University of Cincinnati

Date: 5/15/2015

I, Anubendu Adhikary, hereby submit this original work as part of the requirements for the degree of Doctor of Philosophy in Chemistry.

It is entitled: Synthesis and Catalytic Applications of Nickel and Palladium Pincer Complexes

Student's name: Anubendu Adhikary

This work and its defense approved by:

Committee chair: Hairong Guan, Ph.D.

Committee member: Michael Baldwin, Ph.D.

Committee member: James Mack, Ph.D.

Committee member: David Smithrud, Ph.D.
Synthesis and Catalytic Applications of Nickel and Palladium Pincer Complexes

A Dissertation Submitted to the Graduate School of the University of Cincinnati in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy (Ph.D.)

In the Department of Chemistry of McMicken College of Arts and Sciences

Anubendu Adhikary

Master of Science (M.Sc.), Chemistry Indian Institute of Technology, Kharagpur, India, 2009

Bachelor of Science (B.Sc.), Chemistry Ramakrishna Mission Residential College Calcutta University, India, 2007

Dissertation Advisor: Hairong Guan, Ph.D.
Synthesis and Catalytic Applications of Nickel and Palladium Pincer Complexes

ABSTRACT

This dissertation focuses on the synthesis of nickel and palladium pincer complexes supported by a bis(phosphinite) ligand (also known as a POCOP-pincer ligand), and the study of their reactivity towards fundamentally important organometallic reactions as well as catalytic organic transformations. More specifically, efforts were made to characterize complexes bearing a hydride or formate as the ancillary ligand, and to investigate their properties in alkyne reduction, carbon dioxide hydroboration, and decarboxylation reactions.

Reactions between (POCOP)Pd-H and phenylacetylene result in palladium alkynyl complex, palladium alkenyl complex and dihydrogen along with substoichiometric amount of styrene. Based on the experimental results, a method for catalytic hydrogenation of alkynes has been developed using different palladium pincer complexes as catalyst precursors. The process has been found to be catalyzed by palladium particles, which are being produced from the POCOP-pincer complexes in the presence of dihydrogen.

Carbon dioxide rapidly inserts into Pd-H at room temperature and produces palladium formate complexes. Reaction of these formate complexes with a stoichiometric amount of catechol borane results in the formation of palladium hydrides, palladium bis(catecholato)borate complexes, and some unknown palladium species. It has been found that the reactions between palladium hydrides and catechol borane produce similar unknown palladium species and the palladium bis(catecholato)borate
complexes. In a comparative study between nickel and palladium hydrides for the catalytic CO$_2$ hydroboration, nickel is found to be more efficient than palladium.

An equimolar mixture of *racemic* and *meso* isomers of $P$-stereogenic nickel POCOP-pincer chloride complexes is synthesized, and from the mixture a successful separation of the *racemic* isomer is accomplished through repeated recrystallization. In a substitution reaction of these chloride isomers with potassium *tert*-butoxide, it is found that the *meso* isomer reacts faster than the *racemic* isomer. Similarly, for the formate complexes, the *meso* isomer undergoes faster decarboxylation than the *racemic* isomer.

A kinetic study of the decarboxylation from POCOP-igated nickel and palladium formate complexes has been carried out using carbon disulfide to trap the hydride intermediates. At a higher concentration of CS$_2$, the rates of the reactions have been found to follow a first order kinetics with respect to the formate complexes. Compared to the nickel complexes a faster rate in decarboxylation from the palladium complexes has been observed. The rates of these reactions have also been found to be dependent on the steric nature of $P$-substituents.
Preface

Parts of this thesis have been adapted from articles co-written by the author. The following articles were reproduced in part with permission from the American Chemical Society and the Royal Society of Chemistry.


ACKNOWLEDGEMENTS

I would like to express my deepest appreciation to my advisor Professor Hairong Guan. Hairong, what he prefers to be called, has been an amazing friend and an excellent mentor to me. In these past five and half years, he taught me not only chemistry but also how to be an organized person, how to be an independent researcher, and how to be a good leader. His work ethics, critical thinking in research, and teaching style have constantly inspired me. Without his guidance, advices, suggestions and enormous help this dissertation would not have been possible. In short, Hairong, you are a great advisor.

Special thanks to Dr. Jeanette A. Krause for all her help in solving X-ray structures of my newborn complexes, and teaching me crystallography. She has been one of my best friends I made during my graduate study.

I would like to thank my committee members Professor James Mack, Professor David Smithrud, and Professor Michael Baldwin for their helpful suggestions and comments in my research. I thoroughly enjoyed all the philosophical discussion with Dr. James Mack. I would like to thank Professor Anna Gudmundsdottir for her advices and helps. In addition, I would like to express my thanks to staff scientists Dr. Larry Sallans and Dr. Stephen Macha for solving my mass spectrometry problems, and Dr. Keyang Ding for the help and suggestions in performing NMR spectroscopy experiments.

It is my privilege to be a part of such a wonderful research group, the Guan Group. I learned a lot from my ex-lab mates Dr. Jie Zhang, Dr. Sumit Chakraborty, Dr. Sanjeewa Rodrigo, and Dr. Papri Bhattacharya. I enjoyed working with my current group members Arundhoti Chakraborty, Gleason Wilson, Nadeesha Wellala, Yigze Li, Aaron Bailey, Nathan Eberhardt, Huiguang Dai, Becca Haley, and Becca Ransohoff.
Their friendship was precious. I appreciate all their help, and wish them all the best for their future.

I want to thank all my undergraduate students Jason Schwartz, Kendra Leahy, Andrew Hanson, Lev Lezinsky, and Joel Collett for their willingness to work with me and their dedication in research. Also, I would like to thank summer rotation graduate student Jessie Ringo for her interest to work with me. I wish them all the best for their future.

Finally, I would like to thank my family and friends who continuously helped and supported me to reach this goal. I am grateful to my parents for all the sacrifices they made on my behalf.
# Synthesis and Catalytic Applications of Nickel and Palladium Pincer Complexes

## TABLE OF CONTENTS

### Chapter 1: Introduction

1.1 Importance of Bis(phosphinite)-Ligated Pincer Complexes  
1.2 Catalytic Reactions with Palladium POCOP-Pincer Complexes  
1.3 Chiral POCOP-Pincer Complexes  
1.4 Goals of the Research Projects  

### Chapter 2: Palladium POCOP-Pincer Hydride Complexes: Synthesis and Reactivity with Alkynes

2.1 Introduction  
2.2 Synthesis of Palladium POCOP-Pincer Hydrides  
2.3 Reactions of Palladium Hydrides with Phenylacetylene  
2.4 Mechanism for the Conversion of Phenylacetylene to Styrene  
2.5 Catalytic Hydrogenation of Alkynes  
2.6 Mechanism for Catalytic Hydrogenation of Alkynes  
2.7 Investigations of Ligand-Exchange Reactions with Phenylacetylene  
2.8 Reactions of Palladium Hydrides with Internal Alkynes  
2.9 Conclusions  
2.10 Experimental Section  

### Chapter 3: Nickel and Palladium POCOP-Pincer Hydride Complexes as Catalysts for the Hydroboration of CO₂ and Methyl Formate

3.1 Introduction  
3.2 Insertion of CO₂ into Palladium Hydrides  
3.3 Reduction of Palladium Formate Complexes with HBcat  
3.4 Reactions of Palladium Hydrides with HBcat  

viii
Synthesis and Catalytic Applications of Nickel and Palladium Pincer Complexes

LIST OF FIGURES

Chapter 1: Introduction

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pincer Complexes</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>POCOP-Pincer Complexes and their Applications</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>Palladium POCOP-Pincer Catalysts for Cross-Coupling Reactions</td>
<td>7</td>
</tr>
</tbody>
</table>

Chapter 2: Palladium POCOP-Pincer Hydride Complexes: Synthesis and Reactivity with Alkynes

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>X-ray Crystal Structure of [2,6-((\text{Bu}_3\text{PO})_2\text{C}_6\text{H}_3)]\text{PdCl}</td>
<td>17</td>
</tr>
<tr>
<td>2</td>
<td>X-ray Crystal Structure of [2,6-((\text{Pe}_3\text{PO})_2\text{C}_6\text{H}_3)]\text{PdCl}</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>X-ray Crystal Structure of [2,6-((\text{Bu}_3\text{PO})_2\text{C}_6\text{H}_3)]\text{PdH}</td>
<td>19</td>
</tr>
<tr>
<td>4</td>
<td>X-ray Crystal Structure of [2,6-((\text{Pe}_3\text{PO})_2\text{C}_6\text{H}_3)]\text{PdH}</td>
<td>22</td>
</tr>
<tr>
<td>5</td>
<td>X-ray Crystal Structure of (E)-[2,6-((\text{Pr}_2\text{PO})_2\text{C}_6\text{H}_3)]\text{PdCH=CHPh}</td>
<td>25</td>
</tr>
<tr>
<td>6</td>
<td>X-ray Crystal Structure of [2,6-((\text{Pr}_2\text{PO})_2\text{C}_6\text{H}_3)]\text{PdCH}_3</td>
<td>30</td>
</tr>
<tr>
<td>7</td>
<td>X-ray Crystal Structure of [2,6-((\text{Pr}_2\text{PO})_2\text{C}_6\text{H}_3)]\text{PdC}_6\text{H}_5</td>
<td>40</td>
</tr>
<tr>
<td>8</td>
<td>X-ray Crystal Structure of (E)-[2,6-((\text{Bu}_3\text{PO})_2\text{C}_6\text{H}_3)]\text{PdC}(\text{CO}_2\text{Et})\text{CH}(\text{CO}_2\text{Et})</td>
<td>43</td>
</tr>
</tbody>
</table>

Chapter 3: Nickel and Palladium POCOP-Pincer Hydride Complexes as Catalysts for the Hydroboration of CO\textsubscript{2} and Methyl Formate

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>X-ray Crystal Structure of [2,6-((\text{Bu}_3\text{PO})_2\text{C}_6\text{H}_3)]\text{PdOCHO}</td>
<td>68</td>
</tr>
<tr>
<td>2</td>
<td>X-ray Crystal Structure of [2,6-((\text{Pr}_2\text{PO})_2\text{C}_6\text{H}_3)]\text{PdOCHO}</td>
<td>68</td>
</tr>
<tr>
<td>3</td>
<td>Orientations of the Formato Group in Nickel POCOP-Pincer Complexes</td>
<td>69</td>
</tr>
<tr>
<td>4</td>
<td>X-ray Crystal Structure of {[2,6-((\text{Pr}_2\text{PO})_2\text{C}_6\text{H}_3)]\text{Pd(Pr}_2\text{PH})}^-\text{[OTf]}^-</td>
<td>72</td>
</tr>
<tr>
<td>5</td>
<td>X-ray Crystal Structure of [2,6-((\text{Bu}_2\text{PO})_2\text{C}_6\text{H}_3)]\text{Pd(Bcat}_2\text{)}</td>
<td>74</td>
</tr>
<tr>
<td>6</td>
<td>X-ray Crystal Structure of [2,6-((\text{Pr}_2\text{PO})_2\text{C}_6\text{H}_3)]\text{Pd(Bcat}_2\text{)}</td>
<td>78</td>
</tr>
</tbody>
</table>
LIST OF TABLES

Chapter 2: Palladium POCOP-Pincer Hydride Complexes: Synthesis and Reactivity with Alkynes

Table 1 Palladium-Catalyzed Hydrogenation of Phenylacetylene 29
Table 2 Palladium-Catalyzed Hydrogenation of Diphenylacetylene 31
Table 3 Reactions of Palladium Pincer Complexes with Phenylacetylene 38

Chapter 3: Nickel and Palladium POCOP-Pincer Hydride Complexes as Catalysts for the Hydroboration of CO₂ and Methyl Formate

Table 1 Catalytic Reduction of CO₂ with HBcat 82
Table 2 Hydrogenation of Methyl Formate Facilitated by Nickel Complexes 84
Table 3 Nickel-Catalyzed Hydroboration of Methyl Formate 84

Chapter 5: Kinetic Study of Decarboxylation of Bis(phosphinite)-Ligated Nickel and Palladium Pincer Formate Complexes

Table 1 Kinetic Data for the Reaction of [2,6-(tBu₂PO)₂C₆H₃]NiOCHO with CS₂ at 30 °C 125
Table 2 Kinetic Data for the Reaction of [2,6-(tBu₂PO)₂C₆H₃]NiOCHO with CS₂ at 30-45 °C 127
Table 3 Kinetic Data for the Reaction of [2,6-(R₂PO)₂C₆H₃]NiOCHO with CS₂ at 30-45 °C 129
Table 4 Calculated Activation Parameters for the Decarboxylation of [2,6-(R₂PO)₂C₆H₃]NiOCHO 129
Table 5 Kinetic Data for the Reaction of [2,6-(R₂PO)₂C₆H₃]PdOCHO with CS₂ at 25-40 °C 131
Table 6 Calculated Activation Parameters for Decarboxylation of [2,6-(R₂PO)₂C₆H₃]PdOCHO 131
Table 7 Kinetic Data for the Reaction of [2,6-(tPr₂PO)₂C₆H₃]NiOCHO with CS₂ at 30-45 °C 137
Table 8  Kinetic Data for the Reaction of $[2,6-(\text{tBu}_2\text{PO})_2\text{C}_6\text{H}_3]\text{PdOCHO}$ with CS$_2$
at 25-40 °C

Table 9  Kinetic Data for the Reaction of $[2,6-(\text{iPr}_2\text{PO})_2\text{C}_6\text{H}_3]\text{PdOCHO}$ with CS$_2$ at 25-40 °C
Chapter 1

Introduction
1.1 Importance of Bis(phosphinite)-Ligated Pincer Complexes

Since the first pincer complex was reported by Multon and Shaw in 1976,\(^1\) numerous transition metal pincer complexes have been isolated and their properties have been extensively studied.\(^2\) The vast majority of the applications of this type of complexes are in the area of catalysis.\(^2,3\) Due to the presence of two metallacycles in these metal-ligand systems, pincer complexes have shown an unique balance of stability and reactivity, making them very attractive catalysts (Figure 1a). Among many different types of pincer systems, bis(phosphinite)-ligated pincer complexes, also known as POCOP-pincer complexes (Figure 1b),\(^4\) are of high interest to our group not only due to their remarkable chemical properties, but also because of their straightforward synthetic procedures.

\[\text{M} = \text{transition metal} \quad \text{D} = \text{donor atom} \quad \text{E} = \text{center donor atom} \quad \text{R} = \text{alkyl, aryl groups} \]

\[\text{POCOP} - \text{pincer complexes} \]

---

4 Aliphatic analogs of POCOP-pincer complexes, POC\textsubscript{sp3}OP, are relatively less stable than POCOP-pincer complexes. For references, see: (a) Pandarus, V. M.Sc. Dissertation, Université de Montréal. (b) Pandarus, V.; Zargarian, D. Chem. Commun. 2007, 978. (c) Pandarus, V.; Zargarian, D. Organometallics 2007, 26, 4321.
POCOP-pincer ligands can be readily synthesized from resorcinol and chlorophosphines in the presence of a base. Subsequent cyclometallation can be achieved using commercially available metal precursors, resulting in the desired pincer complexes.\(^5\) In some cases, the pincer complexes could be prepared by mixing the reagents (resorcinol, chlorophosphine, base, and the metal precursor) all together in one pot.\(^6\) In the past decade, POCOP-pincer complexes of various transition metals such as Ir,\(^7\) Rh,\(^8\) Ru,\(^9\) Pt,\(^10\) Ni,\(^11\) and Fe\(^12\) have been synthesized and their catalytic applications have been explored. Some of the reported POCOP-pincer complexes and their catalytic applications are shown in Figure 2.

---

From the reactivity point of view, advantages of using POCOP-pincer complexes for catalysis are: (a) the group trans to the pincer center donor becomes labile due to the strong trans-directing effect of the carbon donor, and (b) various functional groups could be placed on the P-donors and the aromatic ring through the use of different chlorophosphines and resorcinol derivatives, which allow for tuning the electronic and steric properties of the complexes. Although bis(phosphinite)-based pincer ligands have...
been incorporated into many metal systems (Figure 2), in terms of catalytic applications, palladium POCOP-pincer complexes are relatively less explored. This is in contrast to the rich chemistry of palladium complexes established in catalytic transformations\textsuperscript{13} such as cross-coupling reactions and hydrogenations of olefins. As such, investigation of chemical properties and particularly the catalytic applications of POCOP-ligated palladium complexes will be highly valuable. The study could potentially improve existing catalytic systems, and lead to discovery of new reactions.

1.2 Catalytic Reactions with Palladium POCOP-Pincer Complexes

The first bis(phosphinite)-ligated palladium complex was synthesized by both the Jensen group\textsuperscript{14} and the Bedford group\textsuperscript{15} through complexation of the isolated pincer ligand with Pd(COD)Cl\textsubscript{2} and Pd(OCOCF\textsubscript{3})\textsubscript{2}, respectively (Scheme 1). Later on, Uzomi and co-workers synthesized a series of palladium POCOP-pincer iodide complexes via a route involving late-stage phosphorylation (Scheme 1).\textsuperscript{16} In 2007, Song and co-workers reported an one-pot synthetic procedure for these complexes starting from resorcinol, chlorophosphine and PdCl\textsubscript{2}.\textsuperscript{17b} However, this one-pot procedure did not work in the case of complexes having bulky P-substituents such as tert-butyl groups.\textsuperscript{17}

\textsuperscript{17} Polukeev, A. V.; Kuikin, S. A.; Petrovskii, P. V.; Peregudova, S. M.; Smol’yakov, A. F.; Dolgushin, F. M.; Koridze, A. A. Dalton Trans. 2011, 40, 7201.
Many of the reported POCOP-palladium complexes, which are air and moisture stable, have been found to be excellent catalysts in various cross-coupling reactions (Figure 3). In addition, ester-substituted palladium POCOP-pincer complexes have been reported by Domínguez and co-workers as highly active catalysts for the α-arylation of ketones (eq 1).

---

Szabó and co-workers discovered another important catalytic application of palladium POCOP-pincer complex namely the allylation of aldehydes and imines (eq 2).\(^{20}\) In the proposed catalytic cycle for this transformation (Scheme 3), the nucleophilic attack of the allyl unit to the aldehyde or imine was found to be the most important step. The enhanced nucleophilicity of the allyl group induced by the strongly \textit{trans}-influencing carbon donor was demonstrated as the key to the success of these reactions.

Palladium hydrides have been proposed as key intermediates in many organic transformations catalyzed by palladium complexes.\(^{21}\) Study of the reactivity of palladium hydride complexes is therefore critical to the development of new catalytic reactions and

the improvement of existing reactions. However, due to the high reactivity of the palladium-hydrogen bond, isolation of palladium hydride complexes is always challenging. As pincer ligands are known to provide sufficient stability to the metal complexes, it is advantageous to synthesize POCOP-ligated palladium hydride complexes and informative to investigate their reactivity towards various nucleophilic reactions. Furthermore, our group has discovered that the bis(phosphinite)-ligated nickel pincer hydride complexes are efficient catalysts for hydrosilylation of aldehydes, hydroboration of CO$_2$, and dehydrogenation of amine-borane. Because palladium is in the same group (Group 10) of the periodic table as nickel, exploring the reactivity of analogous palladium hydride complexes would provide an excellent opportunity to compare the reactivity between nickel and palladium. Understanding the effects of metals on fundamentally important organometallic reactions will provide valuable guidelines for the rational design of catalysts that can ultimately replace precious metals with the earth-abundant ones.

### 1.3 Chiral POCOP-Pincer Complexes

Pincer complexes have also shown promising results in the area of asymmetric catalysis. However, so far no asymmetric POCOP-pincer complex has been reported in the literature. On the other hand, there are several chiral *phosphinites* ligands that have...
been used in metal-catalyzed stereoselective reactions such as asymmetric hydrogenation of olefins\(^\text{24}\) and ketones,\(^\text{25}\) and asymmetric hydroformylation reactions.\(^\text{26}\) Therefore, metal complexes ligated with \(P\)-stereogenic bis(phosphinite) ligands could be useful catalysts for enantioselective organic transformations.

### 1.4 Goals of the Research Projects

My research projects have been focused on the synthesis of bis(phosphinite)-ligated palladium pincer complexes and the investigation of their reactivity. Emphasis has also been placed on comparing the reactivity of these complexes with the analogous nickel POCOP-pincer complexes. The third goal of my research is to synthesize \(P\)-stereogenic nickel POCOP-pincer complexes as an entry to asymmetric catalysis as well as a means to probe transition states.


Chapter 2

Palladium POCOP-Pincer Hydride Complexes: Synthesis and Reactivity with Alkynes
2.1 Introduction

The reaction of an alkyne with a transition metal hydride is fundamentally important due to its involvement in the catalytic cycles for reduction (e.g., hydrogenation, hydroboration and hydrosilylation) and oligomerization of alkynes. The most common outcome of the reaction is cis-addition of M–H across the C=C bond, although in some cases the trans-addition product has been obtained through either direct insertion or isomerization of the kinetically formed cis-addition product. The interaction between specifically a terminal alkyne and a transition metal hydride is often more complicated and less predictable (Scheme 1). In addition to an (E)-, (Z)-, or α-substituted-alkenyl complex stemmed from cis-1,2-, trans-1,2-, or 2,1-insertion, an alkylidyne complex may be produced via the rearrangement of an η2-alkenyl intermediate. Moreover, facile alkyne-to-vinylidene isomerization makes it possible to incorporate 2

---

equiv of alkyne for the synthesis of a butadienyl complex.\textsuperscript{7} The formation of a $\sigma$-alkynyl complex has also been reported.\textsuperscript{8}

From the hydrogenation point of view, generating a $\sigma$-alkynyl complex from a terminal alkyne and a hydride appears to be the least productive pathway as far as formal oxidation states of the alkyne carbons are concerned. It is, however, not completely irrelevant within the broader context of alkyne reduction. Bianchini and co-workers have shown that $\sigma$-alkynyl complexes are the major organometallic species during a series of reactions between tripodal-ligated Rh(I) hydride complexes and 1-alkynes.\textsuperscript{8a} The organic products of these reactions are mainly consisted of oligomers of alkynes along with some 1-alkenes. Mechanistic analysis has suggested that alkenes are originated from alkyne


insertion followed by the cleavage of the Rh–C(sp²) bond with another alkyne molecule (Scheme 2, pathway A). The net reaction for rhodium hydride complexes is the conversion to σ-alkynyl complexes. A second path to such species involves the loss of H₂ without using alkyne as a sacrificial hydrogen acceptor (pathway B). It should be mentioned that in this study H₂ has been found from the headspace of the reaction mixtures. Several other reports on metal hydrides have proposed pathway A as the single route to σ-alkynyl complexes, all based on a stoichiometric amount of alkene produced as the by-product. Kirchner et al. have suggested a similar process (pathway A) from HC≡CR and MH to σ-alkynyl complexes, which are catalytically active species for dimerization of the alkynes. A study of particular interest to us is that by Johansson and Wendt, which has proposed both pathway A and pathway B being operative for the reaction between a palladium PCP-pincer hydride complex and phenylacetylene (Scheme 3). Although H₂ was not detected by ¹H NMR spectroscopy, likely due to its minute amount in solution, the substoichiometric amount of styrene (0.7 equiv) made during the reaction is

\[ \text{Scheme 2} \]

A study of particular interest to us is that by Johansson and Wendt, which has proposed both pathway A and pathway B being operative for the reaction between a palladium PCP-pincer hydride complex and phenylacetylene (Scheme 3). Although H₂ was not detected by ¹H NMR spectroscopy, likely due to its minute amount in solution, the substoichiometric amount of styrene (0.7 equiv) made during the reaction is

\[ \text{Scheme 3} \]

consistent with the dual process. Unlike the rhodium system described above, the alkenyl complex is not an observable intermediate, suggesting that C–H bond exchange between the alkenyl complex and phenylacetylene is much faster than the insertion step.

Our group has been interested in the chemistry of Group 10 metal hydride complexes bearing bis(phosphinite)-based POCOP-pincer ligands. One of our recent studies has demonstrated that steric and electronic differences between PCP- and POCOP-pincer systems have a profound influence on the reactivity of the hydride moiety. This has made us wonder how different it could be for palladium POCOP-pincer hydride complexes to react with terminal alkynes, and if a well-defined catalytic system could be developed for the hydrogenation of alkynes. In this chapter, I will show that indeed palladium POCOP-pincer hydride complexes behave differently from their PCP analogues when mixed with terminal alkynes. Our study suggests that alkene formation is not a consequence of pathway A, but rather a result of direct hydrogenation.

---

of alkynes by palladium particles that are released from the pincer complexes. We have also studied hydrogenation of alkynes catalyzed by related palladium POCOP-pincer complexes.

2.2 Synthesis of Palladium POCOP-Pincer Hydrides

Although palladium POCOP-pincer complexes have been known for more than a decade now,\(^\text{11}\) their hydride derivatives have never been reported prior to our work. One of the most widely used methods to synthesize compounds of this type is to treat palladium chloride complexes with an appropriate hydride donor such as NaBH\(_4\),\(^\text{12}\) LiAlH\(_4\),\(^\text{13}\) LiEt\(_3\)BH,\(^\text{14}\) or NaH.\(^\text{15}\) Our initial efforts were thus focused on preparing a series of palladium POCOP-pincer chloride complexes as the precursors to the targeted hydride complexes. The \(P\)-substituents of the POCOP-pincer ligand were varied in order to investigate how ligand modification can tune the reactivity at the palladium center.

Complex \(1\text{a}\), which contains a relatively bulky POCOP-pincer ligand, has been previously prepared in 31\% isolated yield via cyclometalation of 1,3-bis(di-\text{\textit{tert}}-butylphophinito)benzene\(^\text{16}\) with Pd(PhCN)\(_2\)Cl\(_2\) in refluxing 2-methoxyethanol.\(^\text{17}\) In our hands a much higher yield was obtained when PdCl\(_2\) was used as the source of palladium and THF was employed as the solvent (eq 1). NMR data of \(1\text{a}\) are consistent with


literature values, and structure of the molecule was further confirmed by X-ray crystallography (Figure 1).

![Molecular structure](image)

**Figure 1.** ORTEP drawing of \([2,6-(t\text{Bu}_2\text{PO})_2\text{C}_6\text{H}_3]\text{PdCl} \ (\text{1a})\) at the 50% probability level. Selected bond lengths (Å) and angles (deg): Pd–Cl(1) 2.3813(8), Pd–C(1) 2.011(3), Pd–P(1) 2.2926(7), Pd–P(2) 2.2954(7), P(1)–Pd–P(2) 160.12(3), C(1)–Pd–Cl(1) 179.55(8).

With a less crowded POCOP-pincer ligand, palladium chloride complexes were more conveniently prepared in a one-pot synthesis without isolating the bis(phosphinite) ligand first (eq 2). Such a strategy has been previously utilized by Song and co-workers\(^\text{18}\) for the synthesis of \([2,6-(\text{Ph}_2\text{PO})_2\text{C}_6\text{H}_3]\text{PdCl} \ (\text{1d})\) and \([2,6-(\text{Cy}_2\text{PO})_2\text{C}_6\text{H}_3]\text{PdCl}\). The new complex \(\text{1c} \ (\text{cPe} = \text{cyclopentyl})\) was characterized by NMR spectroscopy, elemental analysis and X-ray crystallography (Figure 2). The Pd–P and Pd–C\(_{\text{ipso}}\) bonds of \(\text{1c}\) were

---

found to be similar to those of 1b, but slightly shorter (by 0.02 Å) than those of 1a possibly due to reduced steric congestion around the palladium center.

\[
\text{Figure 2. ORTEP drawing of } [2,6-(\text{cPe}_2\text{PO})_2\text{C}_6\text{H}_3]\text{PdCl (1c) at the 50\% probability level. Selected bond lengths (Å) and angles (deg): Pd–Cl(1) 2.3763(9), Pd–C(1) 1.988(4), Pd–P(1) and Pd–P(1A) 2.2748(8), P(1)–Pd–P(1A) 160.38(4), C(1)–Pd–Cl(1) 180.0.}
\]

The synthesis of palladium hydride complexes turned out to be nontrivial. Our previously developed procedures\textsuperscript{10a,c} using LiAlH\textsubscript{4} to convert nickel POCOP-pincer chloride complexes to the corresponding hydrides could be extended the palladium system, but only for the \textsuperscript{1}Bu-substituted POCOP-pincer complex. Thus, palladium hydride 2a was readily isolated as a white solid in good yield after stirring the mixture of 1a and LiAlH\textsubscript{4} in toluene for 48 h (eq 3). The \textsuperscript{1}H NMR spectrum of 2a in C\textsubscript{6}D\textsubscript{6} showed a characteristic hydride resonance as a triplet at –2.48 ppm (\textit{J}_{\text{P–H}} = 16.0 \text{ Hz}). The IR
spectrum of 2a revealed a strong band at 1756 cm$^{-1}$, which is expected for the Pd–H stretch.$^{12a,19}$ The hydride ligand in 2a was also located by X-ray diffraction of its single crystals (Figure 3). The Pd–C$_{ipso}$ bond distance is elongated by 0.02 Å upon conversion from 1a to 2a, which reflects a stronger trans-influence from the hydride. Another noticeable difference between the two complexes is that the Pd–P bonds in 2a are shorter by 0.03 Å, suggesting some degree of flexibility for the pincer backbone.

![Figure 3](image)

**Figure 3.** ORTEP drawing of [2,6-(tBu$_2$PO)$_2$C$_6$H$_3$]PdH (2a) at the 50% probability level. Selected bond lengths (Å) and angles (deg): Pd–H 1.75(3), Pd–C(1) 2.036(2), Pd–P(1) 2.2634(6), Pd–P(2) 2.2627(6), P(1)–Pd–P(2) 159.93(2).

Replacing the tBu groups on the phosphorus donors with smaller groups created some synthetic challenge. Under the same conditions used for the synthesis of 2a, the mixture of 1c and LiAlH$_4$ in toluene turned black within a few hours, a phenomenon that was absent for the reaction of 1a. Standard work-up procedures (filtration followed by

---

solvent evaporation) led to the isolation of a colorless oil. Surprisingly, $^1$H NMR spectrum of this material (in C$_6$D$_6$) showed no resonance that could be assigned to the hydride species. The most notable resonance was a doublet of triplet at 3.30 ppm with coupling constants of 192.0 and 8.0 Hz. $^{31}$P{$^1$H} NMR spectrum of the same material displayed only one resonance at –35.7 ppm. These data are consistent with the formation of (6Pe)$_2$PH, which is likely to be released from degradation of the pincer complex. A similar decomposition pathway involving the cleavage of the pincer P–O bonds has been observed by the Milstein group and us in ruthenium$^{20}$ and nickel$^{10d, 21}$ systems, respectively. The success of synthesizing 2a can thus be explained by well-shielded P–O bonds in 1a that prevent the breakdown of the pincer framework. Reactions of 1b and 1d with LiAlH$_4$ exhibited a similar decomposition process as seen in the case of 1c.

Attempts to synthesize hydrides from 1b-d using other hydride donors such as NaBH$_4$ and NaH also failed. In each case, a complicated mixture of multiple palladium species was obtained, as judged by $^{31}$P{$^1$H} NMR spectroscopy. Somewhat promising results came from the reactions of 1b and 1c with LiBEt$_3$H. Hydride species along with some impurities were identified from the isolated products. After extensive optimization, hydrides 2b and 2c could be isolated in an analytically pure form as long as the reaction and the work-up procedures were performed at low temperatures. The reaction with LiBEt$_3$H must be carried out at –78°C for no more than 1 h (eq 4), and solvent evaporation as well as recrystallization process should be kept below 0°C. However, once isolated as pure compounds, 2b and 2c are thermally stable at room temperature. Boron-containing byproduct (BEt$_3$) or a small amount of unreacted LiBEt$_3$H may

---

facilitate the decomposition of the hydrides at ambient temperature. In \(^1\)H NMR spectra, the hydride resonances of 2b and 2c appeared as triplets at -2.40 ppm (J\(_{P-H}\) = 20.8 Hz) and -2.37 ppm (J\(_{P-H}\) = 20.0 Hz), respectively. A strong IR band in the 1700-1800 cm\(^{-1}\) region (2b: 1765 cm\(^{-1}\); 2c: 1755 cm\(^{-1}\)) further supported the presence of a Pd–H bond. The structure of 2c was also established by X-ray crystallography (Figure 4).\(^{22}\) Compared to 1c, the Pd–C\(_{ipso}\) bond distance of 2c is 0.04 Å longer while the Pd–P bond distances are 0.02 Å longer. Unfortunately, the reaction of 1d with LiBe\(_3\)H gave intractable products even at low temperatures. We\(^{10a}\) and others\(^{23}\) have experienced similar difficulty in preparing Group 10 metal hydride complexes with PPh\(_2\)-containing pincer ligands.

\[ \text{O} \quad \text{PR}_2 \quad \text{Pd} \quad \text{Cl} \quad \text{THF, -78°C, 1 h} \quad \text{LiBe\(_3\)H} \quad \text{O} \quad \text{PR}_2 \quad \text{Pd} \quad \text{H} \quad \text{(eq 4)} \]

\[ 1\text{b} (R = \text{iPr}) \quad 1\text{c} (R = \text{cPe}) \quad 2\text{b} (R = \text{iPr, 42%}) \quad 2\text{c} (R = \text{cPe, 44%}) \]

### 2.3 Reactions of 2a-c with Phenylacetylene

A solution of 2a in C\(_6\)D\(_6\) was treated with an equimolecular amount of *freshly distilled* phenylacetylene, and the reaction was monitored by \(^1\)H and \(^{31}\)P\{\(^1\)H\} NMR spectroscopy. At room temperature, 2a disappeared very slowly, requiring as long as 9 days to be fully converted to phenylacetylide complex 3a (eq 5). H\(_2\) (singlet at 4.47 ppm)

---

22 Two of the cyclopentyl rings show some disorder. A multi-component disorder model is presented.

and a small amount of styrene were also observed by $^1$H NMR. For reasons unknown to us, this reaction was complete within 24 h when the alkyne was not distilled.$^{24}$

Figure 4. ORTEP drawing of [2,6-(Pe$_2$PO)$_2$C$_6$H$_3$]PdH (2c) at the 50% probability level. Selected bond lengths (Å) and angles (deg): Pd–H 1.53(4), Pd–C(1) 2.031(3), Pd–P(1) 2.2518(8), Pd–P(2) 2.2525(9), P(1)–Pd–P(2) 160.25(3).

However, the purity of phenylacetylene appeared to have little effect on the composition of the products. At 50 °C, the reaction of 2a with HC≡CPh (distilled) afforded 3a in 65% yield after 24 h, while styrene was already formed in 10% yield. At that point, H$_2$ remained present in the solution, and some of the starting materials 2a and HC≡CPh were still left unreacted.

![Chemical Reaction Image](image)

$^{24}$ Phenylacetylene from commercial sources sometimes shows light yellow color, but freshly distilled one should be colorless.
The less bulky palladium hydrides 2b and 2c are significantly more reactive. Their reactions with phenylacetylene finished within 15 min, whether or not the alkyne was distilled. The main palladium-containing products were identified as phenylacetylide complexes 3b and 3c, and similar to the observation for 2a, only a negligible amount of styrene was found (eq 6). The anomaly was the reaction of 2b, which gave rise to a second palladium pincer complex 4b with a phosphorus resonance at 187.2 ppm. $^1$H NMR spectrum revealed a broad doublet at 8.20 ppm, and the relatively large coupling constant of 20.0 Hz suggested that 4b could be an (E)-alkenyl complex. The reaction of 2c also generated a second palladium species as judged by $^{31}$P{$^1$H} NMR spectroscopy, although its quantity was too insignificant (~ 1%) to provide any useful structural information.

As further confirmation of the structures proposed in eqs 5 and 6, independent synthesis of 3a-c and 4b were pursued. The phenylacetylide complexes were readily prepared in good yield by mixing 1a-c with a large excess of lithium phenylacetylide (eq 7). Lowering the equivalents of LiC\equivCPh would result in partial conversion of the palladium chloride complexes, suggesting that this reaction might be reversible. Consistent with this hypothesis, mixing pure 3a-c with 1 equiv of LiCl in THF at room temperature for 48 h led to the formation of 1a-c in about 3% yield. Compounds 3a-c
were characterized by NMR and IR spectroscopy as well as elemental analysis. The C≡C stretching frequencies of these molecules (3a: 2100 cm⁻¹; 3b: 2085 cm⁻¹; 3c: 2095 cm⁻¹) are comparable to those reported in the literature for other phenylacetylide complexes.⁸c,²⁵

![Chemical structure](image)

Pure 4b was obtained from salt metathesis reaction of 1b with (E)-2-phenylethenyllithium (prepared in-situ from trans-β-iodostyrene and ⁹BuLi) as illustrated in eq 8. The ¹H and ³¹P{¹H} NMR spectra of 4b in C₆D₆ match well with what has been described for the second observable palladium species during the reaction between 2b and HC≡CPh (eq 6). The characteristic vinylic resonance at 8.20 ppm, however, appeared as a doublet of triplets (J = 20.0 and 4.0 Hz) instead of a broad doublet. The smaller coupling constant of 4.0 Hz, which is presumably due to phosphorus-hydrogen coupling, was somehow better resolved for the pure sample. The configuration of the C=C bond of this compound was unambiguously established by X-ray crystallographic study (Figure 5). Interestingly, the CH=CHPh moiety adopts a conformation that is perpendicular to the coordination plane with a dihedral angle of 89.9(2)° between the two phenyl rings. This is probably due to steric effects rather than driven by back-donation from

---

palladium d\textsubscript{xy} orbital to the \(\pi^*\) orbital of the alkenyl group; the C(27)–C(28) distance of 1.329(5) Å indicates no appreciable elongation from a normal C=C bond.

\[
\begin{align*}
\text{Figure 5.} & \quad \text{ORTEP drawing of } (E)\text{-}[2,6\text{-}(\text{iPr}_2\text{PO})\text{C}_6\text{H}_3]\text{PdCH=CHPh (4b)} \text{ at the 50\% probability level. Selected bond lengths (Å) and angles (deg): Pd–C(1) 2.031(3),} \\
& \quad \text{Pd–C(27) 2.066(3), Pd–P(1) and Pd–P(1A) 2.2549(6), C(27)–C(28) 1.329(5),} \\
& \quad \text{P(1)–Pd–P(1A) 159.45(3), C(1)–Pd–C(27) 179.84(12).}
\end{align*}
\]

2.4 Mechanism for the Conversion of Phenylacetylene to Styrene

The presence of both 3b and 4b in the reaction of 2b with phenylacetylene (eq 6) seem to support the dual mechanism described in Schemes 2 and 3. The fact that styrene was generated in small quantities could be explained by pathway A being the minor
process. Since 4b could be synthesized independently, investigating its reaction with HC≡CPh would give us a better picture about the overall process. It should be mentioned that well-defined reactions of this type are well known in the literature. The Bianchini group has demonstrated in rhodium\textsuperscript{8a} and cobalt\textsuperscript{8b} systems that alkenyl complexes undergo facile M–C(sp\textsuperscript{2}) bond cleavage by HC≡CCO\textsubscript{2}Et to generate alkynyl complexes while release alkenes. They have suggested a mechanism involving oxidative addition of the alkyne C–H bond followed by reductive elimination of the alkene products. Eisen and co-workers have reported similar C–H exchange reactions between alkenyl actinide complexes and HC≡CPr\textsubscript{2},\textsuperscript{26} and have proposed a σ-bond metathesis mechanism as anticipated for f-element complexes. In our case, mixing 4b with 1 equiv of HC≡CPh in C\textsubscript{6}D\textsubscript{6} at room temperature did not yield any styrene within 15 min. However, after 24 h, styrene was obtained in 10% yield along with the same amount of 3b. This result stands in strong contrast to the rapid C–H exchange process postulated for the PCP-pincer system (Scheme 3).\textsuperscript{8f} The reasons for the smaller amount of styrene produced in our POCOP-pincer system are therefore twofold: less favorable formation of the alkenyl species, and more sluggish C–H exchange between the alkenyl species and HC≡CPh. As expected, increasing the ratio of HC≡CPh to 2b from 1 : 1 to 2 : 1 while keeping [2b] same as in eq 6 gave almost the same product ratios for 3b, 4b and styrene after 15 min. Surprisingly, extending the reaction time to 24 h resulted in more styrene (31% yield with respect to 2b) without much expense of 4b. In another word, even if all 4b present in the solution were converted to 3b, it would not account for the amount of styrene generated. This also implies that styrene must be predominantly formed from a different pathway.

Perhaps, 4b acts as a catalyst for the hydrogenation of the excess HC≡CPh using H₂ produced during the reaction, and the hydride 2b is being regenerated. To test this hypothesis, a solution of 4b in C₆D₆ was treated with 1 atm of H₂ and the reaction was monitored by ¹H NMR spectroscopy. At room temperature after 12 h, only 7% of 4b was converted to 2b. If the palladium pincer hydride were a true active species, regenerating it from the hydrogenolysis of 4b would be too slow to be catalytically viable.

Since H₂ was observed during the reactions between the hydride complexes and phenylacetylene, hydrogenolysis of the palladium alkynyl complexes 3a-c could be another mechanism for styrene formation. A solution of 3b in C₆D₆ was then exposed to 1 atm of H₂ and well mixed at room temperature. After 24 h, no styrene was found, thereby ruling out such a mechanistic pathway. An alternative but remote possibility of converting 3b to styrene would be somehow through “borrowing” hydrogen from phenylacetylene. However, mixing complex 3b with 1 equiv of HC≡CPh at room temperature for 24 h did not yield any appreciable product. In contrast, carrying out a similar reaction under 1 atm of H₂ did generate styrene in 5% yield after 24 h. This result is more consistent with a mechanism in which styrene is produced by reduction of the alkyne with molecular hydrogen and this process is catalyzed by 3b. This hypothesis was further substantiated by the fact that ³¹P NMR did not show any new resonance throughout the reaction.

2.5 Catalytic Hydrogenation of Alkynes

Palladium alkynyl complexes 3a-c were then subjected to catalytic studies using phenylacetylene as the substrate and the reactions were conducted at room temperature
under 1 atm of H₂ pressure. As shown in eq 9 and Table 1, in the presence of 20 mol% 3a, after 24 h, only 6% of phenylacetylene was converted to styrene (entry 1). Under the same conditions using 3b as a catalyst (entry 2), a higher conversion of phenylacetylene was observed. The amount of styrene produced in this case (30% yield) is greater than 20%, confirming that this process is catalytic in palladium. Catalyst 3c is slightly less reactive than 3b, providing styrene in 23% yield after 24 h (entry 3).

To further facilitate the hydrogenation process, catalyst structure was modified through the replacement of the alkynyl group with a methyl group. It was hypothesized that the more σ-donating methyl group would promote dihydrogen activation at the palladium center. Palladium POCOP-pincer methyl complexes 5a-c were readily synthesized from the reaction of 1a-c with CH₃Li, and compound 5b was also crystallographically characterized (Figure 6). These methyl complexes indeed are catalytically more reactive than the alkynyl complexes. As shown in Table 1, when 5a was used as a catalyst (entry 4), after 12 h, 92% of phenylacetylene was converted to styrene while the rest of the alkyne substrate was fully reduced to ethylbenzene. By comparison, reactions catalyzed by 5b and 5c under otherwise the same conditions yielded ethylbenzene as the major product (entries 6 and 8). However, when the hydrogenation reactions were stopped at 2 h, styrene became the main hydrogenation product (entries 5 and 7). Another noticeable feature for the reactions catalyzed by 5b and 5c was that after 12 h, about 10% and 20% of palladium species turned into the alkynyl complexes 3b and 3c, respectively. This is due to C–H exchange reaction between the methyl complexes and HC=CPh.
Table 1. Palladium-Catalyzed Hydrogenation of Phenylacetylene$^a$

<table>
<thead>
<tr>
<th>entry</th>
<th>[Pd]</th>
<th>time (h)</th>
<th>PhCH=CH$_2$ (%)$^b$</th>
<th>PhCH$_2$CH$_3$ (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3a</td>
<td>24</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>3b</td>
<td>24</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>3c</td>
<td>24</td>
<td>23</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>5a</td>
<td>12</td>
<td>92</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>5b</td>
<td>2</td>
<td>53</td>
<td>31</td>
</tr>
<tr>
<td>6</td>
<td>5b</td>
<td>12</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>7</td>
<td>5c</td>
<td>2</td>
<td>11</td>
<td>4</td>
</tr>
<tr>
<td>8</td>
<td>5c</td>
<td>12</td>
<td>4</td>
<td>79</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: phenylacetylene (62.5 μmol), palladium catalyst (12.5 μmol), and 1,4-dioxane (25 μmol) in 0.40 mL of C$_6$D$_6$ at room temperature under 1 atm of H$_2$.  
$^b$ NMR yield.

In separate experiments, 5b and 5c were shown to react with HC≡CPh slowly to give 3b and 3c as well as CH$_4$ (eq 10). Similar reaction with the more bulky complex 5a did not proceed at all even at 50 °C.
**Figure 6.** ORTEP drawing of [2,6-\(\text{Pr}_2\text{PO})_2\text{C}_6\text{H}_3\]PdCH\(_3\) (5b) at the 50% probability level. Selected bond lengths (Å) and angles (deg): Pd–C(1) 2.026(3), Pd–C(23) 2.125(3), Pd–P(1) 2.2628(7), Pd–P(2) 2.2591(7), P(1)–Pd–P(2) 158.87(3), C(1)–Pd–C(23) 179.45(12).

\[
\begin{align*}
&\text{O} \quad \text{O} \\
&\text{Pd} \quad \text{Me} \quad + \quad \equiv \text{Ph} \\
&\text{O} \quad \text{O} \\
&\text{C}_6\text{D}_6 \\
&\text{rt}, 24 \text{ h} \\
&\text{eq 10} \\
&5\text{b} (R = \text{^iPr}) \\
&5\text{c} (R = \text{^Me}) \\
&3\text{b} (26\% \text{ conversion}) \\
&3\text{c} (34\% \text{ conversion})
\end{align*}
\]

The hydrogenation protocol could also be applied to internal alkynes such as diphenylacetylene. At room temperature, alkynyl complexes 3a-c did not show any catalytic activity. On the other hand, methyl complexes 5a-c proved to be active catalysts for the hydrogenation of diphenylacetylene (eq 11 and Table 2). Catalytic activity of these palladium complexes followed the decreasing order of 5b > 5c > 5a, which is the same trend observed for the hydrogenation of phenylacetylene. Although *cis*-stilene was
the major hydrogenation product in each catalytic run, a noticeable amount of bibenzyl was detected, indicating that the hydrogenation process did not stop at the olefin stage.

\[
\text{Ph} = \text{Ph} \xrightarrow{20 \text{ mol}\% [\text{Pd}]} \text{H}_2 (1 \text{ atm}) \xrightarrow{\text{C}_6\text{D}_6, \text{rt}, 24 \text{ h}} \text{cis-PhCH=CHPh} \xrightarrow{+} \text{trans-PhCH=CHPh} \xrightarrow{+} \text{PhCH}_2\text{CH}_2\text{Ph}
\]

Table 2. Palladium-Catalyzed Hydrogenation of Diphenylacetylene

<table>
<thead>
<tr>
<th>entry</th>
<th>[Pd]</th>
<th>cis-stilbene (%)</th>
<th>trans-stilbene (%)</th>
<th>bibenzyl (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5a</td>
<td>57</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>5b</td>
<td>82</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>5c</td>
<td>74</td>
<td>5</td>
<td>3</td>
</tr>
</tbody>
</table>

\(^a\) Reaction conditions: diphenylacetylene (62.5 \text{ \SI}{\mu}{\text{mol}}), palladium catalyst (12.5 \text{ \SI}{\mu}{\text{mol}}), and 1,4-dioxane (25 \text{ \SI}{\mu}{\text{mol}}) in 0.40 mL of C\(_6\)D\(_6\) at room temperature under 1 atm of H\(_2\). \(^b\) NMR yield. \(^c\) GC yield.

2.6 Mechanism for Catalytic Hydrogenation of Alkynes

Palladium-catalyzed hydrogenation of alkynes is a well-established process, particularly in the field of heterogeneous catalysis.\(^{27}\) In recent years, there have also been a number of reports focusing on the development of palladium-based homogeneous

catalysts for selective hydrogenation of alkynes.\textsuperscript{28} One common mechanistic feature of these studies involves the intermediacy of a palladium hydride, which is thought to interact with the alkyne substrate to form a palladium alkenyl species. Given these precedents and the observation of 4b from the reaction between 2b and HC≡CPh (eq 6), one might have anticipated that the hydrogenation of alkynes to alkenes described in this chapter would also proceed via alkyne insertion into a palladium-hydrogen bond. However, several pieces of mechanistic information argue against such a mechanism. First, cleavage of the Pd–C bond of 4b by either H\textsubscript{2} or HC≡CPh is much slower than the formation of styrene. Furthermore, it is difficult to rationalize why the palladium methyl complexes 5a-c are catalytically more reactive than the palladium alkynyl complexes 3a-c. Neither class of the complexes reacts with H\textsubscript{2} to give palladium hydrides, the presumed active species.

The substantial amounts of over-reduction products observed in Tables 1 and 2 indicated to us that the hydrogenation reactions might be catalyzed by nano-sized palladium particles released from the metal complexes. Thus, two catalytic reactions (entry 2 in both Table 1 and Table 2) were repeated with added elemental mercury (200 equiv relative to the palladium complexes). After 24 h, neither reaction showed hydrogenation products. The positive mercury test\textsuperscript{29} is in agreement with palladium particles being the true catalytically active species. Further evidence supporting the formation of palladium particles came from the observation that the solution of 5b in


toluene\textsuperscript{30} changed its color from colorless to faint yellow upon exposure to 1 atm of H\textsubscript{2} for 12 h. As a control experiment, the same solution without H\textsubscript{2} remained colorless after 48 h. The former solution was then centrifuged, resulting in some black particles. Analyzing the particle size using dynamic light scattering (DLS) techniques revealed particles distributed in the range of 0.18-0.30 micrometers.

Generating palladium particles from palladium complexes with well-defined structures is not an unusual phenomenon, but the conditions to form these particles in our system are quite rare. A more frequent scenario for palladium particles leached from a pincer complex happens in cross-coupling reactions, where a base and a relatively high temperature are typically used.\textsuperscript{31} A report by the groups of Sherrill, Jones and Weck has suggested that decomposition of pincer complexes is initiated by displacing one of the pincer arms by a base such as triethylamine.\textsuperscript{31a} A different study by Williams and co-workers, although focused on platinum pincer complexes, has shown that CO can initiate a similar decomposition pathway to platinum particles.\textsuperscript{32} By comparison, our reactions of palladium pincer complexes with alkynes as well as catalytic hydrogenation reactions were performed at room temperature, under neutral conditions and without an obvious nucleophile to displace the pincer arms. The control experiment described earlier suggests that the release of palladium particles is caused by H\textsubscript{2}. As mentioned in section 2.4, when 3b was exposed to H\textsubscript{2}, neither 2b nor styrene was observed. However, when H\textsubscript{2} was added to the mixture of 3b and 2c (1 : 1) at room temperature, both 3c and 2b were detected from \textsuperscript{31}P\{\textsuperscript{1}H\} and \textsuperscript{1}H NMR spectroscopy (eq 12).

This result seems to support that the hydrogenolysis of Pd-CCPh yields Pd-H and phenylacetylene, possibly through the oxidative addition of H\textsubscript{2} to 3b. A plausible mechanism is thus outlined in Scheme 4, in which the reaction of H\textsubscript{2} with a Pd(II) pincer complex generates a Pd(IV) intermediate.

**Scheme 4**

\[
\begin{align*}
\text{Pd-CCPh} & \quad \text{H}_2 \quad \text{Pd-H} \\
3b & \quad \text{rt, 24 h} \quad 2b & \quad \text{rt, 24 h} \quad 3c \\
\end{align*}
\]

Subsequent reductive elimination to change the coordination mode of the pincer ligand from meridional to bidentate becomes possible, which leads to the eventual decomplexation of all ligands from palladium. However, during the catalysis, we could
not detect any diphosphinites by $^{31}\text{P}\{^1\text{H}\}$ spectroscopy. It is likely that the amount of diphosphinites is too small to be observed by NMR under reaction conditions. Interestingly, at a higher temperature (60 °C), the reaction of 5b with H$_2$ (1 atm) did provide the free bis(phosphinite) ligand along with 2b, as judged by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (eq 13). Furthermore, when H$_2$ was added to 2b at room temperature, generation of free phosphinites along with several unknown palladium species were observed from the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (eq 14).

The mechanism depicted in Scheme 4 can be used to rationalize the reactivity differences between palladium methyl complexes 5a-c and alkynyl complexes 3a-c in catalyzing the hydrogenation of alkynes. With a more σ-donating methyl group, the former complexes have more electron-rich palladium centers that favor oxidative addition of H$_2$. As a result, palladium particles are more quickly released from the metal complexes, leading to higher catalytic activities. The fact that palladium complexes bearing a 'Bu-substituted pincer ligand are inferior catalysts can be explained by their less
tendency to react with H₂ to generate sterically crowded 6-coordinate Pd(IV) intermediates. Finally, styrene produced in eqs 5 and 6 is a consequence of hydrogenation of HC≡CPh catalyzed by palladium particles that are formed from decomposition of 3a-c and 4b by H₂.

2.7 Investigation of Ligand-Exchange Reactions with Phenylacetylene

Protonation of metal-hydrogen and metal-carbon bonds by an acid is a well-known process. If phenylacetylene serves as an acid, the reactions in eqs 5 and 6 can be viewed as protonation of the Pd-H moiety of 2a-c by phenylacetylene to yield the palladium alkynyl complexes (3a-c) and dihydrogen. To test this hypothesis, a C₆D₆ solution of 2b was treated with one equiv of methanol (pKa = 15.5 in water) at room temperature. After 24 h, only 11% of 2b was consumed according to ³¹P{¹H} NMR spectroscopy. This result would suggest that phenylacetylene (pKa = 23 in water) is not acidic enough to directly protonate the hydride; hence, a different pathway is involved in the reaction between phenylacetylene and the palladium complexes. The possible pathways are: (a) oxidative addition of the phenylacetylene C-H bond to the palladium hydrides followed by reductive elimination of dihydrogen, and (b) σ-bond metathesis between the hydrides and phenylacetylene. For a better understanding of the reaction mechanism, the exchange of a hydride or a carbon-based ligand of a palladium POCOP-pincer complex with PhC≡C⁻ of phenylacetylene was investigated. As the reaction could be dependent on the electronic and steric properties of the pincer ligand, the effect of P-substituents on these reactions was also studied.
As shown in section 2.3, the reaction of phenylacetylene with complex 2a at room temperature took 9 days to complete, whereas the less bulky complexes 2b and 2c showed a complete conversion within just 15 min. Replacing the hydride with methyl group (a carbon-based anionic ligand) resulted in no net reaction for 5a with phenylacetylene even at 50 °C (section 2.5). In contrast, reactions with complexes 5b and 5c at room temperature gave 26% and 34% conversions, respectively (eq 10). The lower reactivity of the complexes 2a and 5a could be explained by the steric hindrance from the bulky tBu substituents. Compared to 2a-c, the lower reactivity of complexes 5a-c further suggests that steric effects may play an important role in these reactions. However, one could also argue that the higher reactivity of 2a-c is due to the stronger σ-donation from the hydride than a methyl group. To differentiate the electronic effects from the steric effects, a number of other palladium POCOP-pincer complexes were synthesized (see experimental section for more details) and their reactivity with phenylacetylene was studied (eq 15). These results including those described earlier are tabulated in Table 3.
Table 3. Reactions of Palladium Pincer Complexes with Phenylacetylene

<table>
<thead>
<tr>
<th>entry</th>
<th>[Pd]</th>
<th>temp</th>
<th>time</th>
<th>conversion (%)^b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2a</td>
<td>rt</td>
<td>24 h</td>
<td>35</td>
</tr>
<tr>
<td>2</td>
<td>2a</td>
<td>50 °C</td>
<td>24 h</td>
<td>65</td>
</tr>
<tr>
<td>3</td>
<td>2b</td>
<td>rt</td>
<td>15 min</td>
<td>92</td>
</tr>
<tr>
<td>4</td>
<td>2c</td>
<td>rt</td>
<td>15 min</td>
<td>98</td>
</tr>
<tr>
<td>5</td>
<td>5a</td>
<td>rt</td>
<td>24 h</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>5b</td>
<td>rt</td>
<td>24 h</td>
<td>26</td>
</tr>
<tr>
<td>7</td>
<td>5c</td>
<td>rt</td>
<td>24 h</td>
<td>34</td>
</tr>
<tr>
<td>8</td>
<td>4b</td>
<td>rt</td>
<td>24 h</td>
<td>10</td>
</tr>
<tr>
<td>9</td>
<td>6a</td>
<td>rt</td>
<td>24 h</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>6b</td>
<td>rt</td>
<td>24 h</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>6c</td>
<td>rt</td>
<td>24 h</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>6a</td>
<td>50 °C</td>
<td>24 h</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>6b</td>
<td>50 °C</td>
<td>24 h</td>
<td>16</td>
</tr>
<tr>
<td>14</td>
<td>6c</td>
<td>50 °C</td>
<td>24 h</td>
<td>12</td>
</tr>
<tr>
<td>15</td>
<td>7b</td>
<td>rt</td>
<td>24 h</td>
<td>0</td>
</tr>
<tr>
<td>16</td>
<td>7b</td>
<td>50 °C</td>
<td>24 h</td>
<td>7</td>
</tr>
</tbody>
</table>

^aReaction conditions: phenylacetylene (12.5 μmol) and palladium complex (12.5 μmol) in 0.40 mL of C₆D₆.  
^bNMR conversion.
The reaction of the alkenyl complex 4b with phenylacetylene at room temperature gave 3b and styrene in 10% conversion (entry 9). Under the same condition, none of the alkynyl complexes (6a-c) reacted with phenylacetylene (entries 10-12). From the steric point of view, one would have anticipated that the palladium center in 6b is more accessible than that in 4b. Thus, the reactivity difference is due to the fact that the alkenyl group is a better σ-donor than the alkynyl groups. These results combined with those shown in entries 3 and 7 (Csp3) further support that the rate of alkynyl formation correlates with the σ-donating ability of the anionic ligands (2b (H−) > 5b (CH3−) > 4b (PhCH=CH−) > 6b (ArC≡C−)). Although at room temperature palladium alkynyl complexes 6a-c were unreactive towards phenylacetylene, the alkynyl exchange reactions for the less bulky 6b and 6c were observed at 50°C (entries 14 and 15). Once again, the inertness of 6a could be attributed to steric reason (entry 13). To rule out the possibility of a thermodynamically uphill forward process in this case, the reverse reaction (3a with 4-ethynyltoluene) was also studied; at 50 °C, no alkynyl exchange was observed (eq 16). A similar study was performed with complexes 3b and 3c, which showed some exchange with the alkynyl group.
Palladium POCOP-pincer phenyl complex \(7b\) was synthesized as another example of an \(sp^2\)-hybridized carbon being bonded to palladium (see experimental section for details). This compound was also characterized by X-ray crystallography (Figure 7). When mixed with phenylacetylene at room temperature, \(7b\) showed no reaction, contrasting to the reaction with \(4b\), which gave \(3b\) in 10\% conversion (entry 9). These results suggest that the reaction is dependent on the steric property of the ligand that is replaced by the phenylacetylide group, as in both cases the carbon donors are \(sp^2\)-hybridized.

![Figure 7](image)

**Figure 7.** ORTEP drawing of \(\left[2,6-\left('Pr_2PO\right)_2C_6H_3\right]PdC_6H_5\) (7b) at the 50\% probability level. Selected bond lengths (Å) and angles (deg): Pd–C(1) 2.030(2), Pd–C(23) 2.085(2), Pd–P(1) 2.2581(4), P(1)#1–Pd–P(1) 159.46(2), C(1)–Pd–C(23) 179.15(9).

To summarize the results, the reactivity order of the palladium POCOP-pincer complexes towards phenylacetylene is shown below.

\[2b, 2c > 2a > 5c > 5b > 4b > 6c, 6b > 7b\]
2.8 Reactions of 2a-b with Internal Alkynes

After the investigation of the reaction of palladium hydride complexes with phenylacetylene, we became interested in studying similar reactions with internal alkynes. Diphenylacetylene was first selected as the substrate. As anticipated, complex 2a did not react even at 50 °C. In the case of 2b, a reaction at 50 °C for 24 h resulted in complete conversion of the hydride to two new pincer complexes (184.6 ppm and 182.7 ppm in $^{31}$P{$^1$H} NMR spectroscopy) with a ratio of 1 : 0.05. As alkynes are known to insert into metal-hydrogen bonds, these new complexes were expected to be palladium alkenyl complexes. When 1 equiv of concentrated hydrochloric acid was added to this mixture, complete conversion to 1b was observed along with the formation of cis-stilbene. The presence of cis-stilbene in the solution was further confirmed by gas chromatography mass spectrometry. This result provided an indirect evidence for the formation of 8b as the major product, which was produced through cis-insertion of diphenylacetylene into the Pd-H bond (eq 17). Unfortunately, the minor product could not be identified due to its low concentration in the mixture. An attempt to isolate the products resulted in decomposition to unknown palladium species.
Cis-insertion of alkynes into metal hydrogen bonds is commonly reported in the literature; however, the presence of strongly electron-withdrawing substituents on the alkyne could change the regioselectivity of the insertion process. The reactivity of 2a-b with diethyl acetylenedicarboxylate was therefore studied next. The addition of one equiv. of diethyl acetylenedicarboxylate to a C₆D₆ solution of 2a resulted in a complete conversion to a new pincer complex (eq 18).

\[
\begin{align*}
2a + \text{EtOOC} & \overset{\text{C₆D₆, rt, 15 min}}{\rightarrow} \text{9a} \\
& \text{100% conversion}
\end{align*}
\]

The appearance of a singlet resonance at 7.5 ppm in ¹H NMR spectrum was indicative of an insertion product. The product (9a) was isolated and characterized by ³¹P{¹H}, ¹H, ¹³C{¹H} NMR spectroscopy and elemental analysis. Its solid-state structure was also studied by X-ray crystallography (Figure 8), which confirmed the trans stereochemistry.
Figure 8. ORTEP drawing of (E)-[2,6-(t-Bu2PO)2C6H3]Pd(CO2Et)CH(CO2Et) (9a) at the 50% probability level. Selected bond lengths (Å) and angles (deg): Pd–C(1) 2.040(3), Pd–C(31) 2.103(3), Pd–P(1) 2.3133(7), Pd–P(2) 2.3045(7), P(1)–Pd–P(2) 157.67(3), C(1)–Pd–C(31) 179.99(9).

The reaction of diethyl acetylenedicarboxylate with complex 2b produced two palladium complexes with a ratio of 1 : 0.28 as shown by 31P{1H} NMR spectroscopy. From the 1H NMR spectrum, two new resonances (singlet) at 7.1 ppm and 6.3 ppm with the same ratio were observed, which indicates that both complexes were insertion products (9b and 9b'). Based on the chemical shifts, the major product is proposed to be the trans-insertion product (eq 19).
2.9 Conclusions

We have investigated stoichiometric reactions between palladium POCOP-pincer hydride complexes and phenylacetylene. Analogous to other reactions involving transition metal hydrides and terminal alkynes, both palladium alkynyl and alkenyl complexes along with styrene have been identified as products. Through isolation of these metal species and examination of their reactivity, we have discounted the commonly proposed mechanism for alkene formation (in this case styrene), which is via a C–H bond exchange process between the alkenyl complexes and phenylacetylene. Instead, we have provided evidence supporting that leached palladium particles are responsible for the reduction of phenylacetylene to styrene. We have also shown that in catalytic hydrogenation of alkynes, palladium methyl or alkynyl complexes are merely the precursors to the active palladium particles. Unlike cross-coupling reactions or related catalytic processes where colloidal metal particles are often produced under harsh conditions (high temperature and in the presence of a base), palladium particles are released from the POCOP-pincer complexes at room temperature under an atmospheric H₂ pressure. These results will have important implications in designing homogeneous palladium catalysts for the reduction of alkynes. To gain a better understanding of the ligand-exchange process, we have studied reactivity of different palladium alkyl, alkenyl and alkynyl complexes with phenylacetylene. The relative reactivity follows the decreasing order of \( LPdH > LPdCH_3 > (E)-LPhCH=CHPh > LPdC≡CAr > LPdPh \) (\( L \) represents the same POCOP-pincer ligand). We have also investigated the reactions of palladium hydride complexes with internal alkynes. Diphenylacetylene favors \( cis-\)
addition of the Pd-H bond across the triple bond, whereas diethyl acetylenedicarboxylate favors trans-addition.

2.10 Experimental Section

General Procedure

Unless otherwise mentioned, all the organometallic compounds were prepared and handled under an argon atmosphere using standard glovebox and Schlenk techniques. Dry and oxygen-free solvents for carrying out synthesis (THF, pentane, and toluene) were collected from an Innovative Technology solvent purification system. Solvents for column chromatography (CH₂Cl₂ and hexanes) were purchased from commercial sources and used without purification or degassing. Benzene-d₆ was distilled from Na and benzophenone under an argon atmosphere. Unless otherwise mentioned, HC≡CPh was freshly distilled prior to use. [2,6-(Ph₂PO)₂C₆H₃]PdCl (1d)¹⁸ and trans-β-iodostyrene³³ were prepared as described in the literature.

Synthesis of [2,6-(tBu₂PO)₂C₆H₃]PdCl (1a). This compound was prepared according to a slightly modified procedure from the one described by Koridze and co-workers.¹⁷ A suspension of NaH (500 mg, 21 mmol) in THF (20 mL) was added dropwise to a Schlenk flask containing a solution of resorcinol (1.10 g, 10 mmol) in THF (40 mL). The resulting mixture was refluxed for 3 h. After cooling to room temperature, a solution of tBu₂PCl (3.98 mL, 21 mmol) in THF (20 mL) was added and the reaction mixture was refluxed again for 3 h. The volatiles were removed under vacuum and the residue was

extracted with pentane (3 × 35 mL). The combined pentane solution was pumped to
dryness to give a white solid, which was mixed with PdCl₂ (1.77 g, 10 mmol) in 60 mL of
THF and then heated to reflux for 36 h. Upon cooling, the insolubles were filtered off,
resulting in a faint yellow solution, which was concentrated under vacuum to yield the
crude product. Further purification was performed by column chromatography (eluted
with 1 : 1 CH₂Cl₂/hexanes) to provide 1a as a white solid (4.30 g, 80%). ¹H NMR (400
MHz, CDCl₃, δ): 1.45 (t, Jₚ-H = 8.0 Hz, CH₃, 36H), 6.56 (d, Jₕ-H = 8.0 Hz, ArH, 2H), 6.97
(t, Jₕ-H = 8.0 Hz, ArH, 1H). ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 27.7 (t, Jₚ-C = 4.0 Hz,
CH₃), 39.6 (t, Jₚ-C = 7.1 Hz, C(CH₃)₃), 105.7 (t, Jₚ-C = 7.1 Hz, ArC), 127.6 (s, ArC), 129.9
(s, ArC), 167.1 (t, Jₚ-C = 6.1 Hz, ArC). ³¹P{¹H} NMR (162 MHz, CDCl₃, δ): 192.2 (s).

**Synthesis of [2,6-(CePO)₂C₆H₃]PdCl (1c).** A mixture of resorcinol (275 mg, 2.5 mmol)
and triethylamine (1.40 mL, 10 mmol) in 40 mL of toluene was stirred at room
temperature for 15 min, after which Ce₂PCl (1.0 mL, 5.2 mmol) was added and the
mixture was stirred for another 15 min. Following the addition of PdCl₂ (443 mg, 2.5
mmol), the reaction mixture was refluxed for 36 h. Upon cooling, the insolubles were
filtered off, and the resulting solution was concentrated under vacuum to give the crude
product. Washing the solid with pentane (10 mL) yielded analytically pure 1c as a white
solid (1.10 g, 75%). ¹H NMR (400 MHz, CDCl₃, δ): 1.58-1.64 (m, CH₂, 8H), 1.76-1.80
(m, CH₂, 8H), 1.88-2.02 (m, CH₂, 16H), 2.53-2.61 (m, PCH₂, 4H), 6.51 (d, Jₕ-H = 8.0 Hz,
ArH, 2H), 6.95 (t, Jₕ-H = 8.0 Hz, ArH, 1H). ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 26.5 (t,
Jₚ-C = 3.5 Hz, CH₂), 26.6 (t, Jₚ-C = 4.5 Hz, CH₂), 27.5 (t, Jₚ-C = 4.2 Hz, CH₂), 28.4 (s,
CH₂), 39.8 (t, Jₚ-C = 12.9 Hz, CH), 106.0 (t, Jₚ-C = 7.2 Hz, ArC), 128.1 (s, ArC), 129.4 (t,
$J_{P-C} = 2.7$ Hz, ArC), $166.1$ (t, $J_{P-C} = 6.7$ Hz, ArC). $^{31}$P{$^1$H} NMR (162 MHz, CDCl$_3$, δ): 177.9 (s). Anal. Calcd for C$_{26}$H$_{39}$P$_2$O$_2$PdCl: C, 53.16%; H, 6.69%; Cl, 6.04. Found: C, 53.26%; H, 6.86%; Cl, 5.93.

**Synthesis of [2,6-(tPrPO)$_2$C$_6$H$_3$]PdCl (1b).** This compound was prepared in 74% yield by a procedure similar to that used for 1c. $^1$H and $^{31}$P NMR data are consistent with the reported values.$^{11b}$

**Synthesis of [2,6-(tBuPO)$_2$C$_6$H$_3$]PdH (2a).** The mixture of 1a (300 mg, 0.56 mmol) and LiAlH$_4$ (317 mg, 8.3 mmol) in 20 mL of toluene was stirred at room temperature for 48 h. The resulting mixture was filtered through a short plug of Celite to give a colorless solution. After the solvent was evaporated under vacuum, the desired hydride 2a was isolated as a white solid (188 mg, 67%). $^1$H NMR (400 MHz, C$_6$D$_6$, δ): –2.48 (t, $J_{P-H} = 16.0$ Hz, PdH, 1H), 1.28 (t, $J_{P-H} = 8.0$ Hz, CH$_3$, 36H), 6.88 (d, $J_{H-H} = 8.0$ Hz, ArH, 2H), 7.01 (t, $J_{H-H} = 8.0$ Hz, ArH, 1H). $^{13}$C{$^1$H} NMR (101 MHz, C$_6$D$_6$, δ): 28.3 (t, $J_{P-C} = 4.0$ Hz, CH$_3$), 38.2 (t, $J_{P-C} = 8.1$ Hz, C(CH$_3$)$_3$), 105.3 (t, $J_{P-C} = 7.1$ Hz, ArC), 128.2 (s, ArC), 145.1 (t, $J_{P-C} = 6.1$ Hz, ArC), 166.8 (t, $J_{P-C} = 6.1$ Hz, ArC). $^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_6$, δ): 213.8 (s). ATR-IR (solid): ν(Pd–H) = 1756 cm$^{-1}$. Anal. Calcd for C$_{22}$H$_{40}$P$_2$O$_2$Pd: C, 52.33%; H, 7.99. Found: C, 52.35%; H, 8.00.

**Synthesis of [2,6-(tPr$_2$PO)$_2$C$_6$H$_3$]PdH (2b).** A 1.0 M solution of LiBEt$_3$H in THF (2.1 mL, 2.1 mmol) was added dropwise to a chilled (−78 °C) Schlenk flask containing a THF (5 mL) solution of 1b (1.0 g, 2.1 mmol). The reaction mixture was stirred at −78 °C for 1
h, followed by evaporation of the solvent while keeping the flask cold (0 °C). The residue was extracted with pentane (2 × 30 mL), and the combined pentane solution was concentrated to 2 mL. Faint yellow crystals were obtained within 24 h when the solution was kept at −35 °C (400 mg, 42%). ¹H NMR (400 MHz, C₆D₆, δ): −2.40 (t, Jₚ-H = 20.8 Hz, PdH, 1H), 1.08-1.18 (m, CH₃, 24H), 2.05-2.08 (m, CH, 4H), 6.90 (d, J₁-H = 7.6 Hz, ArH, 2H), 7.04 (t, J₁-H = 7.6 Hz, ArH, 1H). ¹³C{¹H} NMR (101 MHz, C₆D₆, δ): 17.3 (s, CH₃), 18.6 (t, Jₚ-C = 5.1 Hz, CH₃), 29.4 (t, Jₚ-C = 12.1 Hz, CH), 105.3 (t, Jₚ-C = 7.1 Hz, ArC), 128.6 (s, ArC), 144.2 (t, Jₚ-C = 6.1 Hz, ArC), 165.9 (t, Jₚ-C = 6.1 Hz, ArC). ³¹P{¹H} NMR (162 MHz, C₆D₆, δ): 202.1 (s). ATR-IR (solid): ν(Pd–H) = 1765 cm⁻¹. Anal. Calcd for C₁₈H₃₂P₂O₂Pd: C, 48.17%; H, 7.19. Found: C, 48.35%; H, 7.34.

Synthesis of [2,6-(²Pe₂PO)₂C₆H₃]PdH (2c). This compound was prepared in 44% yield by a procedure similar to that used for 2b. ¹H NMR (400 MHz, C₆D₆, δ): −2.37 (t, Jₚ-H = 20.0 Hz, PdH, 1H), 1.33-1.38 (m, CH₂, 8H), 1.53-1.64 (m, CH₂, 8H), 1.71-1.79 (m, CH₂, 8H), 1.88-1.95 (m, CH₂, 8H), 2.26-2.34 (m, PCH, 4H), 6.93 (d, J₁-H = 8.0 Hz, ArH, 2H), 7.05 (t, J₁-H = 8.0 Hz, ArH, 1H). ¹³C{¹H} NMR (101 MHz, C₆D₆, δ): 26.6 (t, Jₚ-C = 3.6 Hz, CH₂), 26.8 (t, Jₚ-C = 4.2 Hz, CH₂), 29.2 (s, CH₂), 29.3 (t, Jₚ-C = 5.8 Hz, CH₂), 40.6 (t, Jₚ-C = 13.7 Hz, CH), 105.3 (t, Jₚ-C = 6.8 Hz, ArC), 128.7 (s, ArC), 144.5 (t, Jₚ-C = 6.2 Hz, ArC), 165.9 (t, Jₚ-C = 6.8 Hz, ArC). ³¹P{¹H} NMR (162 MHz, C₆D₆, δ): 195.7 (s). ATR-IR (solid): ν(Pd–H) = 1755 cm⁻¹. Anal. Calcd for C₂₆H₄₀P₂O₂Pd: C, 56.47%; H, 7.29. Found: C, 56.17%; H, 7.09.
**Procedures for a stoichiometric reaction between a palladium hydride complex and phenylacetylene**

In a J. Young NMR tube, palladium hydride 2a (12.5 µmol) was mixed with phenylacetylene (12.5 µmol) and 1,4-dioxane (NMR internal standard, 25 µmol) in 0.4 mL of C\textsubscript{6}D\textsubscript{6}. The progress of the reaction at an appropriate temperature was monitored by \textsuperscript{1}H and \textsuperscript{31}P{\textsuperscript{1}H} NMR spectroscopy. NMR yields for phenylacetylride complex 3a and styrene were calculated based on the integrations of their proton resonances versus the integration of \textit{CH}_2 resonance (3.35 ppm) of the internal standard. Selected \textsuperscript{1}H NMR data (400 MHz, C\textsubscript{6}D\textsubscript{6}, \(\delta\)) for styrene: 5.07 (d, \(J_{H-H} = 10.8 \text{ Hz}\)), 5.60 (d, \(J_{H-H} = 17.6 \text{ Hz}\)), 6.58 (dd, \(J_{H-H} = 17.6 \text{ and } 10.8 \text{ Hz}\)). The reactions of other palladium hydride complexes with phenylacetylene were carried out under the same conditions (temperatures, concentrations, and etc.).

**Synthesis of [2,6-(\textit{t}Bu\textsubscript{2}PO)\textsubscript{2}C\textsubscript{6}H\textsubscript{3}]Pd\textsuperscript{\neq}CPh (3a).** A 1.6 M solution of \textit{n}BuLi in hexanes (0.80 mL, 1.28 mmol) was added dropwise to a chilled (–78 °C) Schlenk flask containing a pentane (4 mL) solution of phenylacetylene (154 µL, 1.4 mmol). The flask was gradually warmed to room temperature within 15 min. The resulting suspension was added slowly via a cannula to a THF (16 mL) solution of 1a (300 mg, 0.56 mmol) at –78 °C. After stirring the mixture at room temperature for 1 h, the solvent was removed under vacuum. Extraction of the residue with pentane (2 \(\times\) 30 mL) followed by evaporation of the solvent under vacuum gave the product as a white solid (250 mg, 74%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, \(\delta\)): 1.46 (t, \(J_{P-H} = 8.0 \text{ Hz, } CH\textsubscript{3}, 36H\)), 6.59 (d, \(J_{H-H} = 8.0 \text{ Hz, } ArH, 2H\)), 6.96 (t, \(J_{H-H} = 8.0 \text{ Hz, } ArH, 1H\)), 7.09 (t, \(J_{H-H} = 8.0 \text{ Hz, } ArH, 1H\)), 7.20
(t, $J_{H-H} = 8.0$ Hz, ArH, 2H), 7.28 (d, $J_{H-H} = 8.0$ Hz, ArH, 2H). $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, $\delta$): 28.0 (t, $J_{P-C} = 3.0$ Hz, CH$_3$), 39.5 (t, $J_{P-C} = 8.1$ Hz, C(CH$_3$)$_3$), 105.0 (t, $J_{P-C} = 7.1$ Hz, ArC), 113.2 (t, $J_{P-C} = 16.2$ Hz, C≡CPh), 117.8 (s, C≡CPh), 124.9 (s, ArC), 127.7 (s, ArC), 127.9 (s, ArC), 129.1 (s, ArC), 130.9 (s, ArC), 138.5 (t, $J_{P-C} = 3.0$ Hz, ArC), 167.3 (t, $J_{P-C} = 6.1$ Hz, ArC). $^{31}$P($^1$H) NMR (162 MHz, CDCl$_3$, $\delta$): 200.2 (s). ATR-IR (solid): $\nu$(C≡C) = 2100 cm$^{-1}$. Anal. Calcd for C$_{30}$H$_{44}$P$_2$O$_2$Pd: C, 59.55%; H, 7.33. Found: C, 59.26%; H, 7.26.

**Synthesis of [2,6-($^t$Pr$_2$PO)$_2$C$_6$H$_3$]PdC≡CPh (3b).** This compound was prepared in 71% yield by a procedure similar to that used for 3a. $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 1.28-1.34 (m, CH$_3$, 12H), 1.39-1.45 (m, CH$_3$, 12H), 2.47-2.54 (m, CH, 4H), 6.60 (d, $J_{H-H} = 8.0$ Hz, ArH, 2H), 7.00 (t, $J_{H-H} = 8.0$ Hz, ArH, 1H), 7.10 (t, $J_{H-H} = 7.2$ Hz, ArH, 1H), 7.20 (t, $J_{H-H} = 7.2$ Hz, ArH, 2H), 7.31 (d, $J_{H-H} = 7.6$ Hz, ArH, 2H). $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$, $\delta$): 17.1 (s, CH$_3$), 17.8 (t, $J_{P-C} = 3.2$ Hz, CH$_3$), 29.3 (t, $J_{P-C} = 12.2$ Hz, CH), 105.2 (t, $J_{P-C} = 7.0$ Hz, ArC), 109.7 (t, $J_{P-C} = 17.5$ Hz, C≡CPh), 118.4 (s, C≡CPh), 125.1 (s, ArC), 127.9 (s, ArC), 128.2 (s, ArC), 128.6 (s, ArC), 131.2 (s, ArC), 137.7 (t, $J_{P-C} = 3.8$ Hz, ArC), 166.4 (t, $J_{P-C} = 6.5$ Hz, ArC). $^{31}$P($^1$H) NMR (162 MHz, CDCl$_3$, $\delta$): 192.7 (s). ATR-IR (solid): $\nu$(C≡C) = 2085 cm$^{-1}$. Anal. Calcd for C$_{26}$H$_{36}$P$_2$O$_2$Pd: C, 56.89%; H, 6.61. Found: C, 56.74; H, 6.47.

**Synthesis of [2,6-($^c$Pe$_2$PO)$_2$C$_6$H$_3$]PdC≡CPh (3c).** This compound was prepared in 76% yield by a procedure similar to that used for 3a except that the extraction of the residue was performed using toluene instead of pentane. The use of pentane for extraction would
result in a much lower isolated yield. $^1$H NMR (400 MHz, C$_6$D$_6$, $\delta$): 1.52-1.72 (m, CH$_2$, 8H), 1.76-1.85 (m, CH$_2$, 12H), 1.87-2.08 (m, CH$_2$, 8H), 2.12-2.27 (m, CH$_2$, 4H), 2.56-2.65 (m, PCH, 4H), 6.56 (d, $J_{H-H} = 8.0$ Hz, ArH, 2H), 6.97 (t, $J_{H-H} = 8.0$ Hz, ArH, 1H), 7.09 (t, $J_{H-H} = 8.0$ Hz, ArH, 1H), 7.20 (t, $J_{H-H} = 8.0$ Hz, ArH, 2H), 7.27 (d, $J_{H-H} = 8.0$ Hz, ArH, 2H). $^{13}$C{$^1$H} NMR (101 MHz, C$_6$D$_6$, $\delta$): 26.5 (t, $J_{P-C} = 3.2$ Hz, CH$_2$), 26.7 (t, $J_{P-C} = 4.2$ Hz, CH$_2$), 27.7 (t, $J_{P-C} = 4.1$ Hz, CH$_2$), 28.8 (s, CH$_2$), 40.3 (t, $J_{P-C} = 13.4$ Hz, CH), 105.1 (t, $J_{P-C} = 7.0$ Hz, ArC), 111.3 (t, $J_{P-C} = 17.2$ Hz, C=CPH), 116.9 (s, C=CPH), 124.9 (s, ArC), 127.9 (s, ArC), 128.2 (s, ArC), 128.9 (s, ArC), 131.0 (s, ArC), 137.8 (t, $J_{P-C} = 4.3$ Hz, ArC), 166.2 (t, $J_{P-C} = 6.6$ Hz, ArC). $^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_6$, $\delta$): 183.8 (s). ATR-IR (solid): $\nu$(C=Ph) = 2095 cm$^{-1}$. Anal. Calcd for C$_{34}$H$_{44}$P$_2$O$_2$Pd: C, 62.53%; H, 6.79. Found: C, 62.25%; H, 6.83.

**Synthesis of (E)-[2,6-(iPr$_2$PO)$_2$C$_6$H$_3$]PdCH=CHPh (4b).** A 1.6 M solution of $^n$BuLi in hexanes (0.32 mL, 0.51 mmol) was added dropwise to a chilled (−78 °C) Schlenk flask containing a pentane (5 mL) solution of trans-β-iodostyrene (143 mg, 0.62 mmol). The reaction mixture was warmed to room temperature and stirred for 15 min. The resulting suspension was transferred via a cannula to a THF (15 mL) solution of 1b (200 mg, 0.42 mmol) at −78 °C. After stirring the reaction mixture at room temperature for 15 min, the volatiles were removed under vacuum. Extraction of the residue with pentane (2 × 30 mL) followed by evaporation of the solvent produced 4b as a white solid. The product was further purified by recrystallization from pentane at −35 °C (95 mg, 41%). $^1$H NMR (400 MHz, C$_6$D$_6$, $\delta$): 1.06-1.14 (m, CH$_3$, 24H), 2.02-2.09 (m, CH(CH$_3$)$_2$, 4H), 6.85 (d, $J_{H-H} = 8.0$ Hz, ArH, 2H), 6.97-7.08 (m, ArH + CH=CPH, 3H), 7.30 (t, $J_{H-H} = 8.0$ Hz, ArH,
2H), 7.57 (d, J_H-H = 8.0 Hz, ArH, 2H), 8.20 (dt, J_H-H = 20.0 Hz, J_P-H = 4.0 Hz, CH=CHPh, 1H). $^{13}$C{$^1$H} NMR (101 MHz, C_6D_6, δ): 16.9 (s, CH_3), 17.6 (t, J_P-C = 4.0 Hz, CH_3), 28.7 (t, J_P-C = 12.1 Hz, CH), 105.5 (t, J_P-C = 7.1 Hz, ArC), 124.9 (s, ArC), 125.1 (s, ArC), 128.6 (s, ArC), 128.8 (s, ArC), 139.0 (t, J_P-C = 4.0 Hz, PdCH=CH), 140.9 (t, J_P-C = 5.1 Hz, ArC), 142.7 (s, ArC), 150.9 (t, J_P-C = 13.1 Hz, PdCH=CH), 166.2 (t, J_P-C = 6.1 Hz, ArC). $^{31}$P{$^1$H} NMR (162 MHz, C_6D_6, δ): 187.2 (s). Anal. Calcd for C_{26}H_{38}P_2O_2Pd: C, 56.68%; H, 6.95. Found: C, 56.54%; H, 6.80.

**Synthesis of (E)-[2,6-(tBu_2PO)_2C_6H_3]PdCH=CHPh (4a).** This compound was prepared in 45% yield by a procedure similar to that used for 4b. Relative to 1a, the amounts of trans-β-iodostyrene and nBuLi were increased to 2.5 equiv and 2.25 equiv, respectively. Unfortunately, the isolated material was a mixture of 4a (91%) and palladium iodide complex 10a (9%). Attempt to purify the product through the recrystallization from toluene, toluene/pentane or toluene/diethyl ether was failed. $^1$H NMR (400 MHz, C_6D_6, δ): 1.26 (t, J_P-H = 8.0 Hz, CH_3, 36H), 6.84 (d, J_H-H = 8.0 Hz, ArH, 2H), 6.97-7.10 (m, ArH + CH=CHPh, 3H), 7.29 (t, J_H-H = 8.0 Hz, ArH, 2H), 7.55 (d, J_H-H = 8.0 Hz, ArH, 2H), 8.28 (d, J_H-H = 20.0 Hz, CH=CHPh, 1H). $^{31}$P{$^1$H} NMR (162 MHz, C_6D_6, δ): 193.7 (s).

**Synthesis of [2,6-(tBu_2PO)_2C_6H_3]PdCH_3 (5a).** A 1.6 M solution of CH_3Li in diethyl ether (375 µL, 0.60 mmol) was added slowly to a chilled (−78 °C) Schlenk flask containing a THF (20 mL) solution of 1a (270 mg, 0.50 mmol). The flask was warmed to room temperature and the reaction mixture was stirred at this temperature for 2 h. The volatiles were removed under vacuum and the residue was extracted with pentane (2 × 30
Evaporating the solvent from the combined extracts yielded 5a as a white solid (240 mg, 92%). $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): $-0.01$ (t, $J_{\text{P-H}} = 4.0$ Hz, PdCH$_3$, 3H), 1.33 (t, $J_{\text{P-H}} = 8.0$ Hz, C(CH$_3$)$_3$, 36H), 6.57 (d, $J_{\text{H-H}} = 8.0$ Hz, ArH, 2H), 6.91 (t, $J_{\text{H-H}} = 8.0$ Hz, ArH, 1H). $^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$, $\delta$): $-17.8$ (t, $J_{\text{P-C}} = 10.1$ Hz, PdC$_3$H), 28.0 (t, $J_{\text{P-C}} = 4.4$ Hz, C(CH$_3$)$_3$, 36H), 39.4 (t, $J_{\text{P-C}} = 7.1$ Hz, C(CH$_3$)$_3$, 104.4 (t, $J_{\text{P-C}} = 6.1$ Hz, ArC), 126.7 (s, ArC), 143.1 (t, $J_{\text{P-C}} = 7.1$ Hz, ArC), 165.9 (t, $J_{\text{P-C}} = 6.1$ Hz, ArC). $^{31}$P{$^1$H} NMR (162 MHz, CDCl$_3$, $\delta$): 194.1 (s). Anal. Calcd for C$_{23}$H$_{42}$P$_2$O$_2$Pd: C, 53.23%; H, 8.16. Found: C, 52.98%; H, 8.01.

Synthesis of [2,6-(iPr$_2$PO)$_2$C$_6$H$_3$]PdCH$_3$ (5b). This compound was prepared in 67% yield by a procedure similar to that used for 5a. $^1$H NMR (400 MHz, C$_6$D$_6$, $\delta$): 0.32 (t, $J_{\text{P-H}} = 5.2$ Hz, PdCH$_3$, 3H), 1.08-1.15 (m, CH(CH$_3$)$_2$, 24H), 2.05-2.12 (m, PCH, 4H), 6.86 (d, $J_{\text{H-H}} = 8.0$ Hz, ArH, 2H), 6.99 (t, $J_{\text{H-H}} = 8.0$ Hz, ArH, 1H). $^{13}$C{$^1$H} NMR (101 MHz, C$_6$D$_6$, $\delta$): $-20.0$ (t, $J_{\text{P-C}} = 10.1$ Hz, PdCH$_3$), 17.1 (s, CH(CH$_3$)$_2$), 17.7 (t, $J_{\text{P-C}} = 3.0$ Hz, CH(CH$_3$)$_2$), 29.1 (t, $J_{\text{P-C}} = 11.1$ Hz, CH(CH$_3$)$_2$), 105.3 (t, $J_{\text{P-C}} = 6.1$ Hz, ArC), 127.9 (s, ArC), 143.2 (t, $J_{\text{P-C}} = 7.1$ Hz, ArC), 165.7 (t, $J_{\text{P-C}} = 7.1$ Hz, ArC). $^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_6$, $\delta$): 188.1 (s). Anal. Calcd for C$_{19}$H$_{34}$P$_2$O$_2$Pd: C, 49.31; H, 7.40. Found: C, 49.20; H, 7.38.

Synthesis of [2,6-(cPe$_2$PO)$_2$C$_6$H$_3$]PdCH$_3$ (5c). This compound was prepared in a quantitative yield by a procedure similar to that used for 5a. $^1$H NMR (400 MHz, C$_6$D$_6$, $\delta$): 0.37 (t, $J_{\text{P-H}} = 5.2$ Hz, PdCH$_3$, 3H), 1.31-1.44 (m, CH$_2$, 8H), 1.58-1.66 (m, CH$_2$, 8H), 1.71-1.80 (m, CH$_2$, 8H), 1.84-2.02 (m, CH$_2$, 8H), 2.31-2.40 (m, PCH, 4H), 6.89 (d, $J_{\text{H-H}} =$
8.0 Hz, ArH, 2H), 7.01 (t, J_H-H = 8.0 Hz, ArH, 1H). $^{13}$C{$^1$H} NMR (101 MHz, C$_6$D$_6$, $\delta$): 
−18.6 (t, J_P-C = 10.1 Hz, PdCH$_3$), 26.7 (t, J_P-C = 4.0 Hz, CH$_2$), 26.8 (t, J_P-C = 4.0 Hz, CH$_2$), 28.1 (t, J_P-C = 4.0 Hz, CH$_2$), 28.9 (s, CH$_2$), 40.5 (t, J_P-C = 12.7 Hz, PCH), 105.4 (t, J_P-C = 6.9 Hz, ArC), 128.0 (s, ArC), 143.4 (t, J_P-C = 6.8 Hz, ArC), 165.6 (t, J_P-C = 7.0 Hz, ArH).

$^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_6$, $\delta$): 177.9 (s). Anal. Calcd for C$_{27}$H$_{42}$P$_2$O$_2$Pd: C, 57.20; H, 7.47. Found: C, 57.46; H, 7.55.

**Synthesis of [2,6-(Bu$_2$PO)$_2$C$_6$H$_3$]Pd≡C[4-(CH$_3$)C$_6$H$_4$] (6a).** A 1.6 M solution of BuLi in hexanes (0.27 mL, 0.43 mmol) was added dropwise to a cold (−5 °C; ice-acetone bath) Schlenk flask containing a pentane (5 mL) solution of 4-ethynyltoluene (60 μL, 0.48 mmol). The flask was gradually warmed to room temperature within 15 min. The resulting suspension was added slowly via a cannula to a THF (10 mL) solution of 1a (100 mg, 0.19 mmol) at −78 °C. After stirring the mixture at room temperature for 15 min, the solvent was removed under vacuum. Extraction of the residue with pentane (2 × 30 mL) followed by evaporation of the solvent under vacuum gave the product as a white solid, which was further washed with cold pentane (2 mL) (83 mg, 72%).

$^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 1.46 (t, J_P-H = 8.0 Hz, CH$_3$, 36H), 2.31 (s, CH$_3$, 3H), 6.60 (d, J_H-H = 8.0 Hz, ArH, 2H), 6.95-7.02 (m, ArH, 3H), 7.19 (d, J_H-H = 8.0 Hz, ArH, 2H). $^1$H NMR (400 MHz, C$_6$D$_6$, $\delta$): 1.39 (t, J_P-H = 8.0 Hz, CH$_3$, 36H), 2.10 (s, CH$_3$, 3H), 6.78 (d, J_H-H = 8.0 Hz, ArH, 2H), 6.94 (t, J_P-H = 8.0 Hz, ArH, 1H), 7.00 (d, J_H-H = 8.0 Hz, ArH, 2H), 7.57 (d, J_H-H = 8.0 Hz, ArH, 2H).

$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$, $\delta$): 21.4 (s, CH$_3$), 28.0 (t, J_P-C = 4.0 Hz, CH$_3$), 39.5 (t, J_P-C = 8.1 Hz, C(CH$_3$)$_3$), 105.0 (t, J_P-C = 7.1 Hz, ArC), 111.7 (t, J_P-C = 16.2 Hz, C≡CPh), 117.7 (s, C≡CPh), 126.1 (s, ArC), 127.7 (s, ArC), 128.7 (s, ArC), 128.7 (s, ArC), 128.7 (s, ArC), 128.7 (s, ArC).
130.7 (s, ArC), 134.5 (s, ArC), 138.6 (t, J_P-C = 4.0 Hz, ArC), 167.3 (t, J_P-C = 6.1 Hz, ArC). 

$^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (162 MHz, CDCl$_3$, $\delta$): 200.2 (s). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (162 MHz, C$_6$D$_6$, $\delta$): 200.4 (s). ATR-IR (solid): $\nu$(C≡C) = 2096 cm$^{-1}$.

**Synthesis of [2,6-(iPr$_2$PO)$_2$C$_6$H$_3$]PdC≡C[4-(CH$_3$)C$_6$H$_4$] (6b).** This compound was prepared in 83% by a procedure similar to that used for 6a. $^1\mathrm{H}$ NMR (400 MHz, CDCl$_3$, $\delta$): 1.29-1.33 (m, CH$_3$, 12H), 1.40-1.44 (m, CH$_3$, 12H), 2.32 (s, CH$_3$, 3H), 2.50-2.53 (m, CH, 4H), 6.62 (m, $J_{H-H} = 8.0$ Hz, ArH, 2H), 6.99-7.04 (m, ArH, 3H), 7.23 (d, $J_{H-H} = 8.0$ Hz, ArH, 2H). $^1\mathrm{H}$ NMR (400 MHz, C$_6$D$_6$, $\delta$): 1.09-1.15 (m, CH$_3$, 12H), 1.28-1.34 (m, CH$_3$, 12H), 2.08 (s, CH$_3$, 3H), 2.15-2.22 (m, CH, 4H), 6.79 (m, $J_{H-H} = 8.0$ Hz, ArH, 2H), 6.93-7.00 (m, ArH, 3H), 7.62 (d, $J_{H-H} = 8.0$ Hz, ArH, 2H). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (101 MHz, CDCl$_3$, $\delta$): 17.0 (s, CH$_3$), 17.7 (t, $J_{P-C} = 3.0$ Hz, CH$_3$), 21.3 (s, CH$_3$) 29.2 (t, $J_{P-C} = 12.1$ Hz, CH), 105.1 (t, $J_{P-C} = 7.1$ Hz, ArC), 108.1 (t, $J_{P-C} = 18.2$ Hz, C≡CPh), 118.3 (s, C≡CPh), 125.5 (s, ArC), 128.1 (s, ArC), 128.6 (s, ArC), 131.0 (s, ArC), 134.6 (s, ArC), 137.7 (t, $J_{P-C} = 4.0$ Hz, ArC), 166.3 (t, $J_{P-C} = 6.1$ Hz, ArC). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (162 MHz, CDCl$_3$, $\delta$): 192.6 (s). ATR-IR (solid): $\nu$(C≡C) = 2093 cm$^{-1}$. Anal. Calcd for C$_{27}$H$_{38}$P$_2$O$_2$Pd: C, 57.61%; H, 6.80. Found: C, 57.61%; H, 6.72.

**Synthesis of [2,6-(cPe$_2$PO)$_2$C$_6$H$_3$]PdC≡C[4-(CH$_3$)C$_6$H$_4$] (6c).** This compound was prepared by a procedure similar to that used for 3a except that the extraction of the residue was performed using toluene instead of pentane. $^1\mathrm{H}$ NMR (400 MHz, CDCl$_3$, $\delta$): 1.60-1.61 (m, CH$_2$, 8H), 1.82 (m, CH$_2$, 12H), 1.97 (m, CH$_2$, 8H), 2.19 (m, CH$_2$, 4H), 2.31
(s, CH3, 3H), 2.56-2.62 (m, PCH, 4H), 6.56 (d, JH-H = 8.0 Hz, ArH, 2H), 6.95-7.02 (m, ArH, 3H), 7.17 (d, JH-H = 8.0 Hz, ArH, 2H). 1H NMR (400 MHz, C6D6, δ): 1.39 (m, CH2, 8H), 1.78 (m, CH2, 16H), 1.95-1.98 (m, PCH, 4H), 2.06 (s, CH3, 3H), 2.40-2.43 (m, CH2, 4H), 6.82 (d, JH-H = 8.0 Hz, ArH, 2H), 6.96-6.98 (m, ArH, 3H), 7.59 (d, JH-H = 8.0 Hz, ArH, 2H). 13C{1H} NMR (101 MHz, CDCl3, δ): 21.4 (s, CH3), 26.5 (t, JPC = 3.0 Hz, CH2), 26.7 (t, JPC = 4.0 Hz, CH2), 27.7 (t, JPC = 4.0 Hz, CH2), 28.8 (s, CH2), 40.3 (t, JPC = 13.1 Hz, CH), 105.1 (t, JPC = 7.1 Hz, ArC), 109.7 (t, JPC = 16.2 Hz, C=CPH), 116.8 (s, C=CPH), 125.9 (s, ArC), 128.2 (s, ArC), 128.7 (s, ArC), 130.9 (s, ArC), 134.5 (s, ArC), 137.9 (t, JPC = 4.0 Hz, ArC), 166.2 (t, JPC = 6.1 Hz, ArC). 31P{1H} NMR (162 MHz, CDCl3, δ): 183.7 (s). 31P{1H} NMR (162 MHz, C6D6, δ): 183.4 (s). ATR-IR (solid): ν(C≡C) = 2084 cm⁻¹. Anal. Calcd for C33H46P2O2Pd: C, 63.02; H, 6.95. Found: C, 63.05; H, 6.78.

**Synthesis of [2,6-(Pr2PO)2C6H3]PdPh (7b).** A 2 M solution of PhLi in dibutyl ether (0.62 ml, 1.24 mmol) was added slowly to a chilled (−78 °C) Schlenk flask containing a THF (20 mL) solution of 1b (500 mg, 1.03 mmol). The flask was warmed to room temperature and the reaction mixture was stirred at this temperature for 2 h. The volatiles were removed under vacuum and the residue was extracted with pentane (2 × 30 mL). Evaporating the solvent from the combined extracts yielded 7b as a white solid (450 mg, 83%). The product can be further purified through recrystallization from concentrated pentane solution at −35°C. 1H NMR (400 MHz, C6D6, δ): 0.93-0.99 (m, CH3, 12H), 1.04-1.10 (m, CH3, 12H), 1.97-2.04 (m, CH, 4H), 6.86 (d, JH-H = 8.0 Hz, ArH, 2H), 7.01 (t, JH-H = 8.0 Hz, ArH, 1H), 7.10-7.23 (m, ArH, 1H), 7.33 (t, JH-H = 8.0 Hz, ArH, 2H), 7.72 (d,
$J_{H-H} = 8.0$ Hz, ArH, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, C$_6$D$_6$, $\delta$): 16.8 (s, CH$_3$), 17.5 (t, $J_{P-C} = 4.0$ Hz, CH$_3$), 28.5 (t, $J_{P-C} = 12.1$ Hz, CH), 105.5 (t, $J_{P-C} = 7.1$ Hz, ArC), 122.5 (s, ArC), 127.3 (s, ArC), 128.6 (s, ArC), 129.1 (s, ArC), 140.2 (s, ArC), 159.6 (t, $J_{P-C} = 11.1$ Hz, ArC), 166.3 (t, $J_{P-C} = 7.1$ Hz, ArC). $^{31}P\{^1H\}$ NMR (162 MHz, C$_6$D$_6$, $\delta$): 185.9 (s). Anal. Calcd for C$_{24}$H$_{36}$P$_2$O$_2$Pd: C, 54.92; H, 6.91. Found: C, 55.15; H, 6.96.

**Synthesis of (E)-[2,6-(Bu$_2$PO)$_2$C$_6$H$_3$]PdC(CO$_2$Et)=CH(CO$_2$Et) (9a).** Under an argon atmosphere to a solution of 2a (505 mg, 1.0 mmol) in toluene (10 mL) was added diethyl acetylenedicarboxylate (0.16 mL, 1.0 mmol). The reaction mixture was stirred at room temperature for 15 min. The volatiles were removed under vacuum and a white solid was obtained, which was washed with cold pentane (5 mL) followed by drying under vacuum (608 mg, 90% yield). $^1$H NMR (400 MHz, C$_6$D$_6$, $\delta$): 1.05-1.11 (m, OCH$_2$CH$_3$, 6H), 1.33-1.40 (m, C(CH$_3$)$_3$, 36H), 4.05-4.15 (m, OCH$_2$CH$_3$, 4H), 6.78 (d, $J_{H-H} = 8.0$ Hz, ArH, 2H), 6.98 (t, ArH, $J_{H-H} = 8.0$ Hz, ArH, 1H), 7.54 (s, CH, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, C$_6$D$_6$, $\delta$): 14.6 (s, OCH$_2$CH$_3$), 14.8 (s, OCH$_2$CH$_3$), 27.6 (t, $J_{P-C} = 3.0$ Hz, C(CH$_3$)$_3$), 28.1 (t, $J_{P-C} = 3.0$ Hz, C(CH$_3$)$_3$), 39.8 (t, $J_{P-C} = 8.1$ Hz, C(CH$_3$)$_3$), 40.6 (t, $J_{P-C} = 8.1$ Hz, C(CH$_3$)$_3$), 59.5 (s, OCH$_2$CH$_3$), 59.8 (s, OCH$_2$CH$_3$), 105.2 (t, $J_{P-C} = 7.1$ Hz, ArC), 128.4 (s, ArC), 134.1 (s, ArC), 137.5 (t, $J_{P-C} = 4.0$ Hz, PdCR=CH), 166.8 (t, $J_{P-C} = 6.1$ Hz, ArC), 169.5 (s, CO), 177.0 (s, CO), 188.5 (t, $J_{P-C} = 4.0$ Hz, PdCR=CH). $^{31}P\{^1H\}$ NMR (162 MHz, C$_6$D$_6$, $\delta$): 194.2 (s). ATR-IR (solid): $\nu_{C=O} = 1674$, 1714 cm$^{-1}$. Anal. Calcd for C$_{30}$H$_{30}$P$_2$O$_6$Pd: C, 53.37; H, 7.47. Found: C, 53.63; H, 7.47.
Procedures for catalytic hydrogenation of alkenes

In a J. Young NMR tube, an alkyne substrate (62.5 μmol), a palladium catalyst (12.5 μmol, 20 mol%), and 1,4-dioxane (25 μmol) were mixed in 0.4 mL of C₆D₆. The mixture was degassed by a freeze-pimp-thaw cycle and then placed under 1 atm of H₂ at room temperature. The reaction was monitored by ¹H NMR spectroscopy and the NMR yields for the hydrogenation products were calculated based on integrations of individual peaks. The resonances for trans-stilbene (from the hydrogenation of diphenylacetylene) were obscured by other resonances, and therefore, its yield was obtained from GC using hexamethylbenzene as an internal standard.

Procedures for alkynyl exchange reactions between palladium POCOP-pincer complexes and phenylacetylene

In a J. Young NMR tube, a palladium complex (12.5 μmol) was mixed with phenylacetylene (12.5 μmol) in 0.4 mL of C₆D₆. The progress of the reaction at an appropriate temperature was monitored by ¹H and ³¹P{¹H} NMR spectroscopy.

Procedures for stoichiometric reactions between palladium hydrides and internal alkenes

In a J. Young NMR tube, a palladium hydride (12.5 μmol) was mixed with an alkyne (12.5 μmol) in 0.4 mL of C₆D₆. The progress of the reaction at an appropriate temperature was monitored by ¹H and ³¹P{¹H} NMR spectroscopy.
Synthesis of [2,6-\((\text{Bu}_2\text{PO})_2\text{C}_6\text{H}_3\)]\text{Pd} (10a). Under an argon atmosphere, AgOTf (308 mg, 1.2 mmol) was added to a solution of 1a (540 mg, 1.0 mmol) in 40 mL of THF. The reaction mixture was stirred at room temperature in dark for 45 min before being filtered through Celite. To the filtrate, sodium iodide (225 mg, 1.5 mmol) was added. After stirring the mixture at room temperature for 30 min, the volatiles were removed under vacuum and the residue was extracted with toluene (40 mL). Toluene was evaporated to dryness, providing the product as a white solid (568 mg, 90 % yield). $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 1.47 (t, $J_{P-H} = 8.0$ Hz, CH$_3$, 36H), 6.58 (d, $J_{H-H} = 8.0$ Hz, ArH, 2H), 6.99 (t, $J_{H-H} = 8.0$ Hz, ArH, 1H). $^1$H NMR (400 MHz, C$_6$D$_6$, $\delta$): 1.38 (t, $J_{P-H} = 8.0$ Hz, CH$_3$, 36H), 6.68 (d, $J_{H-H} = 8.0$ Hz, ArH, 2H), 6.88 (t, $J_{H-H} = 8.0$ Hz, ArH, 1H). $^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$, $\delta$): 28.4 (s, CH$_3$), 40.4 (t, $J_{P-C} = 8.1$ Hz, C(CH$_3$)$_3$), 105.6 (t, $J_{P-C} = 7.1$ Hz, ArC), 127.9 (s, ArC), 135.9 (s, ArC), 166.7 (t, $J_{P-C} = 6.1$ Hz, ArC). $^{31}$P{$^1$H} NMR (162 MHz, CDCl$_3$, $\delta$): 198.1 (s). $^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_6$, $\delta$): 198.6 (s).

X-ray structure determinations

Single crystals of 1a and 1c were obtained from recrystallization in toluene/pentane and CH$_2$Cl$_2$/pentane, respectively. Single crystals of 2a were obtained from cold (−30 °C) toluene solution. Single crystals of 2c, 4b, 5b and 7b were obtained from cold (−30 °C for 2c, 4b and 7b, −5 °C for 5b) pentane solutions. Single crystal of 9a was obtained from recrystallization in toluene at −30 °C. Intensity data for 1a, 2a, 2c, 4b, 5b, 7b and 9a were collected at 150K on a Bruker SMART6000 CCD diffractometer using graphite-monochromated Cu Kα radiation, $\lambda = 1.54178$Å. Data for 1c were collected at Beamline 11.3.1 at Advanced Light Source at Lawrence Berkeley National Laboratory. The data
frames were processed using the program SAINT. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structures were solved by a combination of direct methods in SHELXTL and the difference Fourier technique and refined by full-matrix least-squares procedures. Non-hydrogen atoms were refined with anisotropic displacement parameters. The hydride in 2a and 2c was located directly from the difference map and the coordinates refined. The remaining H-atoms were calculated and treated with a riding model. No solvent of crystallization is present in the lattice for any of the structures. Typical disorder was observed in two of the cyclopentyl rings of 2c; a suitable multi-component disorder model was applied.
Chapter 3

Nickel and Palladium POCOP-Pincer Hydride Complexes as Catalysts for the Hydroboration of CO₂ and Methyl Formate
3.1 Introduction

The growing concern about the rise of CO\(_2\) level in the atmosphere coupled with the increasing global demand for energy has spurred the efforts to develop catalytic processes that can convert CO\(_2\) to liquid fuels.\(^1\) Ideally, this transformation should be carried out in conjunction with light harvesting or, alternatively, employ photogenerated H\(_2\). Using main group hydrides (e.g., boranes and silanes) for CO\(_2\) reduction is not going to be an optimal solution for carbon management and energy storage, unless the hydrides can be regenerated inexpensively, but a deeper understanding of the reduction reactions may provide useful guidelines for designing more efficient solar to liquid fuel conversion. In the past several years, boranes have emerged as effective hydrogen sources for the reduction of CO\(_2\), and the process has been shown to be catalyzed by Ni,\(^2,3\) Cu,\(^4\) Ru,\(^5\) Pd,\(^6\) alkaline earth metals,\(^7\) phosphines,\(^8\) nitrogen bases,\(^9\) and group 13

---


\(^3\) Suh, H.-W.; Guard, L. M.; Hazari, N. \(Polyhedron\) 2014, 84, 37-43.


compounds bearing a phosphine moiety. In this context, we have reported reduction of CO$_2$ with boranes catalyzed by nickel bis(phosphinite) pincer (or POCOP-pincer) complexes under very mild conditions (room temperature and 1 atm of CO$_2$). On the basis of NMR studies and DFT calculations, we have proposed a mechanism involving three consecutive formally two-electron reductions from CO$_2$ to a formate species to formaldehyde, and eventually to the methanol derivative (Scheme 1). Because the most challenging step of the catalytic cycles was shown to be the insertion of HCO$_2$BR'_2 into the nickel hydride (highlighted in blue in Scheme 1), we had hypothesized that reducing the steric congestion around the hydride by decreasing the size of R groups would favor the insertion, thus improving the catalytic reaction. Contrary to this hypothesis, we have found that nickel hydrides bearing smaller R groups are more likely to be trapped by boranes to form hydridoborate complexes, resulting in less efficient CO$_2$ reduction.

Despite the higher price of palladium, we became interested in employing related palladium POCOP-pincer complexes for catalytic reduction of CO$_2$ with boranes. It was

---

hoped that if higher reactivity were observed, a less amount of catalyst would suffice, which might offset the cost of catalyst. A direct comparison between palladium and nickel hydrides for their interaction with boranes is unavailable prior to our study. On the other hand, the majority of the literature has pointed out that with the same ancillary ligands, second-row transition metal hydrides are more hydridic than their first-row counterparts from both kinetic\textsuperscript{11} and thermodynamic\textsuperscript{12} points of view. As such, palladium POCOP-pincer hydrides could be more reactive toward HCO\textsubscript{2}BR'\textsubscript{2}, leading to a better catalytic system. A study by Hazari, Kemp, and coworkers, however, has shown more favorable insertion of CO\textsubscript{2} into pincer-ligated nickel hydrides than the insertion into the analogous palladium hydrides.\textsuperscript{13} This result has been rationalized by considering the difference in M–O bond strengths (i.e., the Ni–O bond is stronger than the Pd–O bond).

An encouraging study by Hazari \textit{et al.} has demonstrated that a palladium hydride bearing a PSiP-type pincer ligand\textsuperscript{14} is remarkably active for catalytic hydroboration of CO\textsubscript{2}.\textsuperscript{6} When pinacolborane (HBpin) is used as the boron reagent, the reduction stops at the HCO\textsubscript{2}BR'\textsubscript{2} stage. Interestingly, replacing HBpin with catecholborane (HBcat) gives rise to a complicated product mixture including HCO\textsubscript{2}BeCat and CH\textsubscript{3}OBeCat.


In this chapter, I focus on investigating CO$_2$ insertion into palladium bis(phosphinite) pincer hydride complexes, reduction of the resulting palladium formate complexes by HBcat, and the reactions of the hydride species with HBcat. I also describe the catalytic performance of the palladium hydrides for the reduction of CO$_2$ with HBcat. Results from the stoichiometric and catalytic studies show a profound influence of the metal on the overall reduction process.

### 3.2 Insertion of CO$_2$ into Palladium Hydrides

Studying the reaction of palladium POCOP-pincer hydrides with HCO$_2$BR’$_2$ would be more informative. Unfortunately, it is hampered by the instability of the boryl formate, and therefore, the reaction with CO$_2$ was investigated to gain some insights about the insertion of a carbonyl substrate into the Pd–H bond. Under an atmospheric pressure of CO$_2$, [2,6-(R$_2$PO)$_2$C$_6$H$_3$]PdH (1a-c)$^{15,16}$ rapidly converted to their formate complexes 2a-c (Scheme 2), as judged by $^1$H NMR spectroscopy. The characteristic formate resonance appeared as a triplet$^{17}$ in the low-field region (2a: 8.92 ppm; 2b: 8.76 ppm; 2c: 8.77 ppm). The absence of the hydride resonance (1a: −2.48 ppm; 1b: −2.40 ppm; 1c: −2.37 ppm) within 15 min of reaction suggested that CO$_2$ insertion is a kinetically and thermodynamically favorable process. A similar observation has been made for the insertion of CO$_2$ into nickel and palladium complexes bearing a hydride

---

16 $^{t}$Bu = tertiary butyl group, $^{i}$Pr = isopropyl group, $^{c}$Pe = cyclopentyl group.
17 The coupling constant ($J_{P-H}$) is small (1.6 or 2.0 Hz), so the formate resonance could appear as a singlet if the resolution is not high enough.
ligand trans to a C- or Si-based donor.\textsuperscript{2a,c,13,18} The formate complexes 2a-c were also independently synthesized through protonation of palladium methyl complexes 3a-c by HCO\textsubscript{2}H.

![Scheme 2](image-url)

Compounds 2b and 2c are soluble in benzene and toluene, whereas 2a is sparingly soluble in these solvents. To fully dissolve ~10 mg of 2a in 0.5 mL of C\textsubscript{6}D\textsubscript{6}, the mixture (in a J. Young NMR tube) was gently heated, which resulted in ~20% of 2a reverted back to 1a. The NMR characterization of 2a was thus performed by quickly recording the spectra of a freshly prepared sample in CDCl\textsubscript{3}. A sample aged for 48 h showed a quantitative conversion of 2a to chloride complex 4a (eq 1) along with CHDCl\textsubscript{2} ($\delta_t = 5.28$ ppm) and CO\textsubscript{2} ($\delta_c = 124.8$ ppm). These results support the reversibility of CO\textsubscript{2} insertion. In fact, drying 2a-c under a dynamic vacuum for > 1 h usually gives a sample contaminated with hydride species. In contrast, the analogous nickel formate complexes can sustain prolonged evacuation without losing CO\textsubscript{2}, suggesting that kinetic barriers for decarboxylation are higher with nickel than with palladium.

The structures of 2a and 2b were studied by X-ray crystallography. As shown in Figure 1, palladium of 2a is situated in a distorted square-planar environment with the O3 atom displaced 0.40 Å out of the least-square plane defined by the P1, C1, Pd, and P2 atoms. The formato group adopts a conformation that is nearly perpendicular to the coordination plane; the dihedral angle (θ) between P1–C1–Pd–P2 and C3–O23–C4 planes is measured as 74.7°. This type of orientation has been found in other nickel or palladium pincer formate complexes.\textsuperscript{13,18b,19} The formato group in 2b, however, rotates only slightly out of the coordination plane (Figure 2), creating a dihedral angle of 14.4°. This structural difference between 2a and 2b is not unique to palladium. The nickel POCOP-pincer system also shows different orientations of the –OC(O)H group when the substituents on the phosphorus donors are altered (Figure 3).\textsuperscript{2a,c} Perhaps due to either electronic reasons or crystal packing effects, the formato group has a preference for the “in plane” conformation unless it is sterically prohibited, as in the case of 2a and 5a.

Figure 1. ORTEP drawing of $[2,6-(^t\text{Bu}_2\text{PO})_2\text{C}_6\text{H}_3]\text{PdOCHO}$ (2a) at 50% probability level. Selected bond lengths (Å) and angles (deg): Pd–C1 1.990(2), Pd–O3 2.1056(19), Pd–P1 2.2903(6), Pd–P2 2.3088(6), C23–O3 1.259(4), C23–O4 1.220(4), P1–Pd–P2 160.29(2), C1–Pd–O3 169.60(9), C1–Pd–P1 80.22(7), C1–Pd–P2 80.16(7).

Figure 2. ORTEP drawing of $[2,6-(^i\text{Pr}_2\text{PO})_2\text{C}_6\text{H}_3]\text{PdOCHO}$ (2b) at 50% probability level. Selected bond lengths (Å) and angles (deg): Pd–C1 1.977(2), Pd–O3 2.0986(18),
Pd–P1 2.2927(6), Pd–P2 2.2778(6), C23–O3 1.267(4), C23–O4 1.236(4), P1–Pd–P2 160.79(2), C1–Pd–O3 176.15(9), C1–Pd–P1 80.79(7), C1–Pd–P2 80.34(7).

![Figure 3. Orientations of the Formato Group in Nickel POCOP-Pincer Complexes](image)

3.3 Reduction of Palladium Formate Complexes with HBcat

Having established stoichiometric reduction of CO₂ to 2a-c by the palladium hydrides, our next objective was to probe the reactivity of 2a-c toward HBcat. Each of the formate complexes were treated with 3 equiv of the borane, which according to Scheme 1 is the amount needed to fully convert HCO₂M to CH₃OBcat. Once mixed with HBcat, the suspension of 2a in C₆D₆ became a clear solution. The ¹H NMR spectrum recorded at 15 min showed the expected product CH₃OBcat; however, its NMR yield was only 87%. Extending the reaction time did not further increase the yield, implying that the reaction was already complete. Contrasting to this result, a similar reaction between the nickel formate 5a and HBcat yields CH₃OBcat quantitatively. ³¹P{¹H} spectroscopy gives a better clue about why less amount of CH₃OBcat was obtained from the palladium system. Evidently, HBcat reacts with 2a to form three palladium pincer complexes with phosphorus resonances at 213.8, 192.3, and 192.2 ppm, and their ratio of 76 : 5 : 19 does not change over a period of 12 h. The major resonance corresponds to the hydride 1a, the resonance at 192.3 ppm has not been identified thus far, and the resonance at 192.2 ppm...
is for a palladium bis(catecholato)borate complex (6a) that will be discussed in the next section (eq 2).

The reaction of HBcat with a sterically less bulky formate complex (2b or 2c) is much more complicated. In addition to the expected hydride complex (1b or 1c), more than four palladium species were observed at the beginning of the reaction (< 15 min). Nevertheless, the $^{31}$P{$^{1}$H} NMR spectra recorded after 12 h are more interpretable. In the case of 2b, the initially formed hydride 1b disappears completely, and the major palladium species (186.8 ppm, 91% of all pincer complexes) becomes bis(catecholato)borate complex 6b (eq 3). The identity of a minor species (4%) at 188.0 ppm remains unknown to us at this point. The third palladium species (5%) has characteristic resonances at 197.3 ppm (doublet, $J_{P-P}$ = 32.4 Hz) and 4.1 ppm (triplet, $J_{P-P}$ = 32.4 Hz), which are integrated to a 2 : 1 ratio. The chemical shifts and the splitting pattern are reminiscent of our previous observations of the degradation of POCOP-pincer complexes by a hydride donor or a nucleophilic base.\textsuperscript{2d,15,20} We thus suspected that this species might be a pincer complex bearing a secondary phosphine ligand (7b),\textsuperscript{21} which could be generated via the cleavage of the pincer backbone. The 2c/HBcat reaction was

\textsuperscript{20} Zhang, J.; Medley, C. M.; Krause, J. A.; Guan, H. \textit{Organometallics} \textbf{2010}, 29, 6393-6401.

\textsuperscript{21} The counter anion is unknown at the moment.
quite similar, producing a mixture of 6c (179.5 ppm, 74%), an unknown palladium species (179.7 ppm, 6%), and 7c (a doublet at 186.3 ppm and a triplet at −1.8 ppm, \(J_{P-H} = 32.4\) Hz, 20%) after 12 h. In both cases, the NMR yield for CH$_3$OBcat is not quantitative (≈85%), which is not surprising given the observed side reactions with 2b and 2c.

7b and 7c with a triflate counter anion can be readily synthesized from palladium chloride complexes 4b and 4c, respectively, following the procedures described in eq 4. These secondary phosphine complexes were fully characterized by NMR spectroscopy and elemental analysis as well as X-ray crystal structure determination for 7b-OTf (Figure 4). Due to the counter anion effect, the NMR data for 7b-OTf and 7c-OTf do not match exactly with those described above but are reasonably close. In the $^{31}$P{$^1$H} NMR spectra, 7b-OTf appears as a doublet at 197.8 ppm and a triplet at 1.1 ppm (\(J_{P-H} = 32.4\) Hz), while 7c-OTf shows a doublet at 186.2 ppm and a triplet at −4.7 ppm (\(J_{P-H} = 30.2\) Hz). From $^1$H NMR, the PH resonances of 7b-OTf and 7c-OTf are located at 4.99 and 5.10 ppm, respectively, with a significantly large $^1J_{P-H}$ coupling constant of ≈340 Hz. These resonances were also found from the reactions shown in eq 3, further supporting the proposed structures of 7b and 7c.
3.4 Reactions of Palladium Hydrides with HBcat

From the complicated reactions shown in eqs 2 and 3 including the less than quantitative yield for CH$_3$OBcat, it became obvious to us that palladium POCOP-pincer complexes are not as effective as the related nickel complexes for the conversion of
HCO₂M to CH₃OBcat. Elucidation of all factors that contribute to the lower efficiency of palladium is a challenging task due to the complexity of the overall process. We decided to focus on specifically the reactions of palladium hydrides 1a-c with HBcat, because they are regenerated multiple times during formate reduction and could be intercepted by HBcat leading to various side reactions.

When 1a in C₆D₆ was treated with 1 equiv of HBcat at room temperature or 50 °C for 24 h, the only resonance observable by ³¹P{¹H} NMR spectroscopy is the one for 1a. The ¹H NMR spectrum of the same mixture shows resonances of 1a and HBcat except that the PdH and BH resonances were absent. This phenomenon is no different from the nickel system, and we have previously rationalized it as a result of rapid and reversible hydrogen exchange between palladium and boron.²d In an attempt to recover 1a, the above mixture was placed under the vacuum for 1 h and the residue was redissolved in C₆D₆ to check for purity. Interestingly, other than the expected hydride 1a, two additional ³¹P resonances were found at 192.3 and 192.2 ppm (6a), which account for 3% and 10% of all pincer complexes, respectively. These are the same palladium species observed from the 2a/HBcat reaction (eq 2). Fortunately, increasing the ratio of HBcat : 1a from 1 : 1 to 75 : 1 and following a workup procedure that involves the addition of Et₂O (for details see Experimental Section), 6a could be isolated in a pure form. The number of aromatic hydrogens present in the ¹H NMR spectrum suggests two catecholato groups per palladium, while its ¹¹B NMR spectrum displays a singlet at 4 ppm, indicative of a quaternary boron center. Compound 6a was therefore identified as a palladium POCOP-pincer complex bearing a bis(catecholato)borate ligand. The structure of 6a was unambiguously established by X-ray crystallography. As illustrated in Figure 5, the most
notable feature is the $\kappa^1$-coordination mode for B(cat)$_2^-$, which is unprecedented for transition metal complexes according to Cambridge Structural Database (CSD). More commonly observed coordination modes are $\kappa^2$ using two oxygen atoms or $\eta^6$ through one of the aromatic rings. As one might have expected, the B1–O3 bond is longer than other B–O bonds by 0.06-0.08 Å.

**Figure 5.** ORTEP drawing of [2,6-(t-Bu$_2$PO)$_2$C$_6$H$_3$]Pd(Bcat$_2$) (6a) at 50% probability level. Selected bond lengths (Å) and angles (deg): Pd–C1 1.990(4), Pd–P1 2.3530(12), Pd–P2 2.3384(12), Pd–O3 2.200(3), B1–O3 1.536(6), B1–O4 1.459(6), B1–O5 1.478(6), B1–O6 1.459(6), B2–O3 1.473(6), B2–O4 1.474(6), B2–O5 1.479(6), B2–O6 1.478(6), P1–P2 2.3561(12), P1–O3 2.201(3), P1–O4 1.459(6), P1–O5 1.478(6), P1–O6 1.478(6), P2–O3 2.201(3), P2–O4 1.460(6), P2–O5 1.478(6), P2–O6 1.478(6).


B1–O6 1.471(6), P1–Pd–P2 158.01(4), C1–Pd–O3 173.78(15), C1–Pd–P1 79.41(13),
C1–Pd–P2 79.49(13), O3–B1–O4 103.6(4), O5–B1–O6 105.3(4).

Degradation of HBcat to B(cat)_2^- by nucleophiles or metal hydrides has been
reported in the literature. Marder, Baker, and co-workers have studied the reaction of
tertiary phosphines PR_3 with HBcat, which, depending on the size of the R groups,
produces either [(PR_3)_2BH_2]^+[B(cat)_2]^- or H_3B•PR_3/B_2(cat)_3. They have also shown
that RhH(PMe_3)_4 reacts with HBcat to generate cis-[RhH_2(PMe_3)_4]^+[B(cat)_2]^-, 
[(PMe_3)_2BH_2]^+[B(cat)_2]^-, and many other products. RhH(dppp)_2 (dppp =
Ph_2PCH_2CH_2CH_2PPh_2), which does not have a labile phosphine ligand, reacts with
HBcat to afford [RhH_2(dppp)_2]^+[B(cat)_2]^- and B_2(cat)_3. In contrast, a similar reaction
with coordinatively unsaturated hydride [RhH(dippe)]_2 (dippe = ^3Pr_2PCH_2CH_2P^Pr_2)
yields [Rh(η^6-B(cat)_2)(dippe)]. Beyond rhodium chemistry, Knizek and Nöth have
reported that the reaction between (RO)_3TiH(PMe_3) (R = 2,6-^3Pr_2C_6H_3) and HBcat gives
rise to (RO)_3TiB(cat)_2 and H_3B•PMe_3. Inspired by these studies, we speculate that 1a
interacts with HBcat to form a κ¹ dihydridoborate complex 8a as shown in Scheme 3. It
should be noted that we previously favored [H_2Bcat]^- being a bidentate ligand for a
nickel center bearing the same POCOP-pincer ligand. The palladium system described
here should have a more electron-rich metal center that might discourage [H_2Bcat]^-
from being coordinated to palladium using both hydride ligands. As a consequence, the B–O
bonds of 8a are weakened to the extent that the attack of oxygen on the second HBcat
molecule becomes possible. The resulting compound 9a can further react with HBcat to

25 Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. Inorg. Chem. 1993, 32, 2175-
2182.
26 Westcott, S. A.; Marder, T. B.; Baker, R. T.; Harlow, R. L.; Calabrese, J. C.; Lam, K. C.; Lin, Z.
yield a κ¹-BH₄ complex 10a and B₂(cat)₃. Alternatively, 9a can be converted to 6a with concomitant release of B₂H₆, which should be facilitated under a reduced pressure.

As expected, the less bulky complexes 1b and 1c were found to be more reactive towards catecholborane. According to ¹H NMR spectroscopy, the addition of just one equiv of HBcat to a solution of 1b in C₆D₆ showed formation of dihydrogen within 15 min. At that stage of the reaction, 44% of 1b was converted to 6b (δ_P = 186.8 ppm) and a new species 11b with ³¹P resonance at 200.2 ppm (eq 5). The ratio of 1b, 6b and 11b was 1 : 0.1 : 0.7. Extending the reaction time to 12 h resulted in a 89% conversion of 1b with concomitant growth of 11b and 6b (75% and 7% of all the pincer complexes, respectively). Interestingly, 7b (7%) was also observed by ³¹P{¹H} and ¹H NMR spectroscopy.
Very similar results were obtained in the case of 1c. $^{31}$P$\{^1$H$\}$ NMR spectrum of an equimolar mixture of 1c and HBcat revealed formation of a new complex 11c with resonance at 193.4 ppm (38% with respect to the unreacted 1c) within 15 min. Dihydrogen was detected by $^1$H NMR spectroscopy. After 12 h, 83% of 1c was converted and, 11c was shown as the major pincer complex (45%) present in solution along with 6c (26%) and 7c (12%). The formation of complexes 6 and 7 in eq 5 is consistent with the hypothesis that the side products shown in eq 3 are due to the reactions between 1b-c and HBcat.

The observation of palladium pincer complexes 11b and 11c was interesting and perhaps informative. They could be the intermediates for the formation of the bis(catecholato)borate complexes 6b-c and phosphine complexes 7b-c. In an attempt to synthesize 11b-c, we studied the reactions of 1b-c with a large excess HBcat. Reaction of 1b with 5 equiv of HBcat for 12 h resulted in 11b as the sole product, as observed by $^{31}$P$\{^1$H$\}$ NMR spectroscopy. The $^1$H NMR spectrum of the solution showed dihydrogen and, more importantly, no resonance in the range from 0 to $-$2 ppm, which would be for a borohydride or hydridoborate complex as seen in the nickel case. The reaction of 1c with HBcat was similar, giving rise to dihydrogen and complex 11c. Thus, complexes 11b-c were proposed as palladium-boryl complexes, which were produced from dehydrogenative coupling between the palladium hydrides and the borane.
Unfortunately, attempts to isolate 11b-c from the reaction mixture were unsuccessful, resulting in a partial conversion of 11b-c to 6b-c (26% for 11b and 27% for 11c). The bis(catecholato)borate complexes 6b-c were isolated from the reaction mixtures (see experimental section for more details). Complex 6b was fully characterized by $^1$H, $^{13}$C{$^1$H}, $^{31}$P{$^1$H} NMR spectroscopy and elemental analysis. The structure was further confirmed by X-ray crystallography (Figure 6).

![ORTEP drawing of [2,6-(Pr$_2$PO)$_2$C$_6$H$_3$]Pd(Bcat$_2$) (6b) at 50% probability level.]

Selected bond lengths (Å) and angles (deg): Pd–C1 1.994(3), Pd–P1 2.3072(8), Pd–P2 2.3020(8), Pd–O3 2.1571(18), B1–O3 1.544(4), B1–O4 1.460(4), B1–O5 1.456(5), B1–O6 1.478(5), P1–Pd–P2 160.25(3), C1–Pd–O3 177.36(9), C1–Pd–P1 79.49(13), C1–Pd–P2 80.82(13), O3–B1–O4 102.4(2), O5–B1–O6 105.9(3).

Fortunately, stirring an equimolar mixture of 1c and HBcat for 2 h resulted in complex 11c in a quantitative yield. A fast evacuation of the volatiles followed by extraction with diethyl ether and then slow evaporation of the ether resulted in single
crystals that are suitable for X-ray diffraction. The preliminary structural analysis indeed supported 11c being a palladium boryl complex (Figure 7). Prior to this work, Ozerov and co-workers reported the synthesis of a palladium boryl complex from a reaction between a cationic palladium hydride and HBcat.28 A similar dehydrogenative borylation of PNP-supported nickel pincer hydride was reported by Mindiola et al.29 However, compared to these complexes, 11b-c are less stable, largely due to the boryl group is placed trans to a strongly trans-directing group.

![Figure 7. Ball-and-stick drawing of preliminary structure of [2,6-(Pe2PO)2C6H3]PdBe (11c).](image)

From the experimental results discussed above, we propose a reversible dehydrogenative coupling between 1b-c with HBcat through borane-adducts 8b-c (Scheme 4). In the presence of a large excess HBcat, the equilibria between 1b-c and 8b-c lie towards 8b-c, which increases the likelihood for the formation of 11b-c. However,

---

under a dynamic vacuum, the formation of 6 becomes favorable due to the removal of B$_2$H$_6$ from the system. The pathway for the conversion from 11 to 6 could proceed via complex 8 and 9 or via another path without the involvement of 8 and 9. At this moment, it is not possible to distinguish between these pathways.

3.5 Catalytic Hydroboration of CO$_2$ with Nickel and Palladium Complexes

Unlike nickel formate complexes, which react with HBcat to generate nickel hydride complexes cleanly, palladium formate complexes 2a-c react with HBcat to give 1a-c as well as some side products (eq 2 and 3). If these species were inactive or less reactive, they would undermine the catalytic performance of palladium catalysts. A series of comparisons between the activity of 2a-c and 5a-c in catalytic hydroboration of CO$_2$ was thus made (eq 6). Experimental procedure involved the addition of HBcat (100 equiv with respect to the catalyst) to a solution of the catalyst in C$_6$D$_6$ followed by the introduction of CO$_2$ (1 atm) into the reaction vessel (method A). In the case of 5a, a
quantitative conversion of HBcat to CH3OBcat was observed in 1 h, whereas for 2a, only 85% conversion (or TON = 85) was achieved in 1 h (entries 1 and 2 in Table 1). Extending the reaction time from 1 h to 4 h did not improve the TON. We have already established that 1a reacts with HBcat to yield multiple products; therefore, it is possible that in method A, prior to the addition of CO2, the loss of catalytic activity through the reactions with the borane already takes place. The side reactions between the catalyst and HBcat could potentially be avoided by introducing CO2 first because once the catalytic reaction starts, the insertion of CO2 into the metal hydride could be more competitive than the side reactions between the hydride and HBcat. To test this hypothesis, we first placed the catalyst 2a under an atmospheric pressure of CO2, after which the borane was added to the mixture (method B). Unfortunately, no significant improvement of the TON was observed (entry 3). Likewise, when the less bulky 2b was used as the catalyst, two different methods did not show much difference in terms of the TON (entries 4 and 5).

Interestingly, for all the palladium catalysts examined here, the reactivity was almost same (entries 2-6), contrasting to the nickel system where the P-substituents affect the catalytic performance of the catalyst for the hydroboration of CO2. Monitoring the catalytic reactions with $^{31}\text{P}{}^{1\text{H}}$ NMR spectroscopy did not show the formation of other palladium species, suggesting that the insertion of CO2 into Pd-H bonds of 1a-c followed by the hydroboration is much faster than the side reactions with the HBcat. The hydride/HBcat reaction, though relatively slower, does cause the degradation of the catalyst over the time, which results in a less than quantitative conversion. Although the modification in the sequence of addition (method A vs. B) did not change the TON for 2a-c and 5b, in the case of the nickel complex 5c, a significant improvement of TON was
observed using method B (entry 10) compared to method A (entry 9). It is likely that for 1c, some irreversible and fast reactions with HBcat are operating, and the erosion of the catalytic activity could be avoided in presence of CO₂.

\[
\text{CO}_2 + \text{HBcat} \xrightarrow{\text{catalyst (1 equiv)}} \text{CH}_3\text{OBcat} \quad \text{(eq 6)}
\]

**Table 1.** Catalytic Reduction of CO₂ with HBcat

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Time (h)</th>
<th>Method</th>
<th>TONᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5a</td>
<td>1</td>
<td>A</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>2a</td>
<td>1</td>
<td>A</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>A</td>
<td>85</td>
</tr>
<tr>
<td>3</td>
<td>2a</td>
<td>1</td>
<td>B</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>B</td>
<td>89</td>
</tr>
<tr>
<td>4</td>
<td>2b</td>
<td>1</td>
<td>A</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>A</td>
<td>84</td>
</tr>
<tr>
<td>5</td>
<td>2b</td>
<td>1</td>
<td>B</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>B</td>
<td>81</td>
</tr>
<tr>
<td>6</td>
<td>2c</td>
<td>1</td>
<td>B</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>B</td>
<td>89</td>
</tr>
<tr>
<td>7</td>
<td>5b</td>
<td>4</td>
<td>A</td>
<td>100</td>
</tr>
<tr>
<td>8</td>
<td>5b</td>
<td>4</td>
<td>B</td>
<td>97</td>
</tr>
<tr>
<td>9</td>
<td>5c</td>
<td>12</td>
<td>A</td>
<td>30</td>
</tr>
<tr>
<td>10</td>
<td>5c</td>
<td>1</td>
<td>B</td>
<td>84</td>
</tr>
</tbody>
</table>

ᵃ Reaction conditions: catecholborane (2.5 mmol), catalyst (25 µmol), and hexamethyldisilane (50 µmol) in 2 mL of C₆D₆ at room temperature under 1 atm of CO₂. ᵇ TON = turnover number; calculated by NMR.

### 3.6 Catalytic Hydroboration of Methyl Formate

In the proposed mechanism for the catalytic hydroboration of CO₂ (Scheme 1), there are three steps all involving the insertion of a C=O into a metal hydrogen bond.
The first step is the insertion of CO\(_2\), the second one is the insertion of HCO\(_2\)Bcat, and the last one involves the insertion of HCHO leading to the CH\(_3\)OBcat. The insertion of both CO\(_2\) and HCHO into metal hydrides has been probed experimentally\(^{2a, 2d}\). However, the reactivity of the metal hydrides with the boryl ester could not be easily studied, as the isolation of this compound was challenging. Instead, we have chosen methyl formate as the model substrate to mimic the reaction of HCO\(_2\)Bcat.

When a stoichiometric amount of methyl formate was added to a C\(_6\)D\(_6\) solution of nickel POCOP-pincer hydride 12a, no insertion was observed at room temperature even after several days. However, the addition of 2 equiv of HBcat to this mixture resulted in the formation of CH\(_3\)OBcat and CH\(_3\)OCH\(_2\)OBcat (eq 7), as suggested by \(^1\)H NMR spectroscopy. The less bulky nickel hydride 12b also showed no insertion of methyl formate at room temperature, and the formation of CH\(_3\)OCH\(_2\)OBcat and CH\(_3\)OBcat in the presence of HBcat (2 equiv). The reaction with 12b stopped at 15 min and provided CH\(_3\)OCH\(_2\)OBcat as the major product; however, increasing the reaction time to 5 h gave CH\(_3\)OBcat as the major product.

Catalytic reduction of methyl formate by catecholborane was thus carried out with the more reactive complex 12b in (eq 8; Table 3).
Table 2. Hydroboration of Methyl Formate Facilitated by Nickel Complexes

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
<th>Time</th>
<th>CH$_3$OCH$_2$OBcat (%)$^b$</th>
<th>CH$_3$OBcat (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12a</td>
<td>15 min</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3 h</td>
<td>6</td>
<td>45</td>
</tr>
<tr>
<td>2</td>
<td>12b</td>
<td>15 min</td>
<td>74</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5 h</td>
<td>3</td>
<td>75</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: methyl formate (25 μmol), nickel complex (25 μmol), catecholborane (50 μmol), and hexamethyldisilane (12.5 μmol) in 0.5 mL of C$_6$D$_6$ at room temperature. $^b$ NMR yield.

![Chemical reaction equation]

Table 3. Nickel-Catalyzed Hydroboration of Methyl Formate

<table>
<thead>
<tr>
<th>Time</th>
<th>CH$_3$OCH$_2$OBcat (%)$^b$</th>
<th>CH$_3$OBcat (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 h</td>
<td>28</td>
<td>72</td>
</tr>
<tr>
<td>3 h</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: methyl formate (0.5 mmol), nickel catalyst (25 μmol), hexamethyldisilane (25 μmol) and catecholborane (1 mmol) in 0.5 mL of C$_6$D$_6$ at room temperature. $^b$ NMR yield.

Based on the experimental results described above, it is reasonable to propose that the insertion of an ester carbonyl group into POCOP-ligated nickel hydride is thermodynamically less favorable compared to the insertion of CO$_2$ or HCHO. However, in the presence of HBcat, hydroboration of the ester was observed, suggesting that the subsequent reduction drives the insertion process.
3.7 Conclusions

A series of palladium POCOP-pincer formate complexes have been synthesized and their reactivity with catecholborane has been studied. In the presence of 3 equiv of HBcat, these palladium formate complexes are converted to CH₃OBcat and palladium hydrides as the major metal complex along with a number of other palladium species. Investigation of the reactions between HBcat and palladium hydrides has showed the formation of similar palladium species as observed in the palladium formate/HBcat reactions. Two of these new complexes have been isolated and characterized as the bis(catecholato)borate and phosphine-ligated palladium pincer complexes. From these observations, it can be concluded that the reactions between palladium hydrides and HBcat could be one of the major side reactions during catalytic hydroboration of CO₂. We have also compared the reactivity of palladium and nickel formate complexes in catalytic hydroboration of CO₂ with HBcat. Among all the catalytic systems, the tert-butyl group substituted POCOP-nickel pincer formate complex (5a) has been shown to be the most active catalyst. Lower efficiency of the palladium formate complexes has been observed, which is likely due to the aforementioned side reactions of the catalyst with HBcat. In addition, we have shown that the POCOP-pincer nickel hydrides are effective in catalytic reduction of methyl formate with HBcat. However, these complexes are less efficient in the reduction of the ester than that of CO₂.

3.8 Experimental Section

General Comments. All the organometallic compounds were prepared and handled under an argon atmosphere using standard Schlenk and inert-atmosphere box
techniques. Dry and oxygen-free solvents were collected from an Innovative Technology solvent purification system and used throughout all experiments. Benzene-$d_6$ was distilled from Na and benzophenone under an argon atmosphere. Catecholborane (HBcat) was purified by vacuum distillation prior to use. $^1$H, $^{13}$C{$^1$H} and $^{31}$P{$^1$H} NMR spectra were recorded on a Bruker Avance-400 MHz spectrometer. Chemical shift values in $^1$H and $^{13}$C{$^1$H} NMR spectra were referenced internally to the residual solvent resonances. $^{31}$P{$^1$H} spectra were referenced externally to 85% H$_3$PO$_4$ (0 ppm). Infrared spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR spectrometer equipped with smart orbit diamond attenuated total reflectance (ATR) accessory. Complexes 1a-c, 3a-c, 12a-b and 4b-c were prepared as described in the literature.$^{15, 2a, 2c}$

**Synthesis of [2,6-(tBu$_2$PO)$_2$C$_6$H$_3$]PdOCHO (2a).** Under an argon atmosphere, formic acid (95% purity, 18 μL, 0.45 mmol) was added to a solution of 3a (200 mg, 0.39 mmol) in 10 mL of toluene and the reaction mixture was stirred at room temperature for 15 min. The volatiles were removed under the vacuum and the residue was washed with a small amount of cold pentane. The desired product was isolated as a white solid (128 mg, 60% yield) after drying under the vacuum for a short period of time; extensive drying should be avoided as decarboxylation of the formate complex can occur. If needed, this compound can be further purified via recrystallization in toluene at −30 °C. $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 1.40 (t, $J_{P-H} = 7.6$ Hz, CH$_3$, 36H), 6.51 (d, $J_{H-H} = 8.0$ Hz, ArH, 2H), 6.94 (t, $J_{H-H} = 8.0$ Hz, ArH, 1H), 8.45 (s, PdOCHO, 1H). $^1$H NMR (400 MHz, C$_6$D$_6$, $\delta$): 1.33 (t, $J_{P-H} = 7.6$ Hz, CH$_3$, 36H), 6.62 (d, $J_{H-H} = 8.0$ Hz, ArH, 2H), 6.84 (t, $J_{H-H} = 8.0$ Hz, ArH, 1H), 8.92 (t, $J_{P-H} = 1.6$ Hz, PdOCHO, 1H). $^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$, $\delta$):
27.4 (t, $J_{P\cdot C} = 3.8$ Hz, CH$_3$), 39.3 (t, $J_{P\cdot C} = 7.8$ Hz, C(CH$_3$)$_3$), 105.7 (t, $J_{P\cdot C} = 7.1$ Hz, ArC), 125.8 (t, $J_{P\cdot C} = 3.2$ Hz, ArC), 127.6 (s, ArC), 167.2 (t, $J_{P\cdot C} = 5.8$ Hz, ArC), 167.6 (s, PdOCHO). $^{31}$P{$_1^1$H} NMR (162 MHz, CDCl$_3$, $\delta$): 191.5 (s). $^{31}$P{$_1^1$H} NMR (162 MHz, C$_6$D$_6$, $\delta$): 191.8 (s). ATR-IR (solid): $\nu$(C=O) = 1624 cm$^{-1}$. Anal. Calcd for C$_{23}$H$_{40}$O$_4$P$_2$Pd: C, 50.32%; H, 7.34. Found: C, 50.04%; H, 7.26.

**Synthesis of [2,6-(iPr$_2$PO)$_2$C$_6$H$_3]$PdOCHO (2b).** Under an argon atmosphere, formic acid (95% purity, 20 $\mu$L, 0.50 mmol) was added to a solution of [2,6-(iPr$_2$PO)$_2$C$_6$H$_3]$PdCH$_3$ (3b; 200 mg, 0.43 mmol) in 10 mL of toluene and the reaction mixture was stirred at room temperature for 15 min. The volatiles were removed under the vacuum and the residue was extracted with pentane (60 mL). Evaporation of the solvent resulted in the product as a faint yellow solid (97 mg, 46% yield); extensive drying should be avoided as decarboxylation of the formate complex can occur. In needed, this compound can be further purified via recrystallization from a saturated pentane solution at $-30$ °C. $^1$H NMR (400 MHz, C$_6$D$_6$, $\delta$): 1.08-1.15 (m, CH$_3$, 12H), 1.21-1.30 (m, CH$_3$, 12H), 2.30-2.39 (m, CH, 4H), 6.66 (d, $J_{H\cdot H} = 8.0$ Hz, ArH, 2H), 6.87 (t, $J_{H\cdot H} = 8.0$ Hz, ArH, 1H), 8.76 (t, $J_{P\cdot H} = 2.0$ Hz, PdOCHO, 1H). $^{13}$C{$_1^1$H} NMR (101 MHz, C$_6$D$_6$, $\delta$): 16.9 (s, CH$_3$), 18.0 (t, $J_{P\cdot C} = 3.7$ Hz, CH$_3$), 29.8 (t, $J_{P\cdot C} = 12.0$ Hz, CH), 106.2 (t, $J_{P\cdot C} = 6.7$ Hz, ArC), 126.9 (t, $J_{P\cdot C} = 4.3$ Hz, ArC), 128.6 (s, ArC), 166.3 (s, PdOCHO), 167.3 (t, $J_{P\cdot C} = 6.3$ Hz, ArC). $^{31}$P{$_1^1$H} NMR (162 MHz, C$_6$D$_6$, $\delta$): 187.3 (s). ATR-IR (solid): $\nu$(C=O) = 1594 cm$^{-1}$. Anal. Calcd for C$_{19}$H$_{32}$O$_4$P$_2$Pd: C, 46.31; H, 6.54. Found: C, 46.33; H, 6.48.
Synthesis of [2,6-(iPr2PO)2C6H3]PdOCHO (2c). This compound was prepared in 49% yield by a procedure similar to that used for 2b. 1H NMR (400 MHz, C6D6, δ): 1.35-1.41 (m, CH2, 8H), 1.58-1.66 (m, CH2, 8H), 1.72-1.76 (m, CH2, 4H), 1.93-2.04 (m, CH2, 12H), 2.57-2.70 (m, PCH, 4H), 6.69 (d, JH-H = 8.0 Hz, ArH, 2H), 6.88 (t, JH-H = 8.0 Hz, ArH, 1H), 8.77 (t, JP-H = 2.0 Hz, PdOCHO, 1H). 13C{1H} NMR (101 MHz, C6D6, δ): 26.6 (t, JP-C = 6.0 Hz, CH2), 26.8 (t, JP-C = 3.0 Hz, CH2), 28.3 (s, CH2), 28.7 (t, JP-C = 4.0 Hz, CH2), 40.6 (t, JP-C = 13.7 Hz, CH), 106.2 (t, JP-C = 7.1 Hz, ArC), 126.8 (t, JP-C = 4.0 Hz, ArC), 126.8 (s, ArC), 166.2 (s, PdOCHO), 167.2 (t, JP-C = 7.1 Hz, ArC). 31P{1H} NMR (162 MHz, C6D6, δ): 176.7 (s). ATR-IR (solid): ν(C=O) = 1599 cm⁻¹. Anal. Calcd for C27H40O4P2Pd: C, 54.32%; H, 6.75. Found: C, 54.33; H, 6.64.

General Reaction Procedure for the Reaction of Catecholborane with Palladium Formate Complexes (2a-c): Under an argon atmosphere, to a mixture of a palladium formate complex (0.025 mmol) and hexamethyldisilane (0.008 mmol) in C6D6 (0.5 mL), was added catecholborane (0.075 mmol). The progress of the reaction was monitored by 31P{1H} and 1H NMR spectroscopy.

Synthesis of [{2,6-(iPr2PO)2C6H3}Pd(iPr2PH)]+{OTf}– (7b-OTf). Under an argon atmosphere, silver triflate (31 mg, 0.12 mmol) was added to a solution of 4b (48 mg, 0.10 mmol) in 2 mL of THF. The reaction mixture was kept in the dark and stirred for 2 h before filtered through a short pad of Celite. To the filtrate iPr2PH (10 wt.% solution in hexane, 119 mg, 0.10 mmol) was added and the resulting mixture was stirred for 10 min. Removal of the volatiles under the vacuum resulted in an off-white residue, which was
washed with 5 mL of pentane and then dried. The desired product was isolated as a white powder (50 mg, 70% yield). $^1$H NMR (400 MHz, C$_6$D$_6$, $\delta$): 1.12-1.16 (m, CH$_3$, 24H), 1.22-1.28 (m, CH$_3$, 6H), 1.46-1.51 (m, CH$_3$, 6H), 2.40-2.48 (m, CH, 2H), 2.55-2.62 (m, CH, 4H), 4.99 (dm, $^1$J$_{P-H}$ = 340.0 Hz, PH, 1H), 6.64 (d, $^1$J$_{H-H}$ = 8.0 Hz, ArH, 2H), 6.89 (t, $^1$J$_{H-H}$ = 8.0 Hz, ArH, 1H). $^{13}$C{$^1$H} NMR (101 MHz, C$_6$D$_6$, $\delta$): 16.8 (s, CH$_3$), 18.0 (s, CH$_3$), 21.9 (d, $^1$J$_{P-C}$ = 5.1 Hz, CH$_3$), 22.4 (d, $^1$J$_{P-C}$ = 3.0 Hz, CH$_3$), 24.3 (d, $^1$J$_{P-C}$ = 23.2 Hz, CH), 30.5 (t, $^1$J$_{P-C}$ = 12.1 Hz, CH), 106.2 (t, $^1$J$_{P-C}$ = 7.1 Hz, ArC), 122.7 (q, $^1$J$_{P-C}$ = 324.2 Hz, CF$_3$), 131.1 (s, ArC), 137.7 (d, $^1$J$_{P-C}$ = 79.8 Hz, ArC), 166.0 (t, $^1$J$_{P-C}$ = 5.1 Hz, ArC). $^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_6$, $\delta$): 1.1 (t, $^1$J$_{P-P}$ = 32.4 Hz, $^1$P$_{Pr}$PH, 1P), 197.8 (d, $^1$J$_{P-P}$ = 32.4 Hz, OP$^3$Pr$_2$, 2P). Anal. Caled for C$_{25}$H$_{46}$O$_5$F$_3$P$_3$SPd: C, 41.99; H, 6.48. Found: C, 42.26; H, 6.39.

**Synthesis of [{2,6-(Pe2PO)2C$_6$H$_3$}Pd(Pe2PH)]$^+$[OTf]$^-$ (7c-OTf).** This compound was prepared in 49% yield by a procedure similar to that used for 7b-OTf. $^1$H NMR (400 MHz, C$_6$D$_6$, $\delta$): 1.37-2.20 (m, CH$_2$, 46H), 2.54-2.57 (m, CH$_2$, 2H), 2.70-2.74 (m, CH, 2H), 2.94-3.00 (m, CH, 4H), 5.10 (dm, $^1$J$_{P-H}$ = 342.8 Hz, PH, 1H), 6.70 (dd, $^1$J$_{H-H}$ = 8.0 Hz, $^1$J$_{H-H}$ = 2.0 Hz, ArH, 2H), 6.90 (t, $^1$J$_{H-H}$ = 8.0 Hz, ArH, 1H). $^{13}$C{$^1$H} NMR (101 MHz, C$_6$D$_6$, $\delta$): 26.0 (d, $^1$J$_{P-C}$ = 11.2 Hz, CH$_2$), 26.2 (t, $^1$J$_{P-C}$ = 4.8 Hz, CH$_2$), 26.6 (d, $^1$J$_{P-C}$ = 8.1 Hz, CH$_2$), 26.9 (s, CH$_2$), 28.4 (s, CH$_2$), 30.4 (s, CH$_2$), 33.3 (d, $^1$J$_{P-C}$ = 6.1 Hz, CH$_2$), 34.5 (d, $^1$J$_{P-C}$ = 4.9 Hz, CH$_2$), 34.8 (d, $^1$J$_{P-C}$ = 26.4 Hz, CH), 41.5 (t, $^1$J$_{P-C}$ = 14.1 Hz, CH), 106.2 (t, $^1$J$_{P-C}$ = 6.5 Hz, ArC), 122.5 (q, $^1$J$_{P-C}$ = 324.0 Hz, CF$_3$), 130.8 (s, ArC), 137.8 (d, $^1$J$_{P-C}$ = 80.9 Hz, ArC), 166.3 (t, $^1$J$_{P-C}$ = 3.4 Hz, ArC). $^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_6$, $\delta$): -4.7 (t,
\( J_{P-P} = 30.2 \text{ Hz, } ^3\text{Pe}_2\text{PH, } 1P \), 186.2 (d, \( J_{P-P} = 30.2 \text{ Hz, } OP^2\text{Pe}_2, 2P \)). Anal. Calcd for C_{37}H_{58}O_{3}F_{3}P_{3}SP_{d}: C, 51.01%; H, 6.71. Found: C, 51.29%; H, 6.85.

**Synthesis of [2,6-(\text{Bu}_2\text{PO})_2\text{C}_6\text{H}_3]\text{PdB(cat)}_2 (6a).** Under an argon atmosphere, HBcat (3.23 mL, 30 mmol) was added slowly to a solution of 1a (200 mg, 0.40 mmol) in 10 mL of toluene. The mixture was first stirred at room temperature for 30 min and then concentrated under the vacuum. The resulting white solid was washed with 30 mL of pentane, followed by extraction with 20 mL of diethyl ether. Evaporation of the solvent resulted in a white solid, which was kept under a dynamic vacuum for at least 24 h. The solid was then dissolved in 3 mL of toluene and layered with 6 mL of diethyl ether, at which point gas evolution was noted. After standing for 1 h, the volatiles were removed under the vacuum. The desired product was further purified by recrystallization in benzene at room temperature to provide a white solid (60 mg, 21% yield). \(^1\text{H} \text{NMR (400 MHz, C}_6\text{D}_6, \delta): 1.15 (t, J_{P-H} = 8.0 \text{ Hz, CH}_3, 36\text{H}), 6.43 (d, J_{H-H} = 8.0 \text{ Hz, ArH}, 2\text{H}), 6.74 (t, J_{H-H} = 8.0 \text{ Hz, ArH}, 1\text{H}), 6.81-6.85 (m, ArH, 4\text{H}), 6.89-6.93 (m, ArH, 4\text{H}). \(^{13}\text{C} \{^{1}\text{H}\} \text{NMR (101 MHz, C}_6\text{D}_6, \delta): 27.3 (t, J_{P-C} = 3.8 \text{ Hz, CH}_3), 39.8 (t, J_{P-C} = 7.8 \text{ Hz, C(CH}_3)_3), 106.6 (t, J_{P-C} = 6.1 \text{ Hz, ArC}), 111.0 (s, ArC), 112.6 (s, ArC), 119.4 (s, ArC), 122.9 (s, ArC), 129.5 (s, ArC), 148.2 (t, J_{P-C} = 11.1 \text{ Hz, ArC}), 151.7 (s, ArC), 167.3 (t, J_{P-C} = 5.1 \text{ Hz, ArC}). \(^{31}\text{P} \{^{1}\text{H}\} \text{NMR (162 MHz, C}_6\text{D}_6, \delta): 192.2 (s). \(^{11}\text{B} \{^{1}\text{H}\} \text{NMR (128 MHz, C}_6\text{D}_6, \delta): 4.4 (s). \text{ Anal. Calcd for C}_{34}\text{H}_{47}\text{BO}_6\text{P}_2\text{Pd: C, 55.87; H, 6.48. Found: C, 57.74; H, 6.63.} \text{ The elemental analysis data are better matched with those calculated for C}_{34}\text{H}_{47}\text{BO}_6\text{P}_2\text{Pd} \cdot 0.5\text{C}_6\text{H}_6 (C, 57.72; H, 6.54).
Synthesis of [2,6-(\textit{i}Pr\text{2}PO)\textsubscript{2}C\textsubscript{6}H\textsubscript{3}]PdB(cat)\textsubscript{2} (6b). Under an argon atmosphere, HBcat (27 \(\mu\)L, 0.25 mmol) was added to a solution of 1b (100 mg, 0.22 mmol) in 10 mL of toluene. The mixture was stirred at room temperature for 12 h before subjected to prolonged evacuation (12 h). The residue was washed with 10 mL of pentane and then treated with 1 mL of benzene. The resulting mixture was filtered through a pipette filled with Celite and the filtrate was kept at room temperature. Upon standing for 24 h, the product precipitated out of the solution as colorless crystals (25 mg, 17\% yield). \textsuperscript{1}H NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}, \(\delta\)): 0.89-0.96 (m, CH\textsubscript{3}, 12H), 0.99-1.05 (m, CH\textsubscript{3}, 12H), 2.11-2.18 (m, CH, 4H), 6.49 (d, \(J_{H-H} = 8.0\) Hz, ArH, 2H), 6.75 (t, \(J_{H-H} = 8.0\) Hz, ArH, 1H), 6.77-6.81 (m, ArH, 4H), 6.98-7.01 (m, ArH, 4H). \textsuperscript{31}P{\textsuperscript{1}H} NMR (162 MHz, C\textsubscript{6}D\textsubscript{6}, \(\delta\)): 186.8 (s). \textsuperscript{11}B{\textsuperscript{1}H} NMR (128 MHz, C\textsubscript{6}D\textsubscript{6}, \(\delta\)): 4.4 (s). Anal. Calcd for C\textsubscript{30}H\textsubscript{39}BO\textsubscript{6}P\textsubscript{2}Pd: C, 53.40; H, 5.82. Found: C, 53.13; H, 5.97.

Synthesis of [2,6-(\textit{c}Pe\text{2}PO)\textsubscript{2}C\textsubscript{6}H\textsubscript{3}]PdB(cat)\textsubscript{2} (6c). This compound was prepared by a procedure similar to that used for 6b. \textsuperscript{1}H NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}, \(\delta\)): 1.32-1.39 (m, CH\textsubscript{2}, 8H), 1.53-1.86 (m, CH\textsubscript{2}, 24H), 2.33-2.39 (m, CH\textsubscript{2}, 4H), 6.54 (d, \(J_{H-H} = 8.0\) Hz, ArH, 2H), 6.72-6.75 (m, ArH, 2H), 6.80 (t, \(J_{H-H} = 8.0\) Hz, ArH, 1H), 6.97-6.99 (m, ArH, 4H). \textsuperscript{31}P{\textsuperscript{1}H} NMR (162 MHz, C\textsubscript{6}D\textsubscript{6}, \(\delta\)): 179.7 (s).

Synthesis of [2,6-(\textit{c}Pe\text{2}PO)\textsubscript{2}C\textsubscript{6}H\textsubscript{3}]PdBcat (11c). Under an argon atmosphere, catecholborane (10 \(\mu\)L, 0.10 mmol) was added to a toluene (2 mL) solution of 1c (50 mg, 0.09 mmol). The reaction mixture was stirred at room temperature for 2 h. The volatiles were removed under vacuum and the residue was extracted with diethyl ether (10 mL).
followed by a filtration through glass fiber filter paper. The filtrate was kept under vacuum until the volume was reduced to 5 mL. At this stage, crystals of 11c were observed around the wall of the flask. However, evaporation of the solvent resulted in a white solid (30 mg), which turned out to be a mixture of 11c (74 %) and 6c (26 %). 

\[^{1}\text{H}\] NMR (400 MHz, C\(_{6}\)D\(_{6}\), \(\delta\)): 1.26-1.40 (m, CH\(_2\), 8H), 1.60-1.76 (m, CH\(_2\), 20H), 1.88-1.97 (m, CH\(_2\), 4H), 2.26-2.36 (m, CH\(_2\), 4H), 6.83-6.85 (m, ArH, 4H), 6.94 (d, \(J_{\text{H-H}} = 8.0\) Hz, ArH, 2H), 7.06 (t, \(J_{\text{H-H}} = 8.0\) Hz, ArH, 1H), 7.26-7.28 (m, ArH, 4H). 

\[^{31}\text{P}\{^{1}\text{H}\}\] NMR (162 MHz, C\(_{6}\)D\(_{6}\), \(\delta\)): 193.4 (s).

**Procedures for the Catalytic Reduction of CO\(_2\) with Catecholborane:**  
*Method A:* Under an argon atmosphere, to a solution of catalyst (0.025 mmol) and hexamethyldisilane (0.05 mmol) in C\(_{6}\)D\(_{6}\) (2 mL), was added catecholborane (2.5 mmol) followed by the incorporation of CO\(_2\) into the mixture through freeze-pump-thaw method. The reaction was stirred at room temperature under an atmospheric pressure of CO\(_2\), and the progress of the reaction was monitored by \[^{1}\text{H}\] NMR spectroscopy.  

*Method B:* Under an argon atmosphere, catalyst (0.025 mmol) and hexamethyldisilane (0.05 mmol) were dissolved in C\(_{6}\)D\(_{6}\) (2 mL) followed by the addition of CO\(_2\) into the mixture through freeze-pump-thaw method. Under an atmospheric pressure of CO\(_2\), catecholborane (2.5 mmol) was added to the reaction mixture, which was further stirred at room temperature. The progress of the reaction was monitored by \[^{1}\text{H}\] NMR spectroscopy.
Procedure for Nickel-Catalyzed Hydroboration of Methyl Formate with Catecholborane: Under an argon atmosphere, to a solution of 12b (10 mg, 0.025 mmol), methyl formate (49.1 μL, 0.5 mmol) and hexamethyldisilane (5.2 μL, 0.025 mmol) in C₆D₆ (0.5 mL), was added catecholborane (109 μL, 1.0 mmol). The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by ¹H NMR spectroscopy.
Chapter 4

Synthesis and Reactivity of Asymmetric Nickel POCOP-Pincer Complexes
4.1 Introduction

During the past several decades, tremendous advancements in homogeneous catalysis have been made through the use of transition metal pincer complexes.\textsuperscript{1a, 2a} One attractive application of these complexes has been in the area of asymmetric transformations, where the chirality in the products can be potentially introduced through the catalysis of chiral pincer complexes.\textsuperscript{2} Towards this goal, a number of chiral pincer complexes have been synthesized and their catalytic activities have been studied specifically for organic transformations such as asymmetric addition of phosphines to $\alpha$, $\beta$-unsaturated compounds,\textsuperscript{2c, 2e} hydrogenation of ketones and imines,\textsuperscript{2d} aldol-type reactions,\textsuperscript{2f} aza-Morita-Baylis-Hilman reaction of acrylonitrile,\textsuperscript{2g} and allylation of aldehydes and sulfonimides.\textsuperscript{2h} These pincer complexes have been regarded as versatile chiral catalysts, largely due to the fact that the chiral center can be incorporated in different regions of the ligand (Figure 1).\textsuperscript{2h}

![Figure 1. Pincer Complexes with Possible Chiral Centers](image)


Additionally, due to the presence of two metallocycles, pincer complexes are known to be rigid and the substituents on the pincer backbone have relatively fixed orientations, hence these complexes should have well-defined reactive sites,\(^3\) and make it convenient to investigate the substrate-complex interaction for a better understanding of the transition states in asymmetric reactions. Although introducing chirality at various parts of pincer complexes is possible, the vast majority of asymmetric pincer complexes have been prepared with chiral center attached to the pincer backbone. Yet, if pincer ligands with chiral-donors (D\(^1\)* and D\(^3\)*) such as phosphorous are employed, it is expected to transfer the asymmetry more effectively into the products, as the chiral information is located in the close proximity of the reactive metal site. In the literature there are several \(P\)-stereogenic PCP-pincer ligated metal complexes that have been used in asymmetric reactions;\(^4\) however, no chiral pincer complex of nickel has been reported yet. As our group focused our studies on late transition metal complexes, we became particularly interested in the synthesis of \(P\)-stereogenic chiral nickel pincer complexes and their reactivity and selectivity in asymmetric synthesis.

Recently, our research group has discovered the coupling of aldehydes with acetonitrile using a bis(phosphinite)-ligated nickel pincer cyanomethyl complex as the catalyst (Scheme 1).\(^5\)

---


The Zargarian group has reported that similar nickel pincer complexes are excellent catalysts for the hydroamination of acrylonitrile under mild conditions (Scheme 2).\(^6\)

In both catalytic systems, a new stereogenic center has been created in final nitrile products. These types of nitrile derivatives are useful precursors to nitrogen-based ligands as well as important building blocks for pharmaceutical synthesis. Therefore, developing enantioselective methods to synthesize the chiral versions of these molecules are highly desirable. Because bis(phosphinite)-based pincer (or POCOP-pincer) complexes of nickel are effective for many catalytic processes including the two illustrated in scheme 1 and 2, we wished to synthesize \(P\)-stereogenic bis(phosphinite) nickel pincer complexes as depicted in Figure 2 and study their reactivity and selectivity.

We also intended to use these complexes to probe the transition-state structures of several elementary reactions that are key to many catalytic processes.

![Figure 2. P-stereogenic Nickel Pincer Complexes](image)

### 4.2 Synthesis of Asymmetric Nickel POCOP-Pincer Complexes

One of the challenges associated with chiral trivalent phosphines is the configurational stability of the phosphorous center. There are many studies concerning pyramidal inversion of phosphines at elevated temperatures.\(^7\) Several study have also been done on the relation of inversion energy barrier with electronic and steric nature of the \(P\)-substituents;\(^8\) however, little has been researched on phosphinites where one of the substituents on phosphorous is oxygen. It has been proposed in general the presence of oxygen-based substituents increases the inversion barrier.\(^9\) Several thermally stable chiral phosphinites have been reported and used in asymmetric reactions,\(^10\) though there are also examples where complete loss of chirality has been observed at elevated temperatures.

---


\(^10\) *P-Stereogenic Ligands in Enantioselective Catalysis*, A. Grabulosa, RSC: Cambridge, UK, 2011.
temperatures.\textsuperscript{11} To prevent the possibility of \(P\)-center inversion, we decided to use \textit{tert}-butyl group as one of the phosphinite substituents, as bulky groups typically result in higher inversion barrier. Phenyl group was chosen as the other substituent because phosphinite ligands bearing aromatic groups often result in interesting reactivity for the metal complexes.\textsuperscript{12} In addition, the corresponding chlorophosphines are commercially available, therefore, convenient to start with.

To synthesize the desired bis(phosphinite)-ligated nickel complexes two routes can be followed: (A) starting with the chiral chlorophosphines and synthesize enantiomerically pure ligands followed by complexation, and (B) using the mixture of both isomers of the chlorophosphines to synthesize the complexes first, and then separating the diastereomers and the enantiomers (Scheme 3). Although route A seems less tedious, we decided to focus on route B because free chiral chlorophosphines are optically unstable at room temperature,\textsuperscript{13} which can result enantiomerically impure ligand. On the other hand, upon coordination to metals, phosphinates are expected to be configurationally stable even at elevated temperatures, hence easy to handle with.

First, the bis(phosphinite)-based pincer ligand (1) was synthesized by deprotonating resorcinol using sodium hydride followed by refluxing the mixture with the commercially available \textit{racemic} chloro(\textit{tert}-butyl)phenyl phosphine (Scheme 4). The synthesized ligand was characterized by \(^{31}\text{P}\{\text{\textsuperscript{1}H}\}\) and \(^{1}\text{H}\) NMR spectroscopy. In \(^{31}\text{P}\{\text{\textsuperscript{1}H}\}\) NMR spectrum two signals were found at 127.5 and 127.6 ppm with a 1:1 ratio,

\begin{itemize}
\end{itemize}
suggesting the formation of both racemic and meso isomers. The $^1$H NMR spectrum showed a doublet resonance at 1.03 ppm with a coupling constant of 12 Hz, indicating a phosphorous-coupled tert-butyl group.

After successful isolation of 1, the corresponding nickel chloride complex (2) was synthesized through cyclometallation with NiCl₂. In the $^1$H NMR spectrum the appearance of triplet resonances at ~1.3 ppm for the tBu groups is a result of virtual coupling by two phosphorous atoms that are trans to each other, which confirms the formation of a pincer complex. As in case of the ligand, for the complex 2, two resonances (157.9 & 158.8 ppm) with a 1:1 ratio were observed from $^{31}$P{$^1$H} NMR.
implying the formation of both racemic (2-rac) and meso (2-meso) isomers of the nickel pincer complex. At that stage it was not possible to ascertain which resonance is for which isomer.

After isolation of the chloride complexes (2), the next step was the separation of racemic isomer (2-rac) from the mixture, which was accomplished via repeated recrystallization by layering pentane to the concentrated methylene chloride solution (Scheme 5).
The absolute configuration was established by X-ray crystallography (Figure 3). Additionally, the complex was characterized by $^1$H, $^{31}$P{$^1$H}, $^{13}$C{$^1$H} NMR spectroscopy and elemental analysis. From the filtrates a meso-enriched sample ($2$-rac : $2$-meso = 1:10) was obtained. In $^{31}$P{$^1$H} NMR spectrum, the resonance for $2$-rac is slightly more down field (158.8 ppm) than $2$-meso (157.9 ppm). The tert-butyl proton resonances for the racemic isomer are also more downfield shifted as compared to those of $2$-meso.

**Figure 3.** ORTEP drawing of rac-[(2,6-$(t$Bu)(Ph)PO)$_2$C$_6$H$_3$]NiCl ($2$-rac) at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ni–Cl 2.2087(6), Ni–C(1) 1.895(2), Ni–P(1) 2.1774(6), Ni–P(2) 2.1741(6), P(1)–Ni–P(2) 162.46(3), C(1)–Ni–Cl 179.27(7), C(1)–Ni–P(1) 81.88(6), C(1)–Ni–P(2) 81.43(6).

### 4.3 Attempted Separation of Enantiomers

As planned, the next step was transforming the racemic isomers to diastereomers using another chiral ancillary ligand. We chose chiral carboxylates as the auxiliary due to their commercial availability. In addition, bis(phosphinite)-based nickel pincer carboxylate complexes can be readily synthesized and are generally air stable. To
prepare the carboxylate diastereomers, first we replaced the chloride from racemic complex with a triflate group using silver triflate followed by the substitution with sodium (S)-acetylmandelate (Scheme 6). In $^{31}$P{$^1$H} NMR spectrum, the appearance of two peaks at 158.8 and 159.9 ppm with a 1:1 ratio indicated successful conversion of the enantiomers to the diastereomers of acetylmandelates (4a & 4b). Unfortunately no separation was achieved despite the trials of different solvents and solvent combinations. As the use of bulky auxiliaries could help in separation, we prepared the gibberellate derivative (5) following a similar synthetic route. Once again, the appearance of two resonances at 160.1 and 160.4 ppm in $^{31}$P{$^1$H} NMR supports the formation of diastereomers (5a & 5b). However, no separation has been achieved through recrystallization. Our next attempt to separate these diastereomers will be the use of chiral HPLC.

[Scheme 6]

$^1$H NMR spectra of diastereomers of acetylmandelates (4a & 4b) and gibberellate (5a & 5b).
4.4 Reactivity of Racemic and Meso Complexes

Bis(phosphinite) ligated pincer complexes are believed to be rigid under ambient conditions; however, under some reaction conditions the dissociation of phosphinites arm cannot be ruled out. For a symmetric bis(phosphinite)-based pincer complex, it is highly challenging to know (from an experimental point of view) whether or not such an event takes place because this process does not result in the formation of a new species. In contrast, if the pyramidal inversion proceeds rapidly following the dissociation of phosphinite arm, re-association of the ligand arm would interconvert 2-rac and 2-meso. To test the configurational stability of the nickel chloride complex, a toluene solution of 2-rac-enriched sample and another one of 2-meso-enriched sample were heated at 110°C for days. No change in the isomeric ratio was observed, suggesting that either there is no dissociation of phosphinite arm, or the ligand re-association followed dissociation is much faster than the epimerization at stereogenic phosphorous center.

Although enantiomerically pure P-stereogenic pincer complexes have been isolated before, synthesis and separation of both racemic and meso isomers in a single metal system have never been reported. Having the same ligand backbone and identical substituents on each phosphorous donor, it is expected that the electronic nature of both the racemic and meso isomer should be same; however, the spatial arrangements of P-substituents are different (Figure 4). We became interested to know whether this variation in steric environment around the metal center would lead to any difference in reactivity or not.
4.4.1 Substitution Reaction with tert-Butoxide

Substitution reactions are one of the most fundamental reactions in transition metal chemistry. We first focused our study on the substitution reaction with a 1:1 mixture of 2-rac and 2-meso by using potassium tert-butoxide as the nucleophile. Before performing the experiment with the isomeric mixture of 2, we performed a reaction of 2-rac with potassium tert-butoxide (Scheme 7). Formation of 6-rac was confirmed by different spectroscopic methods; however, attempted isolation resulted in a mixture of unknown pincer species.

![Scheme 7](image)

To monitor the progress of the reaction, we chose $^{31}\text{P-}{^1}\text{H}$ NMR, as isomers of 2 and 6 could be unambiguously assigned. When potassium tert-butoxide was mixed with
2 (2-rac : 2-meso = 1:1) in C₆D₆ at room temperature, interestingly, a faster disappearance of the meso isomer was observed as compared to the racemic isomer with concomitant faster appearance of the meso tert-butoxide complex versus the racemic one (Scheme 8).

This type of reactivity difference between diastereomeric transition metal complexes has been rarely reported in the literature. For square-planar transition metal complexes the incoming nucleophile approaches from the top or bottom faces of the square plane. For 2-rac, one tert-butyl and one phenyl group facing up or down of the square-plane, resulting identical steric environment for the top and bottom faces. In contrast, for the meso isomer, two faces of the square plane are different (Figure 5). Two
tert-butyl groups face towards one direction from the square plane whereas both phenyl groups point to the opposite direction. As tert-butyl group is more bulky than the phenyl group, the incoming nucleophile will favor the less hindered site, i.e., the face having two phenyl groups. Therefore, the approach of the tert-butoxide group from the face consisting two phenyl groups is associated with a lower kinetic energy barrier resulting in a faster reaction with the meso isomer.

![Figure 5. Face-Selective Approach of the Incoming Ligand](image)

4.4.2 Decarboxylation of Formate Complexes

Decarboxylation of metal formate complexes is a crucial step in many catalytic processes such as transfer hydrogenation and formic acid decomposition.\(^\text{14}\) Based on theoretical calculations, the hydrogen from the formate moiety must reach the metal prior to the decarboxylation. In addition, kinetic study has shown that these processes have negative entropies of activation, which supports a more crowded behavior of the transition state structure relative to the starting formate complex.\(^\text{15}\) For hydride transfer


from carbon to metal, a vacant coordination site is needed, and in the case of square planar complexes, it is presumably at the axial position (Figure 6).

![Figure 6. Preferred Transition State of Decarboxylation](image)

Although it has been proposed that decarboxylation is much faster than ligand dissociation, a pathway consisting ligand dissociation followed by an equatorial approach of the hydride cannot be ruled out. If the later scenario were true, we would expect no reactivity difference for the racemic and meso isomers as the steric profiles for both are the same when the incoming group approaches from either equatorial site. The formate complexes (7) were synthesized from 1:1 mixture of 2-rac and 2-meso. No change in isomeric ratio was observed, confirming no epimerization under the reaction conditions. However, the formation of a small amount of nickel hydride was noticed from the NMR spectra. In a separate experiment, starting from 3-rac, racemic formate complex (7-rac) was synthesized (Scheme 9) and characterized by $^{31}P\{^1H\}$, $^1H$, $^{13}C\{^1H\}$ NMR spectroscopy and elemental analysis. The absolute configuration was further established by X-ray crystallography.

---

Heating the mixture of 1:1 formate complexes in benzene for days did not result in any change in the diastereomeric ratio, suggesting no dissociation of phosphinite arms. In addition, formation of hydride complexes was not observed, which was not surprising as the reverse reaction (i.e., CO₂ insertion into metal hydride) is a thermodynamically more favorable process. To drive the decarboxylation of the formate to hydride, we performed the reaction in solid state under vacuum. When 7-rac was kept at 60°C under evacuation, formation of hydride complex was observed (Scheme 10), as evidenced by disappearance of the resonance at 8.7 ppm in ¹H NMR and the formation of a triplet resonance at -7.1 ppm (Jₚ-H = 52 Hz).

---

To compare the reactivity between *racemic* and *meso* formate complexes, we heated a 1:1 mixture of *7-rac* and *7-meso* (solid sample) under vacuum at 60°C. After 30 minutes, a higher conversion to *meso* hydride complex (*8-meso*) than *racemic* was observed (Scheme 11). This observation of a faster reaction for the *meso* isomer than the *racemic* isomer is consistent with our hypothesis that the hydride approaches from the less hindered axial position.

**Scheme 11**

\[
\begin{array}{cc}
\text{O-P('Bu/Ph)} & \text{O-P('Bu/Ph)} \\
\text{Ni-OCHO} & \text{Ni-H} \\
\text{7-rac : 7-meso = 1 : 1} & \text{8-rac : 8-meso}
\end{array}
\]

4.5 Conclusions

*P*-stereogenic bis(phosphinite)-ligated nickel pincer chloride complexes were synthesized and the *racemic* and *meso* isomers were separated through repeated recrystallization. Under the reaction conditions examined, these diastereomers did not interconvert, suggesting either dissociation of the phosphinite arm never happens or dissociation followed by re-association is faster than pyramidal inversion at the stereogenic phosphorous center. Reactivity of *P*-stereogenic nickel pincer chlorides
towards ligand substitution reaction with potassium tert-butoxide was investigated. the meso isomer showed a higher reactivity than the racemic isomer, which provides a direct experimental evidence for an axial approach of the incoming ligand. Decarboxylation of the formate complexes to the corresponding hydrides was also investigated. A similar faster CO$_2$ deinsertion for the meso isomer suggests pre-coordination of the hydride (-OCHO) to the metal from the axial position.

4.6 Experimental Section

**Synthesis of 1,3-[(t-Bu)(Ph)PO]$_2$C$_6$H$_4$ (1).** Under an argon atmosphere, a suspension of sodium hydride (252 mg, 10.5 mmol) in 20 mL of THF was added slowly to a solution of resorcinol (550 mg, 5.0 mmol) in 40 mL of THF. The resulting mixture was refluxed for 6 h. After cooling to room temperature, a solution of PhP(t-Bu)Cl (1.98 mL, 10.5 mmol) in 20 mL of THF was added, and the mixture was refluxed for another 6 h. The volatiles were removed under reduced pressure and the residue was extracted with pentane (60 mL first and then 20 mL). Evaporation of pentane yielded the product as a light yellow oil (1.86 g, 85 % yield). $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 1.03 (d, $J_{P-H} = 13.2$ Hz, $CH_3$, 18H), 6.70 (d, $J_{H-H} = 8.4$ Hz, ArH, 2H), 6.86 (s, ArH, 1H), 7.06 (t, $J_{H-H} = 8.4$ Hz, ArH, 1H), 7.35-7.38 (m, ArH, 6H), 7.49-7.52 (m, ArH, 4H). $^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$, $\delta$): 25.0 (d, $J_{P-C} = 16.2$ Hz, CH$_3$), 33.4 (d, $J_{P-C} = 13.1$ Hz, C(CH$_3$)$_3$), 109.56 (t, $J_{P-C} = 9.1$ Hz, ArC$^2$ of one isomer), 109.62 (t, $J_{P-C} = 9.1$ Hz, ArC$^2$ of the other isomer), 112.3 (d, $J_{P-C} = 11.1$ Hz, ArC), 127.9 (d, $J_{P-C} = 7.1$ Hz, ArC), 129.4 (s, ArC), 129.8 (s, ArC), 130.4 (d, $J_{P-C} = 22.2$ Hz, ArC), 138.5 (d, $J_{P-C} = 29.3$ Hz, ArC), 159.0 (d, $J_{P-C} = 9.1$ Hz, ArC). $^{31}$P{$^1$H} NMR (162 MHz, CDCl$_3$, $\delta$): 127.5 (s), 127.6 (s).
Synthesis of [(2,6-\((t\text{-}Bu)(Ph)PO)\)\(2\text{C}_6\text{H}_3\)]\(\text{NiCl}\) (2). Under an argon atmosphere, 1 (1.84 g, 4.2 mmol) and anhydrous \(\text{NiCl}_2\) (545 mg, 4.2 mmol) were mixed with 40 mL of toluene. The resulting mixture was heated to reflux for 36 h. Removal of the solvent under vacuum gave a yellow solid, which was washed with cold pentane (10 mL). After drying, the desired product (2-\textit{rac} : 2-\textit{meso} = 1 : 1) was isolated as a yellow powder (1.58 g, 71 % yield).

\textit{rac-}\[(2,6-(t\text{-}Bu)(Ph)PO)\]2\(\text{C}_6\text{H}_3\)]\(\text{NiCl}\) (2-\textit{rac}). \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 1.30 (vt, \(J_{P-H} = 8.0\) Hz, \(CH_3\), 18H), 6.52 (d, \(J_{H-H} = 8.0\) Hz, Ar\(H\), 2H), 6.99 (t, \(J_{H-H} = 8.0\) Hz, Ar\(H\), 1H), 7.48-7.50 (m, Ar\(H\), 6H), 8.13-8.15 (m, Ar\(H\), 4H). \(^{13}\)C\{\(^1\)H\} NMR (101 MHz, CDCl\(_3\), \(\delta\)): 25.4 (s, \(CH_3\)), 37.0 (t, \(J_{P-C} = 13.0\) Hz, \(C(CH_3)_3\)), 106.1 (t, \(J_{P-C} = 6.1\) Hz, ArC), 124.3 (t, \(J_{P-C} = 22.3\) Hz, ArC), 128.3 (t, \(J_{P-C} = 4.5\) Hz, ArC), 129.1 (s, ArC), 130.9 (t, \(J_{P-C} = 16.8\) Hz, ArC), 131.1 (s, ArC), 131.8 (t, \(J_{P-C} = 6.2\) Hz, ArC), 167.7 (t, \(J_{P-C} = 10.4\) Hz, ArC). \(^{31}\)P\{\(^1\)H\} NMR (162 MHz, CDCl\(_3\), \(\delta\)): 158.9 (s).

\textit{meso-}\[(2,6-(t\text{-}Bu)(Ph)PO)\]2\(\text{C}_6\text{H}_3\)]\(\text{NiCl}\) (2-\textit{meso}). \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 1.37 (vt, \(J_{P-H} = 8.0\) Hz, \(CH_3\), 18H), 6.53 (d, \(J_{H-H} = 8.0\) Hz, Ar\(H\), 2H), 7.00 (t, \(J_{H-H} = 8.0\) Hz, Ar\(H\), 1H), 7.42-7.46 (m, Ar\(H\), 6H), 8.10-8.12 (m, Ar\(H\), 4H). \(^{13}\)C\{\(^1\)H\} NMR (101 MHz, CDCl\(_3\), \(\delta\)): 25.5 (t, \(J_{P-C} = 2.7\) Hz, \(CH_3\)), 37.5 (t, \(J_{P-C} = 12.5\) Hz, \(C(CH_3)_3\)), 105.9 (t, \(J_{P-C} = 6.1\) Hz, ArC), 124.2 (t, \(J_{P-C} = 22.2\) Hz, ArC), 128.2 (t, \(J_{P-C} = 4.8\) Hz, ArC), 129.1 (s, ArC), 130.7 (t, \(J_{P-C} = 17.5\) Hz, ArC), 131.1 (s, ArC), 131.7 (t, \(J_{P-C} = 6.3\) Hz, ArC), 167.8 (t, \(J_{P-C} = 10.6\) Hz, ArC). \(^{31}\)P\{\(^1\)H\} NMR (162 MHz, CDCl\(_3\), \(\delta\)): 158.0 (s).

Synthesis of \textit{rac-}\[(2,6-(t\text{-}Bu)(Ph)PO)\]2\(\text{C}_6\text{H}_3\)]\(\text{NiOTf}\) (3-\textit{rac}). Under an argon atmosphere, AgOTf (308 mg, 1.2 mmol) was added to a solution of 2-\textit{rac} (532 mg, 1.0
mmol) in 25 mL of CH₂Cl₂. The reaction mixture was stirred at room temperature in dark for 2 h before being filtered through Celite. Removal the solvent from the filtrate yielded the product as a yellow solid (520 mg, 81 % yield). ¹H NMR (400 MHz, CDCl₃, δ): 1.32 (vt, Jₚ-H = 8.0 Hz, CH₃, 18H), 6.48 (d, Jₕ-H = 8.0 Hz, ArH, 2H), 7.03 (t, Jₕ-H = 8.0 Hz, ArH, 1H), 7.53-7.57 (m, ArH, 6H), 8.00-8.03 (m, ArH, 4H). ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 25.5 (t, Jₚ-C = 3.2 Hz, CH₃), 37.2 (t, Jₚ-C = 12.4 Hz, C(CH₃)₃), 106.7 (t, Jₚ-C = 5.9 Hz, ArC), 112.3 (t, Jₚ-C = 22.0 Hz, ArC), 119.2 (q, Jₚ-C = 319.8 Hz, CF₃), 128.8 (t, Jₚ-C = 4.9 Hz, ArC), 129.7 (t, Jₚ-C = 17.2 Hz, ArC), 130.3 (s, ArC), 131.4 (t, Jₚ-C = 6.8 Hz, ArC), 131.8 (s, ArC), 167.9 (t, Jₚ-C = 9.2 Hz, ArC). ³¹P{¹H} NMR (162 MHz, CDCl₃, δ): 160.5 (s). Anal. Calcd for C₂₇H₃₁O₅F₃P₂SnI: C, 50.26;; H, 4.84. Found: C, 50.50;; H, 4.68.

Synthesis of rac-[(2,6-(t-Bu)(Ph)PO)₂C₆H₃]NiO(t-Bu) (6-rac). To a J. Young NMR tube containing a solution of 2-rac (13.3 mg, 0.025 mmol) in C₆D₆ (0.5 mL) was added potassium tert-butoxide (5.6 mg, 0.050 mmol). The color of the reaction mixture changed gradually from yellow to red. The conversion of 2-rac to 6-rac was complete within 12 h, as confirmed by ¹H and ³¹P{¹H} NMR spectroscopy. Attempts to isolate 6-rac in the solid form led to decomposition of the product, mainly due to rapid hydrolysis by adventitious water. ¹H NMR (400 MHz, C₆D₆, δ): 1.11 (s, OC(CH₃)₃, 9H), 1.34 (vt, Jₚ-H = 8.0 Hz, PC(CH₃)₃, 18H), 6.60 (d, Jₕ-H = 8.0 Hz, ArH, 2H), 6.93 (t, Jₕ-H = 8.0 Hz, ArH, 1H), 7.11-7.15 (m, ArH, 6H), 8.15-8.19 (m, ArH, 4H). ¹³C{¹H} NMR (101 MHz, C₆D₆, δ): 26.6 (s, PC(CH₃)₃), 35.9 (s, OC(CH₃)₃), 37.1 (t, Jₚ-C = 10.1 Hz, PC(CH₃)₃), 69.1 (s, OC(CH₃)₃), 105.7 (t, Jₚ-C = 6.0 Hz, ArC), 122.7 (t, Jₚ-C = 25.3 Hz, ArC), 128.6 (s, ArC), 130.6 (s, ArC), 132.3 (t, Jₚ-C = 5.6 Hz, ArC), 133.7 (t, Jₚ-C = 14.1 Hz, ArC), 168.3
(t, \( J_{P-C} = 10.1 \) Hz, ArC); one resonance was obscured by solvent resonances. \(^{31}\)P\(^{1}\)H\) NMR (162 MHz, C\(_6\)D\(_6\), \( \delta \)): 148.5 (s).

**Synthesis of rac-[(2,6-(t-Bu)(Ph)PO)\(_2\)C\(_6\)H\(_3\)]NiOCHO (7-rac).** Under an argon atmosphere, to a solution of 3-rac (400 mg, 0.62 mmol) in 40 mL of THF was added sodium formate (51 mg, 0.75 mmol). After stirring the mixture at room temperature for 1 h, the volatiles were removed under vacuum and the residue was extracted with pentane (40 mL first and then 20 mL). The combined pentane extracts were evaporated to dryness, providing the product as a yellow solid (244 mg, 73 % yield). \(^1\)H NMR (400 MHz, C\(_6\)D\(_6\), \( \delta \)): 1.20 (vt, \( J_{P-H} = 8.0 \) Hz, C\(_H\)\(_3\), 18H), 6.59 (d, \( J_{H-H} = 8.0 \) Hz, Ar\(_H\), 2H), 6.87 (t, \( J_{H-H} = 8.0 \) Hz, Ar\(_H\), 1H), 6.97-7.04 (m, Ar\(_H\), 6H), 8.03-8.07 (m, Ar\(_H\), 4H), 8.65 (s, OCHO, 1H). \(^{13}\)C\(^{1}\)H\) NMR (101 MHz, C\(_6\)D\(_6\), \( \delta \)): 24.9 (t, \( J_{P-C} = 3.0 \) Hz, CH\(_3\)), 36.1 (t, \( J_{P-C} = 12.6 \) Hz, C(CH\(_3\))\(_3\)), 106.7 (t, \( J_{P-C} = 5.8 \) Hz, ArC), 120.9 (t, \( J_{P-C} = 23.2 \) Hz, ArC), 128.6 (t, \( J_{P-C} = 5.0 \) Hz, ArC), 129.6 (s, ArC), 131.2 (t, \( J_{P-C} = 16.2 \) Hz, ArC), 131.4 (s, ArC), 132.2 (t, \( J_{P-C} = 6.8 \) Hz, ArC), 168.2 (s, OCHO), 168.3 (t, \( J_{P-C} = 10.0 \) Hz, ArC). \(^{31}\)P\(^{1}\)H\) NMR (162 MHz, C\(_6\)D\(_6\), \( \delta \)): 160.0 (s). ATR-IR (solid): \( \nu_{C=O} = 1629 \) cm\(^{-1}\). Anal. Calcd for C\(_{27}\)H\(_{32}\)O\(_4\)P\(_2\)Ni: C, 59.92; H, 5.96. Found: C, 60.03; H, 6.01.

**Synthesis of [(2,6-(t-Bu)(Ph)PO)\(_2\)C\(_6\)H\(_3\)]NiOCHO (7-rac/7-meso = 1 : 1).** The 1 : 1 mixture of 7-rac/7-meso was prepared in 72% yield from 2-rac/2-meso by generating the triflate complex 3-rac/3-meso in situ followed by the addition of sodium formate. The work-up procedures were the same as those used for the purification of 7-rac. \(^1\)H NMR of 7-meso (400 MHz, C\(_6\)D\(_6\), \( \delta \)): 1.31 (vt, \( J_{P-H} = 7.6 \) Hz, CH\(_3\), 18H), 6.59 (d, \( J_{H-H} = 8.0 \) Hz, Ar\(_H\), 2H), 6.87 (t, \( J_{H-H} = 8.0 \) Hz, Ar\(_H\), 1H), 6.97-7.04 (m, Ar\(_H\), 6H), 8.03-8.07 (m, Ar\(_H\), 4H), 8.65 (s, OCHO, 1H). \(^{13}\)C\(^{1}\)H\) NMR of 7-meso (101 MHz, C\(_6\)D\(_6\), \( \delta \)): 24.8
(s, CH₃), 36.7 (t, J_P-C = 12.4 Hz, C(CH₃)₃), 106.5 (t, J_P-C = 5.8 Hz, ArC), 120.9 (t, J_P-C = 16.9 Hz, ArC), 129.6 (s, ArC), 131.2 (s, ArC), 131.4 (t, J_P-C = 16.2 Hz, ArC), 131.7 (t, J_P-C = 6.8 Hz, ArC), 168.4 (t, J_P-C = 10.0 Hz, ArC), 168.6 (s, OCHO); one resonance was obscured by solvent resonances. ³¹P{¹H} NMR of 7-meso (162 MHz, C₆D₆, δ): 158.7 (s).

**Ligand Substitution Reaction of 2 with tert-Butoxide.** In a J. Young NMR tube, the 1 : 1 mixture of 2-rac and 2-meso (13.3 mg, 0.025 mmol) was dissolved in 0.6 mL of C₆D₆, resulting in a yellow solution. Potassium tert-butoxide (5.6 mg, 0.050 mmol) was then added and mixed thoroughly with the solution. The progress of the reaction was monitored by ¹H and ³¹P{¹H} NMR spectroscopy.

**Decarboxylation of Nickel Formate Complex to Form Nickel Hydride Complex.** A J. Young NMR tube was loaded with a 1 : 1 mixture of nickel formate complex 7-rac and 7-meso (13.5 mg, 0.025 mmol), and then attached to a vacuum line. The sample was subjected to continuous evacuation (to remove any gases or volatiles that were generated) while being heated at 90 °C with an oil bath. After 30 min, the residue was dissolved in C₆D₆ (~ 0.5 mL) and the NMR spectra were recorded. Extended heating resulted in decomposition of the hydride species. Attempts to isolate nickel hydride 8-rac or a mixture of 8-rac and 8-meso in an analytically pure form failed due to instability of the hydride complex. ¹H NMR of 8-rac (400 MHz, C₆D₆, δ): –7.14 (t, J_P-H = 52.0 Hz, NiH, 1H), 1.14 (vt, J_P-H = 8.0 Hz, CH₃, 18H), 6.94 (d, J_H-H = 8.0 Hz, ArH, 2H), 7.04-7.11 (m, ArH, 7H), 8.08-8.13 (m, ArH, 4H). ¹³C{¹H} NMR of 8-rac (101 MHz, C₆D₆, δ): 25.7 (t, J_P-C = 3.8 Hz, CH₃), 35.3 (t, J_P-C = 14.8 Hz, C(CH₃)₃), 105.7 (t, J_P-C = 6.2 Hz, ArC), 129.4 (s, ArC), 130.8 (s, ArC), 132.6 (t, J_P-C = 18.2 Hz, ArC), 133.2 (t, J_P-C = 7.4
Hz, ArC), 141.7 (t, $J_{P-C} = 17.6$ Hz, ArC), 167.5 (t, $J_{P-C} = 10.6$ Hz, ArC); one resonance was obscured by solvent resonances. $^{31}$P{$^1$H} NMR of 8-rac (162 MHz, C$_6$D$_6$, δ): 193.8 (s). The hydride resonance of 8-meso (400 MHz, C$_6$D$_6$, δ): –7.21 (t, $J_{P-H} = 52.0$ Hz).

$^{31}$P{$^1$H} NMR of 8-meso (162 MHz, C$_6$D$_6$, δ): 193.3 (s).

**X-ray Structure Determination.** Single crystals of 2-rac were grown from slow evaporation of a saturated solution in CH$_2$Cl$_2$ at room temperature. Crystal data collection and refinement parameters are summarized in Table S1. Intensity data were collected at 150K on a Bruker SMART6000 CCD diffractometer using graphite-monochromated Cu Kα radiation, λ = 1.54178 Å. The data frames were processed using the program SAINT. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structures were solved by a combination of direct methods in SHELXTL and the difference Fourier technique and refined by full-matrix least-squares procedures. Non-hydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located directly or calculated and subsequently treated with a riding model. No solvent of crystallization is present in the lattice.
Chapter 5

Kinetic Study of Decarboxylation of Bis(phosphinite)-Ligated Nickel and Palladium Pincer Formate Complexes
5.1 Introduction

Decarboxylation of transition metal formate complexes to generate metal hydrides has been proposed as a key step in many catalytic transformations such as dehydrogenation of formic acid,\(^1\) transfer hydrogenation involving formic acid or formate ion,\(^2\) the water-gas shift reaction,\(^3\) and reductive dehalogenation of aryl halides with formate anion.\(^4\) For a better understanding of this particular reaction, a number of metal formate complexes have been synthesized and their reactivity towards decarboxylation has been investigated. The challenges encountered when studying this process include: (1) poor stability of metal formate complex or metal hydride complex or both and (2) reversibility of the process. It has been found that for most metal systems decarboxylation is reversible, and often the reverse reaction (i.e., the insertion of CO\(_2\) into metal hydride) is thermodynamically more favorable. For instance, decarboxylation of \((\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{OCHO}\) was studied under a CO atmosphere by Darensbourg and co-workers.\(^5\) It was proposed that the hydride complex \((\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{H}\) was the...
deinsertion product; however, isolation of the hydride species was unsuccessful due to its poor stability. Alper and co-workers reported the synthesis of binuclear palladium formate complexes, \([\text{trans-(PPh}_3\text{)}_2\text{Pd}(R)\text{OCHO]}\) \((R = \text{Ph, CH}_3)\), \(^6\) and observed deinsertion of \(\text{CO}_2\) at 15 °C. Although a pathway involving a hydride complex was proposed, a Pd(0) species was isolated as the end product. Gladysz and co-workers investigated the decarboxylation of an optically active rhenium formate complex, \((S)-(\eta^5-\text{C}_5\text{H}_5)\text{Re(NO)(PPh}_3\text{)}\text{OCHO}\) \(^7\) and isolated the corresponding hydride complex. Additionally, they were able to calculate the kinetic parameters associated with the process by \(^1\text{H}\) NMR spectroscopy. Another important kinetic investigation by Daresbourg group was performed on the decarboxylation of Group 10 metal formate complexes, \(\text{trans-(PCy}_3\text{)}_2\text{M(H)OCHO} \) \((M = \text{Ni, Pd})\) through exchange reaction with \(^1\text{C}\)-labeled \(\text{CO}_2\). \(^8\) In that work, a comparative study between Ni and Pd towards decarboxylation was carried out. It was found that the calculated kinetic parameters were less precise for the palladium system than the nickel system, possibly due to the lower stability of palladium formate and hydride complexes. Although these studies have shed some light on the mechanism of the decarboxylation process, there is a lack of suitable systems for a full understanding of electronic and steric effects of the ligands as well as the effect of the metal on the rate of the reaction.

Our group has discovered that bis(phosphinite)-ligated nickel and palladium pincer formate complexes are efficient catalysts for the decomposition of formic acid to

---

\(^6\) Grushin, V. V.; Bensimon, C.; Alper, H. *Organometallics* **1995**, *14*, 3259.
CO₂ and H₂ (eq 1).⁹ We have also found that this process can be catalyzed by the corresponding metal hydride complexes (3a-b and 4a-b). For the stoichiometric reaction between the metal hydrides and formic acid, formate complexes and dihydrogen were observed as the products (eq 2). From these observations a two-step mechanism can be proposed for this catalytic process (Scheme 1).

\[
\text{HCOOH} \xrightarrow{\text{catalyst}} \text{CO}_2 + \text{H}_2 \]  
\text{eq 1}

\[
\begin{align*}
\text{M} &= \text{Ni}(1); R = \text{Bu(a)}, \text{Pr(b)} \\
\text{M} &= \text{Pd}(2); R = \text{Bu(a)}, \text{Pr(b)}
\end{align*}
\]

\[
\text{M-H} + \text{HCOOH} \xrightarrow{\text{toluene}, 30 \text{ min}} \text{M-OCHO} + \text{H}_2 \]  
\text{eq 2}

\[
\begin{align*}
\text{M} &= \text{Ni}; 3\text{a-b} \\
\text{M} &= \text{Pd}; 4\text{a-b}
\end{align*}
\]

100% Conversion

Scheme 1

---

As illustrated in the catalytic cycle, the deinsertion of CO$_2$ form the metal formate is a crucial step for the overall catalytic reaction. In order to better understand this process, we became interested in the kinetics of the CO$_2$ deinsertion step. These nickel and palladium complexes represent an excellent system to study the decarboxylation reaction, as all the nickel and palladium POCOP-pincer formate and hydride complexes have been isolated and well characterized. In addition, the POCOP-pincer system will allow us to study the process using different substituents on the phosphorous donors, thereby providing a good opportunity to investigate the effects of the ligand on the decarboxylation reaction. This chapter will be focused on the kinetic study of the CO$_2$ deinsertion from bis(phosphinite)-ligated nickel and palladium formate complexes with two different $P$-substituents (tert-butyl and isopropyl groups).

5.2 Decarboxylation of Nickel and Palladium POCOP-Pincer Formate Complexes

When a solution of 1a in $C_6D_6$ was heated at 60 °C, formation of the hydride complex 3a was not observed even after 24 h. Under the same condition, the other three metal formate complexes (1b, 2a-b) behaved similarly. These results were not surprising as the reverse process, namely the insertion of CO$_2$ into the metal hydrides 3a-b and 4a-b was found to be a thermodynamically more favorable process (eq 3).$^{10,11}$

---


$^{11}$ See Chapter 4.
However, when a $^{13}$C-labeled nickel formate complex 1a-$^{13}$C was mixed with CO$_2$ (1 atm) in C$_6$D$_6$, formation of 1a was observed by $^{13}$C{$^{1}$H} NMR spectroscopy (eq 4). This result supports a reversible deinsertion of CO$_2$ from the metal formate complex to the hydride, though the equilibrium lies to the formate complex side.

To drive the equilibrium towards the formation of the metal hydride and CO$_2$, a solid sample of a formate complex was heated under a dynamic vacuum. In all cases, the formation of the hydride species was observed by $^{31}$P{$^{1}$H} and $^{1}$H NMR spectroscopy (eq 5).
Thus, conversion of the formate complexes to the hydride complexes could be a favorable process if CO₂, one of the products, could be removed. Although the decarboxylation can be observed using this method and the conversion can be quantified by NMR spectroscopy, the progress of the reaction is difficult to monitor. In addition, this method cannot be performed in solution and thus not suitable for kinetic study of the CO₂ deinsertion step.

An alternative approach favoring the decarboxylation step could be the removal of the metal hydride with carbon disulfide. To study the reactivity of the hydride complexes, an equimolar amount of CS₂ was added to a solution of hydride (3a-b or 4a-b) in C₆D₆ at room temperature, which resulted in the formation of a thioformate complex (5a-b or 6a-b) within 15 min (eq 6). In ¹H NMR spectra, disappearance of the signal for the formate resonance at ~ 8.5 ppm along with the appearance of a new singlet resonance at ~ 12 ppm confirms the formation of a CS₂ inserted product. Complexes 5a-b and 6a-b were fully characterized by ¹H, ³¹P{¹H}, ¹³C{¹H} NMR spectroscopy and elemental analysis.

![Chemical reaction](image)

Interestingly, heating a solid sample of complex 5 or 6 at 60 °C under a dynamic vacuum did not produce 3 or 4 after 2 h, implying that unlike the formate complexes 1a-b
and \(2a-b\) (eq 5), \(\text{CS}_2\) insertion into the nickel and palladium hydride complexes is irreversible. This observation also suggests that the kinetic barrier is relatively higher for the deinsertion of \(\text{CS}_2\) than that for the deinsertion of \(\text{CO}_2\), consistent with the fact that the \(\text{C}=\text{S}\) bond energy of \(\text{CS}_2\) (136 kcal/mol) is lower than the \(\text{C}=\text{O}\) bond energy of \(\text{CO}_2\) (190 kcal/mol). Next, stoichiometric reactions between the formate complexes (1a-b, 2a-b) and \(\text{CS}_2\) were studied. As expected, for the room temperature reactions between 1a-b and an excess amount of \(\text{CS}_2\), complete conversion to complexes 5a-b was observed within 48 h (eq 7). In the case of 2a-b, it took 6 h for a quantitative conversion to complexes 6a-b. A two-step reaction mechanism is proposed in Scheme 2.

![Scheme 2](image)

Under the reaction conditions, carbon disulfide competes more effectively than \(\text{CO}_2\) for the insertion into the metal hydride intermediate, resulting in a thioformate complex as the final product. To further test the irreversibility of the process, \(\text{CO}_2\) was
passed through a solution of 5a (or 5b) in C₆D₆ at room temperature. After 2 h no nickel formate species was detected by ³¹P{¹H} or ¹H NMR spectroscopy.

5.3 Pseudo-First Order Kinetics of CO₂ Deinsertion

The mechanistic details of CO₂ deinsertion were probed by monitoring the reaction between 1a and CS₂ at 30 °C (eq 8). The rate of the reaction was derived from disappearance of the formate resonance in ¹H NMR spectra as a function of time. With varying concentrations of CS₂, it was found that the rate constant became independent of [CS₂] at higher concentrations (Table 1), while the reaction consistently showed an exponential decay of the formate complex, suggesting that the overall reaction is first-order dependent on [Ni-OCHO] (Figure 1).

![Chemical reaction diagram](image)

**Table 1.** Kinetic Data for the Reaction of 1a with CS₂ at 30 °C

<table>
<thead>
<tr>
<th>[CS₂]₀ (M)</th>
<th>kₐ₀ × 10⁵ (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.27</td>
<td>1.8</td>
</tr>
<tr>
<td>0.54</td>
<td>2.1</td>
</tr>
<tr>
<td>0.81</td>
<td>2.4</td>
</tr>
<tr>
<td>1.08</td>
<td>2.4</td>
</tr>
<tr>
<td>1.34</td>
<td>2.6</td>
</tr>
</tbody>
</table>

*a* Reaction conditions: CS₂ was added to a solution of 1a (0.014 M) and 1,4-dioxane (2 μL) in toluene-d₈ at 30 °C. *b* Reaction was monitored by ¹H NMR spectroscopy.
Figure 1. A Representative Kinetic Trace for the Reaction of 1a with CS$_2$ at 30 °C

The zeroth order dependence on [CS$_2$] and the overall first-order kinetics rule out any bimolecular process for CO$_2$ deinsertion. Assuming that a steady-state approximation can be applied to the nickel hydride intermediate as shown in Scheme 2, pseudo-first order kinetics should be expected for the decarboxylation at high [CS$_2$] (Scheme 3). The rate law also suggests that at low [CS$_2$] the decarboxylation process should be slower, which is consistent with the results shown in Table 1.
5.4 Kinetic Study of CO₂ Deinsertion from 1a-b and 2a-b

To calculate the activation parameters, decarboxylation reactions at different temperatures (30-45 °C) were carried out and the kinetic data were summarized in Table 2.

**Table 2.** Kinetic Data for the Reaction of 1a with CS₂ at Different Temperatures

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>[CS₂]₀ (M)</th>
<th>(k_{obs} \times 10^5) (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 °C</td>
<td>0.81</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>1.08</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>1.34</td>
<td>2.6</td>
</tr>
<tr>
<td>35 °C</td>
<td>0.81</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>1.08</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>1.34</td>
<td>4.7</td>
</tr>
<tr>
<td>40 °C</td>
<td>0.27</td>
<td>9.2</td>
</tr>
<tr>
<td></td>
<td>0.54</td>
<td>9.4</td>
</tr>
<tr>
<td></td>
<td>0.81</td>
<td>9.2</td>
</tr>
<tr>
<td>45 °C</td>
<td>0.40</td>
<td>14.1</td>
</tr>
<tr>
<td></td>
<td>0.54</td>
<td>15.1</td>
</tr>
<tr>
<td></td>
<td>0.81</td>
<td>14.1</td>
</tr>
<tr>
<td></td>
<td>1.08</td>
<td>15.1</td>
</tr>
</tbody>
</table>

\(^a\) Reaction conditions: CS₂ (0.40-1.08 M) was added to a solution of 1a (0.014 M) and 1,4-dioxane (2 μL) in toluene-\(d_8\) at 30 °C. \(^b\) Reaction was monitored by \(^1\)H NMR spectroscopy.
Plotting $\ln(k/T)$ vs $1/T$ resulted in a straight line (Figure 2). Using the Eyring equation (eq 9) the activation parameters were calculated as $\Delta H^\neq = 21.6 \pm 1.1$ kcal•mol$^{-1}$ and $\Delta S^\neq = -8.5 \pm 3.6$ e.u.

$$\ln \frac{k}{T} = -\frac{\Delta H^\neq}{R} \cdot \frac{1}{T} + \ln \frac{k_B}{h} + \frac{\Delta S^\neq}{R} \quad (\text{eq 9})$$

![Eyring Plot](image)

**Figure 2.** Eyring Plot for the Calculation of Activation Parameters for the Reaction of 1a with CS$_2$

To study how the less bulky $P$-substituents impact the decarboxylation rate, the reactivity of complex 1b towards CS$_2$ was studied. The kinetic data for decarboxylation of 1b as well as those of 1a are listed in Table 3, and the calculated activation parameters are summarized in Table 4.
Table 3. Kinetic Data for the Reaction of 1a-b with CS$_2$ at 30-45 °C$^a,b$

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>1/T (K$^{-1}$)</th>
<th>$k_1 \times 10^5$ (s$^{-1}$)</th>
<th>ln($k/T$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>0.00330</td>
<td>2.5 ± 0.1</td>
<td>3.8 ± 0.1</td>
</tr>
<tr>
<td>308</td>
<td>0.00325</td>
<td>4.7 ± 0.1</td>
<td>6.9 ± 0.1</td>
</tr>
<tr>
<td>313</td>
<td>0.00319</td>
<td>9.3 ± 0.1</td>
<td>12.4 ± 0.3</td>
</tr>
<tr>
<td>318</td>
<td>0.00314</td>
<td>14.7 ± 0.2</td>
<td>23.9 ± 0.3</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: CS$_2$ (0.40-1.08 M) was added to the solution of nickel complex (0.014 M for 1a and 0.013 M for 1b) and 1,4-dioxane (2 μL) in toluene-$d_8$. $^b$ Reaction was monitored by $^1$H NMR spectroscopy.

Table 4. Calculated Activation Parameters for the Decarboxylation of 1a-b

<table>
<thead>
<tr>
<th></th>
<th>1a</th>
<th>1b</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H^\ne$ (kcal/mol)</td>
<td>21.6 ± 1.1</td>
<td>21.9 ± 0.9</td>
</tr>
<tr>
<td>$\Delta S^\ne$ (e.u.)</td>
<td>-8.5 ± 3.6</td>
<td>-6.5 ± 2.8</td>
</tr>
</tbody>
</table>

For the decarboxylation of nickel formate complex trans-(PCy$_3$)$_2$Ni(H)OCHO,$^8$ the Darensbourg group calculated the activation parameters as $\Delta H^\ne = 22.1 \pm 0.9$ kcal•mol$^{-1}$ and $\Delta S^\ne = -5 \pm 3$ e.u., which are similar to those calculated for our nickel system. The entropy of activation for nickel formate complexes 1a-b is found to be negative, which indicates a more crowded structure for the transition state compared to the ground state. In the literature, it has been proposed that during CO$_2$ deinsertion, the hydrogen of the formate group approaches the metal center, resulting in a four-membered cyclic transition state (Figure 3).$^6,7,8$ Additionally, computational study of several metal systems has also supported this type of transition states.$^{12}$

In a study by a previous group member, a kinetic isotope effect ($k_{HH}/k_{HD} = 2$) was observed for the decarboxylation of 1b when labeling the formate hydrogen with deuterium.\textsuperscript{13} This result indicates the breaking of the formate C-H bond in the transition state. Therefore, in the case of POCOP-pincer systems, both the entropy value and the kinetic isotope effect support the transition-state structure in Figure 3, where the C-H bond significantly weakened through the interaction with the metal center.

The rate constants in Table 3 also suggest that CO$_2$ deinsertion is faster in the case of 1b. The faster rate for the less bulky nickel complex can be rationalized by the metal being more accessible for the approach of formate hydrogen. In Chapter 4 decarboxylation of $P$-stereogenic bis(phosphinite)-based pincer nickel formate complexes have been shown to adopt a transition state involving the approach of formate hydrogen to the metal center from the axial site. In the case of 1b, the approach of the formate hydrogen is more favorable due to the presence of less bulky isopropyl groups in comparison with 1a, which contains tert-butyl groups. The less negative $\Delta S^\neq$ value for 1b (Table 4) further supports the transition-state structure because in this less crowded environment, the approach of the formate hydrogen should be more favorable.

Decarboxylation of the analogous palladium formate complexes (2a-b) were studied next. The rate was found to be first-order in [Pd-OCHO], and the rate constants were measured at four different temperatures (25-40 °C) and listed in Table 5. The

\textsuperscript{13} Zhang, J.; Guan, H. *Unpublished Results.*
activation parameters were calculated using the same procedure for the nickel system and the data are summarized in Table 6.

**Table 5. Kinetic Data for the Reaction of 2a-b with CS2 at 25-40 °C**

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>$k_1 \times 10^4$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 °C</td>
<td>6.2 ± 0.2</td>
</tr>
<tr>
<td>30 °C</td>
<td>14.3 ± 0.1</td>
</tr>
<tr>
<td>35 °C</td>
<td>23.1 ± 0.6</td>
</tr>
<tr>
<td>40 °C</td>
<td>38.0 ± 0.2</td>
</tr>
</tbody>
</table>

*$^a$ Reaction conditions: CS$_2$ (0.51-1.53 M) was added to the solution of nickel complex (0.013 M) and 1,4-dioxane (0.3 μL) in toluene-$d_8$. *$^b$ Reaction was monitored by $^1$H NMR spectroscopy.

**Table 6. Calculated Activation Parameters for Decarboxylation of 2a-b**

<table>
<thead>
<tr>
<th></th>
<th>1a</th>
<th>1b</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔH$^\ne$ (kcal/mol)</td>
<td>21.5 ± 0.9</td>
<td>24.7 ± 0.9</td>
</tr>
<tr>
<td>ΔS$^\ne$ (e.u.)</td>
<td>-1.1 ± 0.4</td>
<td>7.3 ± 2.6</td>
</tr>
</tbody>
</table>

As seen from the rate constant values, decarboxylation from the palladium center is much faster than from the nickel center (57 times faster for $^t$Bu-substituted complexes and 10 times faster for $^t$Pr-substituted complexes at 30 °C; Table 3 and 5). As mentioned earlier, the faster decarboxylation rate for complex 1b (compared to 1a) is due to more favorable approach of formate hydrogen in the transition state. Using the same argument, the larger size (or more diffused orbital) of palladium would render formate hydrogen approach to the palladium center more readily than nickel, resulting in a faster decarboxylation reaction. The less negative entropy of activation values for 2a-b than
1a-b (Table 4 and 6) are also consistent with the notion that in the case of palladium, the transition state should be less crowded because of the larger size of the metal.

Interestingly, a higher reactivity for more bulky palladium formate complex was observed; at 30 °C, decarboxylation of 2a is 3.7 times faster than 2b, which is in contrast to the relative reactivity between nickel complexes 1a-b. Based on the $\Delta S^\neq$ values (Table 6), decarboxylation of 2b is entropically more favorable than the more bulky formate complex 2a, which is in line with the more accessible metal center to interact with formate hydrogen. However, the $\Delta H^\neq$ value is more positive in the case of 1b, which makes the decarboxylation process less favorable. A possible explanation involves the dissociation of a stronger Pd-O bond of 1b. However, the solid-state structures of 2a and 2b showed comparable Pd-O bond lengths (2b: 2.0986(18) Å, 2a: 2.01056(19) Å). The difference in the rates for 2b and 2a may arise from other factors that remain unclear to us at the moment.

5.5 Conclusions

Deinsertion of CO$_2$ from bis(phosphinite)-supported nickel and palladium pincer formate complexes was accomplished with the addition of CS$_2$. In the presence of a large excess CS$_2$, pseudo-first order kinetics of decarboxylation with respect to the metal formate complexes was observed. The zeroth order dependence of CS$_2$ on the rate of the reaction is consistent with the fact that CS$_2$ competes with CO$_2$ more effectively for the insertion into the metal hydride intermediate. Kinetics of decarboxylation of bis(phosphinite)-ligated nickel and palladium pincer formate complexes were studied at various temperatures. Faster decarboxylation rates were observed for palladium
complexes compared to nickel analogs. It was hypothesized that the larger size of the palladium allows a more favorable approach of the formate hydrogen to the metal center. In the case of nickel formate complexes, isopropyl substituted formate complex was found to react at a rate faster than the tert-butyl substituted complex. It is likely that the presence of bulky groups on phosphorous hinders the approach of hydrogen to the metal, resulting in a slower decarboxylation rate. However, in the case of palladium complexes, a faster decarboxylation rate was observed for the more bulky formate complex. Based on the enthalpy of activations, it was believed that for palladium complexes, breaking Pd-O bond plays a crucial role in determining the decarboxylation rate.

5.6 Experimental Section

General Comments. All the organometallic compounds were prepared and handled under an argon atmosphere using standard Schlenk and inert-atmosphere box techniques. Dry and oxygen-free solvents were collected from an Innovative Technology solvent purification system and used throughout all experiments. Benzene-\textit{d$_6$} and toluene-\textit{d$_8$} were distilled from Na and benzophenone under argon atmosphere. $^1$H, $^{13}$C{$^1$H} and $^{31}$P{$^1$H} NMR spectra were recorded on a Bruker Avance-400 MHz spectrometer. $^1$H NMR spectra for the kinetic measurement of decarboxylation of nickel formate complexes were recorded on Bruker Avance-400 MHz spectrometer. In the case of decarboxylation of palladium formate complexes, Bruker Avance-500 MHz spectrometer was used to record $^1$H NMR spectra. Chemical shift values in $^1$H and $^{13}$C{$^1$H} NMR spectra were referenced internally to the residual solvent resonances.
$^{31}$P{$^1$H} spectra were referenced externally to 85% H$_3$PO$_4$ (0 ppm). Complexes 1a-b, 2a-b, 3a-b and 4a-b were prepared as described in the literature.$^{10,11,14}$

**Synthesis of [2,6-(iBu$_2$PO)$_2$C$_6$H$_3$]NiSCHS (5a).** Under an argon atmosphere, CS$_2$ (0.52 mL, 8.80 mmol) was added to a solution of 3a (200 mg, 0.44 mmol) in toluene (20 mL) and the mixture was stirred at room temperature for 2 h. The volatiles were removed under vacuum and the resulting yellow solid was crystallized from toluene/hexane (1 : 1) to yield the product as orange crystals (207 mg, 88% yield). $^1$H NMR (CDCl$_3$, 400 MHz, δ): 1.47-1.43 (m, CH$_3$, 36H), 6.47 (d, $^3$J$_{H-H} = 8.0$ Hz, Ar, 2H), 7.00 (t, $^3$J$_{H-H} = 8.0$ Hz, Ar, 1H), 11.50 (t, $^4$J$_{P-H} = 1.8$ Hz, SCHS, 1H). $^{13}$C{$^1$H} NMR (CDCl$_3$, 101 MHz, δ): 28.37 (s, C(CH$_3$)$_3$), 40.10 (t, $^1$J$_{C-P} = 7.7$ Hz, C(CH$_3$)$_3$), 104.91 (t, $^3$J$_{C-P} = 5.7$ Hz, Ar), 128.22 (t, $^2$J$_{C-P} = 19.1$ Hz, Ar), 129.64 (s, Ar), 168.76 (t, $^2$J$_{C-P} = 8.7$ Hz, Ar), 233.95 (s, SCHS). $^{31}$P{$^1$H} NMR (CDCl$_3$, 162 MHz, δ): 190.56. Anal. calcd for C$_{23}$H$_{40}$NiO$_2$P$_2$S$_2$: C, 51.80; H, 7.56. Found: C, 51.96; H, 7.45.

**Synthesis of [2,6-(iPr$_2$PO)$_2$C$_6$H$_3$]NiSCHS (5b).** This compound was prepared in 66% yield by a similar procedure that used for 5a. $^1$H NMR (CDCl$_3$, 400 MHz, δ): 1.38-1.22 (m, CH(CH$_3$)$_2$, 24H), 2.29-2.26 (m, CH(CH$_3$)$_2$, 4H), 6.71 (d, $^3$J$_{H-H} = 7.7$ Hz, Ar, 2H), 7.00 (t, $^3$J$_{H-H} = 7.6$ Hz, Ar, 1H), 11.55 (s, SCHS, 1H). $^{13}$C{$^1$H} NMR (CDCl$_3$, 101 MHz, δ): 16.84 (s, C(CH$_3$)$_3$), 17.44 (s, C(CH$_3$)$_3$), 29.48 (t, $^1$J$_{C-P} = 11.9$ Hz, CH(CH$_3$)$_2$), 105.01 (t, $^3$J$_{C-P} = 5.9$ Hz, Ar), 129.59 (t, $^2$J$_{C-P} = 19.5$ Hz, Ar), 129.65 (s, Ar), 168.08 (t, $^2$J$_{C-P} = 9.2$ Hz, Ar), 233.59 (s, SCHS). $^{31}$P{$^1$H} NMR (CDCl$_3$, 162 MHz, δ): 190.67. Anal. calcd for C$_{19}$H$_{32}$NiO$_2$P$_2$S$_2$: C, 51.80; H, 7.56. Found: C, 51.96; H, 7.45.

**Synthesis of [2,6-(tBu$_2$PO)$_2$C$_6$H$_3$]PdSCHS (6a).** Under an argon atmosphere, CS$_2$ (6.0 μL, 100 μmol) was added to a solution of 4a (25 mg, 50 μmol) in toluene (1 mL)

---

and the mixture was stirred at room temperature for 30 min. The resulting solution was
layered with 1 mL of pentane and kept at –10°C. Within 24 h, the desired product
appeared as white crystals, which were isolated by filtration and drying under vacuum
(20 mg, 70% yield). ¹H NMR (C₆D₆, 400 MHz, δ): 1.30 (t, Jvirtual = 8.0 Hz, CH₃, 36H),
6.66 (d, JH-H = 8.0 Hz, ArH, 2H), 6.88 (t, ³JH-H = 8.0 Hz, ArH, 1H), 11.99 (s, SCHS, 1H).
¹³C{¹H} NMR (C₆D₆, 101 MHz, δ): 27.83 (t, JCP = 4.0 Hz, C(CH₃)₃), 40.17 (t, JCP = 8.1
Hz, C(CH₃)₃), 105.97 (t, JCP = 6.1 Hz, ArC), 129.17 (s, ArC), 134.49 (s, ArC), 167.11 (t,
JCP = 9.1 Hz, ArC), 232.25 (s, SCHS). ³¹P{¹H} NMR (C₆D₆, 162 MHz, δ): 194.40.
Anal. Calcd for C₂₃H₄₀O₂P₂S₂Pd: C, 47.54; H, 6.94. Found: C, 47.90; H, 7.09.

**Synthesis of [2,6-(iPr₂PO)₂C₆H₃]PdSCHS (6b).** Under an argon atmosphere,
CS₂ (6.8 µL, 112 µmol) was added to a solution of 4b (25 mg, 56 µmol) in toluene (1
mL) and the mixture was stirred at room temperature for 30 min. The volatiles were
removed under vacuum and the residue was extracted with 3 mL pentane. Evaporation of
the solvent resulted in pure product as a faint yellow solid (18 mg, 62% yield). This
compound can be further recrystallized from pentane at –35°C. ¹H NMR (C₆D₆, 400
MHz, δ): 1.04-1.09 (m, CH(CH₃)₂, 12H), 1.15-1.22 (m, CH(CH₃)₂, 12H), 2.10-2.17 (m,
CH(CH₃)₂, 4H), 6.68 (d, JH-H = 7.6 Hz, ArH, 2H), 6.89 (t, JH-H = 7.6 Hz, ArH, 1H), 11.93
(s, SCHS, 1H). ¹³C{¹H} NMR (C₆D₆, 101 MHz, δ): 16.67 (s, CH(CH₃)₂), 17.10 (t, JCP =
3.0 Hz, CH(CH₃)₂), 30.20 (t, JCP = 12.1 Hz, CH(CH₃)₂), 106.16 (t, JCP = 7.1 Hz, ArC),
129.34 (s, ArC), 134.31 (s, ArC), 166.47 (t, JCP = 6.1 Hz, ArC), 233.94 (s, SCHS).
³¹P{¹H} NMR (C₆D₆, 162 MHz, δ): 192.00 (s). Anal. Calcd for C₁₉H₃₂O₂P₂S₂Pd: C,
43.47; H, 6.14. Found: C, 43.38; H, 6.01.
Rate Constant Measurement for the Reactions of [2,6-(R₂PO)₂C₆H₃]NiOCHO (1a-b) Complexes with CS₂. In a resealable NMR tube, to a solution of [2,6-(R₂PO)₂C₆H₃]NiOCHO (4.4 mg, 8.8 µmol, 0.014 M in the case of 1a and 3.6 mg, 8.1 µmol, 0.013 M in the case of 1b) in toluene-d₈, was added 1,4-dioxane (2 µL) as the internal standard. To the resulting solution 20 to 100 equivalent of CS₂ (10.5 µL, 0.27 M - 52.8 µL, 1.34 M) was added. In each experiment the combined volume of CS₂ and toluene-d₈ was maintained as 0.65 mL. The first ¹H NMR spectrum of the mixture was recorded within 5 min as an initial point, and the spectra were recorded in every 5-30 min interval at the desired temperature for 3-5 half-lives. The probe temperature was calibrated using 100% ethylene glycol. The concentration of the formate complex (1a-b) was monitored by the integration for the NiOCHO resonances compared to the integration for the internal standard in ¹H NMR spectra.

Rate Constant Measurement for the Reactions of [2,6-(R₂PO)₂C₆H₃]PdOCHO (1a-b) Complexes with CS₂. In a resealable NMR tube, to a solution of [2,6-(R₂PO)₂C₆H₃]PdOCHO (4.6 mg, 8.4 µmol, 0.013 M in the case of 2a and 4.2 mg, 8.4 µmol, 0.013 M in the case of 1b) in toluene-d₈, was added 1,4-dioxane (0.3 µL) as the internal standard. To the resulting solution 40 to 120 equivalent of CS₂ (20 µL, 0.51 M - 60 µL, 1.53 M) was added. In each experiment the combined volume of CS₂ and toluene-d₈ was maintained as 0.65 mL. The first ¹H NMR spectrum of the mixture was recorded within 5 min as an initial point, and the spectra were recorded in every 2.5-5 min interval at the desired temperature for 3-5 half-lives. The probe temperature was calibrated using 100% ethylene glycol. The concentration of the
formate complex (1a-b) was monitored by the integration for the PdOCHO resonances compared to the integration for the internal standard in $^1$H NMR spectra.

**Decarboxylation of Complexes 1a-b and 2a-b in the Solid State.** Under an argon atmosphere, in a J. Young NMR tube a solid sample of formate complex (0.025 mmol) was added and the NMR tube was connected to a vacuum line. Under a dynamic vacuum, the NMR tube was placed in a preheated oil bath at 60 °C. After 5 h, under an argon atmosphere, C₆D₆ was added to the resulting solid and the conversion was calculated by $^{31}$P{$^1$H} and $^1$H NMR spectroscopy.

**Table 7.** Kinetic Data for the Reaction of 1b with CS₂ at 30-45 °C

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>[CS₂]₀ (M)</th>
<th>$k_{obs} \times 10^5$ (S⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 °C</td>
<td>0.25</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>3.8</td>
</tr>
<tr>
<td>35 °C</td>
<td>0.25</td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>6.9</td>
</tr>
<tr>
<td>40 °C</td>
<td>0.25</td>
<td>13.1</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>12.1</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>12.1</td>
</tr>
<tr>
<td>45 °C</td>
<td>0.25</td>
<td>24.1</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>24.1</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>24.1</td>
</tr>
</tbody>
</table>
Table 8. Kinetic Data for the Reaction of 2a with CS₂ at 25-40 °C

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>[CS₂]₀ (M)</th>
<th>$k_{obs} \times 10^4$ (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 °C</td>
<td>0.51</td>
<td>6.2</td>
</tr>
<tr>
<td></td>
<td>1.02</td>
<td>6.2</td>
</tr>
<tr>
<td></td>
<td>1.53</td>
<td>6.2</td>
</tr>
<tr>
<td>30 °C</td>
<td>0.51</td>
<td>14.3</td>
</tr>
<tr>
<td></td>
<td>1.02</td>
<td>14.5</td>
</tr>
<tr>
<td></td>
<td>1.53</td>
<td>14.3</td>
</tr>
<tr>
<td>35 °C</td>
<td>0.51</td>
<td>22.4</td>
</tr>
<tr>
<td></td>
<td>1.02</td>
<td>23.1</td>
</tr>
<tr>
<td></td>
<td>1.53</td>
<td>23.8</td>
</tr>
<tr>
<td>40 °C</td>
<td>0.51</td>
<td>38.2</td>
</tr>
<tr>
<td></td>
<td>1.02</td>
<td>38.0</td>
</tr>
<tr>
<td></td>
<td>1.53</td>
<td>37.8</td>
</tr>
</tbody>
</table>

Table 9. Kinetic Data for the Reaction of 2b with CS₂ at 25-40 °C

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>[CS₂]₀ (M)</th>
<th>$k_{obs} \times 10^4$ (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 °C</td>
<td>0.51</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>1.02</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>1.53</td>
<td>1.7</td>
</tr>
<tr>
<td>30 °C</td>
<td>0.51</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>1.02</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>1.53</td>
<td>3.9</td>
</tr>
<tr>
<td>35 °C</td>
<td>0.51</td>
<td>8.8</td>
</tr>
<tr>
<td></td>
<td>1.02</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td>1.53</td>
<td>7.6</td>
</tr>
<tr>
<td>40 °C</td>
<td>0.51</td>
<td>13.6</td>
</tr>
<tr>
<td></td>
<td>1.02</td>
<td>12.6</td>
</tr>
<tr>
<td></td>
<td>1.53</td>
<td>12.6</td>
</tr>
</tbody>
</table>