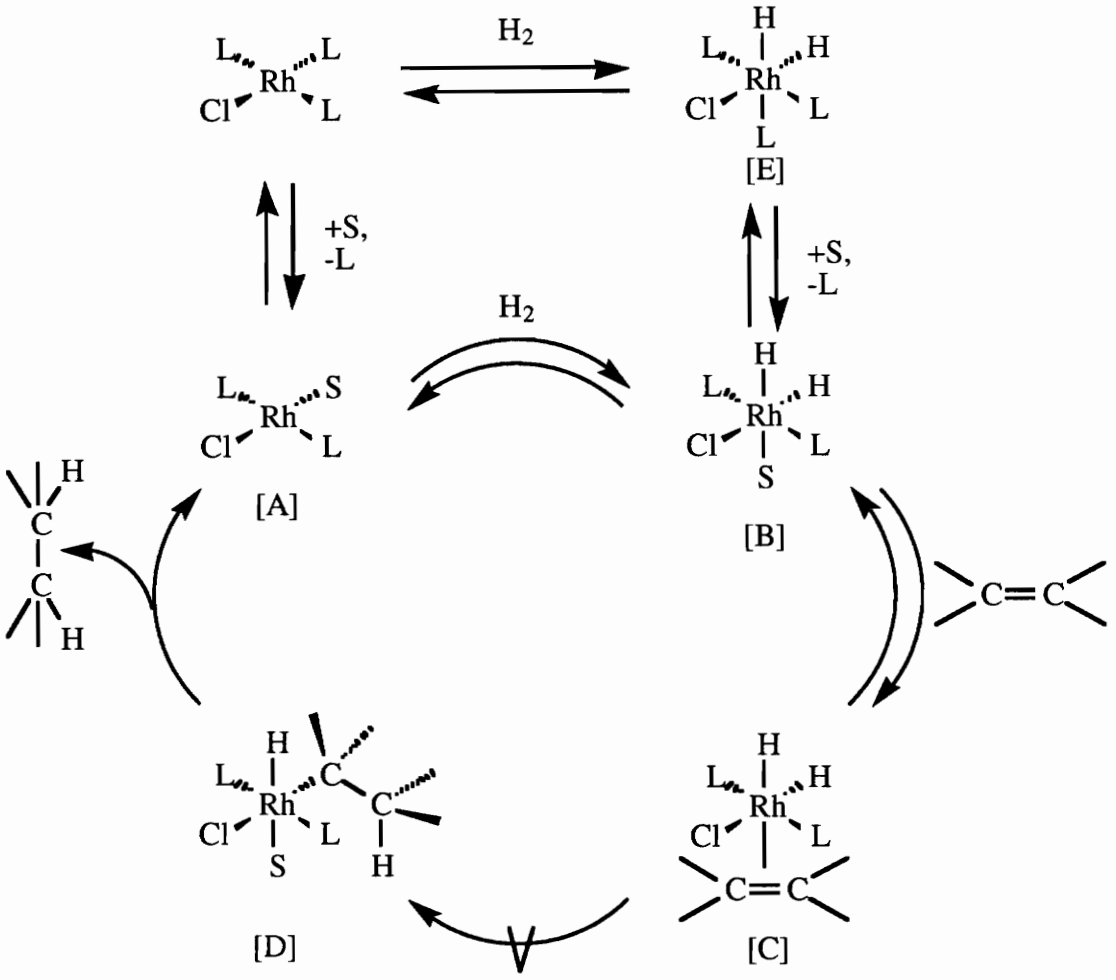


Figure 1.2 Mechanism of olefin hydrogenation by Wilkinson's complex.

In this mechanism, the first step of the catalytic cycle is oxidative addition of H_2 to [A]. However, a π complex could first be formed between the Rh(I) complex and the olefin. Then this complex could undergo oxidative addition of H_2 to give the hydrido-olefin complex. This process does occur in some catalytic reactions. The particular process that is followed depends

on the complex and its affinity for the olefin and H_2 and on the relative concentrations of the reactants. Figure 1.3 illustrates the generalized mechanisms of olefin hydrogenation taking both routes into consideration.[9]

In cycle A, H_2 first oxidatively adds to a coordinatively unsaturated species L_nM, step (a). Complexation of an olefin in step (b) gives the dihydrido-olefin complex [M]. Step (e) is the olefin insertion into one of the M-H bonds yielding a hydrido-alkyl complex that on reductive elimination of step (f) liberates an alkane with the regeneration of the coordinatively unsaturated L_nM complex. This species reacts further with H_2 to drive the catalytic cycle A in an anti clockwise direction.

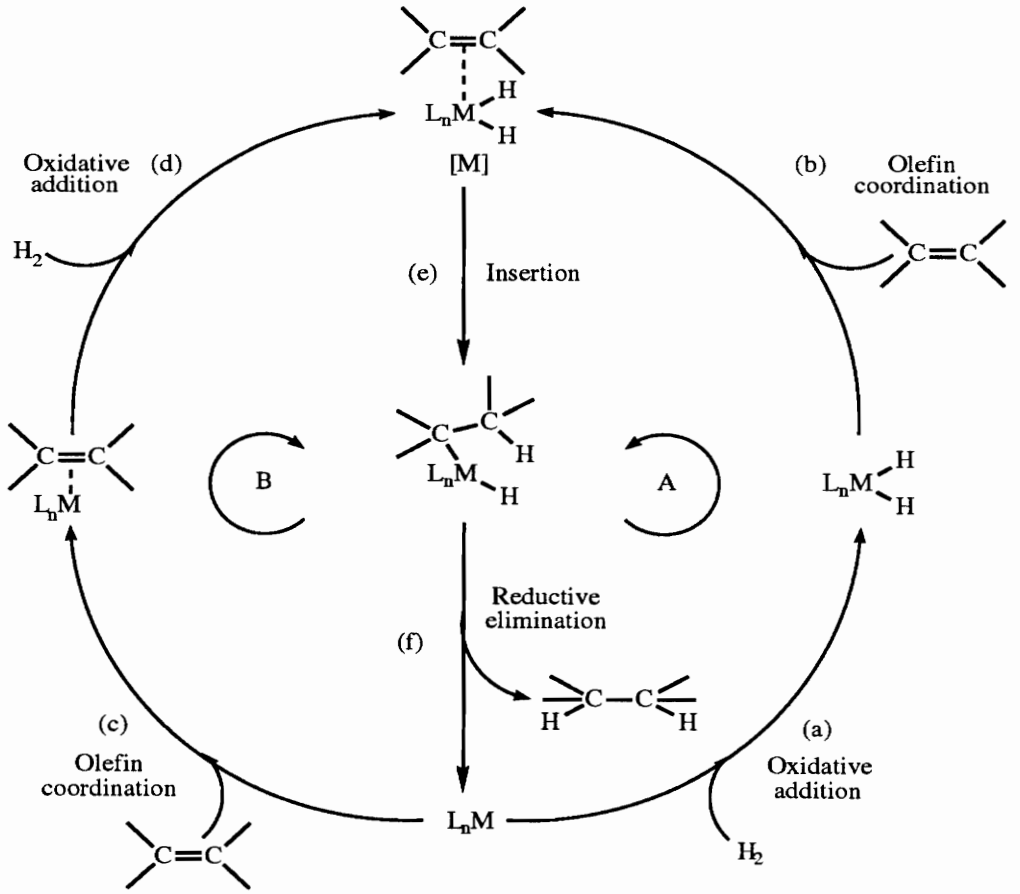


Figure 1.3 Two possible catalytic cycles in olefin hydrogenation with a transition metal complex catalyst

Figure 1.3 also illustrates cycle B, involving initial olefin complexation to L_nM in step (c). Molecular hydrogen oxidatively adds to the olefin complex in step (d) to give the dihydrido-olefin species [M] that undergoes olefin insertion and reductive elimination of alkane. This regenerates L_nM and thus drives the catalytic cycle B in a clockwise direction.

Determining which catalytic cycle is operating is not easy. However, pertinent information can often obtained by examining the rates of addition of olefin and H_2 and by carrying out kinetic studies on the individual elementary steps.

Section 1.3: Iridium-Phosphine Catalysts

Platinum group metals have demonstrated great potential to be active homogeneous hydrogenation catalysts. However, the analog of $RhCl(PPh_3)_3$ was determined to inactive in the reduction of unsaturates.[10] The complex was catalytically inactive because it irreversibly bound molecular hydrogen to the metal center. Furthermore, the complex did not dissociate a triphenylphosphine allowing the substrate to bind to the metal center.[10] Despite the inactivity of this iridium complex, extensive research has been performed on the chemistry of coordinatively unsaturated iridium complexes. Consequently, the most active homogeneous catalysts developed are iridium based.[11]

Crabtree and co-workers examined complexes of the type $[Ir(COD)L_2]PF_6$ (L = tertiary phosphine) for their catalytic activity. Schrock and Osborn first prepared this type of complexes. Moreover, their catalytic activity was determined to be poor in polar solvents such as acetone, ethanol, and tetrahydrofuran.[12] Crabtree hoped to allow the substrate free access to the metal center. Since these polar solvents could bind to the center, they were eliminated.

Common chlorinated solvents, such as chloroform, methylene chloride, and chlorobenzene, were chosen by Crabtree since they were noncoordinating.[11] These solvents had the advantage of polarity but they also had negligible coordinating power. The results of

these systems were outstanding. Two of the most active were [Ir(COD)PCy3(py)]PF_6 and [Ir(COD)(PMePh2)2]PF_6. For the reduction of 1-hexene in methylene chloride at 0 °C, these complexes had turnover frequencies of 6400 and 5100 per hour, respectively.[11] It should be noted that the iridium systems were at least one order of magnitude greater than their rhodium counter parts under the same conditions. Thus, Crabtree proposed that two different mechanisms exist for the iridium and rhodium systems.

In order to understand the mechanisms that operated in each system, Crabtree studied the nature of each system. During the investigations, various dihydrido olefin complexes were isolated. These complexes had the general structure of *cis*-[Ir(H)2(diolefin)L2]PF_6. Moreover, low temperatures were necessary to isolate these compounds since at normal temperatures the olefin was readily reduced. The compounds were identified by ^1H and ^{31}P NMR spectroscopy.

Chelating phosphines such as 1,2-bis(diphenylphosphino)ethane [DPPE] were used as ligands. Similar *cis* dihydrido complexes were isolated.[11] This complex was isolated in the solid state and was identified by infrared spectroscopy as having metal hydrides. The ^1H NMR spectrum has two upfield resonances and were from the metal hydrides. The furthest upfield resonance was a triplet. The splitting was from the two *cis* phosphines. The other resonance was a doublet of doublets and was from the hydride being split by one *trans* and one *cis* phosphines. The ^{31}P NMR spectrum had two resonances. Both were doublets from the two inequivalent phosphines splitting each other.

While Crabtree's catalysts are the most active homogeneous hydrogenation catalysts, many other iridium phosphine catalysts existed before Crabtree's. However, these did not have the same activity. Vaska's complex, *trans*-IrCl(CO)(PPh3)3 was found to reversibly add molecular hydrogen at 25 °C.[13] Moreover, Vaska and co-workers reported catalyzed hydrogenation of ethylene, propylene, and acetylene by using this complex in benzene or toluene at 40 to 60 °C and 1 atm H_2.[14] The yields were somewhat better than when using the

rhodium analog: at 60 °C in 18 hr, ethylene gave 40% ethane, propylene gave 10% propane, and acetylene gave 10% ethylene and 5% ethane. Slow reduction of the metal occurred at higher temperatures. James and co-workers observed very slow hydrogenation of 1-hexene, styrene, and cyclohexene in benzene at 50 °C and 1 atm H_2.[15]

Several bis-bidentate complexes have been synthesized by Heiber and Frey,[16] Sacco and co-workers,[17] Taylor,[18] and Vaska and Catone.[19] $Ir(DPPE)_2^+$ was found to undergo reversible oxidative addition of molecular hydrogen at 25 °C; however, the related complex $IrCO(Ph_2PCH_2PPh_2)_2^+$ and the nonionic $IrBr(Ph_2PCH_2CH_2SPh)_2$ do not react with 1 atm of hydrogen.[20] The presence of chelating phosphines inhibits the catalytic activity at ambient conditions;however, at 150 to 175 °C with 100 atm of molecular hydrogen, reduction of 1-hexyne/1-octene mixtures occurred.[21] The order of activity was

$$IrBr(Ph_2PCH_2CH_2SPh)_2 < [Ir(DPPE)_2]Cl < [IrCO(Ph_2PCH_2PPh_2)_2]Br$$

In all cases the 1-hexyne was reduced faster than the 1-octene (to hexene and hexane).

The activity of these cationic iridium catalysts can be altered dramatically by changing the reaction conditions: solvent, substrate, pressure, temperature, etc. This activity can be used reduce olefins that were not reduced by traditional homogeneous systems.

Section 1.4: Water-Soluble Ligands and Catalysts

Since numerous complexes with a low oxidation state metal center are stabilized by phosphorous-containing ligands, it is no surprise that much research has been performed to tailor these ligands with appropriate substituents, including carboxylic, amino, hydroxyl, and sulfonate functions, which induce water solubility.

In 1958 Chatt and co-workers prepared the first sulfonated phosphine ligand by addition of dilute oleum (20% SO_3-H_2SO_4) to triphenylphosphine. Under the reported conditions, the monosulfonated ligand, $Ph_2P(m\text{-}C_6H_4SO_3Na)$, was obtained after neutralization with sodium hydroxide.[22]

Several years later, Kuntz showed that careful control of the reaction conditions produced the trisubstituted ligand, P(*m*-$C_6H_4SO_3Na)_3$ although it was obtained with mono- and disulfonated ligands as well as with significant amounts of the corresponding oxides.[23] Since the trisubstituted ligand had high performance in aqueous catalysis, a high-yield synthetic route was derived. In short, increasing the SO_3:triphenylphosphine concentration molar ratio and using an oleum with 33% SO_3 in H_2SO_4, minimized the mono- and disubstituted phosphines.[23] Rhodium complexes similar to Wilkinson's catalyst have been prepared and were very active aqueous hydrogenation catalysts.[23]

Phosphines for which water solubility was achieved by quaternary amines as functional groups were also synthesized. Aminoalkyl- and aminoarylphosphines have been prepared by treating chlorodiakyl- or chlorodiarylphosphines with Grignard reagents derived from ω-bromoamines according to Eq. (1).[24]

$$R_2PCl + Me_2NCH_2MgBr \longrightarrow Me_2NCH_2PR_2 + \text{"MgClBr"} \qquad (1)$$

Alternative preparations involve direct attack by a chlorophenylphosphine on a secondary amine in the presence of triethylamine, as shown in Eq. (2).[25,26]

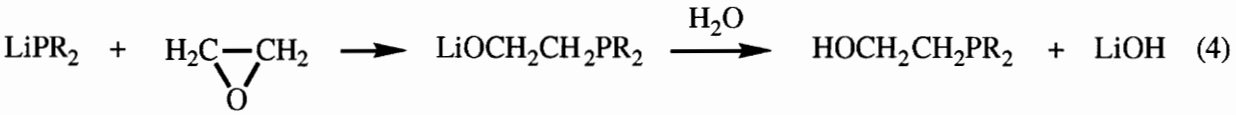
$$PhPCl_2 + 2\,MeNHCH(Me)Ph \xrightarrow{Et_2O/NEt_3} PhP[N(Me)CH(Me)Ph]_2 \qquad (2)$$

Likewise, condensation of a lithium diarylphosphine with ω-haloamine yields the unexpected aminodiarylphosphine as shown in Eq. (3).[27,28,29]

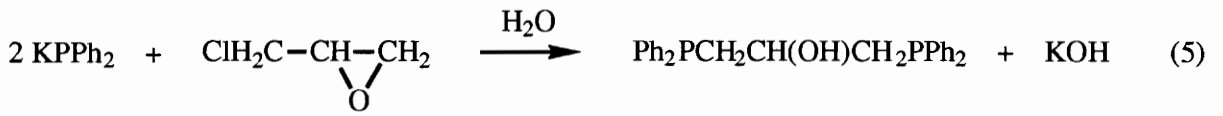
$$PhP(MgBr)_2 + Et_2NCH_2CH_2Br \longrightarrow PhP(CH_2CH_2NEt_2)_2 \qquad (3)$$

Water soluble phosphines have also been synthesized that involve hydroxyl or ether a functional group. Condensation of a primary or secondary alkyl- or arylphosphine with ketones or aldehydes in the presence of hydrochloric acid produces hydroxylalkyl-phosphines.[30] The reaction can also be performed starting with PH_3.[31]

Addition of a phosphide salt to an oxirane, or more generally to a cyclic ether, produces, after hydrolysis, the corresponding hydroxyalkylphosphine, as seen in Eq. (4) and (5).[32,33,34]

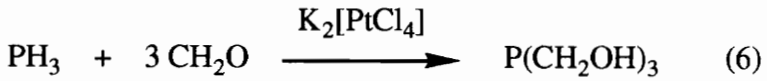


$$LiPR_2 + H_2C(O)CH_2 \longrightarrow LiOCH_2CH_2PR_2 \xrightarrow{H_2O} HOCH_2CH_2PR_2 + LiOH \quad (4)$$



$$2\,KPPh_2 + ClH_2C{-}CH(O){-}CH_2 \xrightarrow{H_2O} Ph_2PCH_2CH(OH)CH_2PPh_2 + KOH \quad (5)$$

Preparation of the water-soluble $P(CH_2OH)_3$ ligand has been accomplished by addition of phosphine gas to formaldehyde in water in the presence of $K_2[PtCl_4]$, as seen in Eq. (6).[35]



$$PH_3 + 3\,CH_2O \xrightarrow{K_2[PtCl_4]} P(CH_2OH)_3 \quad (6)$$

Investigations are currently underway using these and other water-soluble ligands in aqueous hydrogenation systems. Furthermore, aqueous hydroformylation investigations are also being examined and have had excellent results.

Merola *et. al.* reported the reduction of acetylenes, olefins, and ketones in aqueous media under mild conditions (60 °C, 6-8 atm of H_2) using a dihydrido iridium complex: *cis, mer*-$[Ir(H)_2(PMe_3)_3X]$, where X = Cl, O(CO)Ph.[36] When organic solvents were used

instead of water, no catalytic activity was seen. However, the aqueous catalytic activity for these catalysts was not very high, with turnover frequencies of 40 cycles per day.[36]

The catalytic cycle was deduced for the hydrogenation reactions and the schematic is shown in Figure 1.4.

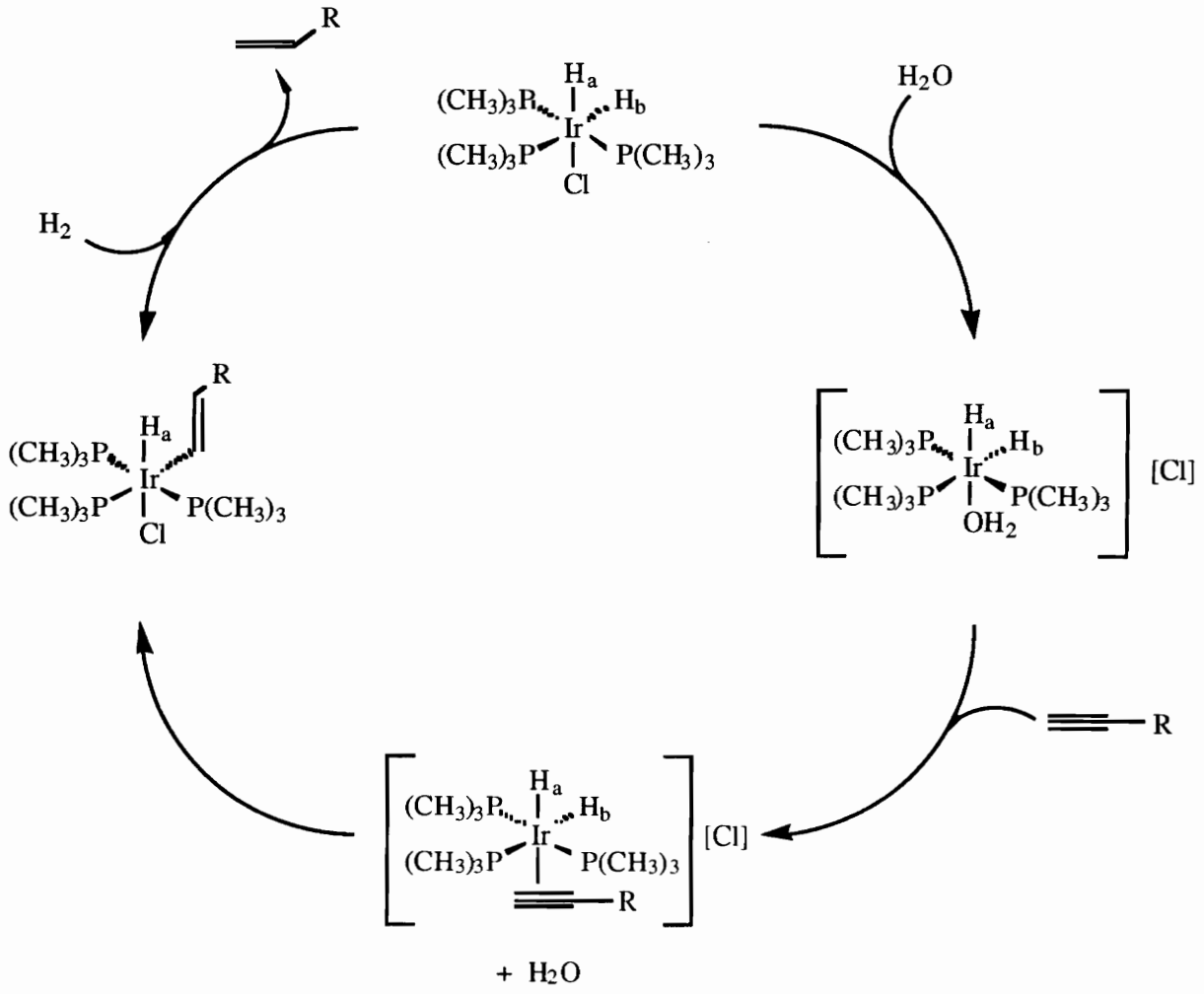


Figure 1.4 Mechanism of olefin hydrogenation by Ir(H)2[P(CH3)3]3Cl complex.[36]

The first step in the catalytic cycle, and also the rate determining step, was the dissociation of the chloride ion and the coordination of water to the iridium center. Next, substrate attacks the metal center displacing the water ligand. The substrate then inserts into the metal-hydride bond creating a hydrido-alkyl complex that reductively eliminates the reduced substrate in the following step while molecular hydrogen oxidatively adds to the metal center regenerating the catalyst. When the substrate was an alkyne, the product was an olefin that subsequently was reduced to the alkane.

This review of the chemical literature has shown the vast quantity of research concerning the catalytic chemistry of iridium. However, very little was reported on aqueous homogeneous catalysis. Thus, the intent of this thesis is to describe the synthesis, characterization, and catalytic activity of novel iridium phosphine complexes, where the phosphines are either bidentate or water-soluble.

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Chapter 2: Synthesis of Iridium Phosphine Complexes

Section 2.1: Introduction

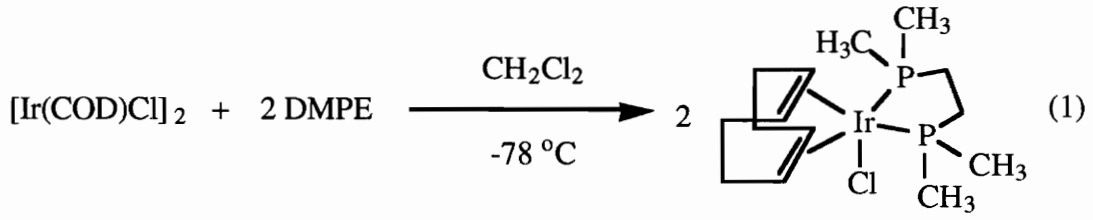
The surprising aqueous catalytic activity of $Ir(H)_2(PMe_3)_3Cl$ brought about many interesting questions regarding synthesizing platinum group metal complexes which are aqueous catalysts. Since the activity of the $Ir(H)_2(PMe_3)_3Cl$ is limited by chloride displacement by water, better activity could be expected if an open coordination site existed on the metal center to increase the water to metal interaction. This could be accomplished by using one bidentate phosphine ligand instead of the three monodentate trimethylphosphine ligands. Previously, bidentate phosphine complexes of iridium have been found to be active catalysts for the reduction of olefins in organic solvents.[1]

Another possible way of generating better catalytic activity might be accomplished by using water soluble phosphines as ligands. This would no longer make chloride loss necessary for water solubility; and in principle, increase the activity by having more of the active complexes in solution. Previously, water soluble phosphines have been used to generate catalytically active complexes for the hydrogenation of olefins[2] and for hydroformylation of olefins.[3] The targets would also be interesting for the fact that they would bridge the gap between classical inorganic chemistry of Werner type compounds with those organometallic compounds that have been studied more recently.[4]

Section 2.2: Synthesis of Bidentate Phosphine Complexes

Due to their structure and commercial availability, two bidentate phosphines were chosen: 1,2-bis(dimethylphosphino)ethane [DMPE] and 1,2-bis(diethylphosphino)ethane [DEPE]. When DMPE was dissolved in a solution of methylene chlorine and added to an orange methylene chlorine solution of $[Ir(COD)Cl]_2$ at

room temperature or at 0 °C, the reaction mixture turn dark brown and a complex mixture of products was produced. However, when the reaction was performed at -78 °C, the solution turned light yellow in color. Upon warming and evaporation of solvent, a yellow solid was formed and has been identified as Ir(COD)(DMPE)Cl, as seen in Eq. (1).



(1)

Ir(COD)(DMPE)Cl was identified by ^{1}H, ^{31}P, ^{13}C NMR spectroscopy and elemental analysis. The complex was soluble in water, alcohols, and most polar solvents and was insoluble in nonpolar solvents. When the complex was dissolved in water, the solution was a dark red color, not the yellow color seen in most polar solvents. The dramatic color change was determined to be from chloride dissociation and solvation of the metal center.

The ^{1}H NMR spectrum of Ir(COD)(DMPE)Cl in CD_2Cl_2 displays a broad singlet at 3.65 ppm corresponding to the olefinic COD resonances, two broad multiplets, one appearing at 2.19 ppm and the other at 2.00 ppm, corresponding to the aliphatic COD resonances, a doublet at 1.77 ppm corresponding to the methylene backbone of the phosphine, and a doublet at 1.47 ppm corresponding to the methyl groups of the phosphine.

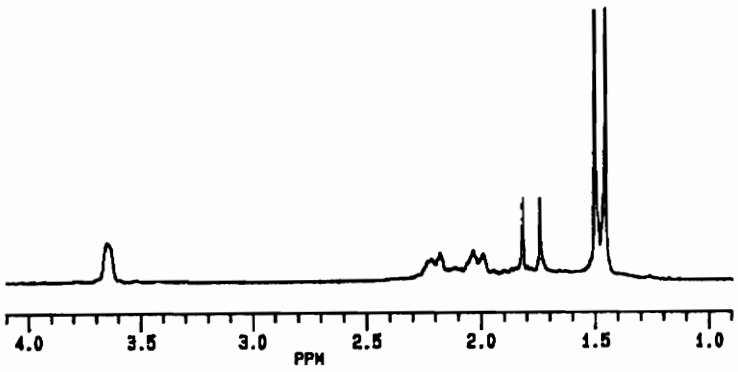
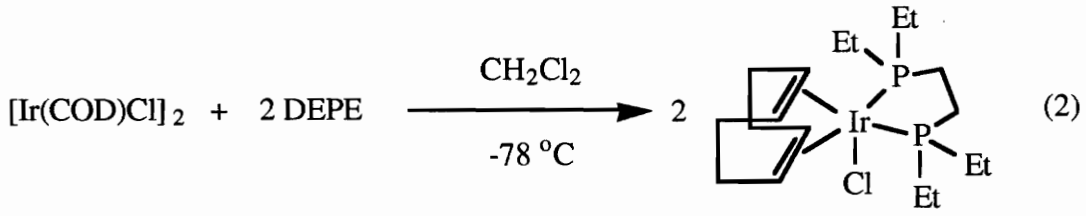


Figure 2.1: 200 MHz ^{1}H NMR Spectrum of Ir(COD)(DMPE)Cl in CD_2Cl_2

In a similar experiment, 1,2-bis(diethylphosphino)ethane [DEPE] was allowed to react with $[Ir(COD)Cl]_2$, as seen in Eq. (2). The product was analogous to the DMPE complex, having the structure, Ir(COD)(DEPE)Cl.



(2)

Like the DMPE complex, the DEPE complex was soluble in water, alcohols, and most polar solvents and was insoluble in nonpolar solvents. Moreover, when the complex was dissolved in water, the solution was a dark green color, not the yellow color seen in most polar solvents. Again, the dramatic color change was determined to be from chloride dissociation and solvation of the metal center. Ir(COD)(DEPE)Cl was identified by ^{1}H, ^{31}P, ^{13}C NMR spectroscopy and elemental analysis.

The ^{1}H NMR spectrum of Ir(COD)(DEPE)Cl in CD_2Cl_2 displays a broad singlet at 3.79 ppm corresponding to the olefinic COD resonances, a broad multiplet, appearing at 2.18 ppm corresponding to half the aliphatic COD resonances, a broad doublet of quartets at 1.90 ppm corresponding to half the aliphatic COD resonances and the methylene part of

the ethyl groups, a doublet at 1.70 ppm corresponding to the methylene backbone of the phosphine, and a doublet of triplets at 1.06 ppm corresponding to the methyl part of the ethyl groups.

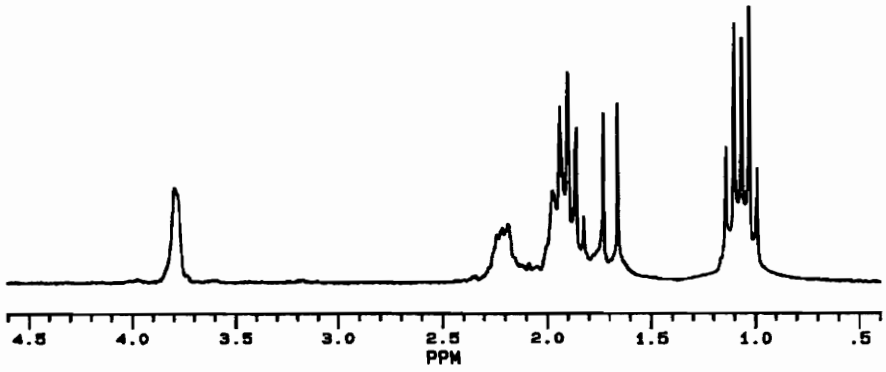


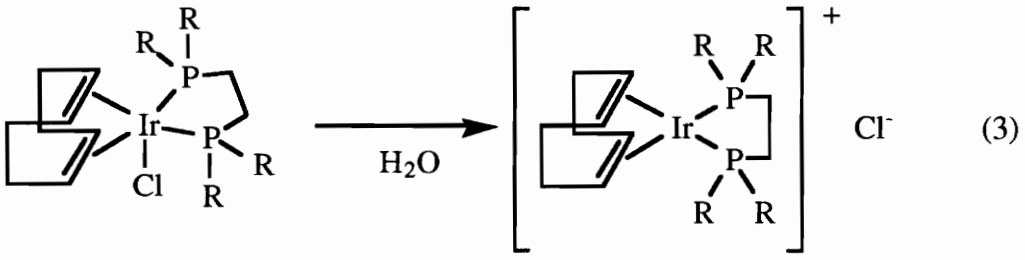
Figure 2.2: 200 MHz ^{1}H NMR Spectrum of Ir(COD)(DEPE)Cl in CD_2Cl_2

For the DMPE and DEPE complexes, several possible geometries exist, depending on the coordination number of the metal center. If the chloride ion is attached to the iridium, the complex is five coordinate and can adopt either a square pyramidal or a trigonal bipyramidal geometry. The conversion between these two geometries often times takes place quite rapidly, resulting in chemically equivalent configurations. This behavior of this type of stereochemically nonrigid molecule is known as fluxionality.[5] NMR spectroscopy is particularly useful in determining fluxionality, since the time scale used in a typical NMR experiment is in the range 10^{-2} to 10^{-5} seconds.[6] Therefore for fluxional molecules, nuclei appear to be equivalent, even though these atoms could be in different environments. The DMPE and DEPE complexes are five coordinate in most solvents such as methylene chlorine.

To confirm that these complexes were in fact five coordinate, low temperature ^{31}P NMR spectroscopy was used. Since the rate at which a complex interconverts is dependent on temperature, cooling the complex will slow the rate down. At room temperature, Ir(COD)(DEPE)Cl displayed a singlet in the ^{31}P NMR spectrum at 33.64

ppm. When the ^{31}P NMR spectrum was obtained at - 90 °C, the signal broadened and moved down field to 36.25 ppm. Since a change was seen when the temperature was lowered, this confirms that the species was fluxional. The signal change was from ^{31}P atoms in different chemical environments. If the complex was four coordinate and non-fluxional, the environments of the ^{31}P atoms would not change with temperature. Thus, the ^{31}P NMR signals would not change.

If, however, the chloride ligand dissociates in solution or acts as a counter ion in the solid state, the iridium complex is four coordinate and adopts a square planar geometry. Although a tetrahedral geometry is possible for a four coordinate transition metal complex, compounds of the second and third row metals rarely adopt this configuration.[7] These complexes are four coordinate in water, as seen in Eq. (3).



(3)

NMR spectroscopy was used to determine that the chloride ion dissociates in water from the iridium center and that ion pair is solvated by water molecules. The ^{1}H NMR spectrum of [Ir(COD)DMPE]Cl in D_2O displays a broad singlet at 4.74 ppm corresponding to the olefinic COD resonances, two broad multiplets, one appearing at 2.15 ppm and the other at 2.00 ppm, corresponding to the aliphatic COD resonances, a doublet at 1.70 ppm corresponding to the methylene backbone of the phosphine, and a doublet at 1.46 ppm corresponding to the methyl groups of the phosphine.

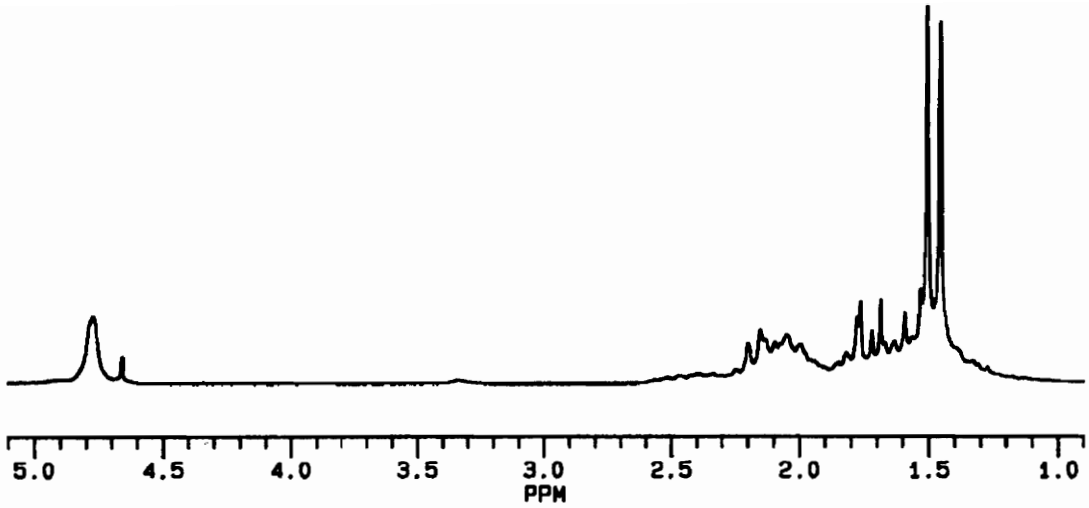


Figure 2.3: 200 MHz ^{1}H NMR Spectrum of [Ir(COD)DMPE]Cl in D_2O

The ^{1}H NMR spectrum of [Ir(COD)DEPE]Cl in D_2O displays a broad singlet at 4.73 ppm corresponding to the olefinic COD resonances, a broad singlet appearing at 2.05 ppm corresponding to the aliphatic COD resonances, a doublet of quartets at 1.83 ppm corresponding to the methylene part of the ethyl groups, a doublet at 1.75 ppm corresponding to the methylene backbone of the phosphine, and a doublet of triplets at 0.99 ppm corresponding to the methyl part of the ethyl groups.

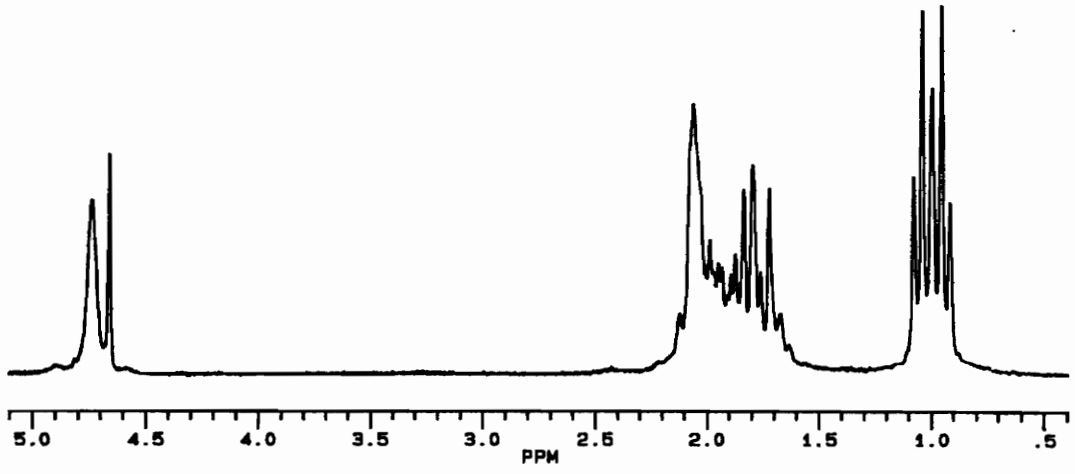


Figure 2.4: 200 MHz ^{1}H NMR Spectrum of [Ir(COD)DEPE]Cl in D_2O

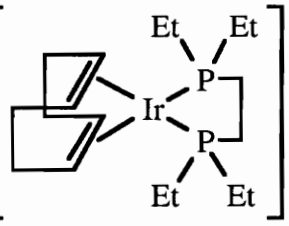
In several syntheses of the Ir(COD)(DMPE)Cl complex, a complex mixture of products were produced. It was concluded that the DMPE molecule was bonding across the chloride bridge of the $[Ir(COD)Cl]_2$ forming a bimetallic product. It was postulated that if the iridium chloride bridges could be split by another incoming ligand, the resulting adduct could be allowed to react with DMPE and form the desired monometallic [Ir(COD)DMPE]X compound. One such synthesis was reported by Mueterties,[8] in which $[Ir(COD)Cl]_2$ and acetonitrile are allowed to react in the presence of silver tetrafluoroborate to produce an iridium-acetonitrile adduct and precipitated silver chloride, as seen in Eq. (4).

$$[Ir(COD)Cl]_2 + \text{xs } CH_3CN \xrightarrow{2\ AgBF_4} 2 \left[\text{Ir}(NCCH_3)_2 \right] BF_4^- \quad (4)$$

The addition of DMPE to a yellow methylene chloride solution of $[Ir(COD)(CH_3CN)_2]BF_4$ produced a dark red solution. When the solvent was evaporated, a reddish brown solid precipitated and was identified as $[Ir(COD)DMPE]BF_4$, as seen in Eq. (5). This compound was identified by ^1H, ^{31}P, ^{13}C NMR spectroscopy and elemental analysis.

$$[Ir(COD)(CH_3CN)_2]BF_4 + DMPE \xrightarrow{CH_2Cl_2} \left[\text{Ir}(P(CH_3)_2CH_2CH_2P(CH_3)_2) \right]^+ BF_4^- \quad (5)$$

In a similar experiment, DEPE was added to methylene chloride solution of $[Ir(COD)(CH_3CN)_2]BF_4$. The resulting product was a dark green solution. When the solvent was evaporated, a dark green solid precipitated and was identified as $[Ir(COD)DEPE]BF_4$, as seen in Eq. (6). The compound was identified by ^1H, ^{31}P, ^{13}C NMR spectroscopy and elemental analysis.

$$[Ir(COD)(CH_3CN)_2]BF_4 + DEPE \xrightarrow{CH_2Cl_2} \left[\text{  }\right] BF_4^- \quad (6)$$

The BF_4^- salts were slightly soluble in water and very soluble in acetone and methylene chloride. Since these salts are soluble in water, this solubility is believed to be a result of open coordination sites on the metal center.

To best illustrate that the chloride complexes have the chloride ion dissociate in water and not in other solvents, Table 1 lists the ^{31}P NMR signals of the chloride and tetrafluoroborate complexes in various solvents. The chloride complexes in D_2O similar resonance positions with the tetrafluoroborate complexes in non-aqueous solvents. However, the chloride complexes have farther upfield positions of the ^{31}P NMR signal in non-aqueous solvents. This demonstrates that when the chloride ion is attached to the metal center, the ^{31}P NMR signals are shifted dramatically upfield.

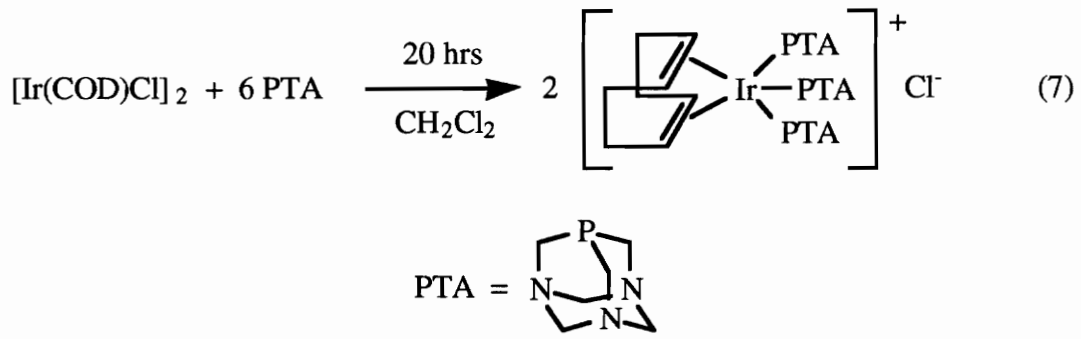
Table 1: ^{31}P NMR Signal Comparison

Complex	Solvent	^{31}P Signal (ppm)
Ir(COD)(DMPE)Cl	CD_2Cl_2	14.39
Ir(COD)(DMPE)Cl	D_2O	29.28
Ir(COD)(DMPE)BF_4	d_6-acetone	32.99
Ir(COD)(DEPE)Cl	CD_2Cl_2	34.11
Ir(COD)(DEPE)Cl	D_2O	52.69
Ir(COD)(DEPE)BF_4	CD_2Cl_2	52.90

Section 2.3: Synthesis of Water Soluble Phosphine Complexes

Two water soluble monodentate phosphines, 1,3,5-triaza-7-phosphaadamantane [PTA] and tris(hydroxymethyl)phosphine [THP] were chosen for investigation. The selection was based on their similar size and reactivity to trimethylphosphine, and their relatively simple preparation. The PTA and THP ligands were prepared following the literature methods.[9,10]

When PTA was added to an orange methylene chlorine solution of $[Ir(COD)Cl]_2$ at room temperature, a white precipitate formed upon addition. After allowing the reaction mixture to stir overnight, the white solid was filtered and dried and identified as $[Ir(COD)(PTA)_3]Cl$, as seen in Eq. (7).



$[Ir(COD)(PTA)_3]Cl$ was identified by ^1H, ^{31}P, ^{13}C NMR spectroscopy and elemental analysis. The complex was soluble in hydrogen bonding solvents, such as water, alcohols and methyl sulfoxide, and the complex was insoluble in chlorinated solvents, such as methylene chlorine and chloroform.

The ^1H NMR spectrum of $[Ir(COD)(PTA)_3]Cl$ in D_2O displays a singlet at 4.47 ppm corresponding to the methylene resonances of the PTA ligand with two alpha nitrogens, a singlet at 3.99 ppm corresponding to the methylene resonances of the PTA ligand with one alpha phosphorous and one alpha nitrogen, a broad singlet at 3.60 ppm

corresponding to the olefinic COD resonances, and two broad multiplets, one appearing at 2.31 ppm and the other at 2.21 ppm, corresponding to the aliphatic COD resonances.

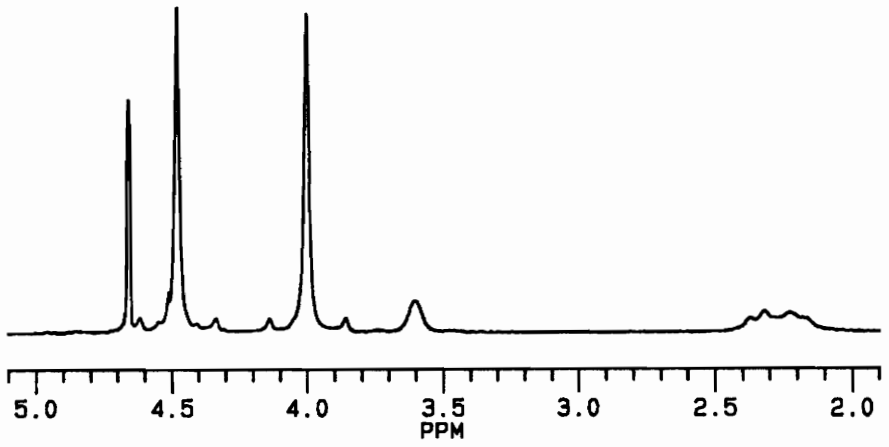


Figure 2.5: 200 MHz ^{1}H NMR Spectrum of [Ir(COD)(PTA)$_3$]Cl in D_2O

When THP was added to a solution of [Ir(COD)Cl]$_2$ and deionized water at room temperature, the water soluble phosphine slowly reacts with the dimer and draws the iridium into solution. After allowing the reaction mixture to stir overnight, the unreacted iridium dimer was filtered from the water. The filtrate was then evaporated leaving a white oily solid. The solid was dried and has been identified as [Ir(COD)(THP)$_3$]Cl, as seen in Eq. (8).

$$[Ir(COD)Cl]_2 + 6\,THP \xrightarrow[H_2O]{20\ hrs} 2\left[\text{Ir(COD)}\left(P(CH_2OH)_3\right)_3\right]^{+} Cl^{-} \qquad (8)$$

[Ir(COD)(THP)$_3$]Cl was identified by ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy. The complex was soluble in hydrogen bonding solvents, such as water, alcohols and

methyl sulfoxide, and the complex was insoluble in chlorinated solvents, such as methylene chlorine and chloroform.

The ^1H NMR spectrum of [Ir(COD)(THP)3]Cl in D_2O displays a singlet at 4.16 ppm corresponding to the methylene resonances of the THP ligand, a broad singlet at 3.74 ppm corresponding to the olefinic COD resonances, and two broad multiplets, one appearing at 2.30 ppm and the other at 2.15 ppm, corresponding to the aliphatic COD resonances. Since the spectrum was obtained using D_2O as the solvent, the proton on the hydroxyl group is not seen because of deuterium exchange.

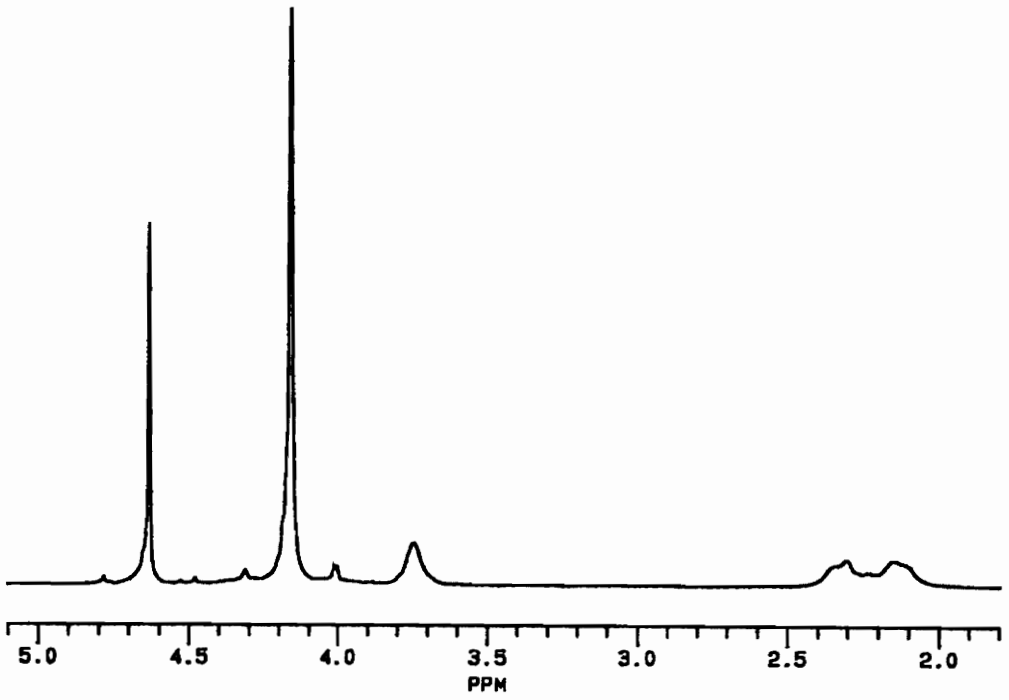


Figure 2.6: 200 MHz ^1H NMR Spectrum of [Ir(COD)(THP)3]Cl in D_2O

Section 2.4: Experimental

General Comments

All reactions were carried out on a Schlenk line under an atmosphere of argon, using oven-dried glassware. Bidentate ligands were purchased from Strem Chemical Company and were used as received. The solvents were purchased from Fisher Scientific. Pentane and diethyl ether were distilled from potassium/sodium under nitrogen. Toluene was distilled from potassium/benzophenone under nitrogen. Methylene chloride was distilled from phosphorus pentaoxide under nitrogen. Deuterated solvents were purchased from Cambridge Isotope Laboratories and dried over molecular sieves. Iridium trichloride was purchased as the hydrate from Johnson Matthey and used as received. Iridic acid was purchased from PGM Chemicals and used as received.

^{1}H NMR spectra were obtained using either a Bruker WP-200 or WP-270 NMR Spectrometer. ^{31}P NMR spectra were obtained on a Bruker WP-200 Spectrometer. ^{13}C NMR spectra were obtained using a Varian UN-400 NMR spectrometer. Chemical shift data are reported in δ units and referenced to the residual solvent peak. Air sensitive manipulations were carried out in a MB-150-M glove box purchased from M. Braun, Germany. Elemental analyses were performed by Atlantic Microlab, Norcross, Georgia.

Synthesis of $[Ir(COD)(CH_3CN)_2]BF_4$: RJPI077

$[Ir(COD)Cl]_2$ (0.5045 g, 0.751 mmol) was placed in a 100 mL side arm flask with a magnetic stir bar. CH_3CN (20 mL) was charged via syringe into the flask. While stirring, $AgBF_4$ (o.225 g, 0.4459 mmol) was added to the reaction mixture. Upon addition of the salt, a white precipitate (AgCl) formed readily. The reaction mixture was stirred for 18 hours. Upon completion, the red colored solution went to a yellow solution with a white precipitate. The yellow solution was filtered from the solid with a cannula

and filter paper into a 50 mL side arm flask. The excess CH_3CN was the removed via vacuum. A yellow solid precipitated out and this solid was dried for 18 hours. The dried solid was weighed (0.5985 g, 1.275 mmol) and the percent yield was determined (84.89%). ^1H NMR (200 MHz, $CDCl_3$): δ 4.23 (s, 4.0 H, CH=CH), 2.56 (s, 6.2 H, CH_3CN), 2.23 and 1.75 (br m, 8.4 H, CH_2CH_2). Spectroscopy and yield consistent with the literature.[8]

Synthesis of Ir(COD)(DMPE)Cl: RJPI105

$[Ir(COD)Cl]_2$ (0.4930 g, 0.7339 mmol) was placed in a 200 mL side arm flask with a magnetic stir bar. Methylene chloride (40 mL) charged via syringe into the flask forming an orange solution. The flask was placed into a dry ice/acetone bath and was cooled to -78 °C. A pressure equalizing addition funnel and gas adapter were attached to the flask. Methylene chloride (30 mL) was then added to the funnel. DMPE (0.240 mL, 1.440 mmol) was charged into the funnel. Additional methylene chloride (30 mL) was then added to the funnel to facilitate mixing. The DMPE solution was then added dropwise at a very slow rate into the flask. The addition took 30 minutes and turned the reaction mixture yellow. The mixture was stirred and warmed to room temperature over a period of eight hours. Evaporation of solvent to ca. 1-2 mL followed by addition of pentane (10 mL) gave a yellow solid which was dried via vacuum for 15 hours. The dried solid was weighed (0.6095 g, 1.254 mmol) and the percent yield was determined (85.96%). ^1H NMR (200 MHz, CD_2Cl_2): δ 3.65 (s, 4.0 H, CH=CH of COD), 2.19 and 2.00 (br m, 8.2 H, CH_2CH_2 of COD), 1.77 (d, J_{H-P} = 15 Hz, 4.3 H, CH_2CH_2 backbone), 1.47 (d, J_{H-P} = 10 Hz, 12.5 H, CH_3). ^{31}P NMR (200 MHz, CD_2Cl_2): δ 14.39 (s). ^{13}C NMR (100MHz, CD_2Cl_2): δ 65.25 (s, C=C COD), 33.03 (s, C-C COD), 28.93 (d J_{C-P} = 25 Hz, CH_2CH_2 backbone), 12.75 (d J_{C-P} = 30 Hz, CH_3).

Elemental analysis: Calc'd for $C_{14}H_{28}IrP_2Cl$: C: 34.6%; H: 5.81%. Found: C: 33.9%; H: 5.84%. ^1H NMR (200 MHz, D_2O): δ 4.74 (s, 4.0 H, CH=CH of COD), 2.15 and 2.00 (br m, 8.1 H, CH_2CH_2 of COD), 1.74 (d, J_{H-P} = 10 Hz, 1.2 H, CH_2CH_2 backbone-attached Cl), 1.72 (d, J_{H-P} = 16 Hz, 4.2 H, CH_2CH_2 backbone), 1.55 (d, J_{H-P} = 12 Hz, 3.2 H, CH_3-attached Cl), 1.47 (d, J_{H-P} = 10 Hz, 12.3 H, CH_3). Some other complex signals are present. ^{31}P NMR (200 MHz, D_2O): δ 29.28 (s, 4.5 P, complex with chlorine not attached), 15.32 (s, 1.0 P, complex with chlorine attached).

Synthesis of [Ir(COD)(DMPE)]BF_4: RJPI289

[Ir(COD)$(CH_3CN)_2$]Cl (0.4020 g, 0.857 mmol) was placed in a 100 mL side arm flask with a magnetic stir bar. Methylene chloride (20 mL) charged via syringe into the flask forming an yellow solution. A pressure equalizing addition funnel and gas adapter were attached to the flask. Methylene chloride (20 mL) was then added to the funnel. DMPE (0.143 mL, 0.855 mmol) was charged into the funnel. Additional methylene chloride (10 mL) was then added to the funnel to facilitate mixing. The DMPE solution was then added dropwise at a very slow rate into the flask. The addition took 30 minutes and turned the reaction mixture yellow-brown. The mixture was stirred and warmed to room temperature over a period of eight hours. Evaporation of solvent to ca. 1-2 mL followed by addition of pentane (10 mL) gave a yellow-brown solid which was dried via vacuum for 15 hours. The dried solid was weighed (0.4070 g, 0.757 mmol) and the percent yield was determined (88.33%). ^1H NMR (200 MHz, d_6-acetone): δ 4.88 (s, 4.0 H, CH=CH of COD), 2.23 (br m, 8.4 H, CH_2CH_2 of COD), 2.00 (d, J_{H-P} = 15 Hz, 4.1 H, CH_2CH_2 backbone), 1.70 (t d, J_{H-P} = 10 Hz, 12.1 H, CH_3). ^{31}P NMR

(200 MHz, d_6-acetone): δ 32.99 (s). Elemental analysis: Calc'd for $C_{14}H_{28}IrP_2BF_4$: C: 31.29%; H: 5.28%. Found: C: 32.11%; H: 5.68%.

Synthesis of Ir(COD)(DEPE)Cl: RJPI131

$[Ir(COD)Cl]_2$ (0.3680 g, 0.548 mmol) was placed in a 200 mL side arm flask with a magnetic stir bar. Methylene chloride (40 mL) charged via syringe into the flask forming an orange solution. The flask was placed into a dry ice/acetone bath and was cooled to -78 °C. A pressure equalizing addition funnel and gas adapter were attached to the flask. Methylene chloride (30 mL) was then added to the funnel. DEPE (0.250 mL, 1.07 mmol) was charged into the funnel. Additional methylene chloride (30 mL) was then added to the funnel to facilitate mixing. The DMPE solution was then added dropwise at a very slow rate into the flask. The addition took 30 minutes and turned the reaction mixture yellow-brown. The mixture was stirred and warmed to room temperature over a period of eight hours. Evaporation of solvent to ca. 1-2 mL followed by addition of pentane (10 mL) gave a yellow-brown solid which was dried via vacuum for 15 hours. The dried solid was weighed (0.5123 g, 0.945 mmol) and the percent yield was determined (86.22%). ^1H NMR (200 MHz, CD_2Cl_2): δ 3.81 (s, 4.0 H, CH=CH of COD), 2.20 (br m, 4.4 H, half CH_2CH_2 of COD), 1.90 (br d q, J_{H-H} = 7.5 Hz and J_{H-P} = 8 Hz, 13.1 H, half CH_2CH_2 of COD and CH_2), 1.70 (d, J_{H-P} = 14 Hz, 3.9 H, CH_2CH_2 backbone), 1.06 (d t, J_{H-H} = 7.5 Hz and J_{H-P} = 15 Hz, 12.7 H, CH_3). ^{31}P NMR (200 MHz, CD_2Cl_2): δ 34.11 (s). ^{13}C NMR (100MHz, CD_2Cl_2): δ 65.18 (s, C=C COD), 33.34 (s, C-C COD), 24.03 (d, J_{C-P} = 25 Hz, CH_2CH_2 backbone), 17.44 (d, J_{C-P} = 29 Hz, CH_2), 12.75 (s, CH_3). Elemental analysis: Calc'd for $C_{18}H_{36}IrP_2Cl$: C: 39.9%; H: 6.69%. Found: C: 37.3%; H: 6.41%. ^1H NMR (200 MHz, D_2O): δ 4.73 (s, 4.0 H, CH=CH of COD), 2.05 (br m, 7.9 H, CH_2CH_2 of

COD), 1.83 (d q, J_{H-H} = 8.0 Hz and J_{H-P} = 7.5 Hz, 8.1 H, CH_2), 1.75 (d, J_{H-P} = 15 Hz, 4.1 H, CH_2CH_2 backbone), 0.99 (d t, J_{H-H} = 7.5 Hz and J_{H-P} = 17 Hz, 13 H, CH_3). Some other complex signals are present. ^{31}P NMR (200 MHz, D_2O): δ 52.69 (s).

Low Temperature, ^{31}P NMR Experiment of Ir(COD)(DEPE)Cl: RJPI291

Ir(COD)(DEPE)Cl (20.0 mg, 0.0369 mmol) was placed in a screw cap NMR tube with Teflon septum. Methylene chloride-d_2 (1 mL) charged via syringe into the tube forming a yellow solution. A ^{31}P NMR Spectrum was obtained at room temperature, 295 K. ^{31}P NMR (200 MHz, CD_2Cl_2): δ 33.64 (s). The sample was then cooled to - 50 °C, 223 K and allowed to equilibrate for 10 minutes. ^{31}P NMR (200 MHz, CD_2Cl_2): δ 35.18 (s). The sample was then cooled to - 85 °C, 188 K and allowed to equilibrate for 10 minutes. ^{31}P NMR (200 MHz, CD_2Cl_2): δ 36.24 (br s). The sample was then cooled to - 90 °C, 183 K and allowed to equilibrate for 10 minutes. ^{31}P NMR (200 MHz, CD_2Cl_2): δ 36.26 (br s).

Synthesis of [Ir(COD)(DEPE)]BF_4: RJPI289

[Ir(COD)$(CH_3CN)_2$]Cl (0.4020 g, 0.857 mmol) was placed in a 100 mL side arm flask with a magnetic stir bar. Methylene chloride (20 mL) charged via syringe into the flask forming an yellow solution. A pressure equalizing addition funnel and gas adapter were attached to the flask. Methylene chloride (20 mL) was then added to the funnel. DEPE (0.200 mL, 0.855 mmol) was charged into the funnel. Additional methylene chloride (10 mL) was then added to the funnel to facilitate mixing. The DEPE solution was then added dropwise at a very slow rate into the flask. The addition took 30 minutes and turned the reaction mixture green. The mixture was stirred and warmed to room

temperature over a period of eight hours. Evaporation of solvent to ca. 1-2 mL followed by addition of pentane (10 mL) gave a dark green solid which was dried via vacuum for 15 hours. The dried solid was weighed (0.4613 g, 0.777 mmol) and the percent yield was determined (90.67%). ^{1}H NMR (200 MHz, CD_2Cl_2): δ 4.78 (s, 4.0 H, CH=CH of COD), 2.20 (br s, 8.1 H, CH_2CH_2 of COD), 1.82 (m, J_{H-H} = 7.6 Hz and J_{H-P} = 7.7 Hz, 8.1 H, CH_2), 1.82 (m, J_{H-P} = 13 Hz, 4.1 H, CH_2CH_2 backbone), 1.15 (d t, J_{H-H} = 7.6 Hz and J_{H-P} = 17 Hz, 12.8 H, CH_3). ^{31}P NMR (200 MHz, CD_2Cl_2): δ 52.90 (s).

Synthesis of [Ir(COD)(THP)$_3$]Cl: RJPI273

Tris(hydroxymethyl)phosphine (THP) (0.557 g, 4.464 mmol) was placed in a 50 mL side arm flask with a magnetic stir bar. Deionized water (20 mL) charged via syringe into the flask completely dissolving the THP. $[Ir(COD)Cl]_2$ (0.500, 0.744 mmol) was charged into the flask. The red colored dimer slowly disappears. The mixture was stirred for a period of ten hours. Evaporation of solvent to ca. 0.5 mL followed by addition of pentane (10 mL) gave a white solid which was dried via vacuum for 15 hours. The dried solid was weighed (0.912 g, 1.288 mmol) and the percent yield was determined (86.56%). ^{1}H NMR (200 MHz, D_2O): δ 4.16 (s, 12.3 H, CH_2), 3.74 (s, 4.0 H, CH=CH of COD), 2.23 (br m, 8.2 H, CH_2CH_2 of COD). ^{31}P NMR (200 MHz, D_2O): δ -17.57 (s).

Synthesis of [Ir(COD)(PTA)$_3$]Cl: RJPI161

$[Ir(COD)Cl]_2$ (2.000 g, 2.977 mmol) was placed in a 100 mL side arm flask with a magnetic stir bar. Methylene Chlorine (50 mL) was charged via syringe into the flask forming an orange solution. 1,3,5-triaza-7-phosphaadamantane (PTA) (2.807 g, 17.86

mmol) was charged into the flask. Upon addition of the phosphine, a white precipitate slowly formed. The reaction mixture was stirred for 18 hours. Upon completion, a copious amount white precipitate had formed. The excess solvent was filtered from the solid with a cannula and filter paper into a 50 mL side arm flask. A white solid was dried for 18 hours. The dried solid was weighed (4.412 g, 5.465 mmol) and the percent yield was determined (91.79%). ^{1}H NMR (200 MHz, D_2O): δ 4.47 (s, 18.1 H, NCH_2N), 3.99 (s, 18.2 H, PCH_2N), 3.59 (s, 4.0 H, CH=CH of COD), 2.25 (br m, 8.2 H, CH_2CH_2 of COD). ^{31}P NMR (200 MHz, D_2O): δ -87.13 (s). ^{13}C NMR (100MHz, D_2O): δ 70.56 (s, NCH_2N), 69.38 (s, C=C COD), 53.42 (m, PCH_2N) 33.52 (s, C-C COD). Elemental analysis: Calc'd for $C_{26}H_{48}IrN_9P_3Cl \cdot 2H_2O$: C: 37.0%; H: 6.21%. Found: C: 37.1%; H: 6.29%.

Section 2.5: References

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Chapter 3: Hydrogenation of Iridium Phosphine Complexes

Section 3.1: Introduction

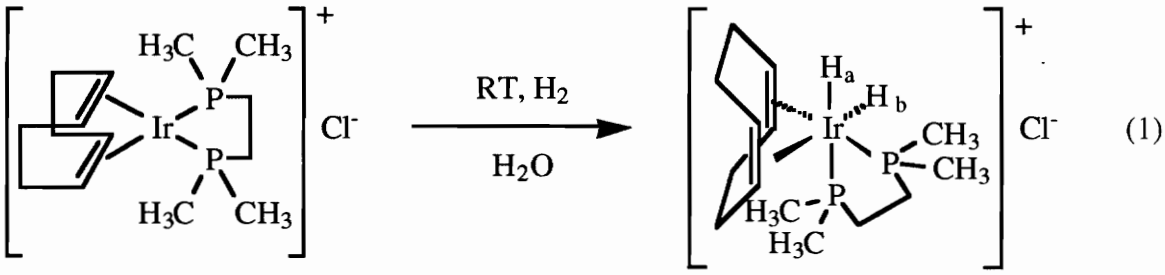
Transition metal hydride compounds are complexes which contain one or more hydrogen atoms bonded directly to the metal via a covalent bond. The first known complexes with metal hydride bonds were the hydridocarbonyls $H_2Fe(CO)_4$ and $HCo(CO)_4$ prepared by Hieber in the 1930's.[1] In their early history, metal hydrides were not fully understood and were thought of as chemical oddities. Since their humble beginnings, metal hydrides have been investigated by industry and academia. Investigators have found a plethora of complexes. Moreover, all d-block metals except hafnium are known to form metal hydride bonds.[2]

These hydrido compounds can undergo a variety of chemical reactions, in particular, hydrogenation, isomerization, hydroformylation, oligomerization and polymerization.[3] Many dihydride compounds are used as catalysts or as catalytic precursors. Moreover, these complexes can give insight into a catalytic system by being used as models for intermediate species never actually seen.

Section 3.2: Hydrogenation of Bidentate Phosphine Complexes

When [Ir(COD)DMPE]Cl was placed in a NMR tube and dissolved with D_2O, the solution turned red from the dissociation of the chloride ion form the metal center. When molecular hydrogen was added via syringe to the tube, the solution turned pale yellow. The ^1H NMR spectrum of this solution displayed two upfield resonances, one a doublet of doublets at -10.38 ppm and the other a triplet at -15.16 ppm. This indicated the presence of two metal-hydride ligands from the oxidative addition of molecular hydrogen. Since

these hydrides were in the presence of an electron rich metal center, they were shielded and thus their resonances appeared at high chemical shifts. The doublet of doublets at -10.38 ($J_{H\text{-}Pcis}$ = 19 Hz, $J_{H\text{-}Ptrans}$ = 89 Hz) corresponds to H_a the hydride trans to one phosphine and cis to the other while the triplet at -15.16 ($J_{H\text{-}Pcis}$ = 19 Hz) corresponds to H_b the hydride cis to two phosphines. Since the dihydrido complex was octahedral and no longer fluxional, the four COD olefinic protons had distinct resonances at 4.59 ppm, 4.21 ppm, 4.10 ppm, and 3.92 ppm. The methyl groups of the DMPE ligands displayed a broad doublet resonance at 1.76 ppm while the methylene groups of the phosphine backbone displayed a broad doublet resonance 1.38 ppm. The aliphatic COD protons showed a complex pattern from 1.50 ppm to 2.75 ppm. The ^{31}P NMR spectrum in D_2O showed two doublets at 9.87 ppm ($J_{P\text{-}P}$ = 12 Hz) and 2.38 ppm ($J_{P\text{-}P}$ = 12 Hz). The phosphine trans to the COD ring was at 9.87 ppm while the phosphine trans to the hydride was at 2.38 ppm. Since an octahedral complex is no longer fluxional and the two phosphines were in different environments, the presence of two signals was further confirmation of the dihydrido complex.



(1)

The stability of this dihydrido complex was investigated. After two hours in D_2O at room temperature, the hydrides exchanged with the deuterium of the solvent. Attempts were made to isolate the dihydride complex in the solid state; however, all have currently

failed and have yielded the original phosphine complex. Although the dihydrido complex was not obtained in the solid state, this result shows the ability of the complexes to undergo facile oxidative addition/ reductive elimination reactions. A quality that is very desirable for homogeneous hydrogenation catalysts.

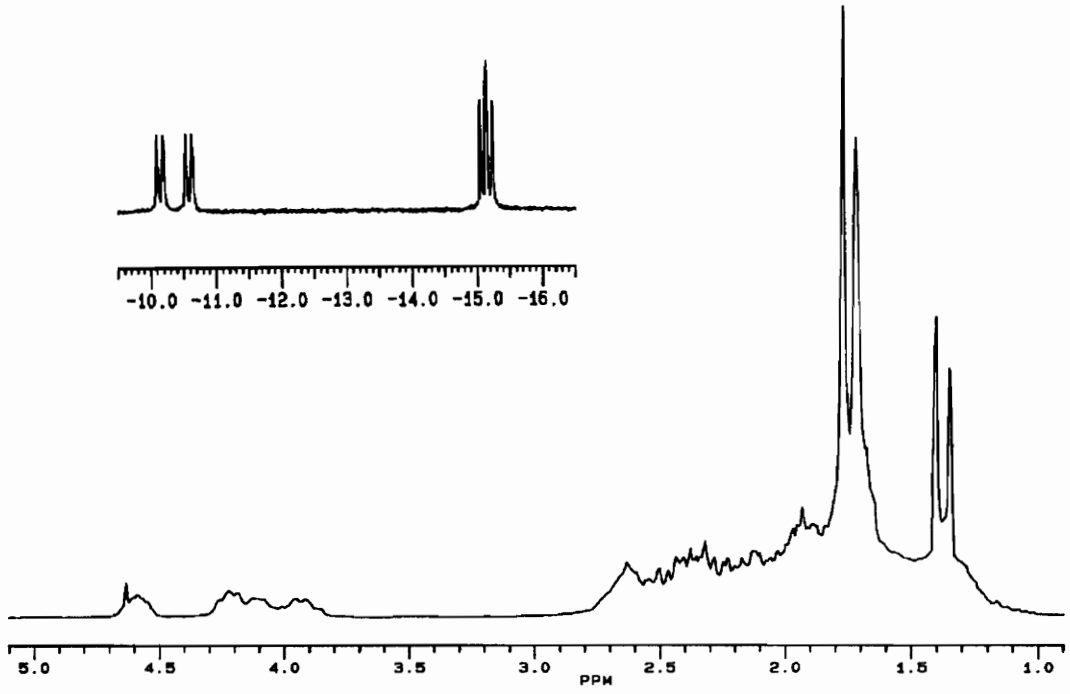
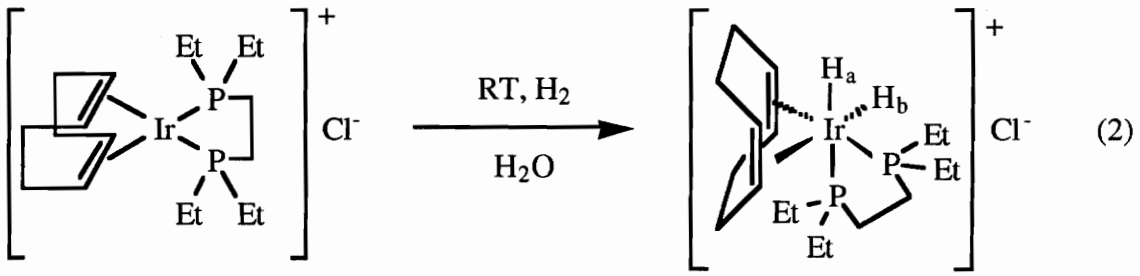


Figure 3.1: 200 MHz ^{1}H NMR Spectrum of [Ir(COD)(H)$_2$(DMPE)]Cl in D$_2$O

In a similar experiment, the aqueous hydrogenation of [Ir(COD)(DEPE)]Cl was studied. When D_2O was added to [Ir(COD)DEPE]Cl was in a NMR tube, the solution turned dark green from the dissociation of the chloride ion form the metal center. When molecular hydrogen was added via syringe to the tube, the solution turned pale yellow. The ^{1}H NMR spectrum of this solution displayed two up field resonances, one a doublet of doublets at -10.49 ppm and the other a triplet at -15.40 ppm. This indicated the presence of two metal-hydride ligands from the oxidative addition of molecular hydrogen. The

doublet of doublets at -10.49 ($J_{H\text{-}Pcis}$ = 18 Hz, $J_{H\text{-}Ptrans}$ = 85 Hz) corresponds to H_a the hydride trans to one phosphine and cis to the other while the triplet at -15.40 ($J_{H\text{-}Pcis}$ = 18 Hz) corresponds to H_b the hydride cis to two phosphines. Since this dihydrido complex was also octahedral and no longer fluxional, the COD olefinic protons had distinct resonances at 4.60 ppm, 4.25 ppm, and two at 4.00 ppm. The methyl groups of the ethyl part of the DEPE ligand displayed a broad fourteen line multiplet resonance at 0.85 ppm while the rest of the spectrum is complex from the methylene backbone of DEPE, the aliphatic COD protons, and the methylene part of the ethyl groups. The ^{31}P NMR spectrum in D_2O showed two doublets at 35.50 ppm ($J_{P\text{-}P}$ = 12 Hz) and 23.62 ppm ($J_{P\text{-}P}$ = 12 Hz). The phosphine trans to the COD ring was at 35.50 ppm while the phosphine trans to the hydride was at 23.62 ppm.



(2)

The stability of this dihydrido complex was also investigated. After two hours in D_2O at room temperature, the hydrides exchanged with the deuterium of the solvent. Attempts were also made to isolate the DEPE dihydride complex in the solid state; however, all have currently failed and have yielded the original phosphine complex. This likewise showed the facile oxidative addition/reductive elimination capabilities of these bidentate complexes.

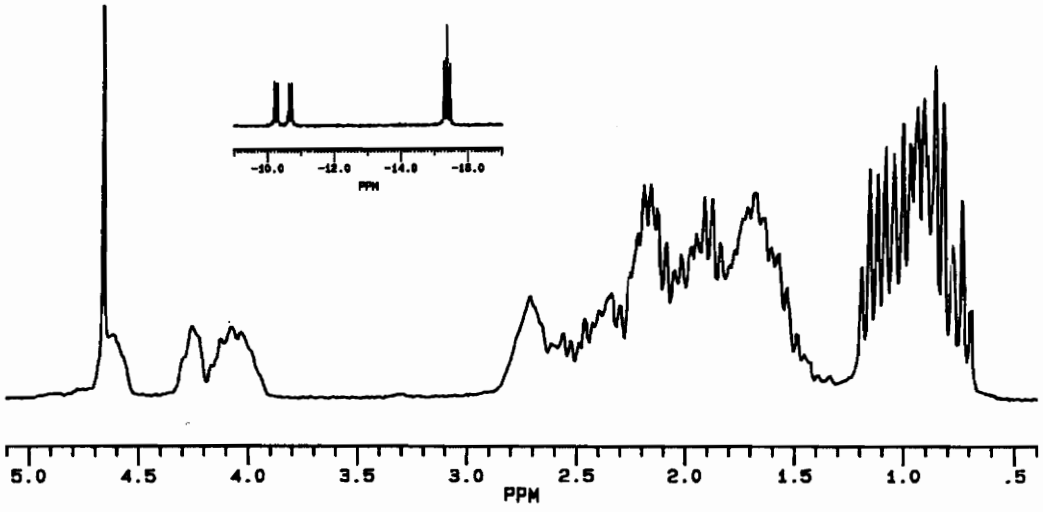


Figure 3.2: 200 MHz ^{1}H NMR Spectrum of [Ir(COD)(H)$_2$DEPE]Cl in D_2O

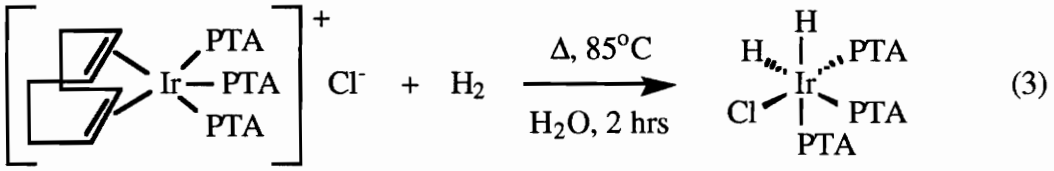
When [Ir(COD)DMPE]BF_4 and [Ir(COD)DEPE]BF_4 were hydrogenated in D_2O, [Ir(COD)(H)$_2$(DMPE)]BF_4 and [Ir(COD)(H)$_2$(DEPE)]BF_4 were produced. These complexes were identified by ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy. The NMR spectra were identical to their chloride counterparts since the chloride and tetrafluoroborate anions were solvated by the D_2O. It should be noted that the tetrafluoroborate salts had poor solubility in aqueous media.

When the hydrogenation of [Ir(COD)DMPE]Cl and [Ir(COD)DEPE]Cl were performed in non-aqueous solvents such as methylene chloride, chloroform, acetone or benzene, the respective dihydrido species seen in water were formed. When only one equivalent of molecular hydrogen was added via syringe, the dihydride quickly underwent reductive elimination of molecular hydrogen to produce the starting [Ir(COD)DMPE]Cl or [Ir(COD)DEPE]Cl, respectively. However, if more than one equivalent of molecular hydrogen was added, further reactivity was observed. The COD ring was reduced partially or completely to cyclooctene or cyclooctane, respectively. This dramatic reactivity demonstrates the ability of these complexes to act as hydrogenation catalysts under mild conditions.

When [Ir(COD)DMPE]BF_4 and [Ir(COD)DEPE]BF_4 were hydrogenated in non-aqueous solvents, the [Ir(COD)$(H)_2$(DMPE)]BF_4 and [Ir(COD)$(H)_2$(DEPE)]BF_4 complexes were produced. Further reactivity was not seen for these dihydride complexes. Reduction of the COD ring was not seen even when excess molecular hydrogen was added. Therefore, the chloride anion must aid in the reduction of the 1,5-cyclooctadiene.

Section 3.3: Hydrogenation of Water Soluble Phosphine Complexes

When [Ir(COD)$(PTA)_3$]Cl was hydrogenated in deionized water at 85°C for two hours, the solution turned from light white to yellow-brown. When the water was evaporated, a yellow-brown solid crystallized. This solid was determined to be the facial isomer of Ir$(H)_2(PTA)_3$Cl.



(3)

Ir$(H)_2(PTA)_3$Cl was identified by ^1H, ^{31}P, ^{13}C NMR spectroscopy and elemental analysis. The complex was soluble in hydrogen bonding solvents, such as water, alcohols and methyl sulfoxide, and the complex was insoluble in chlorinated solvents, such as methylene chlorine and chloroform.

The ^1H NMR spectrum of Ir$(H)_2(PTA)_3$Cl in D_2O displays a singlet at 4.50 ppm corresponding to the axial proton resonances of the methylene group of the PTA ligand with two alpha nitrogens, a singlet at 4.44 ppm corresponding to the equatorial proton resonances of the methylene group of the PTA ligand with two alpha nitrogens, a doublet at 3.95 ppm corresponding to the methylene proton resonances of the PTA ligand with one

alpha phosphorous and one alpha nitrogen, and pseudo doublet of triplets at -14.00 ppm corresponding to the hydrides.

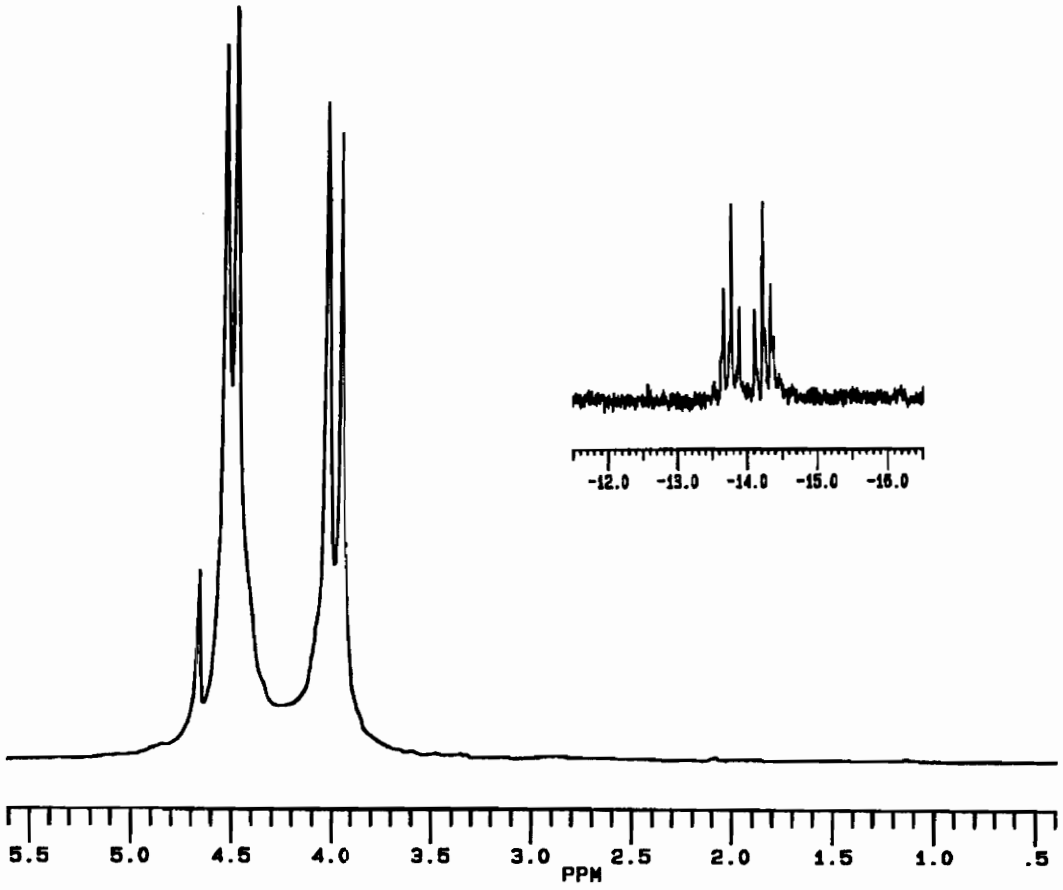
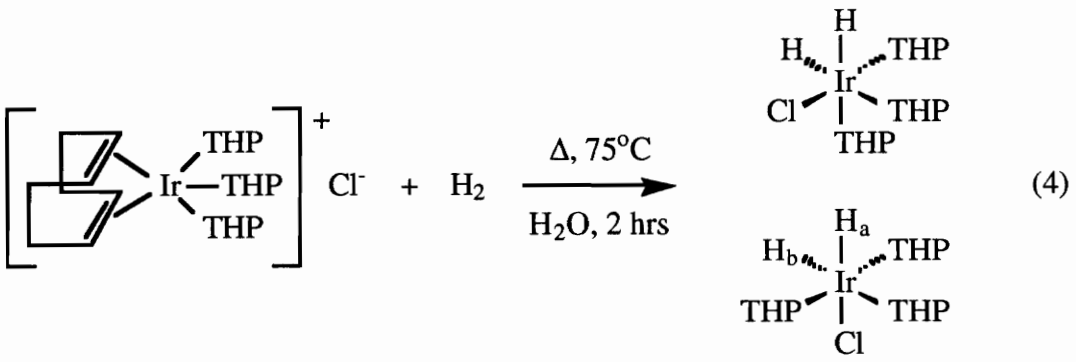


Figure 3.3: 200 MHz ^{1}H NMR Spectrum of Ir(H)2(PTA)3Cl in D2O

When [Ir(COD)(THP)3]Cl (THP = $P(CH_2OH)_3$) was hydrogenated in deionized water at 75°C for two hours, the solution turned from clear to light yellow. When the water was evaporated, a yellow oily solid formed. This solid was elucidated to be a mixture of the facial and meridonal isomers of Ir(H)2(THP)3Cl.



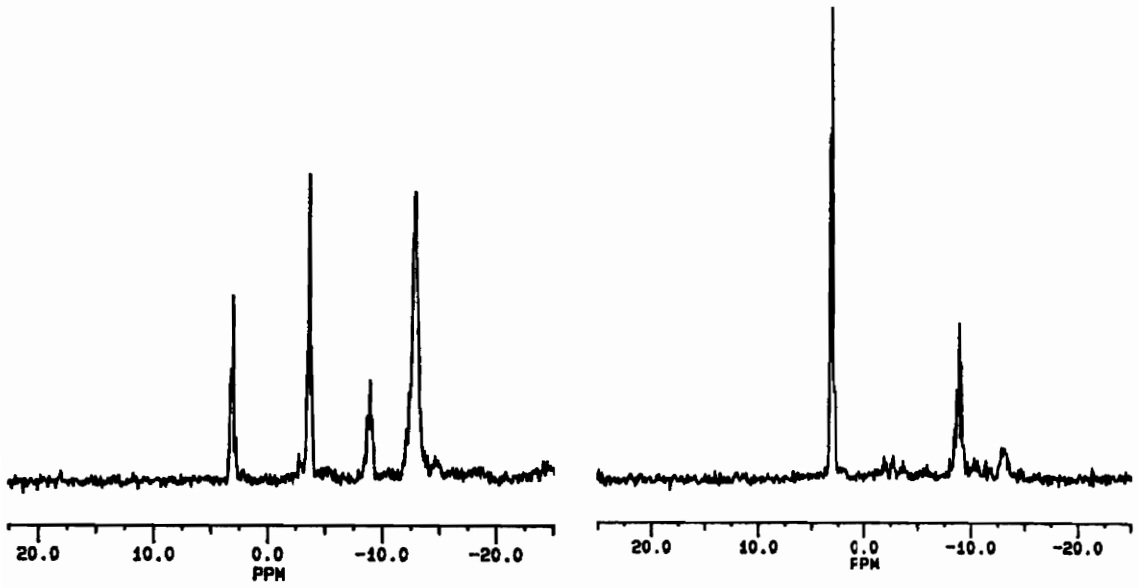
(4)

$Ir(H)_2(THP)_3Cl$ was identified by ^1H and ^{31}P NMR spectroscopy. The complex was soluble in hydrogen bonding solvents, such as water, alcohols and methyl sulfoxide, and the complex was insoluble in chlorinated solvents, such as methylene chlorine and chloroform.

The ^1H NMR spectrum of $Ir(H)_2(THP)_3Cl$ in D_2O displays a complex 5.0 to 3.5 ppm region. This was from the over lap of the facial and meridonal isomers. However, the dissociated COD resonances were no longer seen since it was evaporated with the solvent. The hydride region of the ^1H NMR spectrum shows three resonances: a doublet of triplets at -11.4 ppm, an overlapping doublet of triplets at -14.0 ppm, and an overlapping doublet of quartets at -25.3 ppm. The meridonal isomer has two chemically inequivalent hydrides. The hydride that is *trans* to one phosphine and *cis* to two phosphines gave the resonance at -11.4 ppm while the hydride *cis* to three phosphines and *trans* to the chloride gave the resonance at -25.3 ppm. The facial isomer has two hydrides but these are in equivalent environments; thus, their resonances were the same at -14.0 ppm.

In order to try and make only one isomer, a series of experiments were performed to hydrogenate $[Ir(COD)(THP)_3]Cl$ at different temperatures. The starting complex was dissolved in D_2O and then hydrogenated for 30 minutes at a specified temperature. NMR spectroscopy was obtained on the sample. Then the sample was hydrogenated for 30

minutes longer. Figure 3.6 displays the ^{31}P spectra for the experiments performed at 95 °C. In the spectrum for the 30 minute experiment, four signals are seen: 3.0 ppm, -3.8 ppm, -9.0 ppm, and -13.0 ppm. The spectrum for the 60 minute experiment has enhancements of the 3.0 ppm and -9.0 ppm signals while the -3.8 ppm and -13.0 ppm are dramatically decreased in their intensity. From these experiments, the thermodynamically favored isomer is the one which is present in the 60 minute spectrum. This corresponds to the meridonal isomer. The kinetically favored isomer is the facial since it is formed first but over time it converts to the meridonal over time. This is consistent with the findings of Eisenberg on the concerted addition of molecular hydrogen to square planar complexes with different substitutes.[4]



30 min 60 min

Figure 3.4: 80 MHz ^{31}P NMR Spectrum of mer-and fac-Ir(H)2(THP)3Cl in D_2O at 95 °C

Section 3.4: Catalytic Activity

Since the complexes [Ir(COD)DMPE]Cl and [Ir(COD)DEPE]Cl reacted with molecular hydrogen under ambient conditions, it seemed likely that the compounds could act as homogeneous hydrogenation catalysts or as precursors. In order to best understand the aqueous hydrogenation chemistry, a model system was used that had been developed to keep both substrate and product in the water.[5] The system used allyl alcohol as the substrate since it and the resulting n-propanol were water soluble. The reaction was monitored by ^1H NMR spectroscopy. Thus, D_2O was used as the solvent medium. The advantage of this system was that the disappearance of allyl alcohol and the formation of n-propanol could be monitored since their resonances do not over lap on the ^1H NMR spectrum. The integration of the signals can be used to determine consumption of reactants and formation of products. Figure 3.5 shows a typical ^1H NMR spectrum for the hydrogenation of allyl alcohol to n-propanol.

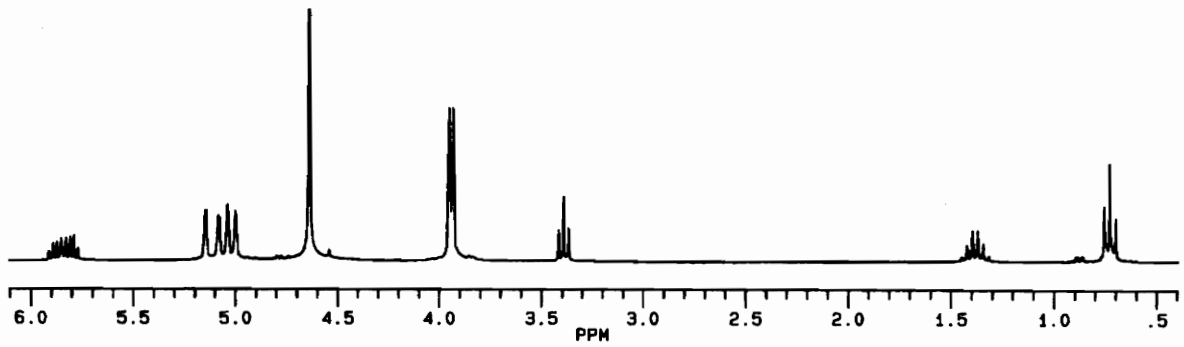


Figure 3.5: 270 MHz ^1H NMR Spectrum of the Hydrogenation of Allyl Alcohol in D_2O

Allyl alcohol displays a triplet at 3.95 ppm corresponding to the methylene protons alpha to the alcohol, two doublets at 5.02 and 5.06 ppm corresponding to the vinyl methylene protons, and a multiplet at 5.82 ppm corresponding to the olefinic methyne proton. The

resonances from n-propanol are a multiplet at 3.40 ppm corresponding to the methylene protons alpha to the alcohol, a multiplet at 1.39 ppm corresponding to the internal methylene protons, and a triplet at 0.72 ppm corresponding to the methyl protons. These resonances were used to determine the concentrations of substrate and product in solution after each catalytic experiment. Since ^1H NMR spectroscopy is the measurement source for percent conversion, an error of +/- 10% of the peak are obtained for the integration is assumed.

The hydrogenation reactions of allyl alcohol with the iridium bidentate phosphine complexes were carried out in a Parr 4841 stainless steel high pressure reactor. A ratio of substrate to catalyst of 2000:1 was used and the reaction was performed at 50 °C and with 200 psi of H_2. Unfortunately, quantitating the amounts was not possible for the reactor had been contaminated with rhodium metal and heterogeneous catalysis was also occurring. a rough estimate can be made by subtracting the percent conversion of the catalytic experiment by an experiment that had the same amount of substrate but no catalyst.

For $[Ir(COD)(DMPE)(H)_2]Cl$ complex, the estimated percent conversion corresponds to a turnover frequency of approximately 250 cycles per hour. For the $[Ir(COD)(DEPE)(H)_2]Cl$ complex, the estimated turnover frequency was approximately 300 cycles per hour. These numbers show that these complexes are aqueous homogeneous catalysts.

The fac-$Ir(H)_2(PTA)_3Cl$ complex was also investigated for its catalytic activity. Once again the results must be used qualitatively, not quantitatively. For a catalytic experiment with a 2000:1 ratio of substrate to complex at 50 °C and 200 psi of H_2, the estimated turnover frequency was 600 cycles per hour. This data shows that the fac-$Ir(H)_2(PTA)_3Cl$ complex is an aqueous homogeneous catalyst. At the time of this thesis, the $Ir(H)_2(THP)_3Cl$ complex had not been studied for its catalytic activity.

Section 3.5: Experimental

Hydrogenation Study of Ir(COD)(DMPE)Cl in D_2O: RJPI275

Ir(COD)(DMPE)Cl (20.0 mg, 0.0412 mmol) was placed in a screw cap NMR tube with Teflon septum. D_2O (1 mL) charged via syringe into the tube forming a red solution. Initial ^1H and ^{31}P NMR Spectra were obtained to confirm the starting material. Two complexes are seen in the NMR spectra. One in which the chlorine is not attached to the iridium center and one where it is. ^1H NMR (200 MHz, D_2O): δ 4.74 (s, 4.0 H, CH=CH of COD), 2.15 and 2.00 (br m, 8.1 H, CH_2CH_2 of COD), 1.74 (d, J_{H-P} = 10 Hz, 1.2 H, CH_2CH_2 backbone-attached Cl), 1.72 (d, J_{H-P} = 16 Hz, 4.2 H, CH_2CH_2 backbone), 1.55 (d, J_{H-P} = 12 Hz, 3.2 H, CH_3-attached Cl), 1.47 (d, J_{H-P} = 10 Hz, 12.3 H, CH_3). Some other complex signals are present. ^{31}P NMR (200 MHz, D_2O): δ 29.28 (s, 4.5 P, complex with chlorine not attached), 15.32 (s, 1.0 P, complex with chlorine attached).

One half molar equivalent of molecular hydrogen (0.5 mL, 0.02 mmol) was added via syringe to the tube. The tube was vigorously shaken for two minutes. The solution turned pale yellow in color. ^1H and ^{31}P NMR Spectra were obtained for the resulting product. ^1H NMR (200 MHz, D_2O): δ 4.74 (br s, 2 H, CH=CH of COD-starting), 4.59 (br s, 1 H, CH=CH of COD-dihydride), 4.21 (br s, 1 H, CH=CH of COD-dihydride), 4.10 (br s, 1 H, CH=CH of COD-dihydride), 3.92 (br s, 1 H, CH=CH of COD-dihydride), 1.76 (d, J_{H-P} = 10 Hz, 12 H, CH_3-dihydride), 1.55 (d, J_{H-P} = 12 Hz, 2 H, CH_3-starting), 1.47 (d, J_{H-P} = 10 Hz, 6 H, CH_3-starting), 1.38 (d, J_{H-P} = 12 Hz, 4 H, CH_2CH_2 backbone-dihydride), -10.38 (d d, J_{H-Pcis} = 19 Hz, $J_{H-Ptrans}$ = 89 Hz, 1.0 H, hydride trans to one phosphine and cis to other phosphine), -15.16 (t, J_{H-Pcis} = 19 Hz, 1.0 H, hydride cis to two phosphines). The rest of the spectrum is complex. ^{31}P NMR (200 MHz, D_2O): δ 29.21 (s, starting material), 15.32 (s, starting material-attached Cl),

9.02 (d, J_{P-P} = 12 Hz, phosphorus trans to COD), 1.37 (d, J_{P-P} = 12 Hz, phosphorus trans to hydride).

An additional one half molar equivalent of molecular hydrogen (0.5 mL, 0.0206 mmol) was added via syringe to the tube. The tube was vigorously shaken for two minutes. ^{1}H and ^{31}P NMR Spectra were obtained for the resulting product. ^{1}H NMR (200 MHz, D_2O): δ 4.59 (br s, 1 H, CH=CH of COD-dihydride), 4.21 (br s, 1 H, CH=CH of COD-dihydride), 4.10 (br s, 1 H, CH=CH of COD-dihydride), 3.92 (br s, 1 H, CH=CH of COD-dihydride), 1.76 (d, J_{H-P} = 10 Hz, 12 H, CH_3-dihydride), 1.55 (d, J_{H-P} = 12 Hz, 2 H, CH_3-starting), 1.38 (d, J_{H-P} = 12 Hz, 4 H, CH_2CH_2 backbone-dihydride), -10.38 (d d, J_{H-Pcis} = 19 Hz, $J_{H-Ptrans}$ = 89 Hz, 1.0 H, hydride trans to one phosphine and cis to other phosphine), -15.16 (t, J_{H-Pcis} = 19 Hz, 1.0 H, hydride cis to two phosphines). The rest of the spectrum is complex. ^{31}P NMR (200 MHz, D_2O): δ 15.32 (s, starting material-attached Cl), 9.02 (d, J_{P-P} = 12 Hz, phosphorus trans to COD), 1.37 (d, J_{P-P} = 12 Hz, phosphorus trans to hydride).

Additional aliquots of molecular hydrogen were added in one molar equivalents until four molar equivalents had been added. ^{1}H and ^{31}P NMR Spectra were obtained after each addition. Very slight differences where seen in the ^{1}H NMR spectra after the second addition of hydrogen. In the ^{31}P NMR Spectra, the peak at 15.32 ppm decreased in intensity until it was finally gone while the peaks at 9.02 ppm and 1.37 ppm increased slightly with each addition aliquot.

Hydrogenation Study of Ir(COD)(DMPE)Cl in CD_2Cl_2: RJPI277

Ir(COD)(DMPE)Cl (20.0 mg, 0.0412 mmol) was placed in a screw cap NMR tube with Teflon septum. Methylene chloride-d_2 (1 mL) charged via syringe into the tube forming a yellow solution. Initial ^{1}H and ^{31}P NMR Spectra were obtained to confirm the starting material. One half molar equivalent of molecular hydrogen (0.5 mL, 0.02 mmol)

was added via syringe to the tube. The tube was vigorously shaken for two minutes. ^{1}H and ^{31}P NMR Spectra were obtained for the resulting product. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 4.69 (br s, 2.0 H, CH=CH of COD-dihydride), 4.36 (br s, 1.0 H, CH=CH of COD-dihydride), 4.12 (br s, 1.0 H, CH=CH of COD-dihydride), 3.65 (s, 3.1 H, CH=CH of COD-starting), 2.16 (d, J_{H-P} = 10 Hz, 4.5 H, CH_2CH_2 backbone-dihydride), 1.89 (d, J_{H-P} = 10 Hz, 8.9 H, CH_3-dihydride), 1.81 (d, J_{H-P} = 11 Hz, 8.2 H, CH_3-dihydride), 1.47 (d, J_{H-P} = 10 Hz, 9.3 H, CH_3-starting), -10.17 (d d, J_{H-Pcis} = 19 Hz, $J_{H-Ptrans}$ = 89 Hz, 1.0 H, hydride trans to phosphine), -15.10 (t, J_{H-Pcis} = 19 Hz, 1.0 H, hydride trans to COD). The rest of the spectrum is complex. ^{31}P NMR (200 MHz, CD_2Cl_2): δ 14.39 (s, starting material), 10.13 (d, J_{P-P} = 12 Hz, phosphorus trans to COD), 2.68 (d, J_{P-P} = 12 Hz, phosphorus trans to hydride).

An additional one half molar equivalent of molecular hydrogen (0.5 mL, 0.0206 mmol) was added via syringe to the tube. The tube was vigorously shaken for two minutes. ^{1}H and ^{31}P NMR Spectra were obtained for the resulting product. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 4.69 (br s, 2.0 H, CH=CH of COD-dihydride), 4.36 (br s, 1.0 H, CH=CH of COD-dihydride), 4.12 (br s, 1.0 H, CH=CH of COD-dihydride), 2.16 (d, J_{H-P} = 10 Hz, 4.5 H, CH_2CH_2 backbone-dihydride), 1.89 (d, J_{H-P} = 10 Hz, 8.9 H, CH_3-dihydride), 1.81 (d, J_{H-P} = 11 Hz, 8.2 H, CH_3-dihydride), -10.17 (d d, J_{H-Pcis} = 19 Hz, $J_{H-Ptrans}$ = 89 Hz, 1.0 H, hydride trans to phosphine), -15.10 (t, J_{H-Pcis} = 19 Hz, 1.0 H, hydride trans to COD), -21.19 (d d, J_A = 10 Hz, J_B = 15 Hz, 0.04 H), -21.78 (d d, J_A = 10 Hz, J_B = 20 Hz, 0.05 H). The rest of the spectrum is complex. ^{31}P NMR (200 MHz, CD_2Cl_2): δ 13.05 (s), 10.13 (d, J_{P-P} = 12 Hz, phosphorus trans to COD), 2.68 (d, J_{P-P} = 12 Hz, phosphorus trans to hydride), -1.58 (s).

Additional aliquots of molecular hydrogen were added in one molar equivalents until seven molar equivalents had been added. ^{1}H and ^{31}P NMR Spectra were obtained after each addition. In the ^{1}H Spectra, the 10 ppm to 0 ppm region becomes complex with

each addition. The hydride region from 0 ppm to -30 ppm has the original hydride signals at -10.17 ppm and -15.10 ppm decrease in intensity while the far upfield signals at -21.19 ppm and -21.78 ppm increase. In the ^{31}P NMR Spectra, the signals at 10.13 ppm and 2.68 ppm decrease until they are no longer seen while the signals at 13.05 ppm and -1.58 ppm increase.

Hydrogenation Study of [Ir(COD)(DMPE)]BF_4 in CD_2Cl_2: RJPI095

[Ir(COD)(DMPE)]BF_4 (20.0 mg, 0.0372 mmol) was placed in a screw cap NMR tube with Teflon septum. Methylene chloride-d_2 (1 mL) charged via syringe into the tube forming a yellow-brown solution. Initial ^{1}H and ^{31}P NMR Spectra were obtained to confirm the starting material. One half molar equivalent of molecular hydrogen (0.5 mL, 0.02 mmol) was added via syringe to the tube. The tube was vigorously shaken for two minutes. ^{1}H and ^{31}P NMR Spectra were obtained for the resulting product. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 4.69 (br s, 2.0 H, CH=CH of COD-dihydride), 4.36 (br s, 1.0 H, CH=CH of COD-dihydride), 4.12 (br s, 1.0 H, CH=CH of COD-dihydride), 3.65 (s, 3.1 H, CH=CH of COD-starting), 2.16 (d, J_{H-P} = 10 Hz, 4.5 H, CH_2CH_2 backbone-dihydride), 1.89 (d, J_{H-P} = 10 Hz, 8.9 H, CH_3-dihydride), 1.81 (d, J_{H-P} = 11 Hz, 8.2 H, CH_3-dihydride), 1.47 (d, J_{H-P} = 10 Hz, 9.3 H, CH_3-starting), -10.17 (d d, J_{H-Pcis} = 19 Hz, $J_{H-Ptrans}$ = 89 Hz, 1.0 H, hydride trans to phosphine), -15.10 (t, J_{H-Pcis} = 19 Hz, 1.0 H, hydride trans to COD). The rest of the spectrum is complex. ^{31}P NMR (200 MHz, CD_2Cl_2): δ 14.39 (s, starting material), 10.13 (d, J_{P-P} = 12 Hz, phosphorus trans to COD), 2.68 (d, J_{P-P} = 12 Hz, phosphorus trans to hydride).

Hydrogenation Study of Ir(COD)(DEPE)Cl in D_2O: RJPI157

Ir(COD)(DEPE)Cl (20.0 mg, 0.0369 mmol) was placed in a screw cap NMR tube with Teflon septum. D_2O (1 mL) charged via syringe into the tube forming a green solution. Initial ^1H and ^{31}P NMR Spectra were obtained to confirm the starting material. One molar equivalent of molecular hydrogen (0.9 mL, 0.0369 mmol) was added via syringe to the tube. The tube was vigorously shaken for two minutes. The color changed to a pale yellow. ^1H and ^{31}P NMR Spectra were obtained for the resulting product. ^1H NMR (200 MHz, D_2O): δ 4.63 (br s, 1 H, CH=CH of COD-dihydride), 4.25 (br s, 1 H, CH=CH of COD-dihydride), 4.07 (br s, 2 H, CH=CH of COD-dihydride), 0.92 (br m, 12 H ,CH_3), -10.49 (d d, $J_{H\text{-}Pcis}$ = 18 Hz, $J_{H\text{-}Ptrans}$ = 90 Hz, 1.0 H, hydride trans to one phosphine and cis to other phosphine), -15.40 (t, $J_{H\text{-}Pcis}$ = 18 Hz, 1.0 H, hydride cis to two phosphines). The rest of the spectrum is complex. ^{31}P NMR (200 MHz, D_2O): δ 35.50 (d, $J_{P\text{-}P}$ = 14 Hz, phosphorus trans to COD), 23.61 (d, $J_{P\text{-}P}$ = 14 Hz, phosphorus trans to hydride).

Hydrogenation Study of Ir(COD)(DEPE)Cl in CD_2Cl_2: RJPI159

Ir(COD)(DEPE)Cl (20.0 mg, 0.0369 mmol) was placed in a screw cap NMR tube with Teflon septum. Methylene chloride-d_2 (1 mL) charged via syringe into the tube forming a yellow solution. Initial ^1H and ^{31}P NMR Spectra were obtained to confirm the starting material. One molar equivalent of molecular hydrogen (0.9 mL, 0.0369 mmol) was added via syringe to the tube. The tube was vigorously shaken for two minutes. ^1H and ^{31}P NMR Spectra were obtained for the resulting product. ^1H NMR (200 MHz, CD_2Cl_2): δ 4.65 (br s, 2.0 H, CH=CH of COD-dihydride), 4.35 (br s, 1.0 H, CH=CH of COD-dihydride), 4.01 (br s, 1.0 H, CH=CH of COD-dihydride), -10.17 (d d, $J_{H\text{-}Pcis}$ = 19 Hz, $J_{H\text{-}Ptrans}$ = 89 Hz, 1.0 H, hydride trans to phosphine), -15.10 (t, $J_{H\text{-}Pcis}$ = 19

Hz, 1.0 H, hydride trans to COD). The rest of the spectrum is complex. ^{31}P NMR (80 MHz, CD_2Cl_2): δ 36.57 (d, J_{P-P} = 12 Hz, phosphorus trans to COD), 23.83 (d, J_{P-P} = 12 Hz, phosphorus trans to hydride).

Additional aliquots of molecular hydrogen were added in one molar equivalents until seven molar equivalents had been added. ^{1}H and ^{31}P NMR Spectra were obtained after each addition. In the ^{1}H Spectra, the 10 ppm to 0 ppm region becomes complex with each addition. The hydride region from 0 ppm to -30 ppm has the original hydride signals at -10.27 ppm and -15.34 ppm decrease in intensity while a new hydride signal far upfield signal at -21.65 ppm that grows in.

Hydrogenation Study of [Ir(COD)(DEPE)]BF_4 in CD_2Cl_2: RJPI283

[Ir(COD)(DEPE)]BF_4 (20.0 mg, 0.0337 mmol) was placed in a screw cap NMR tube with Teflon septum. Methylene chloride-d_2 (1 mL) charged via syringe into the tube forming a yellow solution. Initial ^{1}H and ^{31}P NMR Spectra were obtained to confirm the starting material. One molar equivalent of molecular hydrogen (0.9 mL, 0.0337 mmol) was added via syringe to the tube. The tube was vigorously shaken for two minutes. ^{1}H and ^{31}P NMR Spectra were obtained for the resulting product. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 4.76 (br s, 1.0 H, CH=CH of COD-dihydride), 4.30 (br s, 1.0 H, CH=CH of COD-dihydride), 4.20 (br s, 1.0 H, CH=CH of COD-dihydride), 4.06 (s, 1.0 H, CH=CH of COD-dihydride), 1.12 (br m, 12 H, CH_3), -10.24 (d d, J_{H-Pcis} = 18 Hz, $J_{H-Ptrans}$ = 90 Hz, 1.0 H, hydride trans to phosphine), -15.22 (t, J_{H-Pcis} = 18 Hz, 1.0 H, hydride trans to COD). The rest of the spectrum is complex. ^{31}P NMR (200 MHz, CD_2Cl_2): δ 36.07 (d, J_{P-P} = 12 Hz, phosphorus trans to COD), 23.43 (d, J_{P-P} = 12 Hz, phosphorus trans to hydride).

Synthesis of $Ir(H)_2(PTA)_3Cl$: RJPI165

[Ir(COD)(PTA)3]Cl (1.000 g, 1.239 mmol) was placed in a 50 mL two-neck flask with stirbar. A gas adapter and reflux condensor was attached to the flask while a septum was placed over the second hole. Deionized water (20 mL) was charged via syringe into the flask forming a pale white solution. Molecular hydrogen was then added at a slow rate through a teflon needle and then the flask was placed in a 85 °C oil bath. The solution was stirred and hydrogenated for two hours. Upon completion, the solution was dark yellow. The solvent was evaporated leaving a light brownish-yellow solid. The solid was dried via vacuum for 15 hours. The dried solid was weighed (0.800 g, 1.141 mmol) and the percent yield was determined (92.09%). ^1H NMR (200 MHz, D_2O): δ 4.50 (s, 9.1 H, NCH_2N-ax), 4.44 (s, 9.1 H, NCH_2N-eq), 3.95 (d, J_{H-P} = 30 Hz, 18.2 H, PCH_2N), -14.0 (m, 2.0 H, hydrides). ^{31}P NMR (160 MHz, D_2O): δ -78.65 (m), -86.80 (m). ^{13}C NMR (100 MHz, D_2O): δ 70.33 (s, NCH_2N), 56.65 (d, J_{C-P} = 170 Hz, PCH_2N) . Elemental analysis: Calc'd for $C_{18}H_{38}IrN_9P_3Cl \cdot 2H_2O$: C: 29.33%; H: 5.74%. Found: C: 29.34%; H: 5.75%.

Hydrogenation of [Ir(COD)(THP)3]Cl in D_2O: RJPI225

[Ir(COD)(THP)3]Cl (20.0 mg, 0.0282 mmol) was placed in a screw cap NMR tube with Teflon septum. D_2O (1 mL) charged via syringe into the tube forming a clear solution. Initial ^1H and ^{31}P NMR Spectra were obtained to confirm the starting material. Molecular hydrogen was bubbled via syringe into the tube. The tube was heated at 95 °C for thirty minutes. ^1H and ^{31}P NMR spectra were obtained for the resulting product. ^1H NMR spectrum was complex. ^{31}P NMR (200 MHz, D_2O): δ 3.0 (br s), -3.8 (br s), -9.0 (br s), -13.0 (br s). The tube was then heated for heated for an addition 30 minutes and ^1H

and ^{31}P NMR spectra were obtained. The ^{1}H NMR spectrum was complex. ^{31}P NMR (200 MHz, D_2O): δ 3.0 (br s), -9.0 (br s).

General Procedure for Hydrogenation Reactions

The following procedure was used for hydrogenation reactions with bidentate phosphine catalysts:

Into the Parr 4841 stainless steel autoclave, solvent and substrate were charged. The autoclave was attached to the reactor and stirred magnetically at half power. All valves were closed and the reactor was heated to the desired temperature with a heating mantle and allowed to equilibrate for fifteen minutes. The catalyst was then added and molecular hydrogen was then flushed through the system several times to expel the air from the reactor. The system was then charged to the desired pressure of hydrogen and sampled at appropriate time intervals. The aliquots were transferred into NMR tubes and sealed until analysis was performed. Percent conversions were determined from integration values with error of $\pm$ 10%.

The following procedure was used for hydrogenation reactions with water soluble phosphine catalysts:

Into the Parr 4841 stainless steel autoclave, catalyst, solvent, and substrate were charged. The autoclave was attached to the reactor and stirred via magnetic stirrer at half power. All valves were closed and the reactor was heated to the desired temperature via heating mantle and allowed to equilibrate for fifteen minutes. Molecular hydrogen was then flushed through the system several times to expel the air from the reactor. The system was then charged to the desired pressure of hydrogen and sampled at appropriate time intervals.

The aliquots were transferred into NMR tubes and sealed until analysis was performed.

Percent conversions were determined from integration values with error of ± 10%.

Section 3.5: References

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Chapter 4: Conclusions and Future Work

Section 4.1: Conclusions

The research in this thesis were aimed at the design, synthesis and application of water soluble iridium complexes using bidentate phosphines and water soluble phosphines as ligands. These novel complexes were examined for their catalytic activity in homogeneous hydrogenation.

In this thesis, the synthesis of several novel iridium-phosphine complexes were reported. The dimeric complex $[Ir(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) has been found to undergo bridge-splitting reactions with bidentate phosphine ligands to produce coordinatively unsaturated, 16 electron complexes of the form [Ir(COD)(P-P)]Cl (P-P) = [DMPE] and [DEPE]. These compounds have been found to be both water soluble and reactive towards molecular hydrogen at room temperature. When hydrogenated in water, the product was an 18 electron coordinatively saturated compound $[Ir(COD)(H)_2(P\text{-}P)]Cl$.

Water-soluble ligands were also allowed to react with $[Ir(COD)Cl]_2$. In these cases, the product was analogous to $[Ir(COD)(PMe_3)_3]Cl$ complex. Two water-soluble phosphines were examined: 1,3,5-triaza-7-phosphaadamantane [PTA] and tris(hydroxy-methyl)phosphine [THP]. When these complexes were hydrogenated in water, the PTA complex underwent an oxidative addition of molecular hydrogen with the loss of COD to form the facial isomer of $Ir(H)_2(PTA)_3Cl$. However, the THP made both meridonal and facial isomers of $Ir(H)_2(THP)_3Cl$ upon hydrogenation. The facial was determined to be the kinetically favored product while the meridonal was the thermodynamically favored product.

The complexes Ir(COD)(DMPE)Cl, Ir(COD)(DEPE)Cl, and Ir(H)2(PTA)3Cl were determined to aqueous hydrogenation catalysts. They catalyzed in the reduction allyl alcohol to n-propanol under relative mild conditions.

Section 4.2: Future Work

Qualitative catalytic activity was determined for three of the compounds. The THP complexes need to be investigated for their possible catalytic activity. Moreover, all of the complexes need quantitative data collected on their catalytic activity; that is, activation energies, turnover frequencies, and product distributions. A solvent investigation needs to be performed to see how the bidentate complexes compare to Crabtree's catalysts. Furthermore, since these bidentate complexes are coordinatively unsaturated, they might also be catalysts for hydroformylation, hydrosilation, or hydrocyanation.

The water-soluble complexes both hydrogenated and not need to be examined in the same manner as did the [Ir(COD)(PMe3)3]Cl complex; that is, oxidative addition reactions of N-H, O-H, B-H, etc. Since these compounds are highly water soluble, with the right ligands added, they could have biologically activity similar to the iridium-amino acid complexes that use PMe3.

Vita

Robert J. Pafford, IV was born in Vermillion, South Dakota on January 5, 1970 to Robert and Charlsie Pafford. After graduating from Cave Spring High School in Roanoke, Virginia in 1988, he enrolled at Virginia Tech, pursuing a degree in Chemical Engineering. After two long years of confusion, he switched his major and life to Chemistry. After graduating Virginia Tech with a B.S. in Chemistry in 1992, he decided to continue his education at Virginia Tech and joined the Merola group in the spring of 1993. Here he spent the next two years researching aqueous homogeneous catalysis and finding himself. While at Virginia Tech, Robert was a member of Alpha Chi Sigma, Phi Lambda Upsilon, and the American Chemical Society - Student Affiliates. Robert will continue his chemical education at the University of Illinois Urbana-Champaign.