

**INVESTIGATIONS INTO THE MECHANISMS OF CATALYTIC ALIPHATIC
DEHYDROGENATION BY TRANSBISPHOSPHINE IRIIDIUM
COMPLEXES**

A THESIS SUBMITTED TO THE GRADUATE DIVISION OF THE UNIVERSITY OF
HAWAII IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

IN

CHEMISTRY

AUGUST 2012

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ACKNOWLEDGEMENTS

I would like to acknowledge the following persons:

Professor Craig Jensen for his support, insight and encouragement in the completion of my thesis.

Professor Kristin Kumashiro, Chemistry Department Chair, and Peter Garrod, the Interim Assistant Vice Chancellor for Research and Graduate Education for their assistance and cooperation in getting me reinstated into the graduate program.

The Jensen Research Group graduate students, post docs and researchers for answering my many questions and generously offering their expertise in numerous areas.

Wes Yoshida and Dr. Walt Niemczura for technical NMR support.

All of my teachers and students over the years.

Thank You.

ABSTRACT

*trans*bisphosphine iridium complexes represent a class of homogeneous catalysts with high potential for alkane to olefin transformation applications. The chemical industry is almost exclusively olefin-based and catalysts are responsible for the manufacture of most of the products. Consequently, the design and synthesis of a catalyst that can selectively produce the desired olefins from the enormous stock of alkanes available from petroleum and natural gas, is highly desirable. An understanding of the fine mechanistic processes occurring during the catalytic cycle is invaluable to the successful synthesis of a practical system. Therefore, we investigated the mechanisms of catalytic aliphatic dehydrogenations by *trans*bisphosphine iridium complexes.

A deuterium labeling study was undertaken to probe agostic interactions in the dehydrogenation reaction pathways of four related *trans*bisphosphine iridium complexes in order to understand what role intramolecular interactions play in the catalyst's performance. The labeling studies included a rate study to compare the catalysts' agostic activities. These studies were followed with reaction of the complexes in neat neohexene to further elucidate the mechanisms.

The results of these investigations reveal how agostic interactions stabilize significant intermediates and even stimulate important reaction steps of the catalytic cycle. The higher activity of the pincer type catalysts was shown to be attributable to their agostic access facility endowed by their molecular structure.

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LIST OF ABBREVIATIONS

α	Alpha
A	Pre-exponential factor
\AA	Angstrom(s)
β	Beta
B	Boron
Bu^t	Tertiary butyl
χ	Gamma
C	Carbon
cal	Calorie(s)
Cl	Chlorine
$^{\circ}\text{C}$	Degree(s) Celsius
δ or Δ	Delta
D or d or ^2H	Deuterium
dacoda	1,5-diazacyclooctane-N,N -diacetate
DIPPX	Diisopropylphosphinoxylene
e^-	electron(s)
E_a	Activation Energy
Et	Ethyl
η	Eta
g	Gram(s)
G	Gibbs Free energy
GC	Gas chromatography
h	Hour(s)
H	Hydrogen

H	Enthalpy
HOMO	Highest occupied molecular orbital
Ir	Iridium
IR	Infrared spectroscopy
ⁱ Pr	Isopropyl
J	Coupling constant
J	Joule(s)
k	Rate constant
K	Kelvin
k-	Kilo-
l	Liter(s)
ln	Natural log
LUMO	Lowest unoccupied molecular orbital
μ	Micro
m	Meter(s)
M	Molar
m-	Milli-
<i>m</i> -	Meta-
Me	Methyl
min.	Minute(s)
Mo	Molybdenum
mol	Mole(s)
N	Nitrogen
NMR or nmr	Nuclear magnetic resonance
O	Oxygen
π	Pi

P	Phosphorus
ph	Phenyl
ppm	Parts per million
py	Pyridine
pz	Pyrazole
R	Represents a general organic group in a molecule
R	Molar gas constant
Rh	Rhodium
Ru	Ruthenium
σ	Sigma
s	Second(s)
S	Sulphur
S	Entropy
T	Temperature
Tbe or tbe	<i>Tert</i> -butyl ethylene
~	Approximately
°	Degree(s)
/ or ⁻¹	Per
=	Equals
[]	Concentration of whatever is inside brackets
%	Percent
®	Registered trademark

CHAPTER 1

Introduction

Small molecule activation is a deeply appealing endeavor for any inorganic chemist and has been an area of intense interest for chemists for decades. From the fixation of nitrogen to methane functionalization, the field presents both practical goals capable of transforming economies and intellectual stimulation. Complexes of CO, NO_x, SO_x, O₂, CS_x, N₂, N₂O, CO₂, and H₂S had all been synthesized at least a decade before alkanes or H₂.¹ The reason is that all those small molecules contain lone pairs or π -electrons, which can coordinate to the metal. Molecular hydrogen and alkane C-H bonds, however, both consist of a localized two-electron sigma bond. Thus, bonding to a metal center involves donation of sigma bond electrons creating a three center-two electron bond. Kubas' tungsten dihydride-hydrogen complex represented the first obvious example of a pure "sigma complex".²

Methane and higher alkanes are part of a class of compounds encompassed by the term small molecules. Alkanes constitute the preponderance of compounds in petroleum and natural gas. Selectively activating and functionalizing these molecules would unlock their potential as feed stocks for clean burning fuels and petrochemicals, including plastics, solvents, synthetic fibers, and pharmaceutical drugs. Moreover, methane, the simplest alkane and major constituent of natural gas has the potential to provide the chemical industry with an inexpensive feedstock. At

standard temperature and pressures, methane exists as a gas and its transport is not feasible due to volume constraints. It begins to condense at its boiling point, -161.6 °C, or can be liquefied by oxidation to methanol.³

Alkanes consist of carbon and hydrogen atoms held together by strong localized bonds. The alkanes' highest occupied molecular orbitals (HOMO) are low in energy but their lowest unoccupied molecular orbitals (LUMO) are high in energy; thereby, barring their participation in chemical reactions. Thus, activation of an alkane C-H bond presents a formidable challenge. Employing harsh reaction conditions, super acids, or radical chemistry can coerce alkanes to react. Unfortunately, these reactions typically produce the more undesirable, highly substituted compounds. Appropriately, "relatively inert" is the phrase used to describe alkane reactivity. In fact, alkanes are often called paraffins, which in Latin means "barely connected" for their slight affinity to other substances.⁴

As usual, Nature manages to do seemingly simple chemistry at ambient temperatures that many research groups spend careers exploring. Biological organisms mock our efforts with their transition metal chemistry: Nitrogenase, Cytochrome_{p450}, and Photosystem II are a few remarkable examples. Cytochrome *P*₄₅₀ is an iron porphyrin enzyme that binds alkane, activates and oxidizes it, transforming it into an alcohol. Molecular oxygen is the oxidant, and the iron dances between oxidation states II-V in the catalytic cycle.⁵

The conventional, non-natural methods used to convert alkanes into other products employed high temperatures or extremely reactive species. Selectivity was poor and usually the most substituted C-H bond was attacked yielding highly substituted products, because C-H bond strength increases from tertiary to primary ($R_3CH < R_2CH_2 < RCH_3$).

Metallo-catalytic bond activation is the process by which a chemical bond is lengthened and ultimately broken by binding to a metal atom.¹ Transition metal activation of alkane C-H bonds began to break ground in the 1970's and early 1980's. Shilov's experiments ignited the field with his platinum catalysts that exchanged hydrogen and deuterium between acetic acid- d_1 and an assortment of alkanes;⁵ subsequently, these catalysts were shown to oxidize alkanes.

Unfortunately, this work was not given its due attention at the time either because it was believed that solid platinum metal was responsible or simply because at that time there was a prejudice against work coming out of Russia. The other early examples involved either cyclometallation or C-H bonds that were attached to π systems. The field gained steam and two reviews established it as a major research area.^{5,6} These early systems were either stoichiometric or only weakly catalytic.

The first high turnover thermal dehydrogenation catalyst system employed $Rh(CO)Cl(PMe_3)_2$.^{7,8} But this system also required 4-20 fold excess tandem sacrificial alkene, which underwent direct alkene hydrogenation.

The development of a practical and efficient complex for catalytic alkane activation is highly desirable. Activity and selectivity are the two greatest challenges facing the

development of practical C-H activation catalysts.⁹ Transition metal complexes typically activate alkanes at the least substituted position producing linear products because of steric effects. For example, dehydrogenation catalysts would give alpha olefins. Practically speaking, linear compounds whether olefins, alcohols, or carboxylic acids are commercially valuable for fine chemical syntheses.

The first system to show high activity for alkane dehydrogenation was the PCP pincer complex, $\text{IrH}_2\{\text{C}_6\text{H}_3(\text{CH}_2\text{PR}_2)_2\text{-2,6}\}$ ($\text{R} = \text{Bu}^t$) **1a**. In the presence of the hydrogen acceptor tert-butylethylene (tbe), **1a** dehydrogenates cyclooctane at a rate of 12 turnovers min^{-1} at 200 °C.⁸ The key to this catalyst's success lays in its unique tunable steric and electronic features.

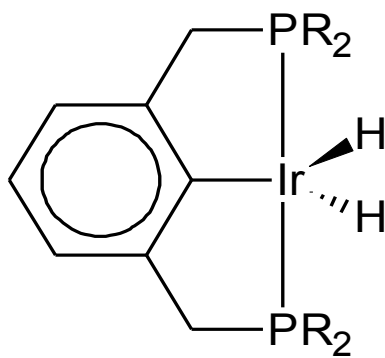


Figure 1. Structure of PCP pincer complex.

The tridentate pincer ligand affords stability and ensures substrates only approach the metal center from the side opposite the xylo-ring. The aromatic ring provides a

framework whereby the electron environment about the metal can be regulated. The electron donating or withdrawing effects can be adjusted by adding different appendages to the ring. Moreover, the size and stability of the ring system can be adjusted as seen in Haenel's "anthrathos" analogues.¹⁰ Replacing the stabilizing terdentate xylo-backbone with chloride would reduce the robusticity of the catalyst and affect the electronic environment at the metal. As well as the ring, sterics and electronics can be adjusted at the phosphines. The present catalyst uses the extremely bulky tert-butyl group, which increases congestion and reduces access to the metal center. Changing the size of the phosphine R-group to isopropyl, for example, would open up access to the iridium, thereby, increasing activity though perhaps reducing selectivity and robustness. In addition to sterics, R-groups can be electron donating or electron depleting. Moreover, there are four different R-groups on the two phosphines (R, R', R'', R'''), which have been utilized to induce chirality. There are an infinite number of combinations.¹¹ Also, the phosphorus can be switched to arsenic, nitrogen, or any atom that works. The PCP pincer is a tunable catalyst awaiting your imagination and synthetic prowess. Finally, the benzylic carbons provide further points of steric and electronic adjustments.

In its present state, **1a** is stabilized by the terdentate chelating effect, the rigid xylo-backbone, and bulky tertiary butyl groups on the phosphines. This accounts for the catalyst's robustness; at 200 °C integrity is maintained indeed beyond complete hydrogen acceptor consumption.⁸ Its activity is attributed to the electronic environment at the iridium and the subtle interplay between metal, surrounding

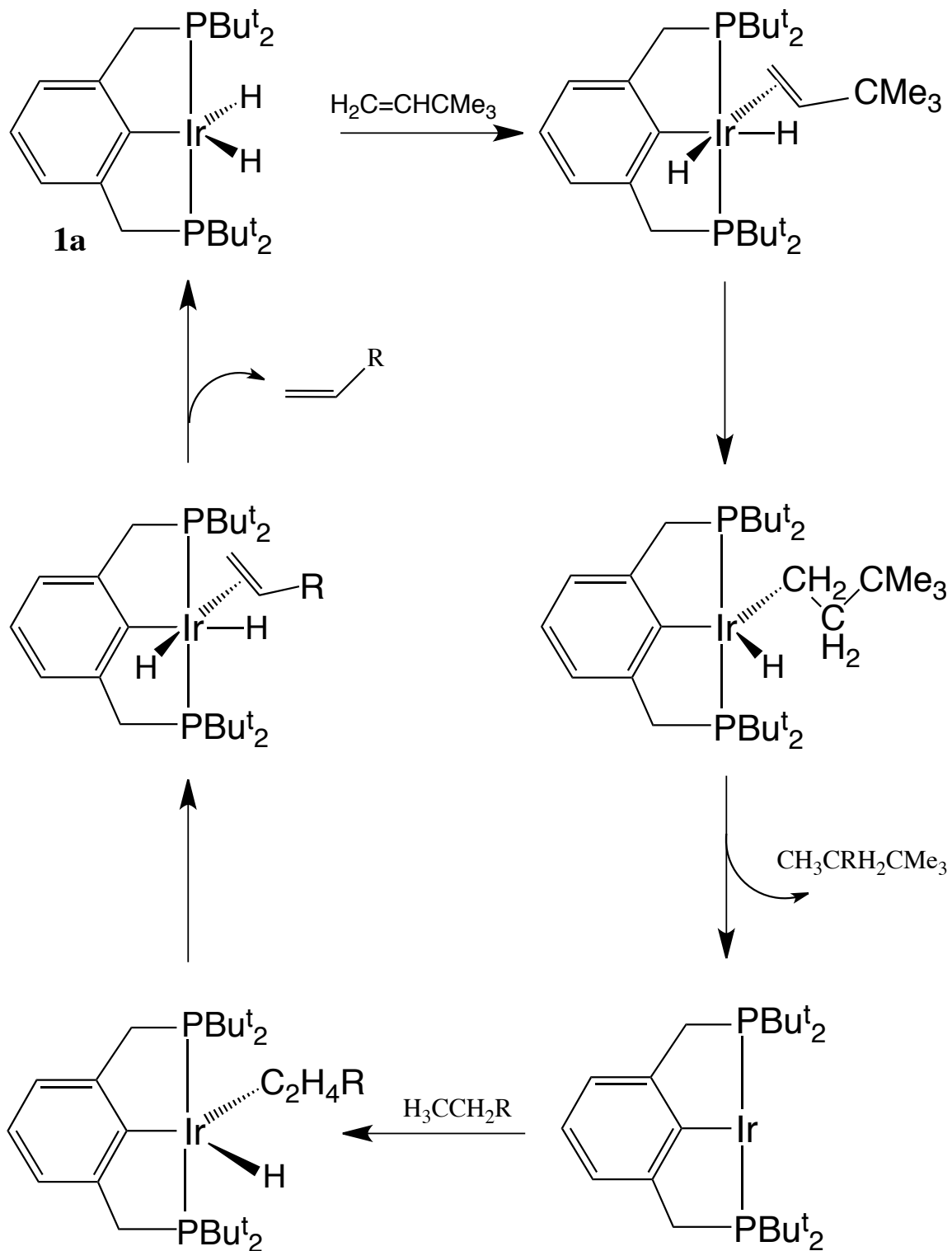
ligands, solvent, and substrate; which naturally leads to an examination of mechanism.

First, a brief discussion of the evolution of **1a** is appropriate. The genesis of **1a** began when the PCP pincer ligand, a tridentate monoanionic aryl bisphosphine, was first synthesized by Moulton and Shaw in 1976.¹² They prepared the synthetic precursor to **1a**, $\text{IrClH}\{\text{C}_6\text{H}_3(\text{CH}_2\text{P}^t\text{Bu})_2\}_{2,6}$ **1a-hcl**, in addition to its rhodium, platinum, palladium, and nickel analogues, noting their high thermal stability. At the end of the decade, Jensen and Kaska recognized that when $\text{RhClH}\{\text{C}_6\text{H}_3(\text{CH}_2\text{P}^t\text{Bu})_2\}_{2,6}$ is dehydrochlorided with $\text{NaN}(\text{SiMe}_3)_2$ in alkane solvent, hydride complexes are produced.¹³ Jensen focused his group research, sixteen years later, on the synthesis and application of **1a** as an alkane dehydrogenation catalyst.^{14,15,16,17,18}

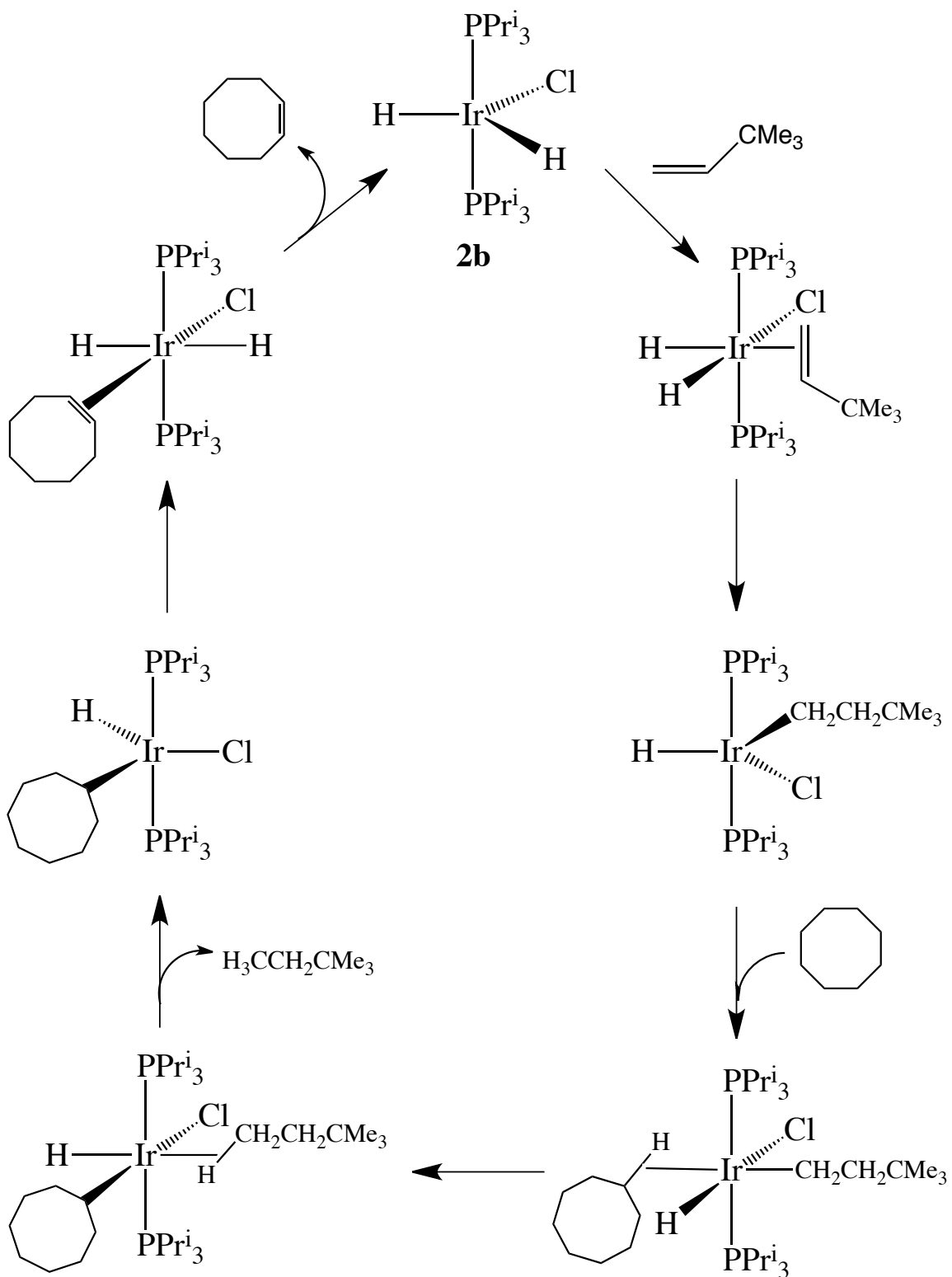
The iridium dihydrido PCP pincer complex has been found to catalyze many transformations: cycloalkanes to arenes, ethylbenzene to styrene, and tetrahydrofuran to furan. Alpha olefins are produced when linear alkanes are dehydrogenated. This complex's unusual stability and reactivity represent a leap forward in the field of catalytic alkane activation. However, the catalyst is impeded by excess olefin in the system; it competes for coordination at the metal center. The smallest olefin, ethylene, binds tightly to the iridium; like cyanide on hemoglobin's iron. Dinitrogen also inhibits the catalyst, producing a stable dimer whose crystal structure shows two pincers clamped onto either end of the nitrogen molecule securely through the metal.

The mechanism of iridium PCP pincer complex catalyzed aliphatic dehydrogenation has been the subject of interest and controversy.^{19,20,21} One proposed pathway proceeds through a 14-electron intermediate as seen in Scheme 1. Initially, the complex transfers its two hydrides to the hydrogen acceptor, 3,3-dimethyl-1-butene (tert-butylethylene (tbe)). First, the tbe coordinates to the iridium center with a donation of its π -electrons to an empty d_z orbital on the metal. Next, the *cis*hydride to the olefin migrates from the iridium to one of the carbons on the double bond via a 1,2-migratory insertion forming the five coordinate alkyl hydride complex. Then, reductive elimination occurs releasing 2,2-dimethylbutane (tba) and generating the 14-electron iridium intermediate. Finally, the doubly unsaturated “hot” three-coordinate iridium(I) complex rapidly inserts across the saturated C-H bond of the alkyl substrate through the process of oxidative addition producing a 16-electron iridium(III) alkyl hydride complex. The putative 14-electron species has never been isolated. Similar square planar complexes proceed through an associative mechanism.²² Reciprocal influence between an aliphatic C-H bond and the metal center is the process by which the hot atom is assuaged.

The proposed mechanism of alkane dehydrogenation catalyzed by **1a** is quite distinct from that which has been proposed for related chloro-*trans*phosphine iridium complexes. Iridium, chlorodihydridobistriisopropylphosphine ($\text{IrClH}_2(\text{PPr}^i_3)_2$) **2b**, is an alkane dehydrogenation catalyst widely studied before the PCP pincer type catalysts gained recognition.^{23,24,25,26} Considering the PCP pincer catalyst **1a**, tba dissociates prior to substrate coordination; it is said to follow a



Scheme 1. Mechanism of aliphatic transfer dehydrogenation by the PCP pincer complex, $\text{IrClH}\{\text{C}_6\text{H}_3(\text{CH}_2\text{P}^t\text{Bu}_2)_2\text{-2,6}\}$, **1a**.



Scheme 2. Mechanism of aliphatic transfer dehydrogenation by $\text{IrClH}_2(\text{PPr}^i_3)_2$, **2b**.

dissociative mechanistic pathway. Distinguishable, **2b** requires alkane association before it releases tba via reductive elimination; it is said to proceed through an associative mechanism. The initial steps of **2b**'s mechanistic path are comparable to those followed by **1a**. Tert-butylethylene coordinates to the iridium center through its double bond followed by a 1,2-migratory insertion producing a 16-electron alkyl hydride complex as seen in scheme 2.²⁷

However, reductive elimination of tba does not occur until the alkane substrate first coordinates to the iridium center. A σ -donation from the saturated C-H bond of the alkane to the five-coordinate, 16-electron iridium(III) alkyl hydride complex occurs, and a six-coordinate, 18-electron iridium(III) complex is formed before tba can reductively eliminate. Aliphatic bond coordination drives elimination of tba.

The PCP pincer catalyst, **1a**, shows much greater catalytic activity than **2b** in aliphatic transfer dehydrogenations. This has been attributed to the pincer ligands geometry "holding back" the phosphinoalkyl groups from the iridium center resulting in less steric crowding.²⁸ However, the divergence in the mechanisms between **1a** and **2b** can also be ascribed to the differences in the electronic environment at the metal center. It is also possible that a third mechanistic model based on an agostic catalytic cycle for the pincer complex may more closely account for the differences in the activity of the catalysts.

The earliest examples of intramolecular C-H-M interactions were presented in the 1960's: Ibers and La Placa²⁹ noticed a close C-H--M distance of 2.6 Å in the x-ray

diffraction data of a five coordinate ruthenium(II) d^6 complex, $\text{RuCl}_2(\text{PPh}_3)_3$; Trofimenko found a pyrazolylborate molybdenum complex with a pseudoaxial methylene having a high-field ^1H NMR signal suggesting hydridic character, supporting IR data suggests “that the two hydrogens are intruding into a suitable empty metal orbital.”³⁰ Six years later, in 1974, Cotton et al.³¹ verified Trofimenko’s implication of a C-H-Mo interaction using X-ray crystallography. Afterwards, Cotton presented the currently accepted three-center, two-electron bonding model to describe the phenomenon.³² Shapley reported C-H-Os bridges in an osmium cluster based upon unusually high ^1H NMR signals and isotope effects observed in the partially deuterated cluster.³³ Despite these early examples³⁴, intramolecular C-H-M interactions did not make their grand entrance onto the chemical research literature scene until Green and Brookhart’s seminal 1983 review.⁶ They coin the term agostic – Greek word which translates to ‘to clasp or hold close to oneself – for these intramolecular aliphatic carbon-hydrogen-transition metal interactions. Afterward, the literature was ripe with examples of agostic interactions.³⁵ The first crystal structure displaying an agostic interaction in a coordination compound was of the cobalt(III) complex, $\text{K}[\text{Co}(\text{dacoda})(\text{SO}_3)] \cdot 5\text{H}_2\text{O}$.³⁶ In their review of Transition Metal Alkane Complexes, Hall and Purutz suggest that the examples of agostic complexes reveal that the initial formational stages of alkyl C-H bond activation proceed through a sigma complex and should prove invaluable in the quest for the elusive alkane complex.³⁷

A C-H agostic bond to a metal is like a coordinated dihydrogen. They both donate their sigma electrons to the metal. If the back donation of electrons from the metal d_x orbital to the aliphatic C-H bond's σ^* orbital is great enough, the C-H bond breaks in a process known as oxidative addition; a C-M-H complex is formed. In the case of the PCP iridium pincer catalyst, the pendant t-butyl group reaches down and coordinates to the metal creating a four-and-a-half membered ring. It is more-or-less a four-and-a-half membered ring because the C-H bond does not approach the metal purely side on like H-H, nor purely end-on like M-H-C but at an angle where the hydrogen atom is slightly closer to the metal than carbon. Crabtree called it canted.⁵

In 1985, he conducted a systematic study employing the structural data of all known C-H--M systems to determine the reaction trajectory for $C-H + M \rightarrow C-M-H$.³⁸ As C-H approaches the metal, the C-H-M angle is about 130° . The angle gets sharper as the C-H bonding electrons get closer to the metal, figure 2. The obtuse angle of approach ($M-H-C = 130^\circ$) may be favored so that the metal d_x can overlap with both the hydrogen 1s and carbon $2sp^3$ hybrid orbitals simultaneously; thereby, maximizing the interaction.¹

This thesis is an investigation of the agostic interactions in *trans*bisphosphine iridium complexes and the possibility of their involvement in alkane activation by this class of compounds. Details gleaned about the mechanism might provide key insights into engineering efficiently functioning catalytic systems. This work was

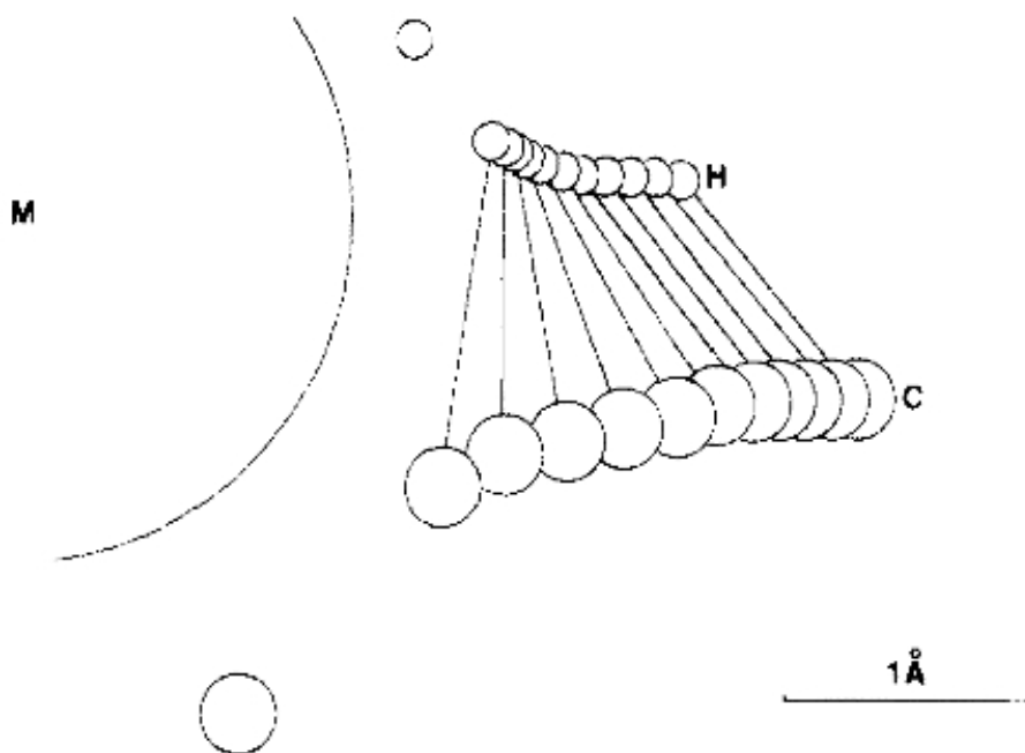


Figure 2. A trace of the reaction $C-H + M$. The course comes from a series of agostic complexes and culminates in the oxidative addition resultant alkyl hydride complex represented by the isolated circles adjacent the large metal sphere. Reprinted with permission.³⁸

carried out to directly probe the possibility that “agostic assistance” accounts for the vastly enhanced activity of the Ir pincer vs. IrP_2X catalysts. The mechanistic differences between the two classes of complexes were probed by a series of labeling experiments and reactions in neat tbe.

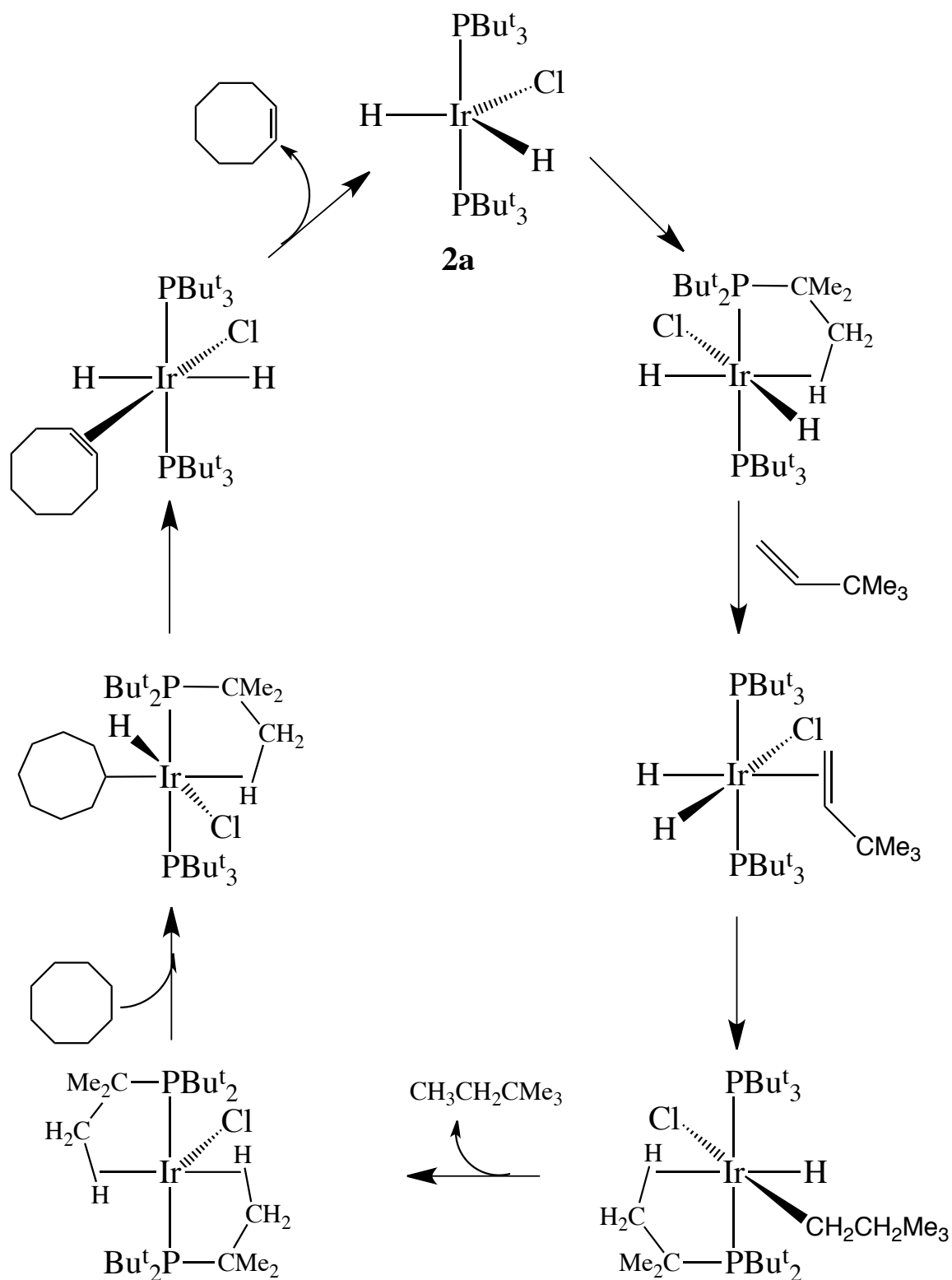
CHAPTER 2

Deuterium Labeling Study to Probe Agostic Interactions in the Dehydrogenation Reaction Pathways.

2.1 Introduction

The accepted mechanisms of aliphatic dehydrogenation by $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-}(\text{CH}_2\text{P}^t\text{Bu}_2)\}$ **1a** and $\text{IrClH}_2(\text{P}^t\text{Pr}_3)_2$ **2b** are dissociative and associative, respectively. The divergence in mechanisms has been ascribed to the ability of the iridium of **1a** to access intramolecular C-H bonds while the iridium of **2b** does not participate in agostic interactions. This study aims to elucidate the reasons for these behavioral differences, to determine whether they can be ascribed to the distinct alkyl phosphine appendages or to the disparate environments at the metal center created by exchange of a chloro-metal group versus a xylo-metal group.

An alternative associative mechanism for aliphatic dehydrogenations, using $\text{IrClH}_2(\text{P}^t\text{Bu}_3)_2$ as catalyst, is presented, Scheme 3. In this mechanism, the reductive elimination is triggered by intramolecular sigma bond coordination from one of the carbon-hydrogen bonds on a phosphine tertiary butyl group to the iridium center. The mechanistic steps are the same as those depicted in scheme 1 for catalytic aliphatic dehydrogenation by $\text{IrH}_2\{\text{C}_6\text{H}_3(\text{CH}_2\text{P}^t\text{Bu}_2)_{2,6}\}$ **1a**, except, each intermediate is stabilized agostically, maintaining an 18-electron iridium center.



Scheme 3. Mechanism of aliphatic transfer dehydrogenation by $\text{IrClH}_2(\text{PBu}^t_3)_2$, **2a**.

Initially, an agostic interaction can satisfy the unsaturated, trigonal bipyramidal 16 e⁻, Ir(III) complex to make an 18 e⁻ octahedral complex. The sigma bond interaction is labile enough to allow the coordination. After olefin coordination, a 1,2-migratory insertion produces an alkyl hydride complex, which again can be coordinatively saturated with agostic assistance. Reductive elimination of alkane gives a complex that is doubly agostically stabilized. To conclude, the labile nature of the intramolecular iridium aliphatic sigma bond interactions makes alkane activation possible. In fact, "C-H-M interactions have not only been found in the ground state but also implicated in the transition states of many important organometallic transformations such as Ziegler-Natta catalysis and sigma bond metathesis."³⁴

In order to test for the involvement of intermediates stabilized by agostic interactions, isotopic iridium deuteride complexes were prepared. The finding of scrambling into the ligand would lend credence to intramolecular aliphatic coordination of the C-H bonds of the phosphine ligands. Therefore, we undertook isotopic labeling experiments of the deuteride complexes.

2.2 Experimental

Standard Schlenk and dry box techniques were employed where appropriate for all chemical manipulations. The following chemicals were purchased and used without further purification: Deuterium gas, 99.8 atom %D (Cambridge Isotope Laboratories, Inc.), Super-Deuteride[®] solution (1.0 M lithium triethylborodeuteride

in THF) (Aldrich). Acetone, $\geq 99.5\%$ (Aldrich), Cyclooctane, 99+% (Aldrich), 1, 2-dibromoethane, $\geq 99\%$ (Aldrich), chlorodiisopropylphosphine, 96% (Aldrich), α , α' -dichloro-m-xylene, 97% (Acros Organics), 3,3-dimethyl-1-ene, 97% (Aldrich), 1,3,5-trimethylbenzene, 98% (Aldrich), and tri-tert-butylphosphine (Strem Chemicals) were all degassed using a freeze-pump-thaw degas method.

Chlorobis(cyclooctene)iridium(I) dimer³⁹ and diisopropylphosphinoxylene (DIPPX)⁴⁰ were prepared by literature methods. Iridium, chlorodideuterobis[tris(1,1-dimethylethyl)]phosphine, **2a-d₂**, iridium, chlorodideuterobis[tris(methylethyl)]phosphine, **2b-d₂**, and iridium, tetradeuterobis[bis(methylethyl)]phosphinoxylene, **1b-d₂** were prepared as previously described and their NMR spectra were found to match those previously reported.^{25,27,28,42} Tetrahydrofuran (THF), pentane, toluene, and diethylether were purchased (Fisher) and purified and degassed on an Innovative Technology, Inc. Solvent Purification System. The ²H and ³¹P{¹H} NMR spectra were recorded on a Varian Unity Inova 500 Spectrometer at 76.8 and 202 MHz.; respectively. Hydrogen (¹H) and Deuterium (²H) chemical shifts are reported in ppm relative to tetramethylsilane (TMS) and are referenced to solvent peaks. ³¹P{¹H} chemical shifts are reported in ppm relative to 85% H₃PO₄ as an external solvent.

Deuterium Scrambling Experiments. Experiments were conducted in J. Young NMR tubes fitted with gas-tight Teflon sealed valves. Typically, the tubes were charged with 0.415ml of a 0.032M solution of IrD₂(PBU^t₃)₂Cl, which was prepared by dissolving 35mg of IrD₂(PBU^t₃)₂Cl into 1.7ml of mesitylene. The tubes

were heated in a silicon oil bath regulated with an IKA-Werke RCT Basic Magnetic Stirrer/Hot Plate equipped with an ETS-D4 fuzzy Temperature Controller at the prescribed temperatures for the set time intervals. The reactions were then quenched, by placing the tubes into a room temperature water bath. Deuterium NMR spectra was recorded before and after heating. The results of these experiments are presented in Table 2.1.

For $[\text{IrD}_4\{\text{C}_6\text{H}_3(\text{CH}_2\text{PPr}^i_2)\text{-2,6}\}]$ (**1b-d₄**), the tubes were stored under an argon atmosphere in an Innovative Technology Glovebox equipped with a Cold Storage Freezer at the prescribed temperatures for the set time intervals. The data is presented in Table 2.2.

2.3 Results

In an effort to delve more deeply into the mechanism of catalytic aliphatic dehydrogenation by *trans*bisphosphine iridium complexes, experiments were designed to explore whether agostic interactions participate in the process and how these interactions might assist in accounting for the activity differences among the catalysts. Initial studies were undertaken whereby 19 mg of **2a-d₂** was dissolved in 0.7 ml of cyclohexane and heated to 120 °C. The sample was analyzed by deuterium NMR before and after heating, revealing deuteride scrambling into the ligands. However, the base of the solvent peak and ligand peak overlapped in the NMR spectrum, eliminating cyclohexane as a possible solvent for the rate study.

Therefore, the non-coordinating solvent mesitylene was selected for the rate study. In order to determine the rate at which deuterium scrambles from the metal to the ligands, samples of $\text{IrClD}_2(\text{P}^t\text{Bu}_3)_2$ **2a-d₂** were heated in mesitylene at various temperatures and times. Twelve samples each containing 35 mg of **2a-d₂** dissolved in 1.7 ml of mesitylene were prepared and analyzed with ^2H NMR at room temperature. The first sample was heated for one hour at 75 °C, quenched, and analyzed with ^2H NMR. The second sample was heated for two hours at 75 °C, the third for three and the fourth for four hours. This procedure was repeated for the next four samples at 95 °C, and the last four at 105 °C. All samples were analyzed via ^2H NMR both before and after heating.

Figure 3 reveals the ^2H NMR spectrum for **2a-d₂** in mesitylene. The two most downfield peaks represent the natural abundance of deuterium (0.015 %) in the undeuterated mesitylene solvent. The larger, at 2.11 ppm, accounts for the nine methyl hydrogens and the smaller, at 6.63 ppm, corresponds to the three ring bound hydrogens. On the complex, the iridium bound deuterides are evinced in the spectra at -34.26 ppm, and the aliphatic deuterium resonates at 1.45 ppm. This peak at 1.45 ppm represents a deuterium atom that has replaced one of the hydrogen atoms on one of the six tertiary butyl groups of the catalyst.

In order to illustrate the behavior illuminated from the NMR spectra data, a data table was generated. Table 2.1 displays the effect of heat on the catalyst dissolved in mesitylene as revealed by the NMR spectra. Qualitatively speaking, longer reaction

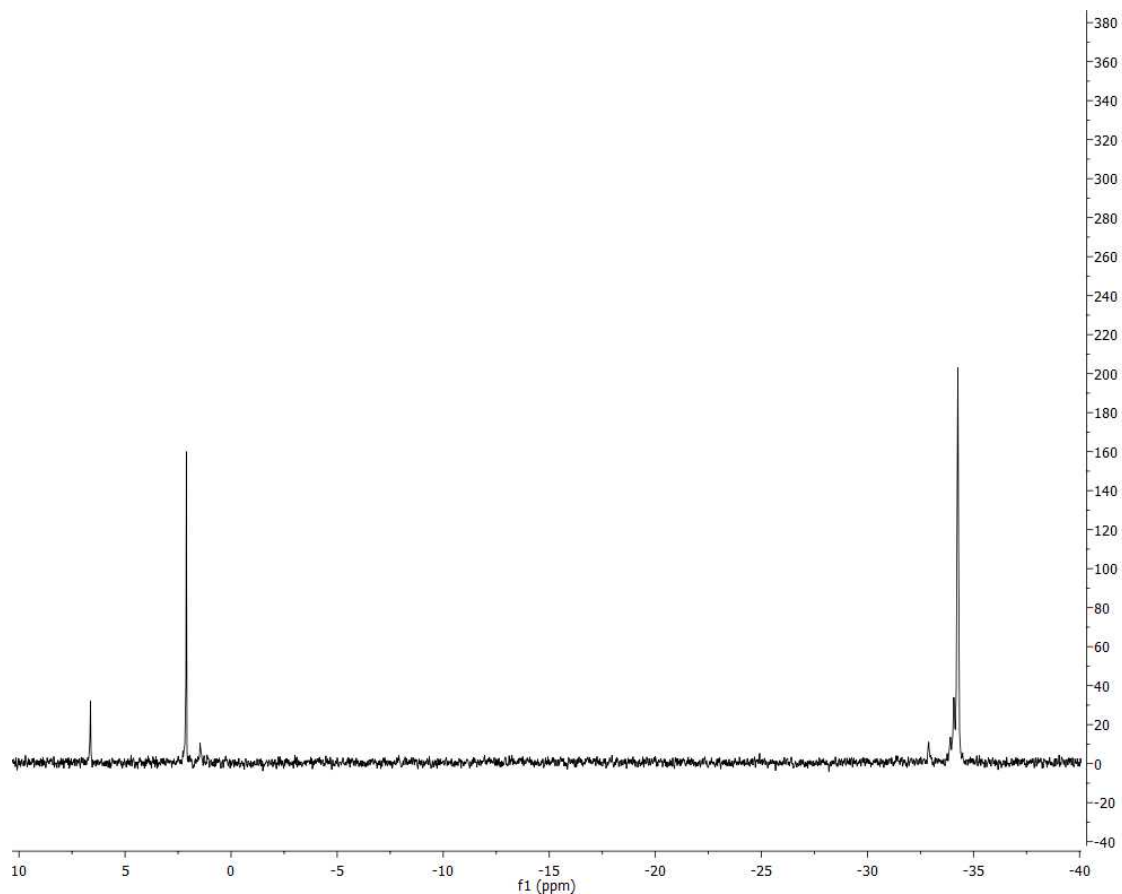


Figure 3. Deuterium NMR spectrum of **2a-d₂** in mesitylene.

Table 2.1. The Effect of Temperature and Time on the Percentage of Deuterium Scrambled into the Aliphatic Position of IrClD₂(PBU^t₃)₂.

		Temperature (°C)		
		<u>75</u>	<u>95</u>	<u>105</u>
Time (h)	1	3.3	7.6	16
	2	4.2	11	28
	3	4.9	13	34
	4	6.2	18	40

times and more heat result in a greater percentage of the deuterium ending up on the aliphatic tertiary butyl-groups of the phosphine ligands. The percentages in the table were generated by integrating the area under the peak corresponding to either the aliphatic deuterium or metal bound deuteride on the ^2H NMR spectra. The peak at 1.45 ppm gets larger, represents more deuteriums, as temperature, strength and duration, increase, Figures 4, 5, and 7. Conversely, the peak at -34.26 ppm gets smaller, represents less deuterides, as temperature, strength and duration, increase.

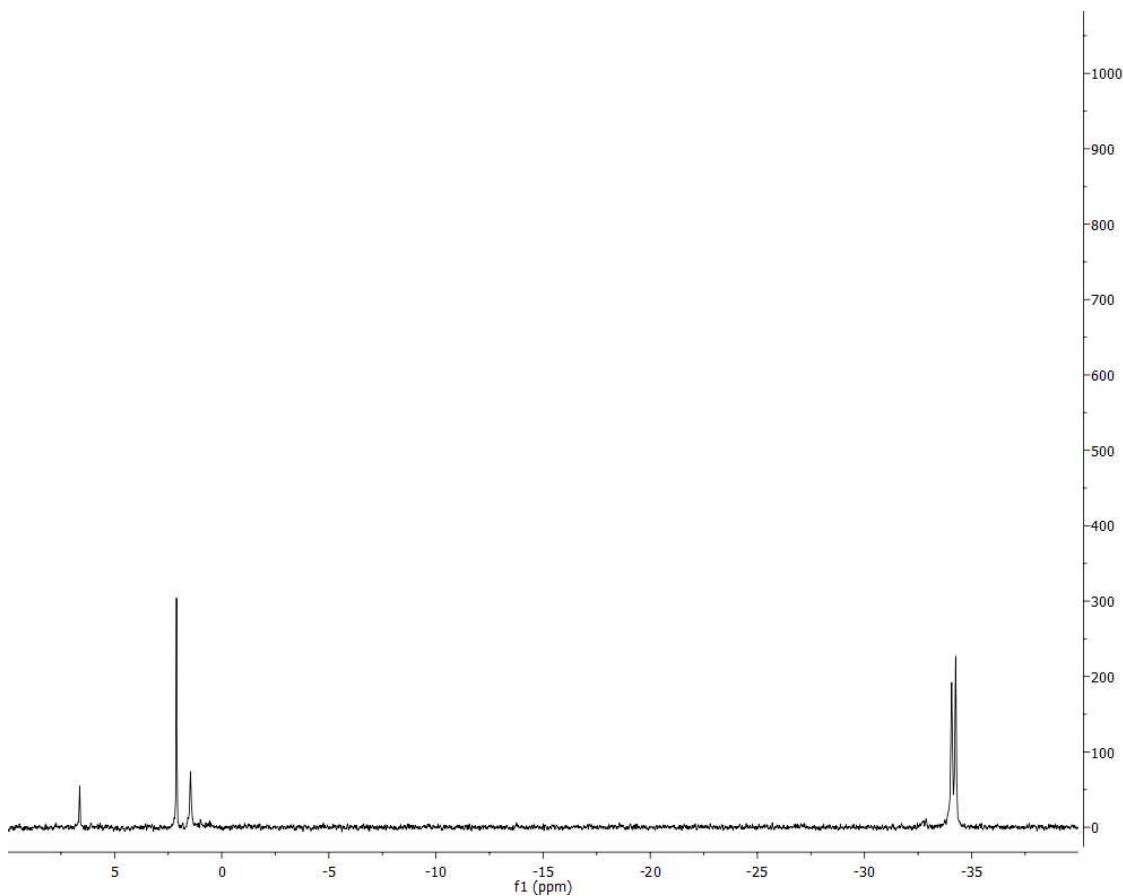


Figure 4. Deuterium NMR spectrum of **2a-d₂** after reacting for 3 h in mesitylene at 95 °C.

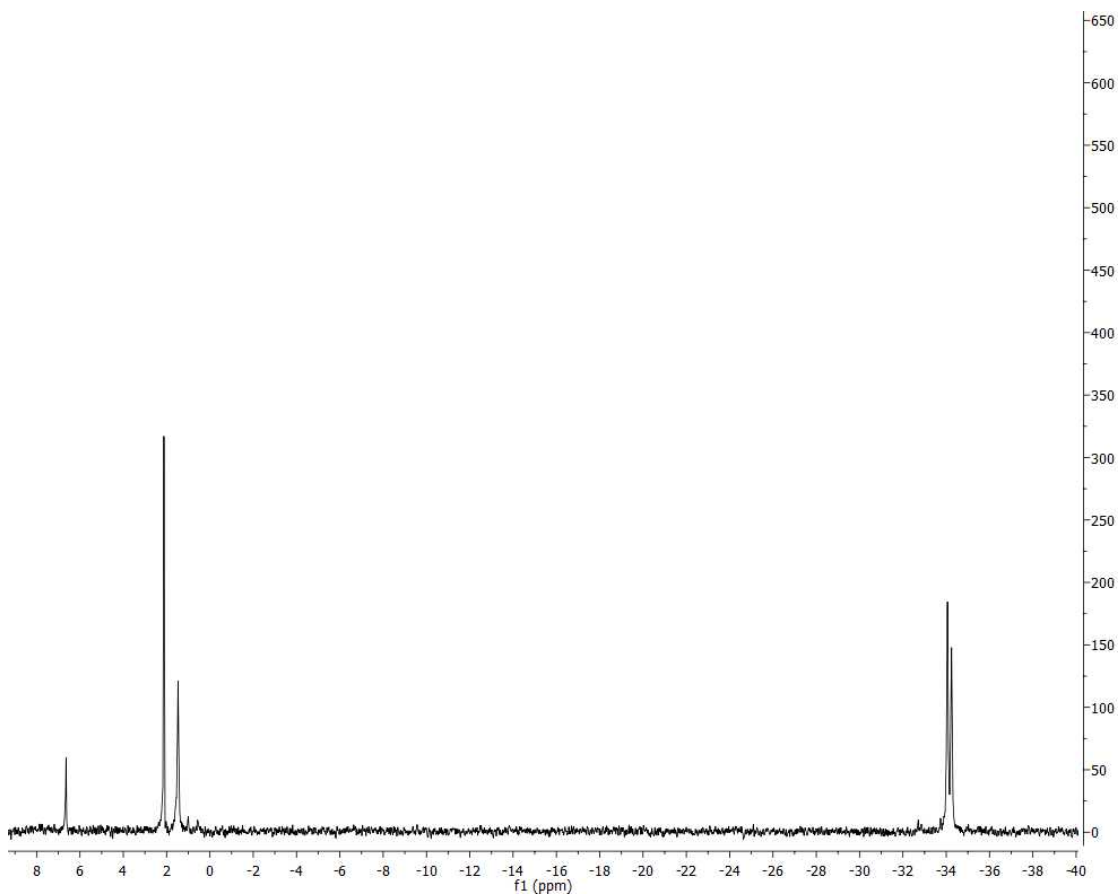


Figure 5. Deuterium NMR spectrum of **2a-d₂** after reacting for 2 h in mesitylene at 105 °C.

An agostic interaction between the C-H σ -bond of the ligand and the iridium center, facilitates the hydrogen/deuteride exchange. The result is deuterium on the ligands and hydrides on the metal center.

Furthermore, figure 6 shows an expansion of the upfield portion of the NMR spectrum of **2a-d₂** in mesitylene after being heated for two hours at 105 °C, revealing the emergence of a sister deuteride resonance at -34.08 ppm. One possible explanation for the appearance of the sister deuteride peak at -34.08 ppm is that an equilibrium exists between the iridium dideuteride complex and the

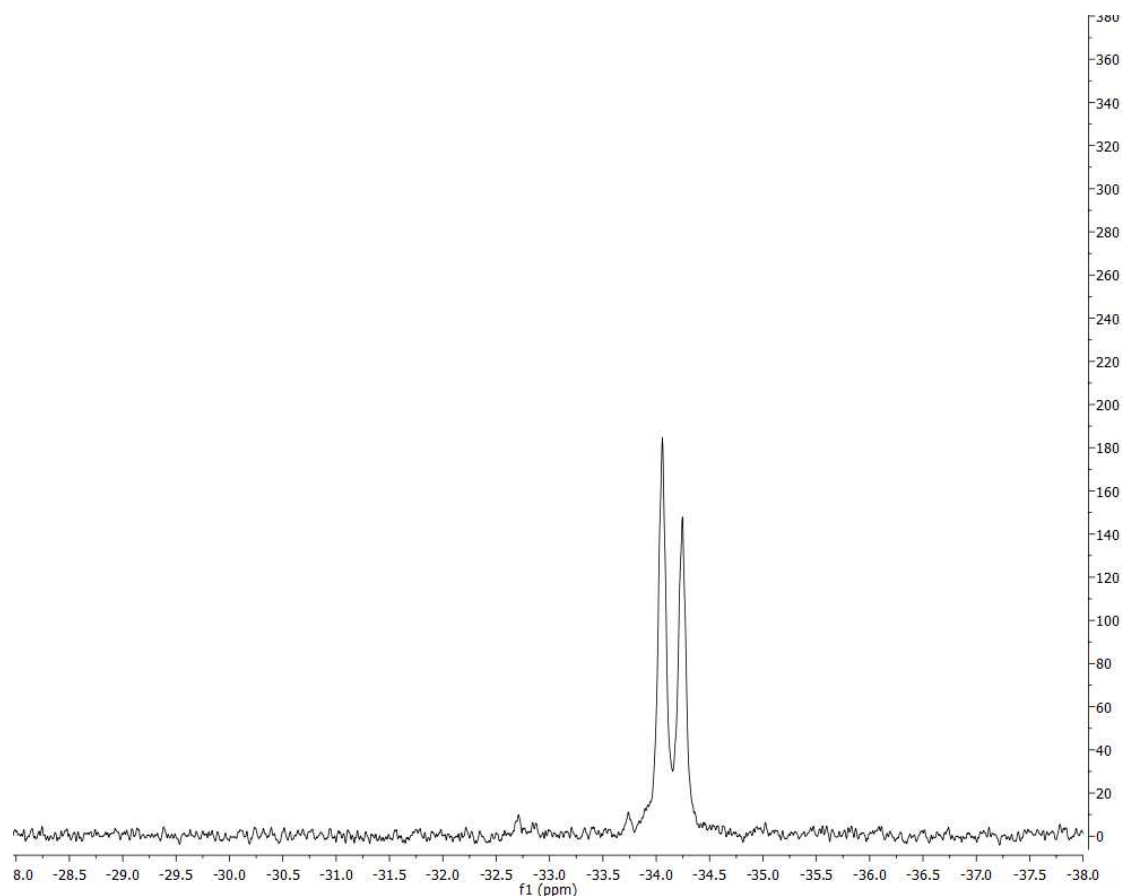


Figure 6. Deuterium NMR spectrum of **2a-d₂** showing hydride/deuteride peak (expanded hydride region from figure 6).

iridium dideuteride agostic complex represented by a single time averaged resonance at -34.26 ppm. The deuteride and bridging hydride exchange places through the process of sigma bond metathesis. Owing to zero-point energy differences, it is preferential for hydrogen to occupy the bridging position and deuterium to take the hydride(deuteride) position. The isotopic perturbation in the equilibrium position generates a second spectral resonance. The resonance represents direct evidence of an agostic interaction caught in the process of sigma bond metathesis.

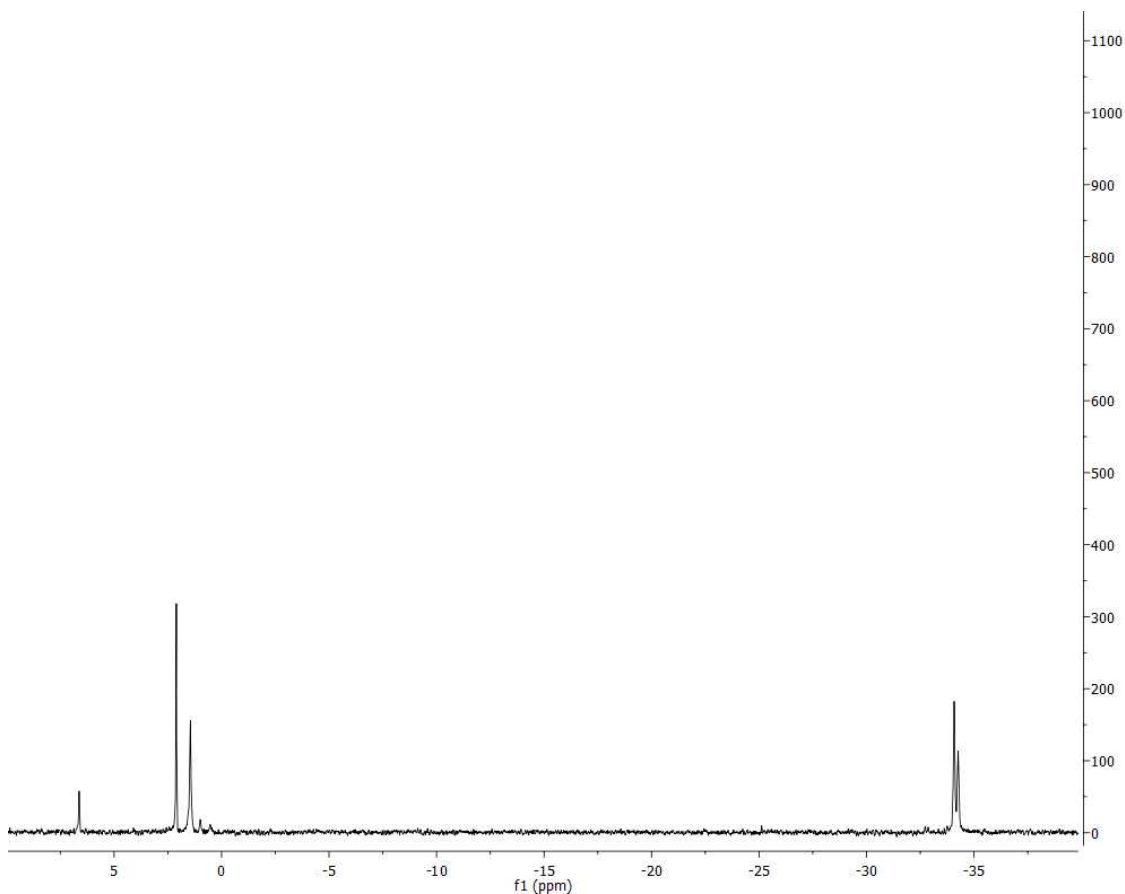


Figure 7. Deuterium NMR spectrum of **2a-d₂** after reacting for 3 h in mesitylene at 105 °C.

In order to quantify the rate of deuteride exchange occurring at 75 °C, 95 °C, and 105 °C, three rate plots were generated. The slope of the rate plot reports the rate of deuterium exchange at the given temperature. At 75 °C, the deuterides on **2a-d₂** transfer to the ligands, exchanging with hydrogen, at a rate 3.5×10^{-3} M/s. At 95 °C, the rate increases to 4.6×10^{-3} M/s. Finally, at 105 °C, the rate of deuterium exchange has climbed to 5.0×10^{-3} M/s.

In order to ascertain the activation energy associated with deuterium scrambling in IrClD₂(PBU^t₃)₂, an Eyring Plot was invoked. The slope of the Eyring Plot describes

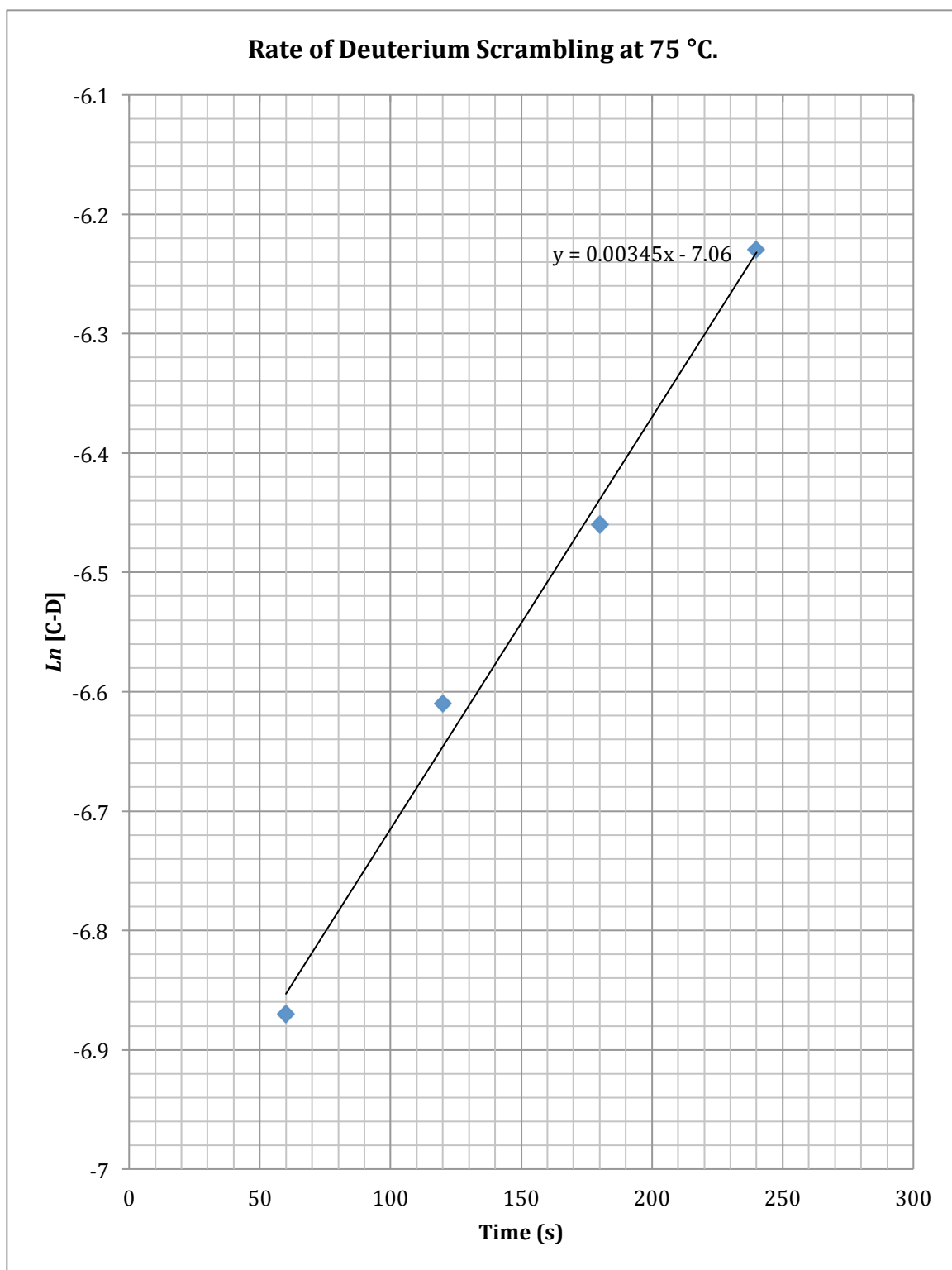


Figure 8. Plot of the natural log of the concentration of deuterium incorporated into the aliphatic position of **2a-d₂** versus time at 75 °C.

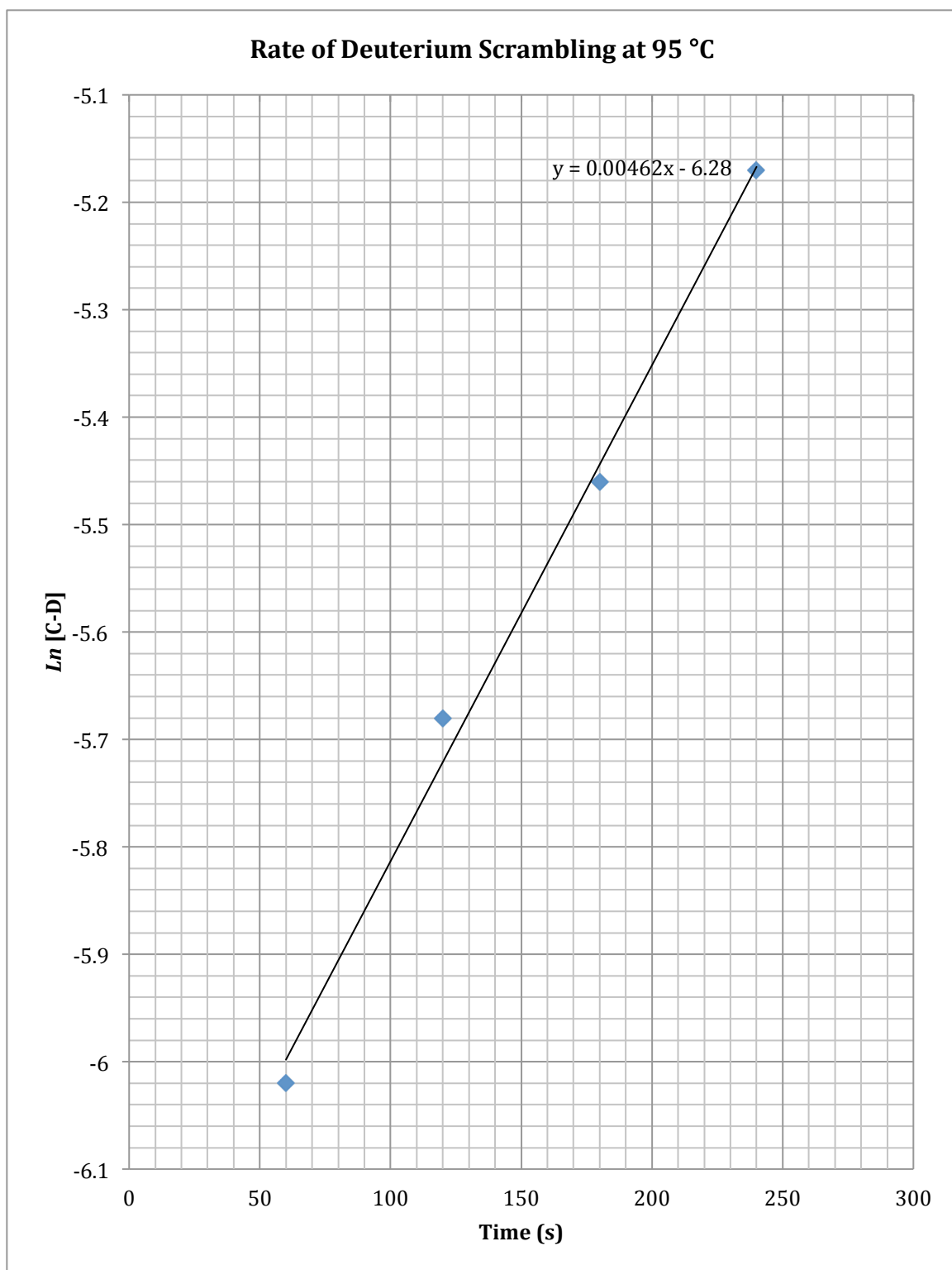


Figure 9. Plot of the natural log of the concentration of deuterium incorporated into the aliphatic position of **2a-d₂** versus time at 95 °C.

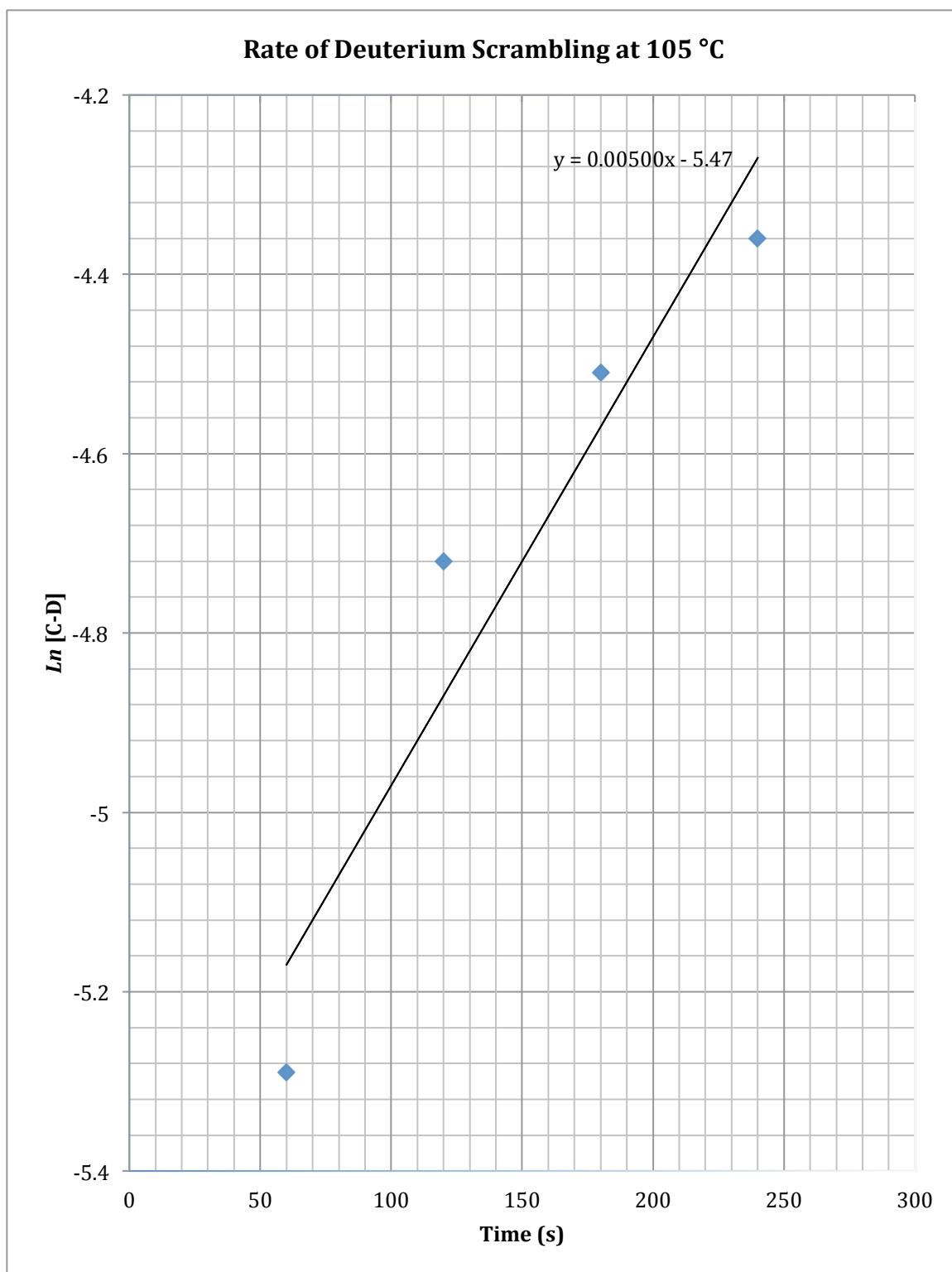


Figure 10. Plot of the natural log of the concentration of deuterium incorporated into the aliphatic position of **2a-d₂** versus time at 105 °C.

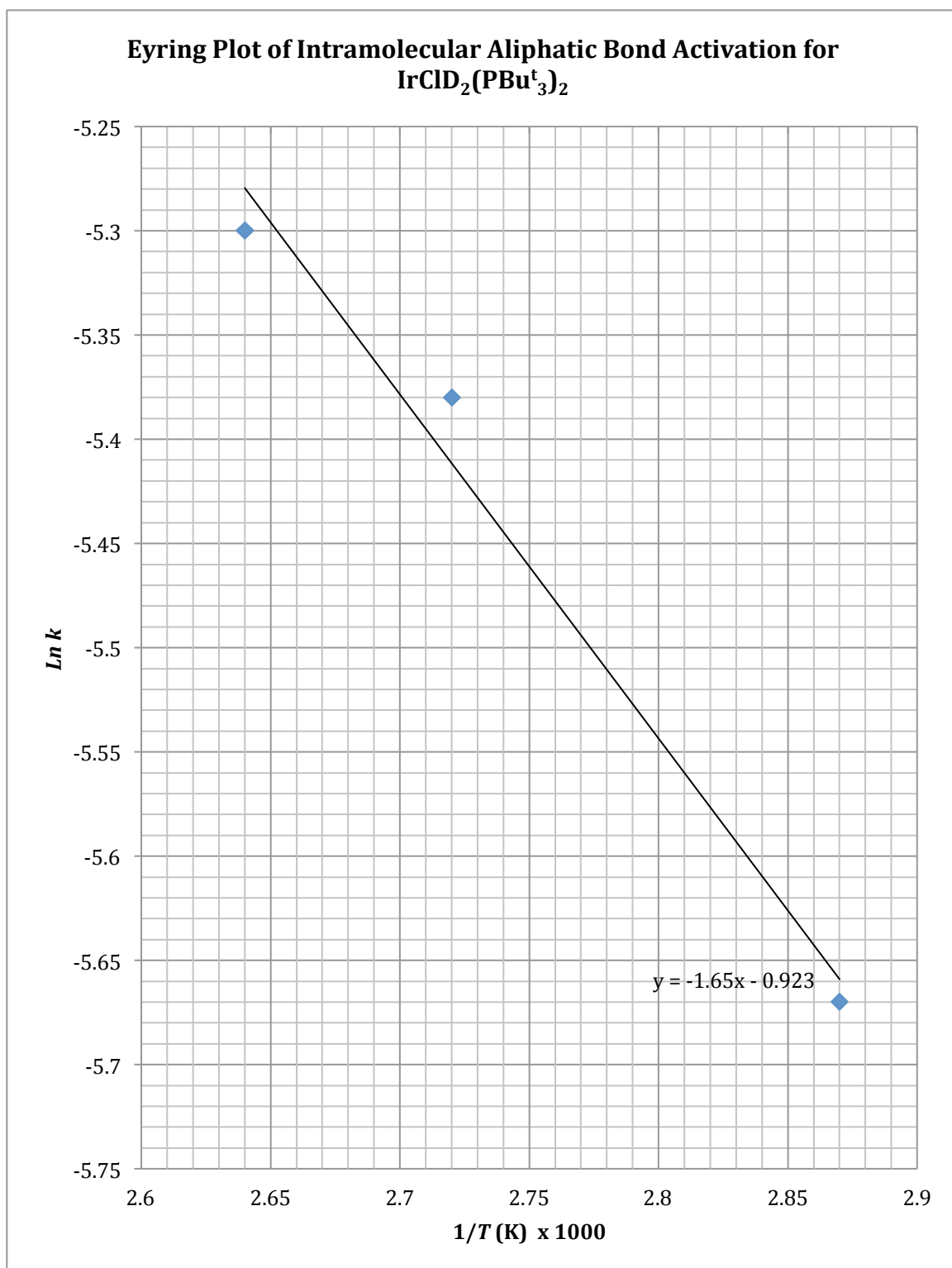


Figure 11. Plot of the natural log of the rate constants versus the inverse of the temperature in Kelvin times 1000.

the activation energy for deuterium exchange. From the equation $k = A e^{(-E_A/RT)}$, where k is the rate constant obtained from the slope of the Rate Plot and E_A is the activation energy, the Eyring plot can be created. Transforming the equation into the familiar form of an equation for a straight line, $\ln k = (-E_A/R)(1/T) + \ln A$. The Eyring Plot of the $\ln k$ versus $1/T$ gives a line whose slope is $-E_A/R$. From this data, we have determined the activation energy for deuterium scrambling in **2a-d₂** to be 14 kJ/mol (3.3 kcal/mol).

In order to determine whether deuterides exchange into the ligands on $[\text{IrD}_4\{\text{C}_6\text{H}_3(\text{CH}_2\text{PPr}^i_2)\text{-2,6}\}]$ **1b-d₄** and the relative rate, the complex was dissolved in mesitylene and analyzed using deuterium NMR. Initial studies exhibited deuterides rapidly transferring to the ligands at room temperature. Aiming to study the exchange, two samples were prepared each containing 0.8 ml of a 3.5 mM solution of **1b-d₄** in mesitylene. After the maiden deuterium NMR analyses, one sample was stored at 25 °C and the other at -40 °C. Subsequent analyses were undertaken after 24 h and 48 h.

The ²H NMR spectrum of **1b-d₄** in mesitylene (figure 12) reveals the expected mesitylene peaks at 6.63 ppm and 2.11 ppm from the natural abundance of deuterium in the solvent. On the complex, iridium bound deuterides exhibit at -9.45 ppm and the aliphatic deuteriums exposed by a large peak at 0.91 ppm. Clearly, there is a low barrier to interaction of the phosphine aliphatic groups with the metal center as the lion's share of deuteriums are on the ligand immediately following solvation at room temperature. Although the speed of deuterium exchange in **1b-d₄**

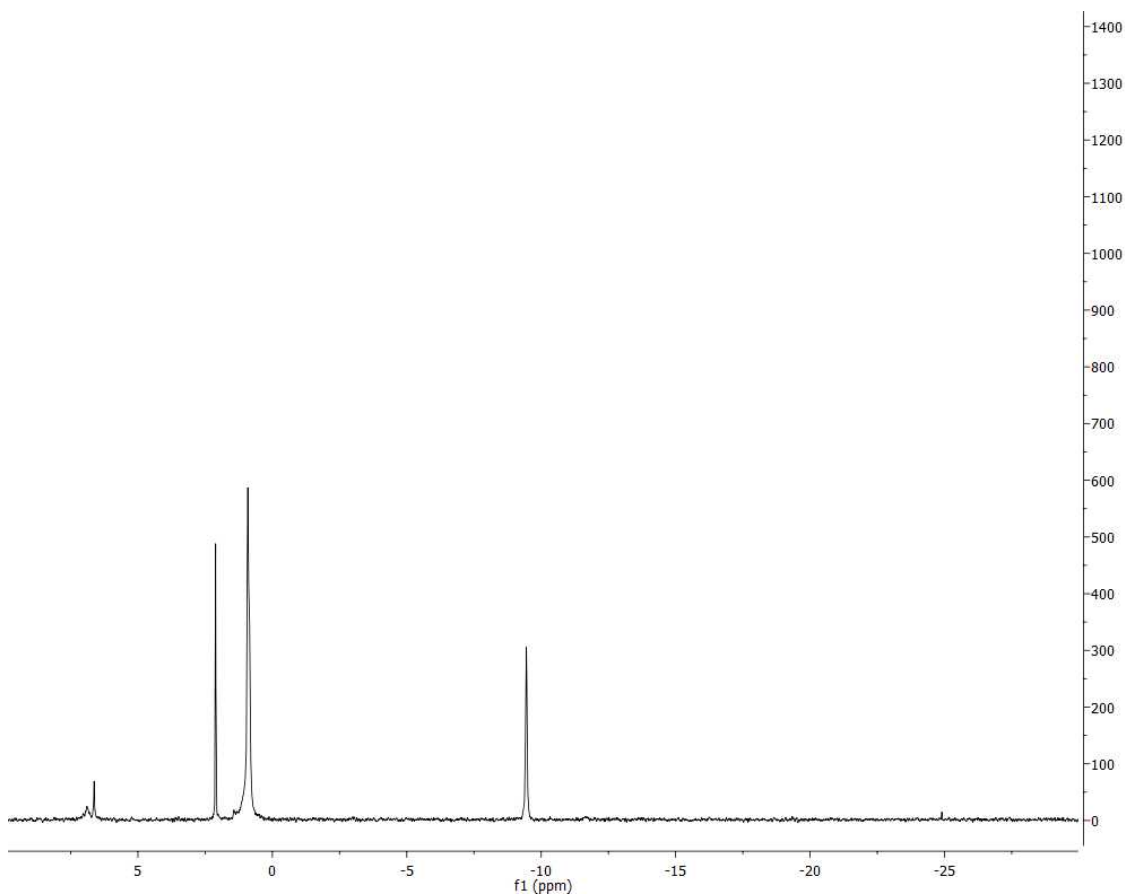


Figure 12. Deuterium NMR spectrum of **1b-d₄** in mesitylene.

precluded the possibility of measuring its rate with a study similar to the one for complex **2a-d₂**, it has been pointed out that a reverse reaction study may be feasible. However, an examination of the behavior of the deuteropincer complex in mesitylene was attempted.

In order to simplify the NMR spectra data, data tables were generated. The first strikingly apparent piece of information gleaned from the data in Table 2.2 and Table 2.3 is that at time zero nearly three-quarters of the deuterium has already scrambled into the aliphatic position on the isopropyl pincer. As expected, deuteride exchange occurred more slowly for the sample stored at -40 °C: 16 %

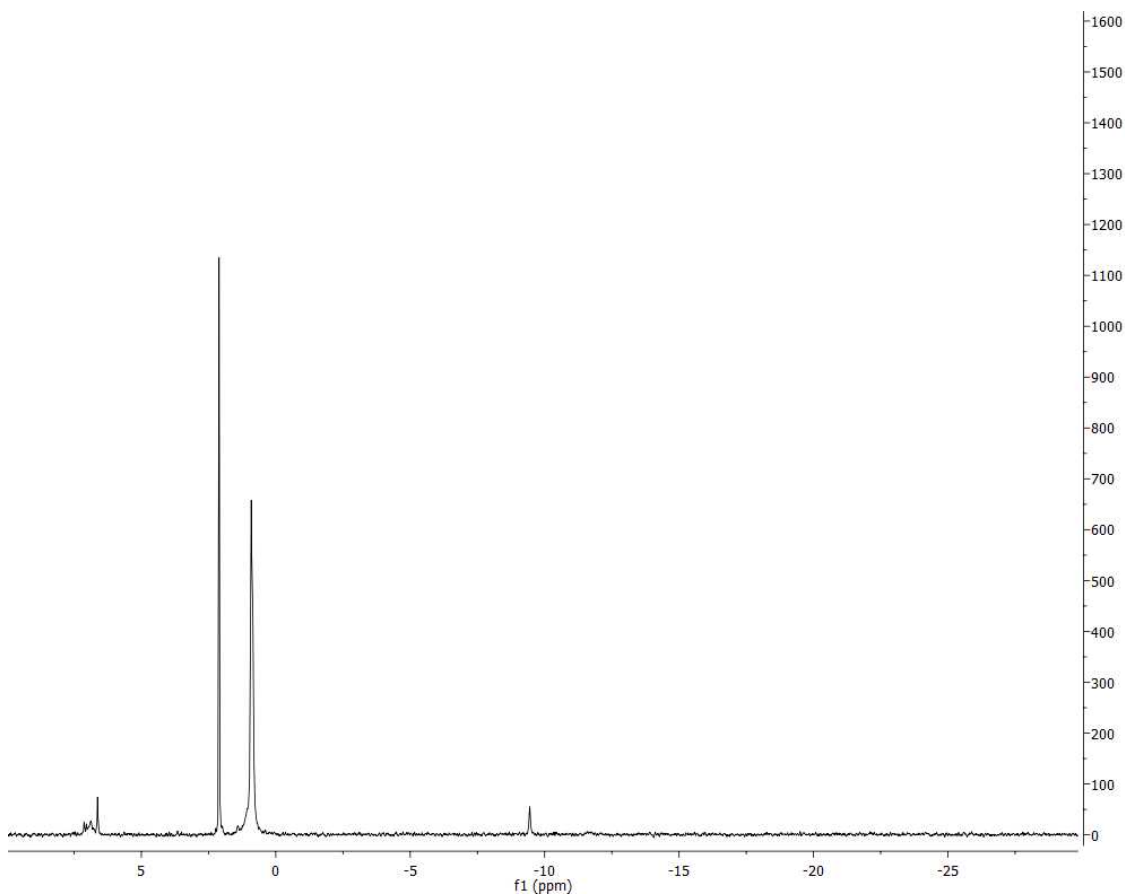


Figure 13. Deuterium nmr spectrum of **1b-d₄** after reaction in mesitylene for 48 h at room temperature.

remains after 24 h compared to 7.6 % for the sample stored at 25 °C. Analogous to the pattern observed for **2a-d₂**, more iridium deuteride scrambles into the aliphatic position of the ligand over time. However, what is novel about **1b-d₄** is that now some of the deuterium is leaking into the mesitylene solvent. In the room temperature study displayed in Table 2.3, apparently up to 17 percent of the deuterium has leaked into the solvent after two days, figure 13. The less sterically hindered isopropyl PCP pincer catalyst allows solvent coordination, and through the process of sigma bond metathesis deuterium ends up leaking into the solvent.

Table 2.2. The Percentage of Deuterium Scrambled into the Aliphatic Ligand Position, the Mesitylene Solvent, or Remaining as Hydride on $[\text{IrD}_4\{\text{C}_6\text{H}_3(\text{CH}_2\text{PPr}^i_2)\text{-}2,6\}]$. A two-day study; sample was stored at $-40\text{ }^\circ\text{C}$ between nmr runs.

Time (hours)		Aliphatic Position	Iridium Deuteride	Solvent
	0	77	21	2.3
	24	81	16	3.7
	48	85	8.7	5.9

Table 2.3. The Percentage of Deuterium Scrambled into the Aliphatic Ligand, the Mesitylene Solvent, or Remaining as Hydride on $[\text{IrD}_4\{\text{C}_6\text{H}_3(\text{CH}_2\text{PPr}^i_2)\text{-}2,6\}]$. A two-day study; sample left at room temperature.

Time (hours)		Aliphatic Position	Iridium Deuteride	Solvent
	0	72	25	3.2
	24	78	7.6	11
	48	78	4.6	17

In order to determine whether deuterium is exchanged from the deuteride to the alkyl groups in $\text{IrClD}_2(\text{PPr}^i_3)_2$, **2b-d₂** was heated in mesitylene and monitored by ^2H NMR. A solution containing 28 mg of **2b-d₂** was dissolved in 0.7 ml mesitylene and heated to 150 °C for 24 hours. The ^2H NMR spectrum of **2b-d₂** in mesitylene before heating shows three peaks: The expected mesitylene peaks at 2.11 ppm and 6.63 ppm in a three to one ratio and a large deuteride peak at 31.3 ppm, figure 14.

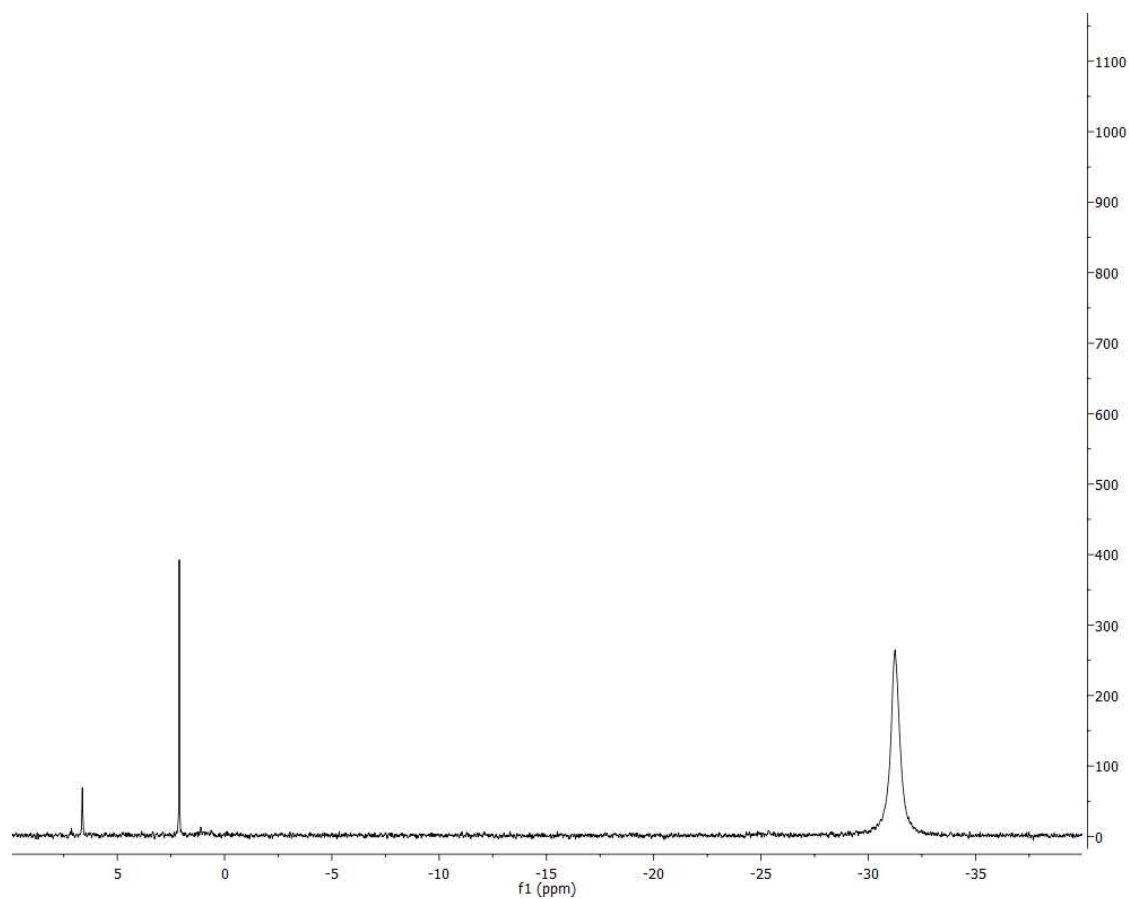


Figure 14. Deuterium NMR spectrum of **2b-d₂** in mesitylene.

After heating, the ^2H NMR spectrum contains a fourth peak at 1.11 ppm, figure 15. Surprisingly, deuterium scrambling was observed, up to 90% was transferred to the aliphatic position of the pendant isopropyl phosphine ligands on **2b-d₂**. These results were unexpected as they are at variance with an earlier study and are probably due to the different solvents employed in the experiments.⁴¹ Further explanations are found in the discussion section.

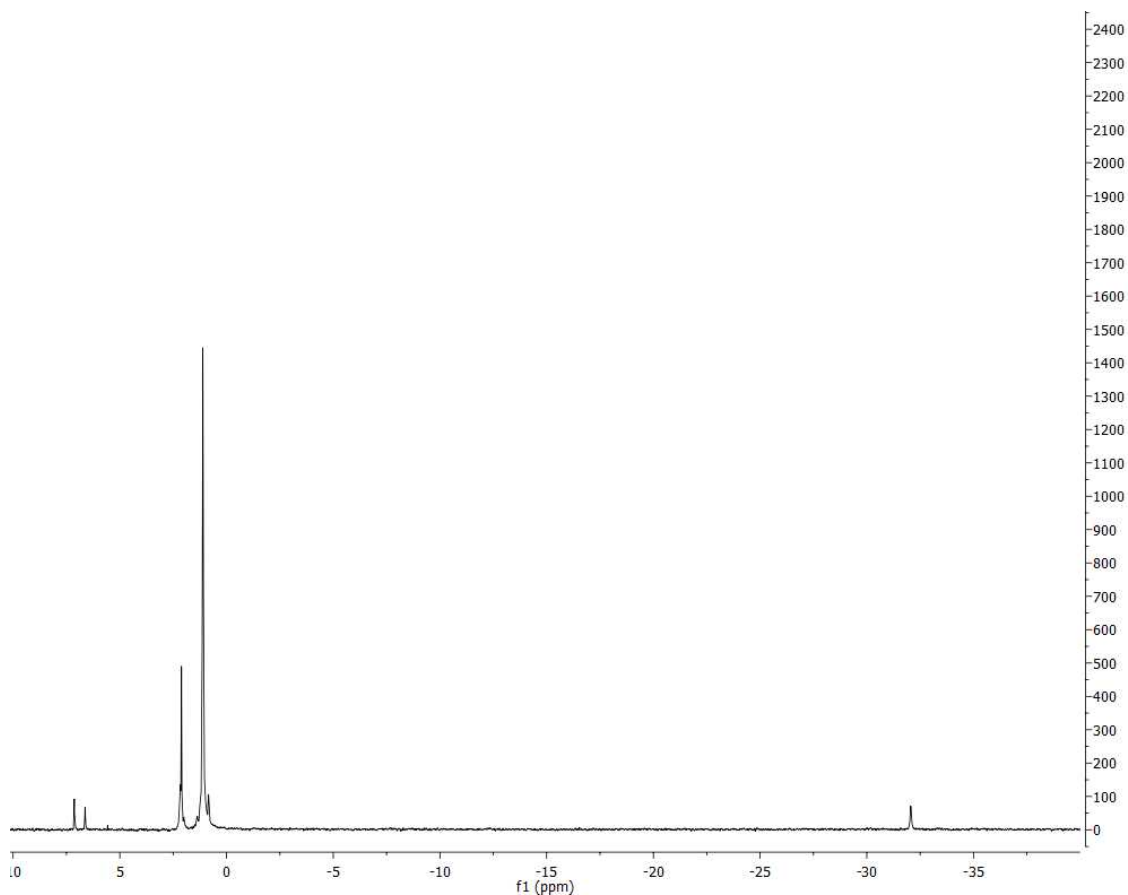


Figure 15. Deuterium NMR spectra of **2b-d₂** after reaction in mesitylene for one day at 150 °C.

2.4 Discussion

All three *trans*bisphosphine iridium catalysts studied, **1b-d₄**, **2a-d₂**, and **2b-d₂**, undergo deuterium scrambling between the metal bound deuterides and the phosphine methyl groups when dissolved in mesitylene. The barrier to deuterium exchange for the PCP pincer complexes, **1a-d₂**, and **1b-d₄**, is low. When **1a-d₂** was dissolved in cyclohexane at 25 °C, “the exchange between the deuteride and tert-butyl methyl ligand was apparent within two hours.”¹⁹ Similarly, at room temperature, more than 70% of the deuterides on **1b-d₄** exchanged with the isopropyl methyl ligands within one hour after being dissolved in mesitylene.

The deuteride exchange in **2b-d₂** contrasts the previous report by Belli, that **2b-d₂** does *not* transfer any deuterium label to the isopropyl methyl groups of the phosphine ligand after being heated for 24 h at 150 °C in toluene.⁴² It is conceivable that in this previous study, the deuterium scrambling was arrested by coordination of the toluene solvent that was used in this investigation. Arenes coordinated in an η^2 fashion could compete with aliphatic C-H bond activation.⁴² A primary reason in choosing mesitylene as the solvent for this study was for its relatively non-coordinating nature.

Selecting an appropriate solvent for these experiments involved research and experimentation. After numerous trials with possible solvents; cyclohexane, toluene, perfluorodecalin, and tetramethylsilane, 1,3,5-trimethylbenzene satisfied the criteria for practicality. It has a high boiling point, 164.7 °C, and is non-polar and

non-coordinating.⁴³ Moreover, the NMR spectrum of mesitylene consists of two sharp singlets (δ 6.63, 2.11) that do not overlap or interfere with the NMR resonances of the methyl hydrogens on the alkyl ligands of the catalysts which respectively are for **2a-d₂**, **2b-d₂**, and **1b-d₄**: δ 1.45, 1.11, 0.91.

Although mesitylene is relatively a non-coordinating solvent, some deuterium does leak into the solvent with catalyst **1b-d₄**. After two days at room temperature up to 17% of the deuterium leaked into the solvent. The astounding activity of **1b-d₄** results in deuterium scrambling even into the mesitylene solvent, which increases over time due to the entropic effect.

The mechanism of deuterium exchange involves intramolecular aliphatic C-H bond coordination followed by sigma bond metathesis. The *trans*phosphine, iridium chloride complexes, **2a-d₂** and **2b-d₂**, are not as active as their pincer correlates, and require heat for the deuterides to scramble into the alkyl ligands. The studies of **2a-d₂** show that at 75 °C deuterides exchange with ligand bound hydrogens at a rate of 3.5×10^{-3} M/sec. As expected, raising temperature accelerates rate, and after four hours at 105 °C, 40 % of the deuterium has ended up in the tert-butyl ligand. In comparison, 90 % of the deuterium is found on the isopropyl ligand of **2b-d₂** after 24 hours at 150 °C.

Agostic coordination and sigma bond metathesis is a facile process for the chloro-*trans*phosphine iridium catalysts. The kinetic barrier or activation energy, ΔH^\ddagger , has been calculated for the process of deuterium scrambling in **2a-d₂** to be

approximately 14 kJ/mol (3.3 kcal/mol). Prior agostic coordination lowers the energy pathway for intramolecular aliphatic C-H bond activation.

The PCP pincer catalysts, **1a** and **1b**, intramolecularly coordinate and transfer deuterides into the ligands with substantially greater facility. Their kinetic barrier to intramolecular sigma bond metathesis is much less than 10 kJ mol⁻¹ (2.4 kcal/mol). A reasonable explanation for their distinguished mutual penetrating influence may be found in the bent P-Ir-P bond angle. The crystal structure of **1a** reveals a P-Ir-P angle of 164.8(1)°.⁴⁴ This abrupt bend from the expected 180° may account for the PCP pincer catalysts' greater agostic bonding propensity and subsequent stronger catalytic activity. In fact, Kubas has found a tungsten bisphosphine, W(CO)₃(PCy₃)₂, where the agostic interaction of the C-H in the cyclohexane ligand distorts the P-W-P angle to 160°.⁴⁵ The energy of this interaction was estimated using the energetics of heptane binding to W(CO)₅ to be about 42-63 kJ mol⁻¹ (10-15 kcal mol⁻¹).¹

The strength and nature of agostic interactions vary widely. Cotton has been extensively cited for his estimates of intramolecular methyl C-H bond activation with molybdenum in [Et₂B(pz)₂]Mo(CO)₂(η³-H₂CCHCH₂) to be 71 kJ mol⁻¹ (17 kcal mol⁻¹). However, this value, based on variable temperature NMR experiments, is "admittedly a very rough estimate".³² A more recent study, applies density functional theory and NMR data to determine the bonding strength of the agostic interaction between phenyl C-H and ruthenium in RuH(H₂)(ph-py)(PⁱPr₃)₂ [ph-py = 2-phenylpyridine] to be approximately 16 kJ/mol (3.8 kcal mol⁻¹).⁴⁶

2.5 Conclusion

The rapidly exchanging fluxional sigma bond donations from the 54 carbon-hydrogen bonds of **2a** or the 36 on **2b** to their respective iridium centers is facile and catalytically stabilizing and significant. Clearly, the terdentate pincer ligand provides stabilization but its kinetic flow radically equips the γ -carbon-hydrogen bonds of the pendent alkyl phosphines to maximize its three-center, two-electron interaction with iridium. The bent (165°) P-Ir-P bond angle helps to bring the ligand C-H bonds close to the iridium center where agostic interactions occur facilely. The PCP pincer complexes undergo deuteride transfer much more readily than their chloro-*trans*bisphosphine iridium cousins. The activation energy for the deuteride transfer or sigma bond metathesis for $\text{IrClD}_2(\text{P}^t\text{Bu}_3)_2$ has been determined by an NMR labeling study to be 3.3 kcal/mol. The *trans*bisphosphine catalyst $\text{IrClD}_2(\text{P}^t\text{Pr}_3)_2$ undergoes deuteride exchange with ligand hydrogens when heated in neat mesitylene. The plausibility of agostic interactions by the phosphine alkyl groups playing a major role in the mechanism of *trans*bisphosphine iridium complex catalyzed aliphatic dehydrogenations is supported.

CHAPTER 3

Reactions of the *trans*Bisphospine Iridium Complexes in Neat Neohexene.

3.1 Introduction

One area of long-standing interest is the development of dehydrogenation catalysts for the production of α -olefins. Alpha olefins are most widely employed as comonomers for polyethylene production and their derivatives are used to make plasticizers and surfactants, synthetic motor oils and lubricants.⁴⁷ The most common production method is ethylene oligomerization using Ziegler catalyst. Annual global consumption of linear α -olefins is expected to increase by three percent through 2014.⁴⁸ More recently, dehydrogenation catalysts have been applied to the development of on-board hydrogen storage systems.^{49,50} Direct dehydrogenation without the use of an acceptor is the only way either of these dehydrogenation catalyst applications will be economically viable.

In the development of a catalyst for C-H activation it was recognized early on that the alkane dehydrogenation is a thermodynamically unfavorable process below 300 °C. The reverse reaction has a ΔH (hydrogenation) of between 30-32 kcal/mol for most alkenes.⁵ However, since we are creating H₂, a gaseous product, the ΔS term in the equation $\Delta G = \Delta H - T\Delta S$ is positive. Therefore, the reaction can be driven

forward at high temperatures. While most heterogeneously catalyzed industrial processes utilize this phenomenon, the more selective and active homogenous catalysts, are less robust. Although the oxidative addition of alkane is thermodynamically unfavorable, the kinetic barrier is relatively low. Consequently, an equilibrium exists between alkyl hydride complex and coordinated alkane complex. Coupling the uphill reaction with subsequent favorable reactions can help overcome the thermodynamic problem.⁵¹ Transfer dehydrogenation is not a practical system for real world industrial processes, but it does provide a raw test of C-H activation. It allows the study of transfer dehydrogenation systems, which serve as a model and provide valuable insights into the design of better dehydrogenation systems in general.

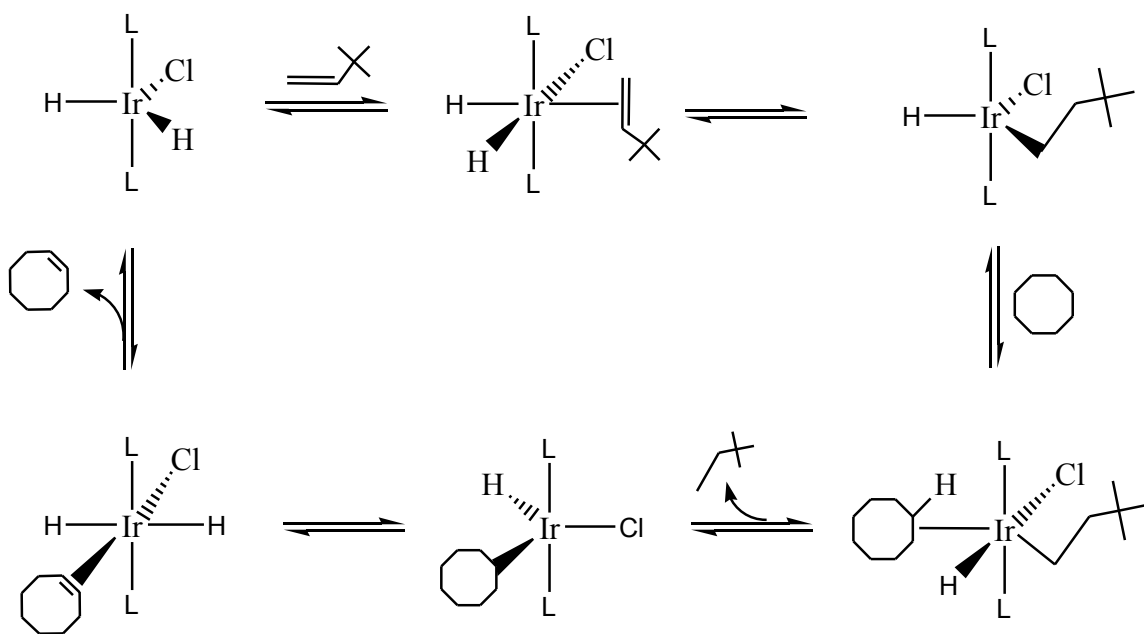
The olefin of choice and most extensively utilized hydrogen acceptor in dehydrogenation catalysis is 3,3-dimethyl-1-butene, commonly known as neohexene or tert-butylethylene (tbe). Crabtree was the first to discover its utility in his iridium complex catalyzed dehydrogenation of cycloalkanes.^{52,53} He advocated tbe's ability to increase product yield by resisting metallation and having sufficient steric bulk; it "seems too bulky to give bis(olefin) complexes."⁵⁴ Moreover, tbe has an exceptionally high heat of hydrogenation (33 kcal/mol), which helps to drive the thermodynamically unfavorable alkane dehydrogenation reaction.⁵

The mechanism of transfer dehydrogenation with iridium catalysts generally involves opening up a coordination site on the complex by removing two hydrogen ligands through their incorporation into the tbe hydrogen acceptor. The

coordinatively unsaturated intermediate oxidatively adds the C-H bond of the substrate. Olefin is produced via β -elimination, regenerating the catalyst. The PCP pincer catalyst is believed to proceed through the aforementioned steps in its transfer dehydrogenation cycle.⁸

For the chloro-*trans*phosphine iridium catalyst **2b**, however, the steps are slightly different. On the basis of what is reported in the literature, the first coordinates to iridium followed by hydride migration. As a consequence of the electron withdrawing nature of the chloro-ligand, this 16 e⁻ alkyl hydride complex cannot undergo reductive elimination to generate the hot 14 e⁻ intermediate.²⁷ Assistance is required for reductive elimination. Coordination of alkyl solvent/substrate can provide the needed associative assistance (scheme 4).

It was previously reported that in neat tbe, **1a** stoichiometrically converts tbe to tba at 25 °C after about an hour.¹⁹ This result corresponds to step one of the 'typical' transfer dehydrogenation catalytic cycle whereby the tbe opens up a coordination site on the catalyst by removing two hydride ligands. On the other hand, when **2b** was reacted with neat tbe at 150 °C, no tba was produced.²⁷ This result is in accord with the associative assistance argument. Recalling the associative mechanism (scheme 4), alkane complexation is required to initiate tba reductive elimination.⁵⁵ Apparently, tbe is too sterically hindered to promote tba reductive elimination by coordinating with the alkyl hydride complex.



Scheme 4. Associative mechanism for aliphatic transfer dehydrogenation.

Based upon the above it is hypothesized that tba production signals the agostic promotion and stabilization of the nominal 14 e⁻ intermediate. Thus, in order to examine whether this sequence occurs in the catalytic systems of **1a**, **1b**, **2a**, and **2b**, the reactions were carried out in neat tbe. If this hypothesis is correct we expect to see tba production in molar amounts corresponding to the moles of catalyst used in complexes operating via a dissociative mechanistic pathway like **1a**, and no tba production for those complexes operating through an intermolecular associative mechanistic pathway like **2b**.

3.2 Experimental

Standard Schlenk and dry box techniques were employed where appropriate for all chemical manipulations. The following chemicals were purchased and used without further purification: Iridium (III) chloride hydrate (Pressure Chemical Co.), Superhydride® (lithium triethylhydridoborate THF solution, 1.0 M) (Aldrich), Acetone, 2-propanol (Fisher), distilled water. Di-tert-butylphosphine, 98% (Aldrich), α,α -dibromo-*m*-xylene, 97% (Aldrich), tert-butylethylene, were all degassed using a freeze-pump-thaw degas method. Di- μ -chloro-bis(cyclooctene)iridium,³⁹ di-tert-butylphosphinoxylene,^{12,13} and iridium, dihydridobis[bis(dimethylethyl)]phosphinoxylene^{45,56} were all prepared via literature methods. Acetonitrile, diethyl ether, toluene, and pentane were purchased (Fisher) and purified and degassed on an Innovative Technology, Inc. Solvent Purification System. Products were analyzed on a temperature-programmed Hewlett Packard 5890 gas chromatograph using a 250 μm x 25 m OV-1 capillary column.

Reaction of $\text{IrH}_2\{\text{C}_6\text{H}_3(\text{CH}_2\text{P}^t\text{Bu}_2)_2\}_2\text{-2,6}$ (1a**) in Neat Tert-butylethylene.**

A Schlenk reaction tube equipped with a magnetic stirring rod was charged with 42.6 mg of **1a** dissolved in 1.0 ml tbe under an argon atmosphere and stirred for 2.7 h at room temperature. The resulting solution was analyzed by GC set at 30 °C with a one minute isotherm (actual start temperature of 32 °C) and a rate of 2 °/min.

Reaction of $\text{IrD}_4\{\text{C}_6\text{H}_3(\text{CH}_2\text{P}^i\text{Pr}_2)_2\}_2\text{-2,6}$ (1b-d₄**) in Neat Tert-butylethylene.** A Schlenk reaction tube equipped with a magnetic stirring rod was

charged with 22.3 mg of **1b** dissolved in 0.5 ml tbe under an argon atmosphere and stirred for 2.0 h at room temperature. The resulting solution was analyzed by GC set at 30 °C with a one minute isotherm (actual start temperature of 32 °C) and a rate of 2 °/min.

Reaction of IrClH₂(PBU^t₃)₂ (2a) in Neat Tert-butylethylene. An NMR tube was charged with 38 mg of **2a** dissolved in 1.0 ml tbe under an argon atmosphere. The tube was fitted with an adapter for Schlenk line manipulations, placed in a liquid nitrogen filled dewar, frozen, and evacuated prior to O₂/CH₄ flame sealing. The sealed tube was then heated for 3 h at 100 °C. The resulting solution was analyzed by GC set at 30 °C with a one minute isotherm (actual start temperature of 32 °C) and a rate of 2 °/min.

Reaction of IrClD₂(PPrⁱ₃)₂ (2b-d₂) in Neat Tert-butylethylene An NMR tube was charged with 43 mg of **2b-d₂** dissolved in 1.0 ml tbe under an argon atmosphere. The tube was fitted with an adapter for Schlenk line manipulations, placed in a liquid nitrogen filled dewar, frozen, and evacuated prior to O₂/CH₄ flame sealing. The sealed tube was then heated for 2.5 hours at 150 °C. The resulting solution was analyzed by GC set at 30 °C with a one minute isotherm and a rate of 2 °/min.

3.3 Results and Discussion

Initially, we want to verify the literature reports¹⁹ of stoichiometric tba production by the Ir pincer complex. In order to do so, we dissolved 42.6 mg of $\text{IrH}_2\{\text{C}_6\text{H}_3(\text{CH}_2\text{PBU}^t_2)_{2-2,6}\}$, **1a**, in 1.0 ml of tbe under an argon atmosphere and stirred for 2.7 h at room temperature. The GC analysis showed a peak for tba corresponding to complete consumption of complex. Next, in order to determine whether the isopropyl homologue, $\text{IrD}_2\{\text{C}_6\text{H}_3(\text{CH}_2\text{PPr}^i_2)_{2-2,6}\}$, **1b-d₄**, produces tba, 22.3 mg of **1b-d₄** was dissolved in 0.5 ml of tbe under an argon atmosphere and stirred for 2.0 h at room temperature. The GC analysis showed a peak for tba corresponding to complete consumption of complex. These results confirm the literature claims that the PCP pincer complex **1a** stoichiometrically produces tba at 25 °C.¹⁹ Similarly, the *i*-PrPCP pincer complex produces tba, indicating that both pincer complexes **1a** and **1b** access a 14 e⁻ agostically stabilized intermediate.

Similar experiments were conducted to verify literature reports of the hydrogenation of tbe to tba by chloro-*trans*phosphine iridium complexes. In this study 43 mg of $\text{IrClD}_2(\text{PPr}^i_3)_2$, **2b-d₂**, was dissolved in 1.0 ml of tbe under an argon atmosphere in an NMR tube. The reactants were frozen, and the tube was evacuated and sealed, and subsequently, immersed in an oil bath and heated to 150 °C for two and one-half hours. Gas Chromatograph analysis of products contained a peak for tba corresponding to complete consumption of complex. A previous room temperature experiment showed no tba production.

In order to determine whether the tert-butyl homologue, $\text{IrClH}_2(\text{P}^t\text{Bu})_2$, **2a**, produces tba, 38 mg of **2a** was dissolved in 1.0 ml of tbe under an argon atmosphere in an NMR tube. The procedure was the same as for **2b-d₂**, except that **2a** was only heated to 100 °C for three hours. Again, GC analysis showed a peak for tba but with an area corresponding to only 5 % consumption of complex. This lower temperature study reveals the reduced activity associated the chloro-*trans*bisphosphine iridium complexes.

The finding of tba production occurring with **2b-d₂** sinks the hypothesis that the difference in the activity between the two catalysts is because agostic promotion occurs only in the case of the pincer catalyst. It had been reported that **2b-d₂** did not stoichiometrically convert tbe to tba when heated neatly in the former solvent.²⁷ The discrepancy between studies may be explained by the techniques employed. Utilizing Schlenk tubes during the initial stages of the study proved troublesome when heating the volatile (b.p. 50 °C.) neohexene solvent. The Teflon/glass seals would not hold when the tubes were submerged up to their seals (so that no reflux takes place) in the 150 °C oil bath. Therefore, an eloquent adjustment was made: NMR tubes were charged with the reactants and sealed with a torch. Submersion of the tubes in the oil bath achieved and experiment successful. Felkin et al. noted similar observations in their study of alkane dehydrogenation catalyzed with ruthenium complexes in which they used tbe as a hydrogen acceptor for cyclooctane at 150 °C in evacuated sealed tubes. "Preliminary experiments carried out in Schlenk tubes at or near the reflux temperature under an atmosphere of argon gave

erratic results, presumably because of the volatility of the olefin.”⁵⁷ The tert-butyl homologue, **2a**, also converted tbe to tba though with significantly lower yields. The lower activity can be attributed to the application of a lower reaction temperature, 100 °C and shorter reaction time. All four of the *trans*phosphine iridium catalysts studied, **1a**, **2a**, **1b-d₂**, and **2b-d₂**, transform a stoichiometric amount of neohexene into neohexane.

Despite the refutation of an earlier study²⁷ and the central hypothesis, tba production indicating agostic promotion and stabilization of the nominal 14 e⁻ intermediate can still be validated. First, tbe hydrogenation is a favorable reaction ($\Delta H = 33$ kcal/mol). Reductive elimination of tba from the iridium(III) complex is the rate limiting step.²¹ Since coordination of tbe and subsequent hydride migration is facile with both complexes, **1a** and **2b**,¹⁹ stabilization of the products eases the reaction along. Agostic interaction through the aliphatic C-H bonds of the ligands provides the stabilization of the putative 14 e⁻ iridium(I) complex. The chloro-*trans*phosphine iridium species necessitate additional heat to drive the reaction. This indicates PCP catalysts can more readily establish agostic interactions due to the bent P-Ir-P bond angle.

These results correspond with the deuterium labeling study of chapter two. They point to the formation of a hot 14-electron iridium intermediate accessible to all of the *trans*phosphine iridium complexes, **1a**, **1b**, **2a**, and **2b**. The stabilization of such complexes may be through solvent coordination or agostic coordination or a

combination of both. In non-coordinating solvents agostic interactions provide reaction stimulus and stabilize unstable intermediates.

3.4 Conclusion

All four *trans*-phosphine iridium catalysts studied, stoichiometrically hydrogenated the olefin tbe to yield tba. The two catalysts supported with a PCP pincer backbone accomplish the conversion at room temperature ($\sim 25\text{ }^{\circ}\text{C}$), while the chloro-*trans*phosphine iridium complexes required additional energy in the form of heat. Despite the fact that the initial premise set forth at the outset of the study was refuted by the experimental results, the central hypothesis, albeit adjusted, still holds that tba production from reactions of the complexes in neat tbe signals the agostic promotion and stabilization of the nominal 14 e^{-} intermediate. Neohexane reductive elimination following from agostic stimulation corresponds with the results of chapter two. A fugacious 14 e^{-} iridium intermediate is obtainable for all four *trans*phosphine iridium complexes examined: **1a**, **1b**, **2a**, and **2b**.

CHAPTER 4

Epilog and Future Studies

The reason for undertaking the research presented in this thesis stems from listening to many presentations on the subject of $\text{IrH}_2\{\text{C}_6\text{H}_3(\text{CH}_2\text{P}^i\text{Bu}^t)_2\}_{2-2,6}$, **1a**, and its chemistry. The numerous talks emphasized the catalyst's ability to access a 14 electron intermediate during its catalytic cycle; the intermediate having been stabilized through intramolecular C-H—M, or agostic interactions. Experimental evidence included deuterium labeling studies and reactions in neat tbe. At the time, the exoticness of agostic interactions drew my interest as did the contrasting behavior of $\text{IrClH}_2(\text{P}^i\text{Pr}_3)_2$, **2b**, which was presented in these lectures. This latter complex could not access a 14 electron intermediate, presumably because of the electron withdrawing nature of the chloro-ligand and its inability to stabilize such an intermediate agositically as was shown through deuterium labeling studies and reactions in neat tbe.

About this time, Goldman's research group at Rutgers was claiming their $\text{IrH}_4\{\text{C}_6\text{H}_3(\text{CH}_2\text{P}^i\text{Pr}_2)_2\}_{2-2,6}$, **1b**, showed higher activity as a dehydrogenation catalyst than $\text{IrH}_2\{\text{C}_6\text{H}_3(\text{CH}_2\text{P}^i\text{Bu}^t)_2\}_{2-2,6}$, **1a**. The question seemed simple and obvious: How does **1b** and $\text{IrClH}_2(\text{P}^t\text{Bu}_3)_2$, **2a**, behave during catalysis? do they participate in intramolecular C-H—M or agostic interactions?

First, $\text{IrClD}_2(\text{PBu}^t_3)_2$, **2a-d₂**, was synthesized and tested for agostic interactions.

“The principal evidence for σ -complex intermediates is derived from the use of isotopic labeling experiments: specifically the observation of deuterium exchange between hydride and alkyl sites.”⁵⁸ The exchange of deuterium between hydride and ligand alkyl sites was affirmed, and the kinetic study commenced.

After a lengthy kinetic study, $\text{IrH}_4\{\text{C}_6\text{H}_3(\text{CH}_2\text{PPr}^i_2)_2\}$, **1b**, was synthesized. This complex is more difficult to prepare than its tertiary butyl homologue. The PCP ligand precursor of **1b** exists as a cloudy white liquid and is more cumbersome and seemingly less stable than the solid white crystals of **1a**'s PCP ligand precursor.

Curiously, the deuterium NMR studies of **1b-d₂** in mesitylene display only a single deuteride peak at -9.45 ppm. It is curious because for **1a**, two species exist: a tetrahydride, $\text{IrH}_4\{\text{C}_6\text{H}_3(\text{CH}_2\text{PBu}^t_2)_2\}$, which appears initially upon synthesis and in hydrogen saturated solutions, and a dihydride, $\text{IrH}_2\{\text{C}_6\text{H}_3(\text{CH}_2\text{PBu}^t_2)_2\}$, which is formed by placing the tetrahydride under vacuum and is believed to be the catalytically active species. The NMR peaks for the hydride species are about -10 ppm and -30 ppm for the tetra- and dihydrides; respectively.

Once it was determined that **1b** was too active at room temperature to be viable for a similar kinetic study, I assumed my thesis research to be complete. My advisor had other plans. I was to verify the literature claims about **2b**; namely that deuterium does not scramble into the ligands. We work so intimately with **1a** that those claims need not be formally verified.

Astonishingly, the hydrides on **2b** scrambled into the terminal aliphatic bonds of the isopropyl phosphine ligands. The reason for starting this research was based upon the claim that they would not undergo deuterium exchange between hydride and ligand alkyl.

Then, the question was asked; how do they react with neat tbe? Again, all four *trans*-phosphine iridium catalysts stoichiometrically converted tbe to tba. The experiments involving the chloro-analogues were especially satisfying because of what I thought at the time was a novel experimental design. However, upon literature research for the write up of this thesis, it was discovered that other researchers conduct experiments in evacuated, flame sealed, NMR tubes when the reaction involves heating volatile solvents in closed system.⁵⁸

For future studies, coupling constants, J_{CH} , are a good initial indicator for the presence and relative strength of an agostic interaction.¹ Furthermore, for interest and research in this area one can examine the equilibrium isotope effects presented in Parkin's studies,^{59,59} or the claims of isolated 14-electron iridium(III) complexes.^{60,61}

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