A COMBINED EXPERIMENTAL AND COMPUTATIONAL APPROACH TO THE
DEVELOPMENT OF ALKANE DEHYDROGENATION CATALYSTS

BY

BENJAMIN MAXWELL GORDON

A dissertation submitted to the

School of Graduate Studies

Rutgers, The State University of New Jersey

In partial fulfillment of the requirements

For the degree of

Doctor of Philosophy

Graduate Program in Chemistry and Chemical Biology

Written under the direction of

Alan S. Goldman

And approved by

__________________________  
__________________________  
__________________________  
__________________________

New Brunswick, New Jersey

May 2022
ABSTRACT OF THE DISSERTATION

A Combined Experimental and Computational Approach to the Development of Alkane Dehydrogenation Catalysts

by BENJAMIN MAXWELL GORDON

Dissertation Director:

Alan S. Goldman

Pincer-iridium catalyzed alkane dehydrogenation is a selective and relatively mild route to the functionalization of an abundant and otherwise inert feedstock. Significant developments have been made since the initial reports of their use in dehydrogenation, however, they suffer from notable limitations that prevent them from being adopted on industrial scale. In this thesis, we identify the origin of regioselectivity for two prototypical pincer catalysts, (tBuPCP) and (tBuPOCOP), and find it to be the result of differing trans-influences in the aryl ring. This varying trans-influence destabilizes a trans-hydride pincer geometry, changing the rate-determining step from beta-hydride transfer to olefin dissociation which favors the formation of 2-olefin. This kinetically disfavored trans-hydride geometry was further explored. The high energy was determined to be the result of a series of hydride reorganization energies, as no such kinetic barrier to dissociation was found with the similar cis-dihydride geometry. We
next examine an asymmetric pincer geometry that favors the formation of a cis-hydride geometry during its catalytic cycle. This geometry leads to a high regioselectivity in alkane dehydrogenation reactions. Unexpectedly, this also leads to an orders of magnitude increase in activity due to resting state destabilization. Finally, we explore of a series of new pincer-molybdenum complexes.
Acknowledgement

I’d like to start by thanking Alan. Something I always tell new students is that “Alan will not be breathing down your neck so you need to really want to be here to do the chemistry.” Despite this, I’ve never met a PI who is so open and available to their students. One of my deepest regrets in graduate school is not taking advantage of his open door policy sooner. Because, luckily, Alan is also the kind of PI whose thoughtful conversation will inspire you to want to do the chemistry. It certainly inspired me.

But what is a Goldman without his group. After nearly 7 years I’ve gotten to work alongside a number of excellent chemists. I’d like to thank those who left before me: Nick, Bo, Andi, Arun, Boris, and Yang for the immense number of things they’ve taught me inside the lab and out. To Santanu, my brother from another continent, and Tariq, my brother in crime, I want to thank you for being the cause of my imposter syndrome. Starting my journey with the two of you gave me something for which to strive. Nick and Bo, I want to thank you two for helping squelch those feelings of inadequacy. For Arun, Nick, and Santanu: a very respectful “King inda Norf”.

To those who came after: Soumya, Souvik, Ashish, Rachel, Jess, Alex, and Soham. I want to thank you for showing me that the group is in good hands. Taking care of this lab is immense amount of work and I’m comforted to know that it’s filled with people who take its upkeep seriously. I’ve gotten to see more of the next generation of Goldpeople then a lot of the people who came before me and it has been wonderfully refreshing to see such new and interesting insight into chemistry I thought I really understood.
I would like to thank Dr. Geeta Govindarajoo for giving me the opportunity to explore new and interesting methods of teaching and outreach. Her guidance outside of teaching was also invaluable in developing my identity as an independent scientist and educator. The trust you put in me to create, in ways that were new to both of us, is something I won’t forget.

I’d like to thank Dr. Warmuth, Dr. Lipke, and Dr. Prokopchuk for serving on my thesis committee. I’d also like to thank Dr. Jing Lee for being on my committee for my IFRP. I’d like to thank Dr. Murali and Dr. Emge, for having the utmost patience with me while I incessantly bugged them about their expertise. I want to also extend a long overdue thank you to my high-school tech teacher, Mr. Eisenberg. For shaping the way I look at tackling problems. I live my life trying to “walk with purpose.”

On the home front, I would like to extend a loving thank you to my family. To my mother for making me always feel loved and supported, and for instilling and fostering a curiosity that persists to this day. Likewise, I’d like to thank my step-father, for teaching me the value of hard work and by setting an example in the art of the schmooze. I’d like to thank my older brother, Andrew, for spending my entire childhood being my partner in heated, if not completely asinine, argument. Our “debates” prepared me for academia far more than I ever thought possible. To my younger brother, Jacob, I want to thank you for helping me keep one foot out of adulthood by being my Gen Z translator.

Finally, I would like to thank Sara, my love, for your patience and for your understanding. I don’t know that I would have been able to finish this without your support. Thank you for being my second half.
Dedication

To my fiancée, my family, and Brando
# Table of Contents

Abstract........................................................................................................................................... ii

Acknowledgements........................................................................................................................... iv

Dedication........................................................................................................................................ vi

Table of Contents ............................................................................................................................. vii

List of Figures .................................................................................................................................... xi

List of Schemes ............................................................................................................................... xiii

List of Tables ..................................................................................................................................... xv

Chapter 1. Introduction ..................................................................................................................... 1

Chapter 2. Computational Investigation into the Origin of Regioselectivity in Pincer-Iridium Complexes .......................................................................................................................... 10

   Introduction ....................................................................................................................................... 12

   Results and Discussion ................................................................................................................... 14

       Energy Profiles for Dehydrogenation Catalyzed by \textsuperscript{tBu}PCP and \textsuperscript{tBu}POCOP 17

       Origin of High Barriers to Loss of Olefin from (Pincer)IrH\textsubscript{2}(olefin) .......... 20

       Origin of the Difference in RDS for Reactions of Pincer Complexes .......... 23

   Summary and Conclusions .............................................................................................................. 29
Chapter 3. Investigating the Kinetic Component of Ligand Dissociation in Pincer-Iridium Complexes

Introduction .................................................................................................................. 36

Results and Discussion ................................................................................................. 38

Isomer Dependent Kinetic Barriers .............................................................................. 39

Computational Studies – Ligand Dissociation ................................................................. 43

Computational Studies – Hydride Reorganization ......................................................... 45

Conclusions .................................................................................................................... 49

Chapter 4. Stoichiometric and Metal Ligand Cooperative Reactions of (tBuPPP)Ir

Introduction .................................................................................................................... 53

Results and Discussion ................................................................................................. 55

Synthesis of tBuHPP and Metalation ............................................................................. 55

Stoichiometric Reactions of (tBuHPP)Ir and (tBuPPP)Ir Complexes ......................... 60

Computational Studies ................................................................................................. 66

Conclusions .................................................................................................................... 69
Chapter 5. Alkane Dehydrogenation by an Extremely Active Terminal Phosphido Iridium Complex

Introduction .................................................................................................................. 79

Results and Discussion .............................................................................................. 81

Alkane Dehydrogenation by (tBuPPP)Ir: Experimental Studies ..................... 81

Alkane Dehydrogenation by (tBuPPP)Ir: DFT Computational Studies .......... 87

Conclusions .................................................................................................................. 94

Link to Supporting Information .................................................................................. 96

References ..................................................................................................................... 97

Chapter 6. The Synthesis of Novel Pincer-Molybdenum Complexes for the Reduction of Nitrogen to Ammonia ................................................................. 100

Introduction .................................................................................................................. 101

Results and Discussion .............................................................................................. 103

Synthesis of an Electrode Mountable Pincer Complex................................. 103

Attempted Synthesis of a Water Soluble Nitrogen Reduction Catalyst . 108

Phosphorus Metal-Ligand Cooperativity in Pincer Molybdenum Complexes ............................................................................................................................. 110

Conclusions .................................................................................................................. 116
List of Figures

Figure 1.1. Schematic Representation of Alkane Metathesis .................................................. 4

Figure 2.1. Mechanism of (pincer)Ir-catalyzed alkane transfer dehydrogenation .......... 17

Figure 2.2. Free-energy diagram for the reaction of (tBuPCP)Ir .................................................. 18

Figure 2.3. Free-energy diagram for the reaction of (tBuPOCOP)Ir ........................................... 19

Figure 2.4. Free-energy diagram for the reaction of (tBuP8-PNP)Ir ........................................ 26

Figure 2.5. Free-energy diagram for the reaction of (tBuP8-PBP)Ir ........................................ 27

Figure 3.1. Generalized energy surface for exoergic ligand binding ........................................ 38

Figure 3.2. Substitution of PPh(OEt)$_2$ by P(OEt)$_3$ (340 mM) in cis-PPh(OEt)$_2$ ............... 41

Figure 3.3. Electronic energies for the dissociation of PPh(OEt)$_2$ from cis-(tBuPCP)IrH$_2$ .. 44

Figure 3.4. Hydride Energy Surface for (tBuPCP)IrH$_2$ ............................................................ 47

Figure 3.5. Hydride Energy Surface for (tBuPOCOP)IrH$_2$ ....................................................... 47

Figure 4.1. Molecular structure of (tBuPPP)IrHCl ................................................................. 57

Figure 4.2. Molecular structure of (tBuP8PP)IrH$_3$ ............................................................... 59

Figure 4.3. Molecular structure of (tBuPPP)Ir(CO) ............................................................... 61

Figure 4.4. Free energy profile for loss of H$_2$ from (tBuP8PP)IrH$_3$. ........................................ 67

Figure 4.5. Free energy profile for the formation of (PPP)IrH(exo-Cl)................................. 68

Figure 5.1. $n$-Octane/1-hexene transfer dehydrogenation catalyzed by (tBuPPP)Ir ........ 82

Figure 5.2. $n$-Octane/1-hexene transfer dehydrogenation catalyzed by (iPrPCP)Ir ........ 82
Figure 5.3. Octane/Propylene transfer dehydrogenation catalyzed by (tBuPPP)Ir .......... 84

Figure 5.4. Octane/Ethylene transfer dehydrogenation catalyzed by (tBuPPP)Ir .......... 85

Figure 5.5. Free energy diagram for 1,2-dehydrogenation of n-hexane by (tBuPPP)Ir .... 87

Figure 5.6. Free energy diagram for 1,2-dehydrogenation of n-hexane by (tBuPCP)Ir .... 87

Figure 5.7. Free energy diagram for 1,2-dehydrogenation of n-hexane by (iPrPCP)Ir ..... 88

Figure 5.8. Buried volume of hemispheres of (tBuPPP)Ir and (tBuPCP)Ir ...................... 92

Figure 6.1. Molecular structure of pyrene(PNP)MoCl_3 ...................................................... 108

Figure 6.2. Molecular structure of p-NMe_2(PNP)MoBr_3 ................................................. 109

Figure 6.3. Molecular structure of (tBu^PPP)MoBr_3 ....................................................... 111

Figure 6.4. Unrefined molecular structure of (tBuPPP)Mo(X)Br ....................................... 113

Figure 6.5. Molecular structure of (tBu^PPP)MoBr_2 ....................................................... 115
List of Schemes

**Scheme 1.1.** The first example of transition metal alkane dehydrogenation ............... 1

**Scheme 1.2.** Alkane Transfer Dehydrogenation by (RPCP)Ir ............................................ 2

**Scheme 2.1.** Transfer Dehydrogenation Catalyzed by a Pincer-Iridium Catalyst .......... 12

**Scheme 2.2.** Pincer-Iridium Catalysts Studied in This Work ........................................... 13

**Scheme 2.3.** Key Metric Parameters for tBuPCP and tBuPOCOP .................................... 22

**Scheme 2.4.** Isoelectronic Relationship of PCP and Azaborinine-Based Ligands .......... 25

**Scheme 3.1.** Reported olefin dissociation TS and adjoining intermediates ............... 37

**Scheme 3.2.** Addition of L to (tBuPCP)IrH2 .................................................................. 39

**Scheme 3.3.** Ligand Substitution of cis-PPh(OEt)₂ with P(OEt)₃ ................................. 40

**Scheme 3.4.** Ligand Substitution of cis-PPh(OEt)₂ with CO ....................................... 42

**Scheme 3.5.** Relaxed potential energy scan for dissociation from cis and trans-L ....... 44

**Scheme 3.6.** Hydride reorganization geometries in (tBuPincer)IrH2 ................................. 48

**Scheme 4.1.** Metal Ligand Cooperative Triphosphorus Pincers ................................. 53

**Scheme 4.2.** Metalation of (tBuPPHP) and Phosphine Activation ................................. 56

**Scheme 4.3.** Synthesis of (tBuPPHP)IrH₃ ........................................................................ 58

**Scheme 4.4.** Stereoselective displacement of H₂ from (tBuPPHP)IrH₃ ......................... 63

**Scheme 4.5.** Proton Transfer in (tBuPPHP)IrH(exo-CO) .............................................. 64

**Scheme 4.6.** Reactions of (tBuPPHP)IrH, (tBuPPP)IrH₂, and (tBuPHP)IrH₃ .................... 65
Scheme 6.1. Alternative Synthesis of \( \text{pyrene}(\text{PNP})\text{MoCl}_3 \) ............................................ 105

Scheme 6.2. Alternative Synthesis of \( \text{pyrene}(\text{PNP})\text{MoCl}_3 \) ............................................ 106

Scheme 6.3. Synthesis of \( p^\text{NMe}_2(\text{tBuPNP})\text{MoBr}_3 \) .......................................................... 109

Scheme 6.4. Synthesis of \( (\text{tBuP}^\text{HPP})\text{MoBr}_3 \) ................................................................. 111

Scheme 6.5. Deprotonation reactions of \( (\text{tBuP}^\text{HPP})\text{MoBr}_3 \) .................................................. 112

Scheme 6.6. Proposed base induced disproportionation of \( (\text{tBuP}^\text{HPP})\text{MoBr}_3 \) ............... 114

Scheme 6.7. Synthesis of \( (\text{tBuP}^\text{HPP})\text{MoBr}_2 \) ......................................................................... 114

Scheme 6.8. Synthesis of proposed \( (\text{tBuPPP})\text{MoBr} \) .............................................................. 116
List of Tables

Table 2.1. Percent Buried Volumes (% VBur) of (8PCP)Ir, (8POCOP)Ir, and (8PCOP)Ir ..... 14

Table 2.2. Calculated Difference in Free Energies ................................................................. 28

Table 3.1. Energies of hydride relaxation from trans-(tBu-pincer)IrH2 .................................. 48

Table 5.1 Calculated Free Energies of Olefin Binding to (Pincer)Ir ........................................ 90

Table 5.2 Percent buried volumes of (tBuPPP)Ir and (tBuPCP)Ir ............................................ 91
Chapter 1: Introduction

1.1 Early Alkane Dehydrogenation

Alkanes are an abundant resource of non-oxidized carbon which is difficult to functionalize into useful materials. This is best represented in sophomore organic chemistry textbooks, where students are typically told that the only way to functionalize alkanes is by radical halogen pathways.¹ Needless to say, this has long since become outdated. By the 1970s, it had long been understood that transition metal complexes were capable of activating aryl C-H bonds, although similar reactions with alkanes remained elusive.²

Scheme 1.1. The first example of transition-metal alkane dehydrogenation

In 1979, Crabtree and coworkers reported the first example of alkane transfer dehydrogenation catalyzed by a transition metal, \([\text{IrH}_2(\text{acetone})_2(\text{PPh}_3)_2][\text{BF}_4]\), using tert-butyl ethylene, TBE, as an acceptor (Scheme 1.1). Crabtree described TBE as being “indispensable as a hydrogen acceptor” as it did not inhibit reactivity by strongly coordinating to the metal center.³ Despite undergoing several dehydrogenations, these reactions were not considered catalytic as the products of dehydrogenation, cyclooctadiene and cyclopentadiene, coordinated to the metal center generating...
stoichiometric products. Shortly after, Felkin and Crabtree independently reported the first examples of catalytic alkane transfer dehydrogenation with rhenium and iridium respectively. In both cases, cycloalkanes were dehydrogenated or even aromatized utilizing TBE as an acceptor.

1.2 Alkane Dehydrogenation by Pincer Iridium Complexes

In 1996, Kaska and Jensen reported the synthesis of the pincer iridium complex, \((^{tBu}PCP)Ir\). The \(\kappa^3\) binding mode of PCP afforded high complex stability even at elevated temperatures. This higher temperature allowed for cyclooctane dehydrogenation rates that were 2 orders of magnitude greater than previously reported. Soon after, the Goldman and Jensen groups reported the synthesis of a less sterically hindered \((^{iPr}PCP)Ir\). Transfer dehydrogenation with this catalyst revealed a high regioselectivity for the formation of 1-olefin (Scheme 1.2). Upon examination of earlier reports of \((^{tBu}PCP)Ir\), it was found that this catalyst too showed high regioselectivity for 1-olefin.

**Scheme 1.2. Alkane Transfer Dehydrogenation by \((^{R}PCP)Ir\)**

Since these early reactions, the field of pincer-iridium chemistry has flourished. There have been countless variations of the standard PCP type pincer framework. In addition to substitution of tBu groups on the phosphine for iPr groups, other groups...
with varying steric and electronic profiles\textsuperscript{9} have been explored. In addition, the bridging methylene between the phosphine and aryl ring have been substituted for heteroatoms, often referred to with the notation (\textsuperscript{8}PECEP)Ir (E = S, N(H or Me), and O)\textsuperscript{10-13}. Substituents have also been added to the para position of the aryl ring in order to alter the electronics of the metal center.\textsuperscript{13-16} The phosphines have also been exchanged for other dative ligands including NHCs,\textsuperscript{17-19} oxazoline,\textsuperscript{20-23} and pyridines.\textsuperscript{24} The central anionic donor has also been modified to be any number of different donors.\textsuperscript{25-27}

Aside from the catalyst itself, many systems that eschew the typical TBE/alkane couple have been developed in an attempt to increase regioselectivity, activity and efficiency. Reactions have been performed in the gas-phase in order to decrease the likelihood of product isomerization.\textsuperscript{28} Typical alkene hydrogen acceptors have been substituted for electrochemical mechanisms, removing the two hydrides as protons and electrons.\textsuperscript{29, 30} A number of these pincer catalysts have also been developed for use as acceptorless dehydrogenation catalysts, whereby H\textsubscript{2} is lost directly without the use of a hydrogen acceptor.\textsuperscript{15, 20, 31, 32}

1.3 Importance of Homogeneous Alkane Transfer Dehydrogenation

Alkane transfer dehydrogenation clearly represents an exceptional opportunity for the functionalization of otherwise inert feedstocks. Pincer-iridium catalysts for dehydrogenation have the advantage of operating at temperatures that are low (100 °C – 200 °C) when compared to heterogeneous catalysts (500+ °C). Additionally, they also exhibit a much higher regioselectivity when compared to the otherwise stochastic
distribution afforded by heterogeneous catalysts.\textsuperscript{33} The ability to use homogenous catalysts at lower temperatures also allows for their use in combination with other catalysts for tandem catalytic reactions.

One promising tandem catalytic reaction examined by the Goldman, Brookhart and Huang groups involves tandem alkane dehydrogenation and olefin metathesis. Early applications sought to use it as a tool for small alkane coupling into medium weight alkanes for use as liquid fuels.\textsuperscript{34-36} Huang later developed a method using this approach to degrade polyethylene using hexane into a similar product distribution.\textsuperscript{37} Pincer iridium catalysts have even been involved in 4-catalyst tandem reactions that convert n-alkanes to n-alcohols.\textsuperscript{38} Despite this success, the temperature ranges are still somewhat prohibitive and the pincer iridium fragment too sensitive for use with other functional group moieties.\textsuperscript{38-41}

![Figure 1.1. Schematic Representation of Alkane Metathesis](image)

**Figure 1.1. Schematic Representation of Alkane Metathesis**

1.4 Research Goals

The development of novel catalysts for alkane dehydrogenation and the elucidation of the factors that govern their activity has been a seminal goal of the Goldman Group. Many advances have been made with regards to the catalytic activity
of pincer-transition metal compounds and the mechanistic underpinning of transfer dehydrogenation reactions. This mechanistic analysis has been greatly bolstered by the use of DFT-based computational analysis. The goal of this thesis is to add to that understanding, and apply the mechanistic and computational understandings gleaned from past catalysts towards the development of more active and selective pincer-iridium catalysts.

In Chapter 2, we detail the computational analysis associated with determining the origin of regioselectivity in two related pincer-iridium complexes. Therein, we discuss how the trans-influence exerted by the central donor atom of PCP-type pincer complexes can have a dramatic effect on the rate-determining step of dehydrogenation. It is determined that the formation of a kinetically-disfavored trans-dihydride complex is culpable in this change in rate-determining step. In Chapter 3, we test this hypothesis in abstract, by trying to observe the relative rates of formation of cis and trans isomers of the same PCP-iridium complex. The trans-hydride complex is, much like in Chapter 2, found to be kinetically inaccessible and forms only due to intramolecular isomerization. The origin of this high kinetic barrier is determined to be composed of a series of endothermic hydride reorganization barriers.

In Chapter 4, we explore the reactivity of a new pincer-iridium complex containing a secondary phosphine. The stoichiometric reactions of this complex are explored and novel examples of phosphorus-based metal-ligand cooperativity are described. Additionally, it is found that reactions with various small molecules are heavily biased to the cis exo-face of the bowl shaped ligand and coordination of olefins
to the 3-coordinate fragment, which typically represents the resting state in alkane dehydrogenation, are unstable and exhibit rapid dissociation. This destabilized resting state and the effects on alkane dehydrogenation are explored in Chapter 5. Therein, we describe the extraordinarily high activity of the triphosphorus fragment towards the dehydrogenation of linear alkanes using 1-hexene, propylene, and even ethylene as hydrogen acceptors. The high activity is attributed to the destabilization of the 4-coordinate olefin complex and a very similar dehydrogenation pathway that differs only from PCP-type pincers in the site of olefin formation. The terminal selectivity for this catalyst is found to be very high, to the detriment of the product distribution, and this is also attributed to the cis-hydride geometry of the resulting olefin complex. This represents a proof of concept of the findings of Chapters 2 and 3. Chapter 6 summarizes the synthesis of a number of complexes intended for use in nitrogen reduction reactions.
Chapter 1 References

39. Lee, D. W.; Jensen, C. M.; Morales-Morales, D., Reactivity of Iridium PCP Pincer Complexes toward CO and CO2. Crystal Structures of IrH(k2-O2COH){C6H3-2,6-(CH2PBut2)2} and IrH(C(O)OH){C6H3-2,6-(CH2PBut2)2}.H2O. Organometallics 2003, 22 (23), 4744-4749.
Chapter 2: Computational Investigation into the Origin of
Regioselectivity in Pincer-Iridium Complexes

 Portions of this chapter are reprinted with permission from:


Copyright 2021 American Chemical Society.

Abstract

PCP-pincer ($\kappa^3$-2,6-C$_6$H$_3$(CH$_2$PR$_2$)$_2$) iridium complexes have been reported to catalyze the transfer dehydrogenation of n-alkanes with high regioselectivity for the terminal position. We find that the very closely related PCOP ($\kappa^3$-2,6-C$_6$H$_3$(CH$_2$PR)(OPR$_2$)) and POCOP ($\kappa^3$-2,6-C$_6$H$_3$(OPR$_2$)$_2$) complexes, in contrast, afford no such regioselectivity. The difference is a true kinetic phenomenon, i.e., it is not a result of isomerization subsequent to the formation of free $\alpha$-olefin. In addition to direct observation of the distribution of n-alkane dehydrogenation products over time, the pronounced difference in regioselectivity is confirmed through intermolecular competition studies of the reverse reaction (olefin transfer hydrogenation) and of the dehydrogenation of
cycloalkane vs n-alkane. Electronic structure (DFT) calculations indicate that the rate- and selectivity-determining step for dehydrogenation by the (PCP)Ir complexes is β-H transfer. C–H activation at the primary position is much more favorable than at secondary positions, but this is not responsible for the terminal regioselectivity; indeed, the formation of α-olefin via C2–H addition and transfer of the C1–H bond is calculated to be slightly more favorable than dehydrogenation proceeding via C1–H addition. For both PCP and POCOP complexes, the formation of the α-olefin iridium dihydride complex is more facile than the formation of internal-olefin complexes. The next step in the catalytic pathway, loss of olefin, is calculated to have an activation energy that is significantly greater than the metal–ligand (thermodynamic) bond energy. In the case of POCOP complexes, the loss of olefin, rather than β-H transfer, is the rate- and selectivity-determining step. The hydrocarbon moiety in the transition state for olefin loss has the character of a fully formed olefin; this favors the formation of internal olefin. The different regioselectivity of (POCOP)Ir vs (PCP)Ir catalysts is thus attributable to the different rate-determining steps of their respective catalytic cycles; this in turn can be explained in terms of different electronic effects of O versus CH₂ linker exerted through the pincer aromatic ring.
**Introduction**

Pincer iridium complexes have been studied extensively as catalysts for the dehydrogenation of alkanes to alkenes. Originally synthesized by Moulton and Shaw,¹ \((\text{tBuPCP})\text{Ir}\), \((1,3\text{-bis((ditertbutylphosphino)methyl)phenyl})\text{iridium}\), has remained relevant as a catalyst for alkane dehydrogenation due to its activity and terminal regioselectivity,²,³ and use as a prime model for elucidating reaction mechanisms.⁴⁻⁶ It has been established that \((\text{tBuPCP})\text{Ir}\) complexes catalyze the dehydrogenation of \(n\)-alkanes with very high selectivity for the terminal olefin. This selectivity is highly desirable,⁷⁻¹⁰ as there are a significant number of applications that benefit from selective dehydrogenation of the terminal position.¹¹

![Scheme 2.1](image)

**Scheme 2.1 – Transfer Dehydrogenation Catalyzed by a Pincer-Iridium Catalyst**

One of the more promising of these reactions utilizes the terminal regioselective dehydrogenation in tandem with an alkene metathesis catalyst.¹²⁻¹⁴ Dehydrogenation at the terminal position would be expected to lead to \(\text{C}_{2n-2}\) \(n\)-alkane plus ethane in such a cycle. Accordingly, when \((\text{tBuPCP})\text{Ir}\) (1) was used as a dehydrogenation co-catalyst, we found that metathesis of \(n\)-hexane gave \(n\)-decane as the major product.¹²,¹³ The selectivity was much lower than the kinetic regioselectivity found for dehydrogenation,
but this could be attributed to olefin isomerization occurring prior to metathesis. In marked contrast, when the dehydrogenation co-catalyst was the bis-phosphinite complex \((^{18}\text{Bu} \text{POCOP})\text{Ir}\) (2; Scheme 2.2), \(n\)-decane was found to be the least abundant of the heavy products potentially resulting from metathesis of \(n\)-hexane. A priori, this could be attributed to more rapid olefin isomerization in the case of 2. Control experiments, however, indicated that 2 was no more active as an olefin isomerization catalyst than 1.\(^{15}\)

![Scheme 2.2. Pincer-Iridium Catalysts Studied in This Work](image)

**Scheme 2.2.** Pincer-Iridium Catalysts Studied in This Work

In view of the importance of selectivity in dehydrogenation and dehydrogenation-based reactions, we decided to conduct an in-depth comparative study of the regioselectivity of dehydrogenation by the two seemingly similar catalysts, 1 and 2, as well as derivatives thereof. Our goal was to obtain insight into the fundamental factors that determine dehydrogenation regioselectivity. Herein, we report the results of such a study, including an entirely unanticipated explanation for the large variations in regioselectivity found among these catalysts. Experiments performed by Dr. Soumik Biswas and Dr. Michael Blessent empirically determined that while \((^{R4}\text{PCP})\text{Ir}\) complexes exhibited a true kinetic regioselectivity for 1-alkene formation, \((^{18}\text{Bu} \text{POCOP})\text{Ir}\) and \((^{iPr}\text{POCOP})\text{Ir}\) showed selective formation of internal alkenes.\(^{16}\) Hybrid phosphine-
phosphinite pincer iridium complexes, (RdPCOP)Ir, showed no appreciable selectivity. In this chapter we describe the computational analysis, started by Dr. Tian Zhou, used to determine the origin of this regioselectivity.

**Results and Discussion**

Although the experimentation performed by Dr. Biswas and Dr. Blessent revealed similar reactivity trends for (tBuPCP)Ir and (iPrPCP)Ir, we sought to quantitatively eliminate the possibility that this regioselectivity was the result of steric influence. The percent buried volume (%VBur) of RPCP, RPCOP, and RPOCOP were probed using the SambVca 2.1 web application for the characterization of catalytic pockets (Table 2.1).17 The smaller size of the O-atom linker when compared with methylene, and the greater C–O–P bond angle caused by the O-atom linker (114 vs 108° in PCP) causes the dialkylphosphino groups to be restrained in fragment (RPOCOP)Ir (C–Ir–P angles are 81.8 and 84.9° in (tBuPOCOP)Ir and (tBuPCP)Ir, respectively).15 This leads to a % VBur that is 0.7% lower for (tBuPOCOP)Ir than for (tBuPCP)Ir. The hybrid (tBuPCOP)Ir fragment, as expected, shows steric congestion intermediate the two complexes.

**Table 2.1.** Percent Buried Volumes (% VBur) of (RPCP)Ir, (RPOCOP)Ir, and (RPOC)Ir (R = tBu, iPr). Sphere Radius = 3.5Å.

<table>
<thead>
<tr>
<th>R</th>
<th>(RPCP)Ir (%)</th>
<th>(RPOCOP)Ir (%)</th>
<th>(RPOC)Ir (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>tBu</td>
<td>84.5</td>
<td>84.2</td>
<td>83.8</td>
</tr>
<tr>
<td>iPr</td>
<td>78.9</td>
<td>78.8</td>
<td>78.2</td>
</tr>
</tbody>
</table>
(iPrPCP)Ir exhibits a % VBur that is much lower than (tBuPCP)Ir, by 6% of the sphere volume, while (iPrPCOP)Ir and (iPrPOCOP)Ir are slightly smaller (Table 2.1). This qualitatively demonstrates that pincer ligands with tBu2P groups have similar steric congestion. The same is found for the much less hindered pincers containing iPr2P groups. Yet, while (iPrPCP)Ir and (tBuPCP)Ir show a high level of terminal regioselectivity, (tBuPCOP)Ir and (tBuPOCOP)Ir afford no such terminal regioselectivity.

Evidently, the O linker strongly disfavors terminal regioselectivity, but not via a simple modulation of crowding at the metal center. With differential steric effects ruled out as the major source of the differences in regioselectivity, the experimental results would indicate that any explanation should be based on electronic effects. However, a priori, we assumed that differences in the electronic demands of the individual reaction steps for terminal dehydrogenation versus internal dehydrogenation would be small; accordingly, it became quite difficult to understand how the subtle differences in the electronic properties engendered by the O vs CH2 linkers could account for striking differences observed in regioselectivity. 18,19,20 We have therefore conducted a computational electronic structure study to elucidate the mechanistic origin of this regioselectivity in the catalytic dehydrogenation of hexane with a focus on (tBuPCP)Ir catalyst 1 and (tBuPOCOP)Ir catalyst 2.

All electronic structure calculations employed the DFT method.21 Geometries were optimized (gas phase) using the M06 functional22 and 6-31G(d,p) basis sets for all atoms, except iridium. 23-26 For Ir, we applied the SDD effective core potential (60e⁻ ECP) and the associated valence basis set.27 Normal mode analysis verified the nature of a
particular stationary point located on the potential energy surface (minimum, transition state) and provided fundamental parameters necessary for the evaluation of enthalpies and Gibbs free energies \((P = 1 \text{ atm}; T = 298.15 \text{ K} = 25 ^\circ \text{C})\) using standard statistical mechanical expressions applicable to an ideal gas. Improved potential energies for all structures were obtained from single-point calculations (at the optimized geometries) applying 6-311+G(d,p) basis sets for all nonmetal atoms. We combined these potential energies with the vibrational zero point and thermal energy corrections already determined to form enthalpies and Gibbs free energies, which approximate energies computed at the higher basis set level (gas phase; \(T = 298.15 \text{ K}, P = 1 \text{ atm}\)).

Further, to better simulate experimental reaction conditions, we adjusted the free energies to include the approximate effect of a condensed phase (i.e., \([n\text{-hexane}] = 7.6 \text{ M} \sim P = 190 \text{ atm at } T = 298.15 \text{ K}\)) and the (statistical) presence of multiple C–H bond activation sites. All energies quoted in the text are free energies obtained through this procedure (unless noted otherwise). Full computational details are available in the Supporting Information.

We have previously proposed that the catalytic transfer dehydrogenation cycle proceeds as shown in Figure 2.1, and, indeed, all of the computational results described herein are consistent with that proposal. While the 14e\(^-\) (pincer)Ir fragment is certainly not the resting state during the catalytic cycle (indeed, we have never succeeded in observing this species despite many attempts to do so), it serves as a convenient zero energy point for the stated thermodynamic parameters, particularly since the nature of the resting state should have no effect on the regioselectivity.
Energy Profiles for Dehydrogenation Catalyzed by 1 and 2: Origin of the Different Regioselectivity

The electronic structure calculations for the reaction of 1 with $n$-hexane indicate that the rate- and selectivity-determining step is β-H transfer by ($^{18}$uCP)Ir(hexyl)(H) (Figure 2.2). The β-H transfer transition state (TS-BHT) leading to ($^{18}$uCP)Ir(H)2(2-hexene) is 3.8 kcal/mol higher in free energy than the lowest TS leading to ($^{18}$uCP)Ir(H)2(1-hexene). Consequently, this value of $\Delta G(\text{TS}_{\text{BHT-int}}) - \Delta G(\text{TS}_{\text{BHT-term}})$ accounts for (or over-accounts for) the observed regioselectivity.
Figure 2.2 – Free-energy diagram for the reaction of \((tBuPCP)Ir\) with \(n\)-hexane. \([Ir] = (tBuPCP)Ir\). (Lowest-energy isomers of each intermediate or TS are shown).

C–H addition at C1 is favored over addition at C2, both kinetically (\(\Delta G^\ddagger = 17.8\) and 19.7 kcal/mol, respectively) and thermodynamically (\(\Delta G^\circ = 14.2\) and 16.6 kcal/mol). Surprisingly, however, the lowest-energy TS leading to the 1-hexene complex is a 2,1-\(\beta\)-H-transfer, i.e., transfer at C1 from the secondary (2-hexyl) hydride, although the difference is small at 26.0 kcal/mol vs 26.8 kcal/mol. Thus, neither the kinetic nor thermodynamic favorability of C–H addition at the primary position of alkanes is calculated to directly influence regioselectivity. Similarly, the most favorable TS leading to the 2-hexene complex is transfer at C2 from the 3-hexyl hydride (29.8 kcal/mol vs 31.8 kcal/mol for transfer at C3 from 2-hexyl hydride).
Chemical intuition suggests that the nature of the linker (O vs CH₂) would not affect the direction of the difference in energy between TS_{BHT-int} and TS_{BHT-term} (ΔΔG-TS_{BHT-int-term}). Indeed, the value of ΔG-TS_{BHT-int/term} for (tBuPOCOP)Ir (3.7 kcal/mol; Figure 2.3) is calculated to be essentially identical to that for (tBuPCP)Ir (3.8 kcal/mol); thus, the formation of 1-alkene dihydride complex is calculated to be strongly favored with either pincer ligand, both kinetically and thermodynamically.

Figure 2.3 – Free-energy diagram for the reaction of (tBuPOCOP)Ir with n-hexane. [Ir] = (tBuPOCOP)Ir. (Lowest-energy isomers of each intermediate or TS are shown).

The origin of the difference in regioselectivity is revealed by calculation when the step following β-H transfer is considered. Whereas β-H transfer is rate and selectivity determining in the case of (tBuPCP)Ir, in the case of (tBuPOCOP)Ir, the rate- and selectivity-determining step is calculated to be the subsequent step, namely, loss of
olefin. The large difference in the energies of terminal and internal β-H transfer TSs is thus not relevant for dehydrogenation by \((^{18} \text{Bu} \text{POCOP})\text{Ir}\). Instead, the relevant parameter is the difference in free energy between the TS for loss of 1-hexene compared with the TS for loss of 2-hexene (27.2 and 25.2 kcal/mol, respectively), consistent with the reversal of regioselectivity compared with catalyst 1.

The fact that such a remarkable difference in selectivity is correctly predicted by the results of the DFT calculations allows us to have a very high level of confidence in the validity of this explanation. However, it clearly raises the question: What is the underlying origin of the high energy of the TS for olefin dissociation from \((^{18} \text{Bu} \text{POCOP})\text{IrH}_2(\text{alkene})\) as compared with the \(^{18} \text{Bu} \text{PCP}\) analogue?

**Origin of High Barriers to Loss of Olefin from (Pincer)IrH\(_2\) (olefin)**

Generally, barriers to ligand loss are assumed to be closely associated with the thermodynamics of the corresponding metal–ligand bonds. As seen in Figures 2.2 and 2.3, however, the thermodynamics of alkene loss from complexes of \((^{18} \text{Bu} \text{POCOP})\text{Ir}\) and \((^{18} \text{Bu} \text{PCP})\text{Ir}\) are both highly exergonic, with the free energy of dissociation from \((^{18} \text{Bu} \text{POCOP})\text{Ir}(1\text{-hexene})\) \((\Delta G = -10.0 \text{ kcal/mol})\) being approximately equal to that for dissociation from \((^{18} \text{Bu} \text{PCP})\text{Ir}(1\text{-hexene})\) \((\Delta G = -10.8 \text{ kcal/mol})\).

The Ir–alkene bond-dissociation enthalpy (BDE) calculated for trans-\(^{18} \text{Bu} \text{PCP})\text{IrH}_2(1\text{-hexene})\) is 9.4 kcal/mol, while that for trans-\((^{18} \text{Bu} \text{POCOP})\text{IrH}_2(1\text{-hexene})\) is 7.7 kcal/mol. The kinetic enthalpic barriers \((\Delta H^\ddagger)\) to olefin loss, however, are significantly greater. The calculated value of \(\Delta H^\ddagger\) is 12.2 kcal/mol for the \(^{18} \text{Bu} \text{PCP}\)
complex. Most importantly, $\Delta H^\ddagger$ is calculated to be 2.6 kcal/mol greater for $(t^3\text{BuPOCOP})\text{IrH}_2(1\text{-hexene})$, at 14.8 kcal/mol, despite the (thermodynamic) BDE being 1.7 kcal/mol less than that of the $t^3\text{BuPCP}$ analogue.

The origin of these high kinetic barriers to olefin loss can be traced to the geometry of the product. As predicted and explained in pioneering work by Eisenstein,$^{33, 34}$ the geometry of trans-$L_2\text{IrXH}_2$ complexes (which are formally analogous to $(R\text{PCP})\text{IrH}_2$ and derivatives) is severely distorted from square pyramidal; a geometry in which hydride ligands are mutually trans would be particularly unfavorable. Completely in accord with that work, we calculate that $\text{H}–\text{Ir}–\text{H}$ angles in $1\text{-H}_2$ and $2\text{-H}_2$ are severely acute, 54.3 and 58.6°,$^{35}$ respectively. The coordination geometry of the olefin-dissociation TS, as is typically expected of a TS for ligand loss, is similar to that of the olefin-bound complex, but with a greatly weakened interaction between the metal and the departing ligand. Most importantly, hydride ligands are situated almost rigorously trans ($<\text{H}–\text{Ir}–\text{H} \text{POCOP} = 178^\circ$ and $<\text{H}–\text{Ir}–\text{H} \text{PCP} = 179^\circ$) in the olefin-dissociation TS, in marked contrast with the $\text{H}–\text{Ir}–\text{H}$ angles in the olefin-loss products.$^{36}$ Conversely, the geometry of the departing olefin in the TS is approximately that of the free ligand as most clearly indicated by the C–C bond distance of 1.34 Å in both TSs, i.e., the same value found in free 1-hexene, as compared with 1.40 Å for the bound olefin. Likewise, the olefin in the TS is approximately planar as compared with the more pyramidalized carbons of bound olefins (key metrical parameters are shown in Scheme 2.3). Indeed, for both complexes, there is very little indication of any olefin $\pi$-bonding in the olefin-dissociation TS. The major Ir-olefin bonding interaction in the transition states is a fairly
long $\sigma$–C–H bonding interaction. Thus, the TS for olefin dissociation requires loss of most of the metal–olefin interaction but realizes none of the energetic benefits of the subsequent relaxation leading to the low energy complex with an acute H–Ir–H angle.

**Scheme 2.3.** Key Metric Parameters (Distances in Å) for TS-BHT, trans-(pincer)IrH$_2$(1-hexene), TS for Loss of 1-hexene, and (Pincer)IrH$_2$ (Product of 1-Hexene Loss) for (a) $^{t}$BuPCP and (b) $^{t}$BuPOCOP

Since the character of TS-Olefin-Diss closely resembles that of trans-(pincer)IrH$_2$ plus free olefin, it is of significantly higher energy than that of the actual products: geometrically unconstrained (pincer)IrH$_2$ plus free olefin. Just as significantly, to the extent this characterization of the TS-Olefin-Diss is valid, and in the limit where the Ir-alkene interaction is energetically negligible, if this is the TS for the rate-determining step, then the catalyst would necessarily favor the formation of the more stable, internal, olefin; hence, this model provides a very direct rationale for the lack of terminal regioselectivity by such catalysts.
Calculations of the other pincer–Ir catalysts investigated in this work generally predict smaller differences between the energies of TS-CH-Add, TS-BHT, and TS-Olefin-Diss. In the case of (iPr)PCP)Ir, TS-BHT is slightly higher in energy than TS-Olefin-Diss for 2-hexene formation, but the difference in energies of the respective TS-BHT isomers is sufficiently large (2.2 kcal/mol) to account for the observed selectivity (Table S2.4). We have not calculated the energetics for the catalysis by (tBu2PCP)iPr)Ir, but assuming that they are somewhere intermediate between the (tBu(PCP)Ir and (iPr(PCP)Ir, then olefin dissociation is not rate determining for any of the three (PCP)Ir complexes.

As would be expected, for PCOP catalysts, the calculated energies are intermediate between those of the PCP and POCOP catalysts. The small differences in calculated energies of the key TSs make any calculation-based predictions of their regioselectivity extremely difficult and questionable. Nevertheless, the trends unambiguously predict relatively lower energies of TS-BHT versus TS-Olefin-Diss as CH₂ linkers are replaced with O atoms. These values correctly “predict” and yield a simple explanation for the highly unexpected effect of the nature of the linkers. We therefore believe that a high level of confidence in this explanation of the differential regioselectivity is justified.

Origin of the Difference in Rate-Determining Steps for Reactions of PCP versus POCOP and PCOP Complexes

As just described, the electronic structure calculations reveal that the differences in selectivity between different (pincer)Ir catalysts are straightforwardly attributable to
different rate-determining steps in their respective catalytic cycles. This, of course, then raises the question as to the origin of this difference.

The O-for-CH₂ linker substitution involved in PCP/PCOP/POCOP variations is expected to decrease the sigma-donating ability, and thereby the trans influence, of the pincer ligand ipso-carbon bound to iridium. This in turn would be expected to lower the energy of TS-Olefin-Diss relative to TS-BHT, as the ipso-carbon in TS-Olefin-Diss is positioned trans to a very weakly bound (almost fully dissociated) olefin, as opposed to an incipient alkyl group at the same coordination site in the case of TS-BHT (Scheme 2.3). The expectedly much greater trans influence of the incipient alkyl group in TS-BHT compared with the departing olefin in TS-Olefin-Diss is highlighted by the much shorter Ir-Cipso bond distance in TS-Olefin-Diss for both PCP and POCOP complexes (approximately 0.1 Å, Scheme 2.3).

Thus, we considered that increased σ-donation by Ir-Cipso lowers the energy of TS-Olefin-Diss relative to TS-BHT, in accord with the calculated energies as well as the experimentally observed regioselectivity. To further test this hypothesis, which implies that the effects of the linker are electronic and specifically exerted via the Ir-bound carbon, we sought to design model compounds in which we could tune the electronic properties of the iridium-bound carbon atom without varying aryl-P linkages. The effect of varying atoms fully contained within the aromatic ring of the pincer ligand was demonstrated through calculations on complexes of 1,4-azaborinine-based pincers (Scheme 2.4), which are isoelectronic with and have the same overall charge as the PCP ligand. In the pincer ligand (²Bu⁺P-B-PNP), the formally anionic ipso-carbon of PCP has been
replaced with a much weaker σ-donor, a neutral N atom, while conversely, in (tBuN-PBP), the coordinating atom of the aryl group is a presumably very strong σ-donor, a formally dianionic boron.

Scheme 2.4. Illustration of the Isoelectronic Relationship of PCP and Azaborinine-Based Pincer Ligands

The substitutions indicated in Scheme 2.4 are calculated to affect the energy profiles for n-hexane dehydrogenation quite dramatically. C–H addition is strongly favored, kinetically and thermodynamically by the weaker σ-donating tBuB-PNP ligand, and conversely disfavored by tBuN-PBP, in accord with results of previous studies (Figure 2.4). With regard to the focus of the present investigation, for (tBuB-PNP)Ir, TS-Olefin-Diss isomers are both significantly higher in energy than the TS-BHT isomers. The TSs of dissociation of 1-hexene and 2-hexene are 12.5 and 12.8 kcal/mol higher, respectively, than the lowest conformer of TS-BHT, which leads to 1-hexene. These differences between TS-Olefin-Diss and TS-BHT are significantly greater than those found for (tBuPOCOP)Ir, where the same comparison reveals differences of only 6.1 and 4.1 kcal/mol (Figure 2.3).
Figure 2.4 – Free-energy diagram for the reaction of (tBu-pB-PNP)Ir with n-hexane. [Ir] = (tBu-pB-PNP)Ir. (Lowest-energy isomers of each intermediate or TS are shown).

For the converse variation of the aromatic ring, (tBu-pN-PBP)Ir, with the formally dianionc B atom coordinated to Ir, calculations of the catalytic cycle show a striking reversal in the energies of TS-BHT relative to TS-Olefin-Diss (Figure 2.5). The TS-Olefin-Diss isomers are more than 12 kcal/mol lower than the lowest isomer of TS-BHT (as opposed to 12.5 and 12.8 kcal/mol higher in the case of (tBu-pB-PNP)Ir).
This very large reversal in the relative energies of TS-Olefin-Diss and TS-BHT for (Bu^4pN-PNP)Ir supports the proposed explanation for the analogous (but much smaller) differences between the TS energies found with (POCOP)Ir and (PCP)Ir complexes; namely, the different electronic properties of the Ir-bound atom of the aromatic ring play a dominant role. We have also investigated (more conventional) derivatizations of the PCP ligand, which display smaller effects as would be expected.

Para-substitution of the aryl ring with a nitro group results in a decrease of the energy gap between TS-BHT and TS-Olefin-Diss (Table 2.2); thus, the effect is in the same direction as the two O-for-CH\textsubscript{2} linker substitutions at the ortho position, although it is much smaller. Constraining the NO\textsubscript{2} group either perpendicular or parallel to the plane
of the aryl ring, in an effort to distinguish π- versus σ-effects, had little effect on TS energetics. To investigate the possible role of π-effects at the linker substituent, we calculated the effects of CF$_2$ and NH linkers, i.e., two groups which are more electron withdrawing than CH$_2$, but with only the latter offering the possibility of substantial π-donation. Both showed a substantial effect of similar magnitude (Table 2.2), in the same direction although smaller in magnitude than the O-for-CH$_2$ linker substitutions. These results are all consistent with an explanation for the effects of varying the pincer linkers that is based primarily on a resulting variation in the σ-donating ability of the pincer ipso-carbon, although π-effects of smaller magnitude can certainly not be excluded.

### Table 2.2 – Calculated Difference in Free Energies (kcal/mol) for TS-BHT(C2,1), and, TS-Olefin-Diss, for Various (tBuPCP)Ir Derivatives

<table>
<thead>
<tr>
<th>Pincer</th>
<th>TS-BHT(C2,1) - TS(OlefinDiss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>tBuPCP</td>
<td>1.2</td>
</tr>
<tr>
<td>tBuPOCOP</td>
<td>-6.1</td>
</tr>
<tr>
<td>tBuPBP-PNP</td>
<td>-12.5</td>
</tr>
<tr>
<td>tBuPN-PBP</td>
<td>12.1</td>
</tr>
<tr>
<td>II-p-NO$_2$-tBuPCP$^a$</td>
<td>0.9</td>
</tr>
<tr>
<td>⊥-p-NO$_2$-tBuPCP$^a$</td>
<td>0.5</td>
</tr>
<tr>
<td>tBuPCP-F$_4$$^b$</td>
<td>-1.3</td>
</tr>
<tr>
<td>tBuPNCNP$^c$</td>
<td>-3.7</td>
</tr>
</tbody>
</table>

a) II-p-NO$_2$ and ⊥-p-NO$_2$ refer to the p-NO$_2$ substituent constrained in the plane and perpendicular to the plane of the aryl ring, respectively. b) tBuPCP-F$_4$ = 2,6-C$_6$H$_3$(CF$_2$P(Bu)$_2$)$_2$. c) tBuPNCNP = 2,6-C$_6$H$_3$(NHP(Bu)$_2$)$_2$.

### Summary and Conclusions
We have demonstrated in this work that (PCP)Ir-based catalysts show high selectivity for dehydrogenation of the terminal position of n-alkanes, whereas (PCOP)Ir and (POCOP)Ir catalysts (analogous complexes with one or two O-atom linkers) are much less terminal selective, or are even selective for the formation of internal olefins. The difference is a genuine kinetic effect and not due to isomerization of free olefin (although such isomerization does lead, eventually, to predominantly internal olefin in all cases studied).

Electronic structure calculations reveal that this difference in selectivity is not due to any variations, among the catalysts studied, in the energy differences between pro-terminal and pro-internal TSs for any given reaction step. For example, the differences in energies, between β-H-transfer TSs leading to terminal versus internal olefins, are nearly identical for (tBuPCP)Ir and (tBuPOCOP)Ir (3.8 and 3.7 kcal/mol, respectively). Indeed, for all catalysts investigated, both 1,2- and 2,1-β-H-transfer TSs leading to terminal dihydride complex are lower than the β-H-transfer TSs leading to internal alkene complex. Thus, 1-alkene dihydride complexes are formed more rapidly than 2-alkene dihydrides in all cases studied—including those catalysts that are not selective for the formation of free terminal olefin. The difference in the observed regioselectivity is instead attributable to a difference in rate-determining steps between the catalysts. In particular, the selectivity is determined by a rate-determining β-H transfer for (tBuPCP)Ir versus a rate-determining olefin dissociation in the case of (tBuPOCOP)Ir.
In the TS for olefin dissociation, the departing olefin moiety has the character of a fully formed olefin, while the remaining fragment has a geometry very similar to that found in the fully bound olefin complex trans-(pincer)IrH₂(alkene). In the limiting case where this (simplified) characterization is valid, and the olefin-metal interaction becomes negligibly weak in the TS for olefin dissociation, the difference in energy between the pro-terminal and pro-internal olefin-dissociation TSs will be equal to the difference between the terminal and internal olefins, and will thus necessarily favor the formation of internal olefin.

The Ir-alkene bond in the trans-(pincer)IrH₂(alkene) intermediate is thermodynamically very weak. For example, bond-dissociation enthalpies for (tBuPCP)IrH₂(1-hexene) and (tBuPOCOP)IrH₂(1-hexene) are calculated as only 9.4 and 7.7 kcal/mol, respectively, while ΔG° for dissociation is actually calculated to be quite negative (−10.8 and −10.0 kcal/mol, respectively). On that basis, it might be expected that the barrier to olefin loss would be small, and the TS for alkene dissociation from (pincer)IrH₂(alkene) would be much lower in energy than the preceding β-H-transfer TS (which is also the TS for the back reaction, i.e., olefin insertion or hydride-to-olefin migration). However, despite the thermodynamically weak binding, the kinetic barrier to olefin loss is surprisingly high. Importantly, it is higher for (POCOP)Ir than it is for (PCP)Ir complexes, for example, ΔG‡ = 12.6 kcal/mol for loss of 1-hexene from trans-(tBuPOCOP)IrH₂(1-hexene) and 8.9 kcal/mol for trans-(tBuPCP)IrH₂(1-hexene), while the corresponding values of ΔH‡ are 14.8 and 12.2 kcal/mol.
The experimental results indicate that the differences in selectivity between catalysts are significant and are not primarily attributable to steric factors. The calculations indicate that the low selectivity in the POCOP and PCOP complexes is due to a high rate- and selectivity-determining kinetic barrier to alkene loss from trans-(pincer)IrH2(alkene) (pincer = POCOP or PCOP), although alkene is quite weakly bound thermodynamically. As a result, the formation of the corresponding 1-alkene complexes is reversible and the major alkene eventually liberated is internal.

Both experimental and computational results indicate that the difference in the rate-determining step, leading to the difference in regioselectivity, is due to electronic differences between PCP, PCOP, and POCOP. In particular, O-atom linkers result in an Ir-bound carbon atom that has a weaker trans-influence relative to that of the Ir-bound carbon of (PCP)Ir. This results, for the POCOP complexes, in a higher energy olefin-dissociation TS relative to the β-H-transfer TS, and this olefin-dissociation TS being rate-determining.

The barrier to ligand dissociation from transition-metal complexes is typically thought of as being determined by the corresponding metal–ligand bond strengths. This is found not to be the case in the present systems, and this is shown to have a dramatic and unexpected effect, leading to major differences in regioselectivity among very closely related alkane dehydrogenation catalysts.

**Supporting Information**
Chapter 2 References


18. For examples of investigations of other effects of varying the phosphido-aryl linkers, see:


35. These H-Ir-H angles are based on geometries of (tBu4POCOP)Ir(H)$_2$ and (tBu4PCP)Ir(H)$_2$ obtained using the LANL2TZ basis set. Using the SDD basis set we were unable to locate an energy minimum for (tBu4PCP)Ir(H)$_2$; all attempts converged with a dihydrogen complex, although an energy minimum was obtained for (tBu4POCOP)Ir(H)$_2$ (>H-Ir-H = 53.6°). Experimentally, however, the 1H NMR spectrum (δ −19.19) clearly indicates that (tBu4PCP)IrH$_2$ is a dihydride as is (tBu4POCOP)IrH$_2$ (δ −17.04; ref (26)). Using the LANL2TZ basis set, dihydride energy minima were obtained (H-Ir-H angles given in text) for both complexes. The actual nature of the complexes (dihydride with acute angle versus dihydrogen complex) does not impact the conclusions of this work since in either case substantial relaxation must occur after dissociation of olefin from trans-(pincer)Ir(H)$_2$(olefin). To minimize inconsistencies, however, we used the LANL2TZ basis set to obtain the geometries of (pincer)Ir(H)$_2$ in both cases, and then conducted single-point calculations using the SDD basis set to determine the energies shown in Figures 1 and 2.
36. It is clearly not possible, based on steric considerations, for the hydrides to approximate the geometry found in the olefin-loss product, which has a very acute H-Ir-H angle, as long as the olefin exhibits even weak pi coordination at the site trans to the pincer ligand ipso-carbon. But the increased Ir-olefin distance seen in TS-OlefinDiss would allow the H-Ir-H angle (ca. 180°) to decrease to some extent. This decrease in the angle is not calculated to occur, however, because even in the complete absence of olefin such a distortion has a significant kinetic barrier (ref (31)). Therefore such a partial “relaxation” would not contribute to a lowering of the energy of the TS; instead it would only further raise the energy of TS-Olefin-Diss.
37. Energies for complexes of tBu4PCOP, iPr4PCP, iPr4PCOP, and iPr4POCOP ligands are available in the Supporting Information.
Chapter 3: Investigating the Kinetic Component of Ligand Dissociation in Pincer-Iridium Complexes.

Abstract

The kinetic barrier to ligand dissociation from cis and trans isomers of ($^t$BuPCP)IrH$_2$L (L = PPhOEt$_2$, POEt$_3$) are examined via ligand exchange. The mechanism of isomerization of cis-($^t$BuPCP)IrH$_2$L to trans-($^t$BuPCP)IrH$_2$L is found to be consistent with an intramolecular trigonal twist mechanism that accounts for the entirety of trans-($^t$BuPCP)IrH$_2$L formation. Direct association to give the trans isomer is thereby found to be kinetically unfavorable and suggests a very high kinetic barrier to dissociation from trans-($^t$BuPCP)IrH$_2$L.

Calculations using DFT find that this kinetic barrier is due to the geometry of the hydrides resulting from the dissociation. Whereas the dissociation from cis-($^t$BuPCP)IrH$_2$L leads to a hydride geometry which is already fully relaxed, dissociation from trans-($^t$BuPCP)IrH$_2$L leads to a very high energy geometry that must undergo a series of hydride reorganizations. In the reverse direction, ligand association, these collective hydride reorganizations result in a significant kinetic barrier preventing ligands from associating trans to the ipso carbon of ($^t$BuPCP)Ir.
Introduction

Ligand dissociation is perhaps the single most common reaction step in organometallic chemistry. Barriers to ligand dissociation are typically, though not always, considered in terms of metal-ligand Bond Dissociation Enthalpy or Free Energy (BDE, BDFE); these, however, are purely thermodynamic properties. The use of BDFE to describe ligand dissociation leads to a systematic discounting of what is a mechanistically complex process. In the previous chapter, we described a system wherein the kinetic barrier to ligand dissociation played a crucial role in governing the regioselectivity of \((tBu_{up}CP)Ir\) and \((tBu_{up}OCOP)Ir\), two catalysts which, a priori, have minimal structural differences. In that work, it was determined that varying the electronic contribution from the ipso atom of the aryl ring had a dramatic effect on the energy of the steps preceding product dissociation and therefore made the oft neglected ligand dissociation step rate-determining. The high energy of the rate-determining product dissociation was attributed to the geometry of the hydrides in the transition state. As the olefin departs, it contributes insignificantly to the metal center and what remains is a geometry where the two hydride ligands are mutually trans (\(\angle H-Ir-H \ 178.0^\circ\)).
Scheme 3.1. Reported olefin dissociation transition state and adjoining intermediates.

This computed transition state, while a useful bellwether for the kinetic barrier of dissociation, is in fact an early geometry for the dissociation of olefin from iridium. Indeed, the transition state described in that work, TS-Olefin-Diss, represents the transition between the iridium pi olefin complex and a σ C-H interaction of the terminal olefin (Scheme 3.1). Despite this, we still presented that transition state as the bridge between the iridium pi olefin complex and the free olefin and lowest energy geometry of (tBuPCP)IrH₂. By doing this, we completely forego the analysis of the hydride reorganization energy. Ligand reorganization energy is not often mentioned when describing thermally driven catalytic cycles, although it remains a foundational component of Marcus Theory when describing electrochemical systems.⁴⁻⁶

In this chapter, we seek to investigate the conclusions of the previous chapter; specifically, that the kinetic barrier to dissociation from the trans-olefin complex is in fact due to the formation of a high energy trans-(tBu-pincer)IrH₂ intermediate. Unfortunately (tBu-pincer)Ir(olefin)H₂ complexes are not stable enough to observe the dissociation directly, as these complexes will instead proceed with the much faster olefin hydrogenation to yield (tBu-pincer)Ir and alkane. Therefore, in order to examine ligand dissociation, we turn to the much more common exoergic ligand dissociation. In this
study, we have chosen phosphines as a mimic of olefins due to their exoergic BDFE, ability to form stable octahedral dihydride complexes without $H_2$ elimination,\textsuperscript{7-9} and pi accepting nature.\textsuperscript{10}

**Figure 3.1.** Generalized energy surface for exoergic ligand binding. The kinetic component is highlighted and the thermodynamic component (BDFE) in red.

**Results and Discussion**

In order to determine the kinetic component of the barrier to ligand dissociation from $trans-\left(\text{tBuPCP}\right)\text{IrH}_2(\text{L})$ “($trans$-$L$)” and $cis-\left(\text{tBuPCP}\right)\text{IrH}_2(\text{L})$ “($cis$-$L$)” we initially set out to measure the rate of ligand association, as this rate would be defined by the kinetic barrier to dissociation (**Figure 3.1**). Given our desire to determine the kinetic components to dissociation for both $cis$ and $trans$-hydride ($^{\text{tBuPCP}}\text{IrH}_2$, we turned to ligands that had been previously identified as having the ability to bind to (PCP)$\text{IrH}_2$ in a
cis and trans fashion, P(OEt)₃ and PPh(OEt)₂.¹¹ These ligands both readily complexed with (tBuPCP)IrH₂ to form a kinetically stable cis-L and a thermodynamically stable trans-L (L = P(OEt)₃ and PPh(OEt)₂), (Scheme 3.2). Similar screens with (tBuPOCOP)IrH₂ were performed but did not give tangible results as L addition was followed by H₂ elimination to give (tBuPOCOP)Ir(L).

Isomer Dependent Kinetic Barriers

Scheme 3.2. Addition of L to (tBuPCP)IrH₂

The rates of addition for P(OEt)₃ and PPh(OEt)₂ to give cis-L were too fast to observe, being seemingly limited by mixing even at temperatures as low as -78 °C. At early time points there was no measurable formation of trans-(tBuPCP)IrH₂(L) by ¹H or ³¹P NMR. While this rapid association to give cis-L and not trans-L would seem to answer our question, it should be noted that these two complexes are exceptions and most L add to (tBuPCP)IrH₂ to give trans-(tBuPCP)IrH₂L. We originally hypothesized that formation of trans-L from cis-L proceeded via a dissociative mechanism: dissociation of L from cis-L and reassociation to give trans-L. Given this assumption, we desired to measure the rate of dissociation from cis-L by conducting a ligand substitution reaction.

One equivalent of PPh(OEt)₂ was added to a toluene-d₈ solution containing (tBuPCP)IrH₂ at -78 °C, leading to rapid formation of cis-(tBuPCP)IrH₂(PPh(OEt)₂) (cis-
PPhOEt$_2$) (Scheme 3.3). This low temperature was used in order to prevent isomerization to trans-(tBu-PCP)IrH$_2$(PPh(OEt)$_2$), (trans-PPh(OEt)$_2$). To this solution was added 20 equivalents of P(OEt)$_3$ as a trapping ligand. The reaction mixture was warmed to 35 °C and observed for ligand exchange. Surprisingly, in addition to ligand exchange to form cis-P(OEt)$_3$ and trans-P(OEt)$_3$, 23% of the starting complex was converted trans-PPh(OEt)$_2$ in spite of the 20-fold excess of trapping ligand (Figure 3.2a).

COPASI modelling software was then used to generate a time course simulation for the appearance of trans-P(OEt)$_3$ (Figure 3.2b). Reaction rates were obtained for the isomerization of cis-PPh(OEt)$_2$ to trans-PPh(OEt)$_2$ ($k_{iso-PPhOEt2}$) and the isomerization of cis-P(OEt)$_3$ to trans-P(OEt)$_3$ ($k_{iso-POE3}$). The rate of substitution ($k_{sub}$) was defined as the rate of formation of both cis-P(OEt)$_3$ and trans-P(OEt)$_3$ in the ligand substitution reaction. Modelling the formation of trans-P(OEt)$_3$ whilst ignoring the possibility of direct association of P(OEt)$_3$ to give trans-P(OEt)$_3$ led to an overestimation of the amount of formed trans-P(OEt)$_3$, despite giving the same rate of formation at initial times of 4µM/s (Figure 3.4c). This over accounting for the formation of trans-P(OEt)$_3$ despite neglecting the direct association pathway, in addition to the surprisingly high amount of trans-PPh(OEt)$_2$, led us to conclude that the isomerization of cis-L to trans-L was in fact proceeding through an intramolecular mechanism.

Scheme 3.3. Ligand Substitution of cis-PPh(OEt)$_2$ with P(OEt)$_3$
**Figure 3.2.** Substitution of PPh(OEt)$_2$ by P(OEt)$_3$ (340 mM) in cis-PPh(OEt)$_2$ (17 mM, toluene-$d_8$, 35 °C) as described in Scheme 3.3. a) Measured experimental values. b) Reaction system modelled using rates from Scheme 3.3 c) Early time points of the modelled and experimentally measured concentrations of trans-P(OEt)$_3$.

This isomerization is well known in less sterically bulky ($^8$PCP)Ir(CO)H$_2$ complexes, but to the best of our knowledge there have been no reports for this occurring in ($^t$BuPCP)Ir(L)H$_2$ complexes. In order to ensure that this isomerization was intramolecular, we performed a ligand substitution reaction with cis-P(OEt)$_3$ under 1 atm of CO (Scheme 3.5). The reaction was mixed by inversion during the duration of the reaction to ensure good gas/liquid mixing. After 12 h, the reaction mixture was composed of 3:1 ($^t$BuPCP)Ir(CO) : trans-P(OEt)$_3$ with the formation of H$_2$. While the majority of complex was converted to the ligand exchange product, we would expect that given the irreversible nature of iridium CO binding (without photolysis), that there would be no isomerization product if indeed the mechanism of isomerization proceeded via ligand dissociation.

**Scheme 3.4 – Ligand Substitution of cis-PPh(OEt)$_2$ with CO**

![Scheme 3.4](image)

This lack of direct formation of trans-L prevented us from obtaining a relative rate of addition and thereby disallowed us from obtaining a value for the kinetic barrier to
dissociation for the \textit{trans}-L complexes. Although we note, that this necessarily means that the kinetic component of the barrier to dissociation from \textit{cis}-L is significantly smaller than that of \textit{trans}-L.

\textbf{Computational Studies}

The experimental results above suggest that not only is there a significant favorability of ligand addition to give \textit{cis}-L, but indeed, there is no association that forms \textit{trans}-L directly. This would imply that there is a large kinetic barrier to the formation of \textit{trans}-L, and therefore a large kinetic component to the energy required to dissociate L directly from \textit{trans}-L. Instead, it seems that formation of \textit{trans}-L proceeds via addition of L to give \textit{cis}-L, which then undergoes an intramolecular isomerization to give \textit{trans}-L. In order to support this observed kinetic preference for the formation of \textit{cis}-L we have performed an electronic structure study using DFT.

\textbf{Ligand Dissociation}

We have experimentally determined that the kinetic component to ligand dissociation from \textit{trans}-L is higher than that for \textit{cis}-L. In order to confirm these observations, we performed a relaxed potential energy scan for the dissociation of PPh(OEt)$_2$ from both \textit{cis}-($^{t\text{Bu}}$PCP)IrH$_2$ and \textit{trans}-($^{t\text{Bu}}$PCP)IrH$_2$. The distance between the Ir and phosphorus atom of the departing ligand were incremented 0.1 Å between optimizations (Scheme 3.5).
Scheme 3.5. Relaxed potential energy scan for dissociation from cis and trans-L

Figure 3.3. Electronic energies for the dissociation of PPh(OEt)$_2$ from cis-(tBuPCP)IrH$_2$ (blue) and trans-(tBuPCP)IrH$_2$ (red). The data points highlighted in yellow mark the first geometry to exhibit hydride relaxation.

The energy of the system increases as the distance between the ligand and iridium center increases, as would be expected for an endergonic ligand dissociation.
of the phosphine on the metal complex becomes sufficiently low to allow for hydride relaxation to lower energy geometries (Figure 3.3, yellow data points). These relaxed hydride geometries differ between the incipient cis-(tBuPCP)IrH₂ and trans-(tBuPCP)IrH₂ complexes. cis-(tBuPCP)IrH₂ relaxes from a T₃H geometry to a distorted trigonal bipyramidal geometry with an acute angle between the hydrides, Yₗ. trans-(tBuPCP)IrH₂, which started as T₃C, relaxes to distorted trigonal bipyramidal geometry with an acute angle between one hydride and the ipso carbon, Yₘ (Scheme 3.5). Attempts to observe this hydride relaxation in similar systems (P(OEt)₃ / (tBuPCP)IrH₂, P(OMe)₃ / (MePCP)IrH₂) were hindered by the formation of sigma C-H interaction at the newly formed vacant site between the trans-(tPcP)IrH₂ fragment and the alkyl chains of the departing ligands.

While the increase in energy caused by the dissociation of ligand was anticipated, what was unanticipated was the lack of stabilization afforded by the hydride relaxations. The 5.5 kcal/mol difference in energy between the system that started as trans-(tBuPCP)IrH₂ and cis-(tBuPCP)IrH₂ is persistent beyond the distances at which the hydrides relax. However, the nature of the relaxed energy scan does not allow for full relaxation from the metastable Y₃H geometry. In order to better understand the remaining steps required to complete ligand dissociation and achieve the free ligand and Yₗ (tBuPCP)IrH₂, we sought to understand the relaxation of the hydrides in (tBuPincer)IrH₂.

Hydride Reorganization Energy
From the ligand dissociation potential energy scan, we have determined that the barrier to ligand dissociation from \((^\text{tBu} \text{pincer})\text{IrH}_2\) is that of the thermodynamic BDE. Once the phosphines were no longer in sufficient proximity to the metal center, the hydrides were allowed to relax. In the case of *cis*-\((^\text{tBu} \text{PCP})\text{IrH}_2\), this relaxation led directly to \(Y_C\) geometry. However, in the case of *trans*-\((^\text{tBu} \text{PCP})\text{IrH}_2\), the incipient trans-hydrides relax into a \(Y_H\) geometry. In order to better understand the process of relaxation for these two geometries, we generated 2-dimensional relaxed potential energy surfaces for the possible geometries of \((^\text{tBu} \text{PCP})\text{IrH}_2\) and \((^\text{tBu} \text{POCOP})\text{IrH}_2\) (Figures 3.4 and 3.5).

Single point energies were taken at 10° increments for \(\angle C-\text{Ir-H}_a\) and \(\angle C-\text{Ir-H}_b\) between 50° and 180°. Geometries where \(\angle C-\text{Ir-H}_a + \angle C-\text{Ir-H}_b \geq 330°\) were omitted due to close interactions between the hydrogen atoms. These conditions generated potential energy surfaces similar to those reported by Eisenstein for \(\text{IrL}_2\text{H}_2\text{Cl}\). For \((^\text{tBu} \text{PCP})\text{IrH}_2\), local energy minimums were found for \(T_C\) and \(Y_H\) geometries. Global energy minimums were found for the \(Y_C\) and \(T_H\) geometries. An energy maximum was found for the idealized trigonal bipyramidal geometry where all angles = 120° (Figure 3.4).
Figure 3.4. Hydride Energy Surface for \((\text{tBuPCP})\text{IrH}_2\) a) Bond angles screened in \((\text{tBuPCP})\text{IrH}_2\) and b) the resulting two-dimensional potential energy surface.

Figure 3.5. Hydride Energy Surface for \((\text{tBuPOCOP})\text{IrH}_2\) a) Bond angles screened in \((\text{tBuPOCOP})\text{IrH}_2\) and b) the resulting two-dimensional potential energy surface.
Interestingly, when the same potential energy surface scan was performed for \((^{\text{Bu}}\text{POCOP})\text{IrH}_2\), there were no local minimum found for \(T_c\) or \(Y_H\) geometries. However, there was a local minimum corresponding to the \(Y_c\) geometry and a global energy minimum for \(T_H\). Just as for \((^{\text{Bu}}\text{PCP})\text{IrH}_2\), there was a significant energy maxima found for the ideal trigonal bipyramidal geometry. The energies for all geometries found in \((^{\text{Bu}}\text{PCP})\text{IrH}_2\) and \((^{\text{Bu}}\text{POCOP})\text{IrH}_2\) are compiled in Table 3.1.

**Scheme 3.6.** Hydride reorganization geometries in \((^{\text{Bu}}\text{pincer})\text{IrH}_2\)

\[
\begin{array}{ccccccc}
 & T_C & Y_H & T_H & Y_C \\
\text{C--Ir} & \text{C--Ir} & \text{C--Ir} & \text{C--Ir} \\
\text{H} & \text{H} & \text{H} & \text{H} \\
\end{array}
\]

**Table 3.1.** Energies of hydride relaxation from trans-\((^{\text{Bu}}\text{pincer})\text{IrH}_2\)

<table>
<thead>
<tr>
<th>(\Delta E) (kcal/mol)</th>
<th>(T_C)</th>
<th>(a^\dagger)</th>
<th>(Y_H)</th>
<th>(b^\dagger)</th>
<th>(T_H)</th>
<th>(c^\dagger)</th>
<th>(Y_C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((^{\text{Bu}}\text{PCP})\text{Ir})</td>
<td>8.6</td>
<td>9.8</td>
<td>9.0</td>
<td>9.4</td>
<td>0.0*</td>
<td>2.1</td>
<td>0.0</td>
</tr>
<tr>
<td>((^{\text{Bu}}\text{POCOP})\text{Ir})</td>
<td>16.7**</td>
<td>-</td>
<td>14.5**</td>
<td>-</td>
<td>0.0*</td>
<td>1.0</td>
<td>0.4</td>
</tr>
</tbody>
</table>

\^ Highest energy barrier between minima or idealized geometries.

* Energy defined as 0.0 kcal/mol.

** Determined by idealized geometries, not a true minimum on the potential energy surface.

While the \(T_H\) and \(Y_C\) are comparable in energy for \((^{\text{Bu}}\text{PCP})\text{IrH}_2\) and \((^{\text{Bu}}\text{POCOP})\text{IrH}_2\), \(Y_H\) and \(T_c\) are significantly higher in energy for \((^{\text{Bu}}\text{POCOP})\text{IrH}_2\). This is likely a result of increased sigma donation of the ipso carbon of the aryl ring to iridium. This difference in energy of the \(T_c\) geometry is what is responsible for the difference in rate determining transitions state in \((^{\text{Bu}}\text{PCP})\text{IrH}_2\) and \((^{\text{Bu}}\text{POCOP})\text{IrH}_2\).
Conclusion

We have demonstrated that there is a significant kinetic barrier to the association of phosphine to trans-\((^{\text{tBu}}\text{PCP})\text{IrH}_2\text{L}\) as compared to cis-\((^{\text{tBu}}\text{PCP})\text{IrH}_2\text{L}\).

Addition of ligand to \((^{\text{tBu}}\text{PCP})\text{IrH}_2\) leads to a single product, cis-\((^{\text{tBu}}\text{PCP})\text{IrH}_2\text{L}\), which then proceeds to form trans-\((^{\text{tBu}}\text{PCP})\text{IrH}_2\text{L}\) via an intramolecular isomerization. Kinetic analysis was performed to confirm that the observed trans-L products were generated solely through this intramolecular mechanism, and not via a dissociative mechanism.

Computational studies were conducted on the ligand dissociation of phosphine from cis and trans (pincer)\(\text{IrH}_2\)\{(phosphine)\} complexes in order to determine the origin of this kinetic selectivity for cis-L. The kinetic barrier of ligand association to give trans-L complexes was found to be a result of a thermodynamic barrier accrued over a series of hydride reorganizations. The energies of these hydride reorganizations is strongly dependent on the strength of the sigma donation provided by the ipso carbon in the case of PCP and its derivatives. This is similarly the case with dissociation of olefin from (pincer)\(\text{IrH}_2\). The BDFE of olefin is very similar for \((^{\text{tBu}}\text{PCP})\text{IrH}_2\) and \((^{\text{tBu}}\text{POCOP})\text{IrH}_2\), however the transient T\(_C\) geometry is much higher in energy for POCOP (+8.1 kcal/mol) due to increased sigma donation from the O-linkers.

Supporting Information
Chapter 3 References


Chapter 4: Stoichiometric and Metal Ligand Cooperative

Reactions of \((t^\text{Bu}PPP)\text{Ir}\).

Portions of this chapter are reprinted with permission from:


Copyright 2022 American Chemical Society.

Abstract: We report the synthesis of a sterically hindered triphosphorus-pincer iridium complex, \((t^\text{Bu}PPP)\text{Ir}\), containing a secondary phosphine that is capable of acting as a proton reservoir to yield a terminal phosphide. A stereoselective loss of \(H_2\) from \((t^\text{Bu}PPP)\text{IrH}_3\), yields a rare example of a four-coordinate iridium monohydride, \((t^\text{Bu}PPP)\text{IrH}\); this complex undergoes a reversible intramolecular proton transfer from phosphorus to iridium to yield \((t^\text{Bu}PPP)\text{IrH}_2\) from which \(H_2\) can be dehydrogenated or displaced to yield the first examples of fully characterized 4-coordinate iridium phosphide complexes. This anionic phosphiido fragment, \((t^\text{Bu}PPP)\text{Ir}\) binds olefin weakly, allowing for rapid exchange of ethylene and propylene in \((t^\text{Bu}PPP)\text{Ir(}\eta^2\text{-olefin})\) complexes.
Introduction

Tridentate pincers have taken a large role in the continued development of Metal-Ligand Cooperativity (MLC) by forcing close interactions between the atoms of interest and metal centers through ancillary phosphine bonds. Pincers where the cooperative atom of interest is bound directly to a metal center have allowed for novel reactivity to be discovered for a number of main group elements. Despite the large number of pincers that explore nitrogen MLC towards H₂ activation, there are surprisingly few reports of pincers that explore the next pnictogen, phosphorus. Indeed, there exists only a handful of examples of H₂ activation across a phosphorus metal bond, with one example of MLC Phosphorus H₂ dissociation and only a single example where these processes were reversible about a metal-phosphenium bond.

Scheme 4.1. Metal Ligand Cooperative Triphosphorus Pincers

While phosphines are ubiquitous in organometallic and coordination chemistry, the field of “non-innocent” phosphorus chemistry is still in its nascency. Pincers exhibiting MLC active phosphorus sites are a significant part of the current driving force behind this non-innocent chemistry. Since the initial report of iPr(PPh₂P)(PPP = bis-(2-di-alkyl-phosphinophenyl)phosphide), MLC-triphosphorus pincers have since
expanded to include N-heterocyclic phosphonium\textsuperscript{28, 29} (1,3-bis(2-diphenylphosphinophenyl)-1,3-diaza-2-phosphenium), and phosphine-oxide\textsuperscript{30} (bis-(2-di-alkyl-phosphinophenyl)phosphide oxide) moieties (Scheme 4.1). Even within scaffolds, there is significant variance to the action of MLC.

In the initial report of $iPr(PP\text{H})_2$, oxidations of a dimeric bridging $iPr(PPP)_2Cu_2$ complex led to a two-step ligand centered reversible oxidation.\textsuperscript{27, 31} The Lee group showed that $iPr(PPP)Ni$ was capable of oxygen\textsuperscript{32, 33} and sulfur\textsuperscript{34} group transfers from nickel to phosphorus with the formation of new P-O and P-S bonds. Aside from group transfer reactions, it was also shown that $iPr(PPP)Ni$ was capable of dimerizing to form a new P-P bond upon irradiation. This dimeric species exhibited E-H (E= N, O) bond cleavage across the Ni-P bond, as well as radical dihydrogen and diphenylhydrazine cleavage upon irradiation with visible light to form new P-H and P-N bonds.\textsuperscript{35} $iPr(PPP)Co$ showed similar P-P dimerization and although substrate cleavage was not observed, radical traps were capable of cleaving the P-P bond to form new P-O bonds. Relevant to the this work, although not an example of Metal-Ligand Cooperativity, are the reports by the Vlugt group of a $Ph(PPP)Ir$ complex. Complexation of $Ph(PP\text{H})$ to [Ir(µ-OMe)(cod)]\textsubscript{2} yielded facially coordinated $Ph(PPP)Ir(cod)$, where the methoxide acts as an internal base to yield the terminal phosphide. Attempts to metalate with other iridium sources were deemed unsuccesful.\textsuperscript{36}

These previous reports of $PP\text{H}$ ligands have utilized isopropyl groups, $iPr(PP\text{H})$, or phenyl groups, $Ph(PP\text{H})$ as steric bulk. These smaller groups allowed for facial coordination or dimerization of the complexes of interest. In order to prevent these
alternative binding modes and enforce a rigid meridional coordination geometry, we synthesized a new PPP ligand with tert-butyl groups, \( {tBu}(PPH) \) as an analogue to the well-studied (PCP)Ir pincer platforms.

Phosphorus has been referred to as “the carbon copy”\(^{37} \) because of numerous similarities between the chemistry, including the coordination chemistry, of these elements. PCP-type pincer ligands, in which the coordinating atom of the central group is typically a formally anionic carbon, have played an important role in organometallic chemistry in recent decades. An example of this of particular interest in our laboratory has been the chemistry of (PCP)Ir complexes as catalysts for alkane dehydrogenation.\(^{38-50} \) In the context of this relationship, and in combination with the potential for an anionic phosphido group to engage in MLC behavior, we have begun an investigation of (PPP)Ir complexes in which the central group is formally anionic phosphido.\(^{23-25, 31, 51-57} \)

**Results and Discussion**

**Synthesis of \( {tBu}HPP \) and Metalation**

(2-bromophenyl)-di-tert-butylphosphine was synthesized according to Shimada.\(^{58} \) Coupling with PCl\(_3\) to give (2-C\(_6\)H\(_4\)P\(_2\)Bu\(_2\))\(_2\)PCl and reduction to give \( {tBu}HPP \) was then conducted as reported by Peters.\(^{52} \) A characteristic resonance expected of the secondary phoshine proton was observed in the \(^1\)H NMR spectrum (\( \delta 6.03, \text{dt, } J = 214.8, 12.3 \text{ Hz} \)) while in the \(^{31}\)P[\(^1\)H] NMR spectrum a doublet (\( \delta 21.35 \)) and a triplet (\( \delta -47.07 \)) were observed with \( ^3J_{pp} = 154 \text{ Hz} \).

Dissolving \( {tBu}HPP \) in a toluene solution with either [Ir(COD)Cl]\(_2\) or Ir(COE)\(_2\)Cl\(_2\) rapidly yields free cyclooctadiene or cyclooctene, respectively, and \( {tBu}HPP \)IrCl (Scheme 4.2),
with signals in the $^{31}P{[^1}H{]}$ NMR spectrum at $\delta$ 76.5 (d, $J = 12.8$ Hz) and $\delta$ 26.3 (t, $J = 12.8$ Hz).\textsuperscript{57,59} Thus, metalation is accompanied by a dramatic decrease in the value of $J_{PP}$, indicative of $k^3$-coordination of a triphosphorus ligand.\textsuperscript{57} The $^1H$ NMR resonance of the phosphine-bound proton shifts upfield to $\delta$ 4.60, while $^1J_{PH}$ increases to 365 Hz ($^3J_{P-H} = 2.7$ Hz).

**Scheme 4.2.** Metalation of ($^tBuPP^tHP$) and Phosphine Activation

Formation of four-coordinate ($^tBuPP^tHP$)IrCl is followed by slow net proton transfer to yield ($^tBuPPP$)IrHCl (**Scheme 4.2**), as monitored in the $^1H$ NMR spectrum by loss of the signal at $\delta$ 4.60 and concomitant appearance of a new hydride signal ($\delta$ -28.0, td, $J = 13.2$, 7.3 Hz).\textsuperscript{60} In the $^{31}P{[^1}H{]}$ NMR spectrum, the resonance corresponding to the central phosphorus ($\delta$ 26.3, t, $J = 12.8$) shifts 70 ppm downfield ($\delta$ 97.2, s) while the terminal phosphine resonance shifts only from $\delta$ 76.5 to $\delta$ 76.3. A crystal suitable for X-ray diffractometry was obtained by vapor diffusion of pentane into a saturated toluene solution and the molecular structure was determined by X-ray diffraction (XRD) (**Figure 4.1**). The unit cell is found to contain two molecules of ($^tBuPPP$)IrHCl where the only notable deviation between them is between the P$_c$-Ir-Cl bond (P$_c$ = central phosphorus) angles. In one molecule, the angle is 124.0°, suggesting a nearly ideal trigonal bipyramidal geometry while in the other it is 144.5°. These values are in contrast with
the C\textsubscript{ipso}-Ir-Cl bond angles, which are very nearly 180°, found for the square-pyramidal geometries of iridium hydrido chloride complexes of PCP-type ligands\textsuperscript{61-63}. The sum of angles around the central (phosphido) phosphorus atom of (\textsuperscript{tBu}PPP)IrHCl is 321.1°, indicating a fully pyramidal geometry. Lastly we note that the chloride is located exo with respect to the bowl-shaped PPP ligand structure. While this might be expected to be thermodynamically favored due to steric crowding, an intramolecular proton transfer from (\textsuperscript{tBu}PP\textsuperscript{H}PP)IrCl would be expected to lead directly to the endo-chloride configuration (Scheme 4.2); this could then be followed by inversion at P\textsubscript{C} to give the observed product.

![Figure 4.1](image)

**Figure 4.1.** Molecular structure of one of the two molecules of (\textsuperscript{tBu}PPP)IrHCl determined by single-crystal XRD. H atoms other than the hydride are omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected distances (Å) and angles (°): P2-Ir1, 2.211(4); P1-Ir1 2.357(4); P3-Ir1, 2.339(4); Cl1-Ir1, 2.379(4); P2-Ir1-Cl1, 124.42(16); P1-
Ir1-Cl1, 98.60(15); P3-Ir1-Cl1, 99.12(15); P1-Ir1-P3, 162.04(14); P1-Ir1-P2, 86.52(14); P3-Ir1-P2, 85.94(15); C1-P2-Ir1, 106.2(5); C7-P2-Ir1, 107.0(5); C7-P2-C1, 107.6(5)

DFT calculations (Figure 4.5) show that the rate-determining proton transfer leads to the initial formation of an unstable square pyramidal (tBuPPP)IrH(endo-Cl) with an apical hydride, much like what is observed in (PCP)Ir and (POCOP)Ir. This unobserved species then undergoes a phosphorus inversion placing the chloride on the exo-face of the ligand. The increased steric influence afforded by the t-butyl groups on the chloride atom allow for this inversion to be thermodynamically favorable by 3.5 kcal/mol as this driving force is not observed in calculations for a similar (Me6PPP)Ir complex. A previously reported (PhPPh)Ir complex was metalated in a similar manner, however, the proton transfer from the secondary phosphine to the iridium was not observed. Complexation was achieved by using a metal source with an internal base, [Ir(µ-MeO)2COD], to deprotonate the secondary phosphine. Additionally, the phenyl groups did not provide enough steric bulk to displace COD from the metal source.56

Scheme 4.3. Synthesis of (tBuPPP)IrH3
Treatment of (tBuPPP)IrHCl with KOtBu under an atmosphere of H₂ in THF rapidly leads to the formation of a complex with a secondary phosphine at the central position, as indicated by an upfield resonance in the ³¹P NMR spectrum (δ 10.7) and a signal in the ¹H NMR spectrum at δ 5.71 with coupling ¹JPH = 335.5 Hz, assigned as (tBuPHP)IrH₃ (Scheme 4.3). The three hydrides are chemically inequivalent due to the unsymmetrical nature of the ligand and they exhibit complex coupling patterns in the ¹H NMR spectrum. The formation of (tBuPHP)IrH₃ involves a net heterolytic cleavage of the dihydrogen bond across the P-Ir bond.

2D ¹H-NOESY-NMR spectroscopy was used to assign the individual hydride resonances. Crystals were obtained through slow evaporation of benzene, and the molecular structure was determined by single-crystal XRD (Figure 4.2).

Figure 4.2. Molecular structure of (tBuPHP)IrH₃ determined by single-crystal XRD. H atoms other than the hydrides and the central phosphino hydrogen are omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected distances (Å) and angles (°): P1-Ir1, 2.2311(8); P2-Ir1, 2.2786(9); P3-Ir1, 2.2880(9); P1-Ir1-P3, 84.78(3);
Stoichiometric Reactions of (tBuHPP)Ir and (tBuPPP)Ir Complexes: Experimental Studies.

A toluene-$d_8$ solution of (tBuHPP)IrH$_3$ was heated at 80 °C under 1 atm ethylene for 15 min, leading the straw-yellow solution to turn dark green. NMR spectroscopy indicated loss of (tBuHPP)IrH$_3$ and formation of (tBuPPP)Ir(C$_2$H$_4$), evidenced by a significant downfield shift in the signal assigned to $P_C$ ($^{31}$P NMR; $\delta$ 155.48) as well as the presence of a peak corresponding to bound ethylene in the $^1$H NMR spectrum ($\delta$ 3.57, 4H, at 0 °C). The $t$-butyl groups of (tBuPPP)Ir(C$_2$H$_4$) are equivalent on the NMR timescale at all temperatures at which spectra were taken (-90 °C to 110 °C), suggesting rapid inversion of the phosphide group.$^{64,65}$ The $^1$H NMR spectrum also revealed formation of 2 equivalents of ethane.

In contrast with (tBuPCP)Ir(C$_2$H$_4$) and (tBuPOCOP)Ir(C$_2$H$_4$),$^{66}$ (tBuPPP)Ir(C$_2$H$_4$) decomposes upon removal of the ethylene atmosphere as manifest by color change and loss of $^1$H and $^{31}$P NMR signals. $^1$H NMR spectra, taken from 25 °C to 110 °C in $p$-xylene-$d_{10}$ solvent, reveal sharp signals at the low end of this range. Broadening of free and bound C$_2$H$_4$ signals is observed at 40 °C and above, indicating exchange on the NMR time scale. The signals attributable to free and bound C$_2$H$_4$ undergo coalescence at 110 °C. Exchange rates were determined, based on line broadening, from 50 °C to 80 °C. An Eyring-type plot of this data yields activation parameters $\Delta H^\ddagger = 19.8(\pm0.7)$ kcal/mol and $\Delta S^\ddagger = 9.3(\pm2)$ eu, consistent with a weakly bound ethylene ligand undergoing rapid reversible dissociation. The analogous propene complex showed an even lower barrier.
to exchange with free propene; coalescence was reached for the three vinylic protons in the $^1$H NMR spectrum in the range 10 °C to 40 °C. Due to the complexity of the spectra, the confidence level in the rate determinations is lower than for ethylene, but the values obtained for propene exchange $\Delta H^\dagger = 17.9$ kcal/mol and $\Delta S^\dagger = 18$ eu, clearly indicate a dissociative process. The corresponding value of $\Delta G^\dagger = 12.5$ kcal/mol at 298 K implies that propene is bound ca. 4 - 5 kcal/mol more weakly than ethylene ($\Delta G^\dagger = 17.0(\pm1.0)$ kcal/mol at 298 K).

The instability of (tBuPCP)Ir(C$_2$H$_4$) precluded its crystallization. Replacement of ethylene with a CO atmosphere resulted in conversion of (tBuPPP)Ir(C$_2$H$_4$) to (tBuPPP)Ir(CO), which represents the first fully characterized four-coordinate terminal-phosphido iridium complex. Crystallization of (tBuPPP)Ir(CO) was successful, and XRD analysis yielded a structure (Figure 4.3) with a unit cell containing two molecules. The sums of the angles around the terminal phosphide are 327.8° and 328.6°, respectively, i.e. both molecules have a fully pyramidal geometry at P. The angles between the CO and terminal phosphide ($\angle P$-Ir-C) are ca. 164°. This deviation from 180° was probed computationally and shown to be a result of the steric influence of the tert-butyl groups.67
Figure 4.3. (a) Molecular structure of \((t^{Bu}PPP)Ir(CO)\) determined by single-crystal XRD. H atoms omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected distances (Å) and angles (°): P1-Ir1, 2.289(3); P2-Ir1, 2.304(3); P3-Ir1, 2.317(3); Ir1-C29, 1.869(11); C29-O1, 1.149(14); P1-Ir1-P2, 83.86(10); P1-Ir1-P3, 83.89(10); P1-Ir1-C29, 166.0(4); P2-Ir1-P3, 160.04(10); C1-P1-C7, 113.3(6); C1-P1-Ir1, 109.5(4); C7-P1-Ir1, 109.2(4). (b) Ball-and-stick style illustration of the same structure, H atoms included, highlighting the difference in crowding between the faces above and below the approximate plane of the iridium and coordinating atoms.

We wished to better understand the mechanism of ethylene hydrogenation by \((t^{Bu}PPP)IrH_3\), and particularly the loss and apparent net transfer of the phosphorus-bound hydrogen. Charging a solution of \((t^{Bu}PPP)IrH_3\) with 1 atm of D\(_2\) led to a rapid and highly selective loss of signals corresponding to the exo and trans hydrides. Signals attributable to the phosphorus-bound proton and the endo-hydride maintained their integration relative to the aromatic peaks of the complex. This result indicates a remarkably stereoselective loss of H\(_2\) (Scheme 4.4), exclusively from the exo face of the complex. Also consistent with loss of H\(_2\) occurring exclusively from the exo face, \((t^{Bu}PPP)IrH_3\) and the labelled \((t^{Bu}PPP)Ir(D)_2(esto-H)\) both yielded exclusively \((t^{Bu}PPP)Ir(esto-CO)(H)\) when treated with 1 atm of CO (Scheme 4.4).
Scheme 4.4. Stereoselective displacement of H₂ from \(^{(\text{tBu}^\text{HPP})}\text{IrH}_3\)

Heating \(^{(\text{tBu}^\text{PPP})}\text{Ir(exo-CO)}(H)\) led to the formation of a mixture of

\(^{(\text{tBu}^\text{PPP})}\text{Ir(exo-CO)}(H)_2\) and \(^{(\text{tBu}^\text{PPP})}\text{Ir(CO)}\) (Scheme 4.5). The mechanism for this

isomerization and ultimately the elimination of the second equivalent of H₂ was initially unclear, as there was no intramolecular mechanism by which we could obtain

\(^{(\text{tBu}^\text{PPP})}\text{Ir(exo-CO)}(H)_2\) from \(^{\text{exo-}(\text{tBu}^\text{PPP})}\text{Ir(H)(CO)}\) as proton transfer from the phosphine should have yielded the trans-hydride isomer of \(^{(\text{tBu}^\text{PPP})}\text{Ir(H)}_2\text{CO}\). We probed the proton transfer mechanism for CO dissociation. The rate of formation of \(^{(\text{tBu}^\text{PPP})}\text{Ir(H)}_2\text{(exo-CO)}\)

from \(^{(\text{tBu}^\text{PPP})}\text{Ir(H)(exo-CO)}\) was tested under both Argon (1atm) and CO (1atm) (Scheme 4.5). Exchanging the CO atmosphere for Argon led to a 15 fold rate enhancement, implicating CO dissociation as a key step in the isomerization to form

\(^{(\text{tBu}^\text{PPP})}\text{Ir(H)}_2\text{(exo-CO)}\). Heating \(^{(\text{tBu}^\text{PPP})}\text{Ir(H)}_2\text{(exo-CO)}\) further under vacuum lead to the formation of \(^{(\text{tBu}^\text{PPP})}\text{Ir(CO)}\). Addition of H₂ to \(^{(\text{tBu}^\text{PPP})}\text{Ir(CO)}\) lead to quantitative formation of \(^{(\text{tBu}^\text{PPP})}\text{Ir(H)}_2\text{(exo-CO)}\) (Scheme 4.5).
The obvious mechanistic pathways for both the isotopic substitution and the displacement of D₂ by CO shown in Scheme 4.4 both proceed through an intermediate, (tBu₃PP)IrH. With that in mind, one equivalent of hydrogen acceptor (t-butyl ethylene, TBE; or norbornene, NBE) was added to a solution of (tBu₃PP)IrH₃. After 24 h at room temperature a dark red solution had formed and NMR spectroscopy indicated conversion to a new species, assigned as (tBu₃PP)IrH. This is a rare example of a square planar iridium monohydride. The ³¹P[¹H] NMR spectrum has signals at δ 102.43 (d, \( J_{PP} = 10 \) Hz) and δ 37.01 (t, \( J_{PP} = 10 \) Hz) in a 2:1 ratio. The phosphorus-bound proton is clearly observed in the ¹H NMR spectrum (δ 4.56, d, \( ^{1}J_{PH} = 320.9 \)), and other signals are unexceptional. Remarkably, however, the hydride of (tBu₃PP)IrH gives rise to a very downfield chemical shift in the ¹H NMR spectrum (δ 4.70, dt, J = 112.9, 18.3 Hz). Selective ³¹P-decoupling confirmed that the coupling of 112.9 Hz was with the central P atom (δ 102.43) and the coupling of 18.3 Hz with the terminal pincer P atoms (δ 37.01).
Scheme 4.6. Reactions of \((t^{Bu}P^{HP})IrH\), \((t^{Bu}P^{PP})IrH_2\), and \((t^{Bu}P^{HP})IrH_3\)

While relatively common for d\(^0\) and d\(^{10}\) metal hydrides,\(^{72-74}\) such downfield chemical shifts are highly unusual, although not completely unprecedented\(^{75-77}\), for other transition metal hydrides. Variable temperature \(^1\)H NMR was performed (10 - 60 °C) and the chemical shift attributable to the hydride was found to be moderately temperature sensitive; however the signals were sharp at all temperatures, indicating that this is not a dynamic NMR phenomena, i.e. due to rapid exchange with a chemically different site.\(^{67}\) The origin of this unusual chemical shift is currently under investigation.\(^{78}\)

Placing a solution of \((t^{Bu}P^{HP})IrH\) under 1 atm of CO led to immediate conversion to \((t^{Bu}P^{HP})Ir(H)(CO)\) (Scheme 4.6), the same complex that only slowly formed upon the addition of CO to \((t^{Bu}P^{HP})IrH_3\) (Scheme 4.4). The much faster reaction of the
monohydride is consistent with its proposed role as an intermediate in the reaction of the trihydride.

Heating \((^{\text{Bu}}\text{P}^{\text{HPP}})\text{IrH}\) at 60 °C for 2 h results in formation of a new complex, with partial loss of signal attributable to the P-bound H and the downfield hydride signal in the \(^1\text{H}\) NMR spectrum. Concomitantly, we observe appearance of a new upfield signal (δ -19.40, dt, \(J = 56.6, 11.4\) Hz, 2 H), which we assign to the formation of \((^{\text{Bu}}\text{PPP})\text{IrH}\)_2 (Scheme 4.6). \((^{\text{Bu}}\text{P}^{\text{HPP}})\text{IrH}\) and \((^{\text{Bu}}\text{PPP})\text{IrH}_2\) exist in equilibrium in a ratio of ~1:2.\(^{70,79}\) As observed with \((^{\text{Bu}}\text{PPP})\text{Ir(CO)}\) and \((^{\text{Bu}}\text{PPP})\text{Ir(C}_2\text{H}_4)\), the \(t\)-butyl groups of \((^{\text{Bu}}\text{PPP})\text{IrH}_2\) appear equivalent in the \(^1\text{H}\) NMR spectrum.

Addition of 1 atm of ethylene to a room-temperature solution containing a mixture of \((^{\text{Bu}}\text{P}^{\text{HPP}})\text{IrH}\) and \((^{\text{Bu}}\text{PPP})\text{IrH}_2\) led immediately to loss of \((^{\text{Bu}}\text{PPP})\text{IrH}_2\) with formation of an equivalent quantity of \((^{\text{Bu}}\text{PPP})\text{Ir(C}_2\text{H}_4)\) while the concentration of \((^{\text{Bu}}\text{P}^{\text{HPP}})\text{IrH}\) was initially unchanged. Thus the five-coordinate \(d^6\) complex \((^{\text{Bu}}\text{PPP})\text{IrH}_2\) reacts much more rapidly with ethylene (to give ethane and an ethylene complex) than does the four-coordinate \(d^8\) \((^{\text{Bu}}\text{P}^{\text{HPP}})\text{IrH}\). Upon heating the resulting mixture for 2 h at 60 °C, however, full conversion to \((^{\text{Bu}}\text{PPP})\text{Ir(C}_2\text{H}_4)\) was observed (Scheme 4.6).

Addition of 1 atm of \(H_2\) to a solution of \((^{\text{Bu}}\text{P}^{\text{HPP}})\text{IrH}\) and \((^{\text{Bu}}\text{PPP})\text{IrH}_2\) at room temperature led to the immediate formation of \((^{\text{Bu}}\text{P}^{\text{HPP}})\text{IrH}_3\), representing a rapid net addition across a metal-phosphorus bond in the case of addition to the dihydride (Scheme 4.6).

Stoichiometric Reactions of \((^{\text{Bu}}\text{P}^{\text{HPP}})\text{Ir}\) and \((^{\text{Bu}}\text{PPP})\text{Ir}\) Complexes: DFT Calculations. The relationship between \((^{\text{Bu}}\text{P}^{\text{HPP}})\text{IrH}_3\), \((^{\text{Bu}}\text{P}^{\text{HPP}})\text{IrH}\), and \((^{\text{Bu}}\text{PPP})\text{IrH}_2\) was investigated
computationally (Figure 4.4). Starting from (tBuP^HPP)IrH$_3$, there is a calculated barrier of $\Delta G^\dagger = 16.7$ kcal/mol to H-H reductive coupling to yield a complex with dihydrogen very weakly bound to the *exo* face. A subsequent dissociation of H$_2$ to give (tBuP^HPP)IrH is essentially barrierless and slightly exothermic. An alternative pathway for hydrogen loss from (tBuP^HPP)IrH$_3$, a concerted heterolytic elimination of H$_2$ across the P-Ir bond of (tBuP^HPP)IrH$_3$ was also considered. The TS was calculated to have a high free energy, 34.8 kcal/mol, leading to a dihydrogen complex, (tBuPPP)Ir(H$_2$)(H) which could then lose H$_2$, rather than leading directly to loss of H$_2$ (Figure 4.4).

Thermodynamically, the overall loss of H$_2$ from (tBuP^HPP)IrH$_3$ is calculated to be slightly endergonic to give either (tBuP^HPP)IrH ($\Delta G^\circ = 2.3$ kcal/mol) or (tBuPPP)IrH$_2$ ($\Delta G^\circ = 1.6$ kcal/mol).

(tBuP^HPP)IrH is calculated to undergo transfer of H (formally H$^+$) from the central phosphorus to iridium to give (tBuPPP)IrH$_2$, with a barrier of $\Delta G^\dagger = 24.3$ kcal/mol. This reaction is approximately thermoneutral with $\Delta G^\circ = -0.7$ kcal/mol. The calculated thermodynamics and reaction barrier are consistent with the experimentally observed equilibrium between (tBuP^HPP)IrH and (tBuPPP)IrH$_2$ ($\Delta G = -0.4$ kcal/mol) and the observed barrier of $\Delta G^\dagger = 25.4$ kcal/mol at 60 °C.\textsuperscript{67}
Figure 4.4. Free energy profile ($\Delta G^\circ$ in kcal/mol) for loss of H$_2$ from (tBuPPP)IrH$_3$.

Reductive elimination of H$_2$ from Ir followed by proton migration (black pathway) is strongly favored over direct heterolytic elimination across P-Ir bond (blue pathway). “‡” indicates a transition state.

While the transfer of H from P to Ir requires an approximate planarization at the central phosphorus for geometric reasons, it should be noted that the barrier to inversion at P in (tBuPPP)IrH$_2$ is calculated to be quite small; the TS has a free energy only 4.6 kcal/mol above (tBuPPP)IrH$_2$. Thus the need for planarity at P is not the major factor contributing to the substantial kinetic barrier for migration of H from P to Ir for (tBuPPP)IrH$_2$ ($\Delta G^\ddagger = 24.3$ kcal/mol). Relatedly, the barrier to proton migration for the conversion of (tBuP$_2$P)IrCl to give (tBuPPP)IrHCl (with Cl in the endo position; Scheme
4.2) is calculated to be very similar, $\Delta G^\dagger = 24.9$ kcal/mol (Figure 4.5); this value is consistent with the experimental observation that the reaction requires ca. 12 hours to reach completion at room temperature. The proton migration is calculated to lead initially to the exo-hydride isomer, as suggested in Scheme 4.2, which then undergoes inversion at $P_C$ with a relatively small barrier, $\Delta G^\dagger = 13.4$ kcal/mol (Figure 4.5).

![Free energy profile](image)

**Figure 4.5.** Free energy profile ($\Delta G^\circ$ in kcal/mol) for conversion of $^{(R}P^\text{HPP})\text{IrCl}$ to $^{(R-PPP)}\text{IrHCl}$ (Cl-exo) via proton migration and inversion at $P_C$. $R = \text{Me, tBu}$. “‡” indicates a transition state.

**Conclusions**

Iridium complexes of a bulky triphosphorus-pincer containing a secondary phosphine have been synthesized and their chemistry explored. The addition and elimination of $D_2$, $H_2$, and CO are found to occur in a facile manner with a high stereoselectivity for the exo-face of the ligand. These reactions proceed through $^{(tBuPP^\text{HPP})}\text{IrH}$. This complex is found to undergo a 1,2-migration of $H$ from phosphorus to
iridium, measured and computed to proceed with a free energy barrier of ca. 25 kcal/mol and is approximately thermoneutral.

The product of this migration, \((^{tBu}PPP)IrH_2\), is found to hydrogenate ethylene to give 4-coordinate olefin complexes similar to that of \((^8PCP)Ir\). Unlike \((^8PCP)Ir\), ethylene and propylene bind weakly to the \((^{tBu}PPP)Ir\) fragment, with BDE of less than 20 kcal/mol. A large hurdle to transfer dehydrogenation using the economical, separable, and regenerable ethylene and propylene is their ability to bind tightly to the 14-electron \((^8PCP)Ir\) fragment, forming \((^8PCP)Ir(\eta^2\text{-olefin})\) a resting state that is too energetically favorable to enter the catalytic cycle. In the next chapter, we will exploit the weak olefin binding in \((^{tBu}PPP)Ir\) to allow us to use ethylene and propylene as hydrogen acceptors.

**Supporting Information**
Chapter 4 References


31. Mankad, N. P.; Harkins, S. B.; Antholine, W. E.; Peters, J. C., Multifrequency EPR studies of [Cu(1.5)Cu(1.5)](+) for Cu2(mu-NR2)2 and Cu2(mu-PR2)2 diamond cores. *Inorg Chem* 2009, 48 (15), 7026-32.


35. Kim, Y. E.; Lee, Y., A P-P Bond as a Redox Reservoir and an Active Reaction Site. *Angew Chem Int Ed Engl* 2018, 57 (43), 14159-14163.


50. CCC-3refs-ChianeseBraunstein, For related “CCC” pincer-Ir complexes with NHC groups in place of the phosphino groups of PCP ligands see for example: .


59. PPPIr, (PhPPP)Ir(COD) and [(PhPHPP)Ir(COD)][PF6] have been reported by Vlugt and co-workers; the triphosphorus ligands adopt a facial coordination mode.

60. A rhodium analogue of (tBuPHPP)IrCl has been reported, (iPrPHPP)RhCl, and was found not to undergo migration of H.


67. SeeSuppInfo, See Supporting Information. In See Supporting Information.


71. While we did not find any non-aromatic solvent suitable for the reaction to give (tBuPHPP)IrH.


76. Haller, L. J.; Mas-Marza, E.; Cybulski, M. K.; Sanguramath, R. A.; Macgregor, S. A.; Mahon, M. F.; Raynaud, C.; Russell, C. A.; Whittlesey, M. K., Computation provides chemical insight into the diverse hydride NMR chemical shifts of [Ru(NHC)4(L)H](0/+) species (NHC = N-heterocyclic carbene; L = vacant, H2, N2, CO, MeCN, O2, P4, SO2, H(-), F(-) and Cl(-)) and their [Ru(R2PCH2CH2PR2)2(L)H](+) congeners. *Dalton Trans.* **2017**, *46*(9), 2861-2873.


78. DFT-ZORA calculations reproduce the downfield shift, the origin of which is currently under investigation. C. Raynaud, O. Eisenstein; personal communication.

79. The only other example, to our knowledge, of MLC interconversion between an iridium monohydride and dihydride also gives an observable equilibrium (reference 70).
Chapter 5: Alkane Dehydrogenation by an Extremely Active Terminal Phosphido Iridium Complex

Portions of this chapter are reprinted with permission from:


Copyright 2022 American Chemical Society.

Abstract
Stoichiometric reactions of (tBuPPP)Ir make apparent a unique distribution of steric bulk around the iridium atom. This distribution, quantified by percent buried volume calculations, disfavors binding of olefin to the site trans to the terminal phosphide. This raises the energy of the 4-coordinate (pincer)Ir(η²-olefin) complex which that is the resting state of transfer alkane dehydrogenation. The geometric constraint also favors a rate-determining beta-hydride transfer transition state which yields olefin cis relative to the central coordinating atom without a significant energetic penalty. By increasing the energy of the resting state without increasing energy of the rate-determining transition state, we observe a rate increase of 3 orders of magnitude for the rate of propene/n-
octane transfer dehydrogenation at 80 °C when compared to the current fastest catalyst, (iPrPCP)Ir.
**Introduction**

Alkanes represent a class of chemicals that are difficult to functionalize selectively despite being available at industrial scales. One of the most successful platforms for the selective functionalization of alkanes are pincer iridium catalysts, which are capable of dehydrogenating alkanes to alkenes.\(^1\)\(^2\) This dehydrogenation is usually coupled with the hydrogenation of a sacrificial alkene in a process known as “transfer dehydrogenation”.\(^3\)\(^4\) This sacrificial alkene is usually chosen to fulfill two main criteria: Firstly, the hydrogenation of the sacrificial alkene must be more exothermic than the target alkane’s dehydrogenation is endothermic; coupling these processes therefore allows for an overall exothermic reaction. Secondly, the sacrificial alkene cannot bind too tightly to the catalyst. It is for this reason that sterically bulky and strained alkenes such as tert-butyl ethylene (TBE) or norbornene (NBE) are frequently used as “hydrogen acceptors”.

However, the use of these specialized alkenes represents a major hurdle in the scaling up of alkane dehydrogenation reactions as the cost of stoichiometric TBE and NBE is prohibitive at industrial scale. If we wish to use an industrial scale amount of alkene, it would be prudent to use an alkene that is already abundant in industrial scales, such as ethylene and propylene which are generated in large amounts as the byproduct of petroleum cracking reactions. These two gaseous alkenes more than fulfill the first requirement of a sacrificial alkene, as hydrogenation of ethylene and propylene are exothermic by 32.5 and 29.6 kcal/mol.\(^5\)\(^-\)\(^7\) Indeed, they have been used successfully
for the dehydrogenation of alkanes\textsuperscript{8-10} and ethers\textsuperscript{11} but have required high temperatures.

These examples remain rare as ethylene and propylene bind strongly to the 14e\textsuperscript{-} (pincer)Ir fragment and therefore inactivate the catalyst. In Chapter 4, we introduced bisphosphine-phosphido complexes which are analogues of the well-developed (PCP)Ir platforms, (tBuPPP)IrH\textsubscript{2} and (tBuPPP)Ir(C\textsubscript{2}H\textsubscript{4}). Importantly, we observed that (tBuPPP)Ir(\eta\textsuperscript{2}-olefin) (olefin = ethylene/propylene) makes weak olefin iridium bonds that readily allow for exchange with free olefin at low temperature (100 °C for C\textsubscript{2}H\textsubscript{4} and 40 °C for C\textsubscript{3}H\textsubscript{6})

The pyramidal geometry of the central phosphorus atom of (tBuPPP)Ir results in a bowl-like ligand structure, analogous to the geometry we have recently reported\textsuperscript{12} for a (PSP)Ru complex. This in turn results in a highly unsymmetrical positioning of the phosphino-t-butyl groups in which one face of the complex is fairly open while the coordination site trans to the central coordinating P atom is very crowded. This was clearly manifest in the addition and elimination of small molecules including H\textsubscript{2}, D\textsubscript{2}, and CO. This architectural motif is found to be particularly advantageous for the catalytic dehydrogenation of \textit{n}-alkanes to give 1-alkenes. We report that the (tBuPPP)Ir fragment is by far the most highly active catalyst for alkane transfer-dehydrogenation developed to date, and affords high regioselectivity; we attribute these properties in large part to this unsymmetrical spatial configuration (See Chapter 4).
Results and Discussion

Alkane Dehydrogenation by \((tBuPPP)Ir: Experimental Studies\). The potential ability of \((tBuPPP)Ir\) to catalyze alkane transfer-dehydrogenation, in analogy with \((^RPCP)Ir\) complexes, was initially explored with \(n\)-octane and with 1-hexene as acceptor (eq 1). Conceptually at least, the use of 1-alkene as an acceptor simplifies analysis of the cycle as the hydrogenation segment of the catalytic cycle is essentially the microscopic reverse of dehydrogenation of the terminal position of the \(n\)-alkane.

\[
n\text{-octane} + 1\text{-hexene} \rightarrow \text{octenes} + \text{hexane} \quad (1)
\]

An \(n\)-octane solution of 1-hexene (0.2 M) and \((tBuPPP)IrH_3\) (2.5 mM) was heated to 100 °C. Within 2 minutes the color was observed to change from golden yellow to a red color similar to that of a solution of \((tBuPPP)IrH_2\) and \((tBuPPP)IrH\). The reaction was monitored by gas chromatography for catalytic transfer dehydrogenation; after 2 minutes of heating 2.2 mM \(n\)-hexane (ca. 1 equiv), but no octenes, were observed. The solution was then subject to further heating at 100 °C. Very early (< 1 min) within the second period of heating, the solution color changed to a green similar to that of \((tBuPPP)Ir(ethylene)\). After 2 min of heating subsequent to the first 2 min, 37 mM octenes (15 TO) and an equal amount of \(n\)-hexane had been produced (Figure 5.1); this represents a rate of catalytic alkane dehydrogenation at such temperature that is remarkably high as compared with any previous reports to our knowledge.\(^{12-25}\) Within 4 min (6 min including the first 2 min without octene formation) 63 mM octenes (25 TO) had formed. The quantity of hexanes formed was within experimental error equal to the quantities of octenes observed at all times, in accord with eq 1, while the disappearance
of 1-hexene was much greater due to isomerization to trans- and cis-2-hexene.

For comparison, an analogous experiment was conducted with \((iPrPCP)Ir\) as the catalyst, which has previously given the fastest rates of alkane/1-alkene transfer-dehydrogenation reported to date.\(^{12-25}\) The reaction rate was much slower, approximately by a factor of 300, than was found for \((tBuPPP)Ir\) (Figure 5.2). Thus \((tBuPPP)Ir\) is apparently by far the fastest catalyst reported to date for \(n\)-alkane-to-alkene transfer dehydrogenation.

At early reaction time it can be seen (Figure 5.2) that the major kinetic product of \(n\)-
octane dehydrogenation by ($t^8$BuPPP)Ir is 1-octene. Thus ($t^8$BuPPP)Ir shows the very desirable regioselectivity for dehydrogenation of the terminal position of $n$-alkane, as has been found with some, although not all, PCP-type iridium-based catalysts$^{26}$. As the reaction proceeds, the ratio of regioisomers shifts in favor of the thermodynamically more favorable 2-olefins. This is presumably due to some combination of double-bond isomerization and hydrogenation that is selective for 1-octene versus internal octenes. Related to this, the rate of transfer dehydrogenation significantly decreases when the 1-hexene is consumed, although the majority of it has been isomerized to 2-hexenes and not hydrogenated; the 2-hexenes are much less effective as hydrogen acceptors. Note that, based on microscopic reversibility, selectivity for hydrogenation of 1-hexene is necessarily correlated with regioselectivity of $n$-alkane dehydrogenation at the terminal position.

While condensed phase olefins are typically preferred as hydrogen acceptors for the sake of convenience, propene offers the advantage over 1-hexene or other 1-alkenes that it cannot undergo isomerization to internal olefins which are seen to be less effective as acceptors. Moreover, with respect to practical considerations at large scale, propene would be much more economical than alpha-olefins. Propene and the propane byproduct also offer the advantage of easy separation from solution, and the possibility of recycling the propane to propene using heterogeneous catalysts$^{27}$ (which are far less effective for the dehydrogenation of higher alkanes in terms of both chemo- and regioselectivity). Accordingly we investigated the use of propene as acceptor for ($t^8$BuPPP)Ir-catalyzed dehydrogenation.
1 atm propene was added at room temperature (9 mL headspace, 0.37 mmol) to an n-octane solution of (P^tBuPP)IrH\textsubscript{3} (2.5 mM, 1.0 mL, 0.0025 mmol). Rapid transfer dehydrogenation resulted at 80 °C, a temperature much lower than that usually employed for alkane dehydrogenation. After 30 min heating, 74 mM (30 TO) total octenes had formed (Figure 5.3), with ca. 12% of the propene hydrogenated. After 80 min heating, 148 mM (59 TO) total octenes was observed.

*Figure 5.3. Octane/Propylene (1 atm, 9 mL headspace) transfer dehydrogenation catalyzed by (tBuPPP)Ir (2.5 mM), 80 °C (a) Octene Products (b) Percent Composition of Propane/Propylene*

For comparison again, a run under the same conditions was conducted with (iPrPCP)Ir as catalyst for n-alkane/propene dehydrogenation. 0.24 TO octenes were observed after 5 hours. Thus catalysis by (tBuPPP)Ir is over 1000 times faster than that by (iPrPCP)Ir under these conditions. Previously (iPrPCP)Ir had been reported to catalyze n-alkane/propene dehydrogenation at 68 TO/min and 9.6 TO/min at 180 °C and 160 °C respectively under 2 atm propene. A crude Eyring-plot extrapolation from these two points gives an expected rate at 80 °C of $4.2 \times 10^{-4} \text{ min}^{-1}$ under those conditions; thus the rate observed in the present experiment (ca. $8 \times 10^{-4} \text{ min}^{-1}$) is not unexpectedly low.
The turnover rate (at initial time) for \( n \)-alkane/propene dehydrogenation by \((^{tBu}PPP)Ir\) varies inversely with propene pressure (1 atm – 4 atm; Figure S5.1). These kinetics indicate a resting state of the composition \((^{tBu}PPP)Ir(\text{propene})\) and a turnover-limiting step in which propene has reversibly dissociated from the catalyst. This is consistent with the rapid reversible dissociation of propene from \((^{tBu}PPP)Ir(\text{propene})\) noted above.

In addition to propylene, ethylene was investigated as a possible hydrogen acceptor. Given the stronger binding of ethylene to \((^{tBu}PPP)Ir\), catalysis was not observed at the temperatures used for propylene. Reactions utilizing 1 atm of ethylene in \( n \)-octane were conducted at 125 °C. The reaction with ethylene was slower, yielding 6 mM octene (2 TON) after 20min.

![Figure 5.4. Octane/Ethylene (1 atm, 9 mL headspace) transfer dehydrogenation catalyzed by \((^{tBu}PPP)Ir\) (2.5 mM), 125 °C, Octene Products.](image)

**Figure 5.4.** Octane/Ethylene (1 atm, 9 mL headspace) transfer dehydrogenation catalyzed by \((^{tBu}PPP)Ir\) (2.5 mM), 125 °C, Octene Products.

**Alkane Dehydrogenation by \((^{tBu}PPP)Ir\): DFT Computational Studies.** DFT calculations on catalysis by \((^{tBu}PPP)Ir\) were conducted using the same computational methods as
recently described\textsuperscript{26} in a study of alkane dehydrogenation by (tBuPCP)Ir and related complexes. Results of the calculations, illustrated in Figures 9 and 10, reveal that the energy profiles for the reaction pathways of (tBuPPP)Ir and (tBuPCP)Ir are remarkably similar – but with two key differences:

(1) In the case of (tBuPPP)Ir the lowest energy pathway proceeds through the isomer of (tBuPPP)Ir(alkene)(H)\textsubscript{2} in which the olefin is coordinated cis to the central coordinating atom (P\textsubscript{c}) of the pincer ligand, and thus the hydrides are mutually cis. In contrast, in the case of the (tBuPCP)Ir the analogous intermediate has mutually trans hydrides, and the olefin is trans to the PCP ipso-carbon.

(2) The out-of-cycle resting state for both tBuPPP and tBuPCP complexes is the four-coordinate Ir(I) complex with 1-alkene positioned trans to the central coordinating atom. The binding of the olefin is calculated to be significantly weaker in (tBuPPP)Ir(1-alkene) than in (tBuPCP)Ir(1-alkene). The rate-determining \(\beta\)-H-transfer (BHT) TSs are similar in energy for tBuPPP and tBuPCP, relative to the respective three-coordinate (pincer)Ir fragments (23.7 kcal/mol and 26.0 kcal/mol); the overall barrier to catalytic turnover, however, is determined by the free energy difference between the rate-determining \(\beta\)-H-transfer TS and the respective four-coordinate iridium-olefin resting state. At 298 K the calculated overall free energies of activation (\(\Delta G^\ddagger\)) are therefore 28.4 kcal/mol and 35.6 kcal/mol for (tBuPPP)Ir and (tBuPCP)Ir, respectively (Figures 5.5 and 5.6). The weaker binding of olefin in the case (tBuPPP)Ir(alkene) can thus be seen as the key factor leading to the much higher activity of (tBuPPP)Ir compared with (tBuPCP)Ir.
Figure 5.5. Free energy diagram (kcal/mol) for 1,2-dehydrogenation of \( n \)-hexane by \((t\text{Bu-PPP})\text{Ir}\) to give 1-hexene. Free energies calculated for \([n\text{-hexane}] = 7.65 \text{ M}\) (concentration of neat solvent), \([1\text{-hexene}] = 1 \text{ M}\). “‡” indicates a transition state.
**Figure 5.6.** Free energy diagram (kcal/mol) for 1,2-dehydrogenation of \(n\)-hexane by \((\text{tBu-PCP})\text{Ir}\) to give 1-hexene. Free energies calculated for \([n\text{-hexane}] = 7.65 \text{ M (concentration of neat solvent), [1-hexene]} = 1 \text{ M. “ǂ” indicates a transition state.}

![Free energy diagram](image)

**Figure 5.7.** Free energy diagram (kcal/mol) for 1,2-dehydrogenation of \(n\)-hexane by \((\text{tBu-PCP})\text{Ir}\) to give 1-hexene. Free energies calculated for \([n\text{-hexane}] = 7.65 \text{ M (concentration of neat solvent), [1-hexene]} = 1 \text{ M. “ǂ” indicates a transition state.}

In the case of \((\text{iPr-PCP})\text{Ir}\), which is sterically much less hindered than \((\text{tBu-PCP})\text{Ir}\), the TSs for \(\beta\)-H-transfer and for olefin loss are calculated to be of comparable free energy, equal within the accuracy limits of the calculations (Figure 5.7). Relative to the respective three-coordinate fragment, both are much lower than the rate-determining TS for either \((\text{tBu-PCP})\text{Ir}\) or \((\text{tBu-PPP})\text{Ir}\). Undoubtedly this results from \((\text{iPr-PCP})\text{Ir}\) being less sterically demanding than \((\text{tBu-PCP})\text{Ir}\). The decreased steric crowding of \((\text{iPr-PCP})\text{Ir}\), however, also
results in much stronger bonding of this fragment to 1-hexene in the resting state. The stronger binding of the olefin to (iPrPCP)Ir can out most of the reduction in free energy of the highest barrier relative to the three-coordinate fragment – although not all of the difference; hence (iPrPCP)Ir is a somewhat more active catalyst than (tBuPCP)Ir with an overall calculated barrier of $\Delta G^\ddagger = 33.2$ kcal/mol under the assumed conditions. This overall barrier, however, is 4.8 kcal/mol greater than that for (tBuPPP)Ir; at 80 °C this difference corresponds to a 900-fold difference in rate which is notably consistent with the experimentally determined difference.

The experimentally determined instability of (tBuPPP)Ir(ethylene) and the dissociation of ethylene on the NMR time scale (with $\Delta H^\ddagger = 19.8$ kcal/mol) is consistent with the calculated weaker binding of olefin to (tBuPPP)Ir versus (tBuPCP)Ir. The experimentally determined activation enthalpy is in good agreement with the calculated enthalpy of ethylene binding in (tBuPPP)Ir(C$_2$H$_4$), $\Delta H^* = -21.9$ kcal/mol compared with $\Delta H^* = -30.6$ kcal/mol for (tBuPCP)Ir(C$_2$H$_4$) (Table S5.16). Since it is this weak binding which appears be critical in explaining the very high activity of (tBuPPP)Ir we investigated this in further detail (Table 5.1).
Table 5.1 Calculated Free Energies of Olefin Binding to (Pincer)Ir

\[
(R\text{PEP})\text{Ir} + \text{alkene} \rightarrow (R\text{PEP})\text{Ir(alkene)} \quad (E = P, C) \quad \Delta G^\circ \text{ (kcal/mol)}
\]

<table>
<thead>
<tr>
<th>alkene</th>
<th>((tBu\text{PPP})\text{Ir(alkene)})</th>
<th>((Me\text{PPP})\text{Ir(alkene)})</th>
<th>((tBu\text{PCP})\text{Ir(alkene)})</th>
<th>((Me\text{PCP})\text{Ir(alkene)})</th>
<th>(\Delta (tBu\text{PCP} - tBu\text{PPP}))</th>
<th>(\Delta (Me\text{PCP} - Me\text{PPP}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethylene</td>
<td>-7.6</td>
<td>-16.0</td>
<td>-22.0</td>
<td>-22.4</td>
<td>8.4</td>
<td>-0.4</td>
</tr>
<tr>
<td>propene</td>
<td>-3.8</td>
<td>-8.9</td>
<td>-21.2</td>
<td>-20.9</td>
<td>5.1</td>
<td>0.3</td>
</tr>
<tr>
<td>1-hexene</td>
<td>-4.7</td>
<td>-9.6</td>
<td>-22.7</td>
<td>-22.3</td>
<td>4.9</td>
<td>0.4</td>
</tr>
<tr>
<td>trans-2-hexene</td>
<td>5.4</td>
<td>-4.7</td>
<td>-20.9</td>
<td>-22.1</td>
<td>10.1</td>
<td>-1.2</td>
</tr>
<tr>
<td>cis-2-hexene</td>
<td>5.9</td>
<td>-3.2</td>
<td>-19.1</td>
<td>-21.8</td>
<td>9.1</td>
<td>-2.7</td>
</tr>
</tbody>
</table>

Olefin binding to \((tBu\text{PPP})\text{Ir}\) is calculated to be significantly weaker than to \((tBu\text{PCP})\text{Ir}\) for all olefins investigated (Table 5.1). To determine if the origin of this effect is electronic or sterically, we calculated bond strengths for the analogous \((Me\text{PPP})\text{Ir}\) \((E = P\ or\ C)\) complexes, for which steric effects are presumably much less significant than the \((tBu\text{PPP})\text{Ir}\) analogs. In strong contrast with the \((tBu\text{PPP})\text{Ir}\) complexes, the \text{Ir}-olefin BDFEs for \((Me\text{PPP})\text{Ir}\) and \((Me\text{PCP})\text{Ir}\) are strikingly similar. The large differences in the \text{Ir}-olefin bond strengths found in the case of \((tBu\text{PPP})\text{Ir}\) complexes are thus primarily attributable to steric effects. This is consistent with reports indicating that terminal phosphido groups have a trans-influence very similar to that of an aryl group.\(^{28}\)

If the significantly weaker binding of olefins to \(tBu\text{PPP}\) versus \(tBu\text{PCP}\) results from greater steric crowding in the former, this raises the question: Why does the increased crowding not raise the energy of the rate-determining TS even more than (or at least as much as) it raises the energy of the four-coordinate (pincer)\text{Ir(olefin)} complex? To
address this question, the steric profiles of $\text{tBuPCP}$ and $\text{tBuPPP}$ were probed using the SambVca 2.1 web application (Figure S5.54).\textsuperscript{29} The mapped catalytic pocket indicates that $\text{tBuPPP}$ is slightly less sterically hindered than $\text{tBuPCP}$ (79.1% buried versus 85.7% buried) (Table 5.2). But more important than the overall buried volume is the arrangement of the steric bulk, which is radically different for the two complexes.

**Table 5.2** Percent buried free volumes of hemispheres centered on three open coordination sites of ($\text{tBuPPP}$)Ir and ($\text{tBuPCP}$)Ir

<table>
<thead>
<tr>
<th></th>
<th>%BurVol total</th>
<th>cis-exo face</th>
<th>cis-endo face</th>
<th>trans face</th>
</tr>
</thead>
<tbody>
<tr>
<td>($\text{tBuPPP}$)Ir</td>
<td>79.1%</td>
<td>66.2%</td>
<td>92.0%</td>
<td>84.9%</td>
</tr>
<tr>
<td>($\text{tBuPCP}$)Ir</td>
<td>85.7%</td>
<td>85.9%</td>
<td>85.6%</td>
<td>78.8%</td>
</tr>
</tbody>
</table>
Figure 5.8. Illustration of buried volumes of hemispheres centered on three open coordination sites of (tBuPPP)Ir and (tBuPCP)Ir.

For a six-coordinate (tBuPEP)Ir (E = C or P) complex, three coordination sites are available. The percent buried volume of the hemisphere approximately centered on each of those three sites was determined. As indicated in Table 5.2 and Figure 5.8, in the case of (tBuPPP)Ir, the hemisphere centered on the (exo) site cis to the central coordinating atom (P_C) is quite uncrowded (BV = 66%). The face trans to P_C is crowded (BV = 85%) and the endo cis face is even more crowded (BV = 92%). In marked contrast, for (tBuPCP)Ir, the faces cis to C_ipso are both significantly more crowded (BV = 86%) than the face trans to C_ipso (BV = 79%).

Viewing the BHT TS as having a geometry approximately resembling the olefin dihydride product to which it leads, the arrangement of steric bulk in (tBuPCP)Ir would
favor the BHT TS that leads to the olefin dihydride isomer with the olefin trans to $C_{ipso}$. It also favors, however, the resting state in which the olefin is trans to $C_{ipso}$, which contributes to an increase in the overall reaction barrier.

In sharp contrast, in the case of ($tBu_2PPP$)Ir, the arrangement of steric bulk favors the BHT TS leading to the olefin dihydride isomer with the olefin at the very uncrowded exo cis site. But while the crowding at the site trans to $P_c$ allows the presence of a hydride (or incipient hydride) without much energetic penalty, it significantly raise the energy of the four-coordinate $d^8$ resting state in which the olefin resides at that site.

The critical factor favoring catalytic activity of ($tBu_2PPP$)Ir versus ($tBu_2PCP$)Ir is thus the destabilization of the four-coordinate (pincer)Ir(olefin) resting state relative to the BHT TS, due to the positioning of steric bulk specifically at the coordination site trans to the central coordinating atom. The steric demands at that site are largely circumvented by a BHT TS that leads to the cis-dihydride olefin $tBu_2PPP$ complex, in contrast with ($tBu_2PCP$)Ir for which the most favorable BHT TS leads to the trans-dihydride. It is noteworthy in this context that what appear to be the most active catalysts for $n$-alkane dehydrogenation previously known, triptycene-based PCP-pincer iridium complexes reported by Bézier and Brookhart, are unusual in that they also have a central coordinating group that is non-planar (tetrahedral carbon).\textsuperscript{14, 21, 23-25}

The different isomeric pathways can have additional implications, beyond relative destabilization of the resting state, for both activity and regioselectivity. $\beta$-H-transfer is rate-determining for both ($tBuPPP$)Ir and ($tBuPCP$)Ir pathways, and the TSs for the two fragments have very similar free energies relative to the respective three-coordinate
fragment. The subsequent step in the cycles, however, loss of olefin, has a TS that is 3.2 kcal/mol higher for \textit{trans}-\((t\text{Bu}PCP)\text{Ir}(1\text{-hexene})H_2\) than for \textit{cis}-\((t\text{Bu}PPP)\text{Ir}(1\text{-hexene})H_2\), although the product of olefin dissociation is actually 4.3 kcal/mol lower for \textit{trans}-\((t\text{Bu}PCP)\text{Ir}(1\text{-hexene})H_2\). This kinetic barrier to loss of alkene is attributable to the formation, as olefin dissociates, of a very high-energy \textit{trans}-dihydride, while relaxation to a dihydride with an acute H-Ir-H angles occurs only after the Ir-olefin bond is essentially fully broken.\textsuperscript{26} In contrast the \textit{cis}-dihydride geometry is only slightly higher than the relaxed geometry\textsuperscript{30}, thus the kinetics of olefin dissociation from the \textit{cis} dihydride (or addition to the \textit{cis} dihydride) are more facile. While the kinetic barrier to olefin loss has no effect on the overall barrier or selectivity in the case of \((t\text{Bu}PCP)\text{Ir}(1\text{-hexene})\), in the case of \((i\text{Pr}PCP)\text{Ir}\) the TS for olefin dissociation is calculated to be very slightly higher than the TS for \(\beta\)-H-transfer, although the difference is too small to be considered meaningful. We have shown, however, that the barrier to olefin dissociation plays an important role in both the rate and selectivity of catalytic alkane dehydrogenation by the closely related fragment \((t\text{Bu}POCOP)\text{Ir}\)\textsuperscript{26} which has oxygen instead of methylene linkers connecting the phosphino groups to the central arene ring. For dehydrogenation by \((t\text{Bu}POCOP)\text{Ir}\), as well as other derivatives with one or two oxygen linkers, the kinetic barrier to olefin dissociation is high enough that it becomes the rate-determining step. This therefore contributes to the overall reaction barrier and, moreover, it was found to be responsible for a lack of regioselectivity for dehydrogenation at the \(n\)-alkane terminal position.\textsuperscript{26}

\textbf{3.3 – Conclusion}
In conclusion, we have demonstrated the catalytic efficacy of a terminal phosphido iridium complex for alkane dehydrogenation utilizing gaseous hydrogen acceptors, the first example of catalysis by a terminal phosphido iridium complex. The steric bulk provided by the tert-butyl groups destabilizes the coordination of ethylene and propylene, allowing for a thermodynamically accessible dissociation to generate the active catalyst, (tBuPPP)Ir.

The (tPPP)Ir fragment is formally analogous to (tPCP)Ir species which are well known to catalyze alkane dehydrogenation. (tBuPPP)Ir is found to catalyze n-alkane transfer dehydrogenation, using propene as a hydrogen acceptor, over a thousand fold faster than (iPrPCP)Ir, the previously reported fastest catalyst for such reactions. Alkane dehydrogenation with appreciable rates can thus be achieved at unprecedentedly low temperatures.31-33

The origin of the high catalytic activity has been elucidated through a combination of mechanistic experimental and computational studies. β-H-transfer (BHT) by the alkyl hydride that is formed by alkane C-H addition is calculated to be the rate-limiting step. The energy of the BHT TS, relative to the (pincer)Ir fragment, is found to be comparable for (tBuPPP)Ir and (tBuPCP)Ir catalysts. In the case of (tBuPPP)Ir, however, the lowest BHT TS leads to a cis-dihydride intermediate with an olefin coordinated cis (exo) to the central coordinating atom of the pincer ligand (Pc). In contrast, in the case of (tBuPCP)Ir, the lowest BHT TS leads to a trans-dihydride complex with the olefin positioned trans to the ipso-carbon of the phenyl ring.
Although the BHT TSs are of similar energy relative to the respective (pincer)Ir fragments, olefin is bound much more weakly in the resting state, (pincer)Ir(olefin), in the case of \((tBuPPP)Ir(olefin)\) than in \((tBuPCP)Ir(olefin)\). Computational studies reveal that the trans influence of \(P_c\) and \(C_{ipso}\) are very similar, but crowding is much greater at the site trans to the central coordinating atom in \((tBuPPP)Ir(olefin)\) and this is responsible for the much weaker olefin binding.

Thus, in the case of \((tBuPPP)Ir\) the very open exo coordination site permits a facile alkane dehydrogenation pathway in which olefin is formed at that site, while the much less sterically demanding hydrides occupy the other two, much more crowded, coordination sites. In the case of \((tBuPCP)Ir\) the most open site is trans to \(C_{ipso}\); this results in a comparably facile pathway in which the olefin is formed at that site. Critically, however, the same lack of crowding at that site also allows strong bonding of olefin in the resting state, \((tBuPCP)Ir(olefin)\), thus increasing the overall barrier to catalysis. Thus, the unprecedented activity of alkane dehydrogenation by \((tBuPPP)Ir\) is largely attributable to the high degree of crowding at the coordination site trans to the central coordination atom, \(P_c\), along with a particular lack of crowding at the (exo) coordination site cis to \(P_c\).

*Supporting Information*
Chapter 5 References


27. PropaneDehtn7Refs, Propane Dehtn 7 Refs.


Chapter 6: The Synthesis of Novel Pincer-Molybdenum Complexes for the Reduction of Nitrogen to Ammonia

Abstract

We report the synthesis of a pyrene-backed (tBuPNP)Mo complex capable of being mounted to a glassy carbon electrode. We also report the synthesis of a para-dimethyl amino (tBuPNP)Mo that was intended for use in aqueous reduction systems. Finally we report a triphosphorus pincer molybdenum complex containing a secondary phosphine that undergoes rapid disproportionation upon deprotonation.
**Introduction**

The development of the Haber - Bosch process (HB) for the reduction of nitrogen to ammonia is arguably one of the most important innovations of the 21st century. It has allowed global population to grow exponentially while preventing mass starvation.\(^1\) For all the good, HB has a number of foundational inefficiencies that make for excellent targets in a modern world where electricity production is rapidly becoming greener and cheaper. These inefficiencies are exacerbated by the sheer scale of HB, consuming 1-2% of the world’s annual energy production and 3% of global CO\(_2\).\(^2,\, 3\) This energy demand and CO\(_2\) production is largely the result of the hydrogen producing steam reformation and water-gas shift of fossil fuels,\(^3\) which accounts for 1% of the global consumption of fossil fuels.\(^4,\, 5\)

There are currently two major pathways to make HB less reliant on fossil fuels; both of these pathways involve the application of electrochemistry. The first involves pivoting the source of hydrogen from processed fossil fuels to water via a water electrolyzer.\(^2\) This pivot should dramatically cut the CO\(_2\) generated from the water-gas shift reaction. This does not mitigate the CO\(_2\) generated by power generation and so is heavily dependent on the local energy infrastructure with the maximum reduction estimated at 75% for full hydropower electrolysis.\(^6\) This method benefits from being able to use the existing infrastructure of modern HB plants, although this comes with a significant drawback in relation to zero-CO\(_2\) emission ammonia: transportation costs. Geographically isolated and developing countries use ammonia at rates an order of
magnitude less than the rest of the world but this could be mitigated via the second electrochemical application of HB, direct electrochemical reduction.

While water electrolysis-HB seeks to modify existing hydrogen feedlines to existing HB plants, direct electrochemical reduction seeks to directly reduce nitrogen to ammonia via addition of hydrogen in the deconstructed form of protons and electrons (Equation 1). This method of ammonia production would allow for complete decoupling from fossil fuels. By removing the fossil fuel proximity requirement, ammonia production could be decentralized to a community level.  

$$\text{N}_2 + 6e^- + 6\text{H}^+ \rightarrow 2\text{NH}_3 \quad \text{Eq (1)}$$

Electrochemical nitrogen reduction to ammonia is a vast field that seeks to improve the chemistry found in naturally occurring nitrogenase enzymes. While nitrogenase utilizes protons from water and requires the hydrolysis of 2 ATP per electron, artificial nitrogen reduction is accomplished using a multitude of proton and electron sources with various catalysts. Within this larger subset of artificial electrochemical catalysts for nitrogen reduction is the study of molecular catalysts for nitrogen reduction. These molecular catalysts offer an arguably more simple system to allow for better understanding of the mechanisms underpinning the reduction of nitrogen.

The proton sources for these molecular catalysts typically employ strong acids, protonated nitrogen species, phosphoniums, ethereal acids, alcohols or, promisingly, water. Less promising is the common use of metal containing chemical reductants like metallocenes, alkali metals, or samarium diiodide. These
important advances signal the coming of a greener alternative, but there is a great need to supplant the use of transition metal complexes as reducing agents. Indeed, there is currently only one example of a molecular catalyst for electrochemical nitrogen reduction, which while mediated by cobaltocene, ultimately utilizes electrons from an electrode.\textsuperscript{17} In this chapter, we discuss a number of different approaches to studying pincer-molybdenum systems for nitrogen fixation.

**Results and Discussion**

**Synthesis of an Electrode Mountable Pincer Complex**

Bridging the gap between heterogeneous and homogenous catalysts is the field of mounted homogeneous catalysts. This catalyst archetype has been employed with great success for electrocatalytic reductions. In 2012, Meyer and Brookhart reported the use of a pyrene functionalized pincer iridium complex for the electrocatalytic reduction of CO\textsubscript{2}.\textsuperscript{25} By appending a pyrene group to the 4-position of the pincer, they were able to mount the catalyst on a Gas-Diffusion Electrode through pi interactions. Inspired by this, we sought to generate an analogue that could be used for nitrogen reduction utilizing the highly successful (PNP)Mo system.\textsuperscript{19, 20, 24}

**Synthesis of (pyrenePNP \textsuperscript{tBu})** starting with commercially available chelidamic acid. A protecting group in the form of an ethyl ester was installed via Fischer esterification with ethanol and catalytic sulfuric acid to yield diethyl chelidamate (1). This compound was then treated with stoichiometric triflic anhydride in dichloromethane to yield 4-trifluoromethanesulfonyl diethyl chelidamate (2). Coupling 2 with 1-pyrene boronic acid
utilizing tetrakis(triphenylphosphine)palladium in dimethylformamide to yield 4-(1-pyrenyl)-diethyl chelidamate (3). The deprotection was then done with sodium borohydride in refluxing ethanol.

The product, 4-(1-pyrenyl)-2,6-(hydroxymethyl)-pyridine (4) precipitates out of solution as a grey solid. This solid is negligibly soluble in a range of solvents including: aromatic solvents (BTX), alcohols (methanol, ethanol, isopropanol, butanol, phenol), halogenated solvents (dichloromethane, chloroform, carbon tetrachloride), ethers (diethyl ether, methyl tert-butyl ether, tetrahydrofuran), and nitrogenous solvents (dimethylformamide, triethylamine, acetonitrile). As such, this compound was not appropriately characterized before being used in the next step.

The diol 4 was suspended in THF before thionyl chloride was added in dropwise. The solid dissolved in solution over time, yielding 4-(1-pyrenyl)-2,6-(chloromethyl)-pyridine (5). This solid was degassed and treated with di-tert-butylphosphine in chloroform before being treated with a mild base to yield (pyrenePNP-tBu).
Scheme 6.1. Alternative Synthesis of $\text{pyrene}(\text{PNP})\text{MoCl}_3$

Due to the length of time to perform the 6 step synthesis, an alternative synthesis for $\text{(pyrenePNP}^{\text{tBu}})$ was devised. The alternative synthesis of $\text{(pyrenePNP}^{\text{tBu}})$ started with commercially available 4-hydroxy-2,6-lutidine. Treatment with excess triflic anhydride and triethylamine as an acid sponge in dichloromethane led to 4-(trifluoromethylsulfonyl)-2,6-lutidine (6). This precursor was dissolved in DMF with 1 equivalent of pyrene-1-boronic acid, triethylamine, and catalytic palladium tetrakis(triphenylphosphine). The mixture was then heated to 90°C for 2 days yielding 4-
(1-pyrenyl)-2,6-lutidine (7) as the coupled product. This product was then converted to the final ligand product via deprotonation of lutidine followed by nucleophilic addition to (tBu)2PCl to give 4-(1-pyrenyl)-2,6-(bis-di-tert-butylphosphinomethyl)pyridine, (pyrenePNP tBu). This ligand was then metalated according to previously reported methods utilizing MoCl3(THF)3 in THF.20

Scheme 6.2. Alternative Synthesis of pyrene(PNP)MoCl3

The resulting product, pyrene(PNP)tBuMoCl3, is paramagnetic and was characterized utilizing Surface Assisted Laser Desorption Ionization – Mass Spectrometry (SALDI-MS) and through single crystal X-Ray Diffraction. The solid state structure revealed the presence of a 90° distortion of the dihedral angle between the pyrene and PNP moieties. Indicating decreased pi-conjugation.

Cyclic voltammetry experiments were performed at UNC-Chapel Hill in the Miller Group by Dr. Brian Lindley. In order to coat the glassy carbon electrode with the carbon
nanotubes onto which the catalyst would be adsorbed, 6 mg carbon nanotubes (CNT, 20-30 nm from Cheap Tubes Inc.) and 6 mL anhydrous DMF were added to a 20 mL vial. The suspension was sonicated for 40 min, forming a fine dispersion. A glassy carbon (GC) electrode (3 mm diameter) was polished with 0.05 micron alumina powder then rinsed with HPLC-grade H2O, acetone, and EtOH, then dried under a stream of air. A drop of the CNT/DMF suspension was added to the GC surface and the DMF was allowed to evaporate in the fume hood, resulting in an electrode surface with black solid adsorbed.\textsuperscript{26, 27}

In order to mount the catalyst, the CNT-GC working electrode was soaked in a solution of \textit{pyrene}(PNP)MoCl\textsubscript{3} (1 mM) and \([\text{nBu}_4\text{N}]\text{PF}_6\) (200 mM) in THF for 30 min. The electrode was rinsed with THF, then submerged in a solution of \([\text{nBu}_4\text{N}]\text{PF}_6\) (200 mM) in THF. Cyclic voltammetry data was collected using a 3-electrode cell comprised of the CNT-GC working electrode, a Pt wire counter electrode and a Ag wire reference electrode (isolated from bulk solution using a fritted capillary tube). The CV features observed for the mounted \textit{pyrene}(PNP)MoCl\textsubscript{3} matched well for those observed in unmounted \textit{pyrene}(PNP)MoCl\textsubscript{3} and (PNP)MoCl\textsubscript{3}. The features for \textit{pyrene}(PNP)MoCl\textsubscript{3} were not reversible. Upon reduction, the solution became colorized. This irreversibility and colorized solution indicated catalyst desorption. Presumably the formation of the anionic \([\textit{pyrene}(PNP)\text{MoCl}_3]^-\) leads to favorable dissolution compared to the non-covalent interactions of the pyrene and CNT.\textsuperscript{27}
Figure 6.1. Molecular structure of $^{\text{pyrene}}$(PNP)MoCl$_3$ determined by single-crystal XRD. H atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability, whilst atoms not placed in the original XRD are placed based on typical C-C bond lengths.

**Attempted Synthesis of a Water Soluble Nitrogen Reduction Catalyst**

Given the desire to use water as the ultimate source of protons and electrons for the reduction of dinitrogen to ammonia, it seemed prudent to synthesize a catalyst that would be readily soluble in highly polar media. We attempted the synthesis of the cationic trimethylammonium complex, $^{p-NMe_3}$($^{tBu}$PNP)MoBr$_3$. $^{p-NMe_2}$($^{tBu}$PNP)MoBr$_3$ has been previously reported, however we synthesized it via a new route (Scheme 6.3). A crystal suitable for X-Ray Diffraction was grown from pentane diffusion into a saturated THF solution. The XRD reveals the planar nature of the dimethylamino group, and explains why there did not seem to be any nucleophilic addition to this site. This project was
abandoned after it became apparent that (\textsuperscript{tBu}PNP)MoBr\textsubscript{3} was an effective precatalyst for nitrogen reduction reactions in water.

**Scheme 6.3. Synthesis of \textsuperscript{p-NMe\textsubscript{2}}(\textsuperscript{tBu}PNP)MoBr\textsubscript{3}**

\[
\begin{align*}
\text{HO-N} & \xrightarrow{\text{POCl\textsubscript{3}, Reflux, 6hr}} \text{Cl-N} + 10\text{eq Me\textsubscript{2}NHCl} \\
& \xrightarrow{11\text{eq NaOH}} \text{H\textsubscript{2}O} \xrightarrow{135^\circ\text{C}, 4 \text{ days}} \\
& \text{N-N} \\
& \text{N-Mo-Br} \xrightarrow{\text{P(tBu)\textsubscript{2}}} \text{N-MoBr\textsubscript{3}} \xrightarrow{\text{MoBr\textsubscript{3}(THF)\textsubscript{3}}} \text{N-P(tBu)\textsubscript{2}}
\end{align*}
\]

1. \textsuperscript{tBu}Li (2.05 eq), Ether, 0°C  
2. 15 hr, reflux  
3. P(tBu)\textsubscript{2}Cl (2eq), -78°C  
4. 15 hr, r.l.

**Figure 6.2.** Molecular structure of \textsuperscript{p-NMe\textsubscript{2}}(PNP)MoBr\textsubscript{3} determined by single-crystal XRD. H atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability,
Phosphorus Metal-Ligand Cooperativity in Pincer Molybdenum Complexes

The Metal-Ligand Cooperativity (MLC) observed between the \( \text{tBu}^{\text{HPP}} \) ligand and iridium described in Chapter 4 led us to explore the chemistry of that ligand with molybdenum. In the case of iridium, we had observed a proton transfer from the phosphorus to the metal center, herein, we described the development of a system we hoped would allow for the proton transfer from phosphorus to a nitrogen bound to molybdenum.

We began by synthesizing \( (\text{tBu}^{\text{HPP}})\text{MoBr}_3 \) in a manner similar to methods reported for other \( \text{L}_3\text{MoX}_3 \) complexes.\(^{28}\) Free ligand was combined with \( \text{MoBr}_3(\text{THF})_3 \) in THF and warmed to 50 °C overnight (Scheme 6.4). The solvent was evaporated and \( (\text{tBu}^{\text{HPP}})\text{MoBr}_3 \) was isolated as a paramagnetic orange solid. The molecular structure was determined by single crystal X-ray diffraction. Analysis of the solid state geometry of \( (\text{tBu}^{\text{HPP}})\text{MoBr}_3 \) revealed hydrogen bonding interactions between the proton located on the secondary phosphine and the bromide ligands of adjacent molecules (Figure 6.3). This interaction indicated that the secondary phosphine proton was highly acidic compared to the free ligand (between 17 and 26 pKa units based on deprotonation studies with KOTBu and KHMDS in THF) and especially the pKa of the analogous secondary phosphine \( \text{Ph}_2\text{PH} \).\(^{29}\)
Scheme 6.4. Synthesis of \((\text{Bu}^{\text{HPP}})\text{MoBr}_3\)

\[
\begin{align*}
\text{Ph} & \quad \text{P(Bu)}_2 \\
\text{H} & \quad \text{P} \\
\text{Ph} & \quad \text{P(Bu)}_2
\end{align*}
\]

\[
\xrightarrow{\text{MoBr}_3(\text{THF})_3, \text{THF}, 50^\circ C}
\]

\[
\begin{align*}
\text{Ph} & \quad \text{P(Bu)}_2 \\
\text{H} & \quad \text{P} - \text{MoBr}_3 \\
\text{Ph} & \quad \text{P(Bu)}_2
\end{align*}
\]

Figure 6.3. a) Molecular structure of \((\text{Bu}^{\text{HPP}})\text{MoBr}_3\) determined by single-crystal XRD. H atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability. b) close P-Br interaction indicative of hydrogen bonding interaction.

Given the acidity of this secondary phosphine proton and the literature precedent of acid promoted nitrogen cleavage by molybdenum complexes,\textsuperscript{30} we sought to explore reactions of base with this complex. A variety of deprotonation reactions were performed with \((\text{Bu}^{\text{HPP}})\text{MoBr}_3\) (Scheme 6.5) varying solvents (toluene or THF), atmosphere (N\textsubscript{2} or Ar, 1 atm), base (KOTBu or NEt\textsubscript{3}, 1 equiv), and reaction temperature (-40 °C and r.t.). All reactions yielded a mixture of products. The facile deprotonation of \((\text{Bu}^{\text{HPP}})\text{MoBr}_3\) by NEt\textsubscript{3}, even at low temperatures, provided an upper bound of approximately 10.8 for the pKa of the P-H bond.
Attempts were made to separate the mixture of products. One yellow product that was separated by pentane wash through a plug of silica was determined to be a 5-coordinate \((\text{TBu}^{\text{p}}\text{pp})\text{Mo}(\text{X})\text{Br}\) \((\text{X} = \text{O}, \text{N})\). The identity of this species was not determined, as the low quality of the crystal did not enable XRD to definitively determine the new atom bound to molybdenum. Interestingly, the newly formed terminal phosphide exhibits a highly planarized geometry (Figure 6.4, sum of angles around phosphorus = 355.01°). In addition to this yellow product, the \(^{31}\text{P}\) NMR of the mixture of products exhibited signals \((\delta^{122.2}, 1\text{P}, \text{t}, J_{\text{PP}} = 16.8 \text{ Hz} \text{ and } \delta^{94.6}, 2\text{P}, \text{d}, J_{\text{PP}} = 16.7 \text{ Hz})\) for a single diamagnetic product that was not free ligand. The high chemical shift observed for the signal corresponding to one phosphorus was consistent to what had been previously observed for terminal phosphido complexes with iridium (Chapter 4).
Figure 6.4. a) Unrefined molecular structure of (tBuPPP)Mo(X)Br (X = O or N) determined by single-crystal XRD. H atoms are omitted for clarity. b) Highlighted bond angles around the planar phosphido moiety.

The solid state structure obtained for the product mixture was that of a either a Mo(IV)-oxo complex or a Mo(V)-nitride complex, the former of which should be paramagnetic and therefore, NMR silent. Stranger still was the presence of only a single bromide ligand. For a stoichiometric reaction, base induced dehydrohalogenation should have yielded, even transiently, a (tBuPPP)MoBr$_2$ complex. Given the low yield of this reaction, as well as the formation of an intractable mixture of species, we proposed that the complex, upon deprotonation was undergoing redox disproportionation reactions (Scheme 6.6).
Scheme 6.6. Proposed base induced disproportionation of \((tBuP^2Hp)MoBr_3\)

![Scheme 6.6. Proposed base induced disproportionation of \((tBuP^2Hp)MoBr_3\)](image)

One key feature of this proposed disproportionation reaction is the single electron reduction to yield a transient \((tBuPPP)MoBr\) species. Given that base induces this proposed rapid disproportionation, we sought to add the electron to the metal complexes prior to addition of base. A toluene-\(d_8\) suspension of \((tBuP^2Hp)MoBr_2\) was treated with 1 equivalent of 0.05% sodium amalgam (Scheme 6.7). Vigorous agitation yielded a dark red solution and white solid. Sharp signals appear in the \(^1H\) and \(^{31}P\) NMR spectra that were attributed to \((tBuP^2Hp)MoBr_2\). The presence of the intact P-H bond is proposed due to the downfield \(^1H\) signal with a very large \(^1J_{PH}\) coupling (12.22 ppm, d, 333.51 Hz, P-H). The signals attributable to the t-butyl groups are also present as doublets (1.17 ppm, d, 13.24 Hz, tBu) and (0.73 ppm, d, 12.68 Hz, tBu).

Scheme 6.7. Synthesis of \((tBuP^2Hp)MoBr_2\)

![Scheme 6.7. Synthesis of \((tBuP^2Hp)MoBr_2\)](image)
A crystal suitable for X-Ray Diffraction was grown by vapor diffusion of pentane into a saturated toluene solution (Figure 6.5). In the solid state structure the \((\text{tBuPP})\) ligand has adopted a facial coordination with the central phosphorus occupying one axial site and the two phosphorus arms in two equatorial sites. This is consistent with the lack of virtual coupling observed in the t-butyl signals in the \(^1\text{H}\) NMR spectrum. It should be noted that \((\text{tBuPP})\text{MoBr}_2\) is not the species we observe for the reactions of \((\text{tBuPP})\text{MoBr}_3\) with base. \((\text{tBuPP})\text{MoBr}_2\) exhibits \(^{31}\text{P}\) NMR signals that do not match the diamagnetic product of dehydrohalogenation.

**Figure 6.5.** Molecular structure of \((\text{tBuPP})\text{MoBr}_2\) determined by single-crystal XRD. H atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability.

In order to generate the 4-coordinate fragment that we propose precedes nitrogen cleavage, \((\text{tBuPP})\text{MoBr}_2\) was generated in situ and treated with potassium tert-butoxide. Vigorous agitation caused the red solution to turn a dark brown. This color change was accompanied by the appearance the diamagnetic signals observed in the base
reaction of \((t^\text{Bu}^\text{H}^\text{PP})\text{MoBr}_3\). This reaction was repeated under both argon and nitrogen atmospheres to the same result. The signals correlating to this species degraded over time under both atmospheres (Scheme 6.8).

Scheme 6.8. Synthesis of proposed \((t^\text{Bu}^\text{PPP})\text{MoBr}\)

Further structural characterization was not obtained. Formation of this common species as both a minor product in the deprotonation of \((t^\text{Bu}^\text{H}^\text{PP})\text{MoBr}_3\) and as a major project in the deprotonation of the already reduced \((t^\text{Bu}^\text{H}^\text{PP})\text{MoBr}_2\) supports the disproportionation hypothesis. Further work on the characterization of the proposed \((t^\text{Bu}^\text{PPP})\text{Mo}\) nitride complex needs to be performed.

Conclusion

In conclusion, we have presented the synthesis of two novel precatalysts for the reduction of nitrogen to ammonia. These complexes were synthesized in order to meet two of the challenges still being faced by homogenous catalytic nitrogen reduction: mitigated the use of chemical reductants by developing an electrode mountable catalyst and appending an amino group in the hope of developing an anionic back bone capable of increasing water solubility.
In addition to this, we have also synthesized a triphosphorus molybdenum catalyst to explore the possibility of phosphorus MLC in nitrogen reduction. While we did not isolate, definitively, the products of nitrogen cleavage, we were able to determine that they might proceed through a 1 electron, 1 equivalent of base pathway.

Supporting Information
Chapter 6 References