INVESTIGATION OF LATE TRANSITION METAL BASED CATALYTIC SYSTEMS FOR POLYMERIZATION OF POLAR VINYL MONOMERS

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Chemistry
by
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Variable-temperature $^1$H NMR studies of the reaction of cationic ($\alpha$-diimine)Pd-alkyl complexes with alkenes are presented. The studies reveal that vinyl bromide coordinates to the Pd(II)-Me complex followed by migratory insertion and $\beta$-bromo elimination, to generate free propene. Propene further reacts to give $\beta$-agostic Pd(II)-tert-butyl species. From the reactions with vinyl bromide, stable chloro-bridged dicationic Pd complex was isolated and characterized. For a series of alkenes (CH$_2$=CHX), the rate for migratory insertion decreases as follows: X = CO$_2$Me > Br > H > Me.

Palladium(1,5-cyclooctadiene)(methyl)(chloride), is a catalyst for the living oligomerization of norbornene. The reaction is attenuated by additives in the following decreasing order, C=C > Cl$^-$ > RC(=O)OR. The insertion of norbornene, endo and exo-5-ethylester-2-norbornene, and endo-5-methylacetate-2-norbornene into the palladium-methyl bond of Palladium(1,5-cyclooctadiene)(methyl)(chloride) was examined. Similar rates were found for all the norbornene derivatives, with the product in every case being derived from insertion through the exo face.

A series of neutral salicylaldiminato Pd(II) complexes, Pd(Me)(Ph-CH=N-R')[3-$^1$Bu-2-(O)C$_6$H$_3$-CH=N-2,6-di-$^1$Pr-C$_6$H$_3$](R=CH$_3$, n-Pr, tert-Bu, Ph, Benzyl) (3a-3e), and Pd(Me)[3-(CH=N-t-Bu)-Py][3-$^1$Bu-2-(O)C$_6$H$_3$-CH=N-2,6-di-$^1$Pr-C$_6$H$_3$] (4) have been synthesized and characterized. Their structure has been confirmed by an X-ray analysis of complexes 3a, 3c-3e, and 4. Nuclear Magnetic Resonance (NMR) studies utilizing 3c
indicate that the complex reacts with CO through a five-coordinate species. The neutral complexes 3a-3e show moderate catalytic activity for the polymerization of methyl acrylate at ambient temperature. In the polymerization reaction, a radical mechanism rather than coordination insertion mechanism is invoked to be operative. The complexes 3a, 3b, 3d, 3e produced poly(norbornene) in low yield.

Neutral Pd(II) complexes, \([3,5\text{-di-}^1\text{Bu-}2\text{-}(\text{OH})\text{C}_6\text{H}_2\text{N}=\text{CH}-2\text{-PPh}_2\text{C}_6\text{H}_4]\text{PdMe}_2 \) (3) and \([3,5\text{-di-}^1\text{Bu-}2\text{-}(\text{OH})\text{C}_6\text{H}_2\text{CH}=\text{N}-2\text{-PPh}_2\text{C}_6\text{H}_4]\text{PdMe}_2 \) (4) have been synthesized and characterized. Their structures have been confirmed by an X-ray analysis of complexes 3 and 4. In the solid state, the structure of the complex 3 significantly deviated from the idealized square planar geometry by virtue of the constraint caused by the large bond length difference between P(1)-C(14) and N(1)-C(8) (1.823(3) and 1.288(3), respectively in the [P,N] six-membered ring. Independently, the title compound did not show catalytic activity for the polymerization or oligomerization of an alkene without an assisting agent. In combination with AlEt₃, 3 and 4 have produced PMA, where 4 showed better activity. The complex 4 with Al(C₆F₅)₃ as a cocatalyst polymerized norbornene or n-butylnorbornene in excellent yield, but with B(C₆F₅)₃, it did not produce any polymeric product. Different reaction pathways between complexes 3 or 4 and Al(C₆F₅)₃ or B(C₆F₅)₃ have been proposed based on the results of the polymerization and the NMR experiments. Utilizing methylaluminoxane (MAO) as a co catalyst, 3 and 4 produced poly(norbornene) in good yield with no activity difference between 3 and 4.
# TABLE OF CONTENTS

LIST OF FIGURES .................................................................................................................. viii

LIST OF TABLES ....................................................................................................................... x

ACKNOWLEDGEMENTS ............................................................................................................. xii

Chapter 1  INTRODUCTION ...................................................................................................... 1

References ................................................................................................................................ 3

Chapter 2  TRENDS IN ALKENE INSERTION IN LATE AND EARLY TRANSITION METAL COMPOUNDS: RELEVANCE TO TRANSITION METAL-CATALYZED POLYMERIZATION OF POLAR VINYL MONOMERS .................................................................................................................. 4

2.1 Introduction ..................................................................................................................... 4

2.2 Results ................................................................................................................................ 5

2.2.1 Generation of Active Species ...................................................................................... 5

2.2.2 1H NMR Study of the Reaction of Cationic (α-diimine)Pd-methyl Complex with Vinyl bromide ............................................................................................. 7

2.2.3 Kinetics of the Reaction of Cationic (α-diimine)Pd-methyl Complex with Alkenes ......................................................................................................................... 11

2.3 Discussion ....................................................................................................................... 13

2.3.1 Formation of Dimer and Deactivation Pathway ....................................................... 13

2.3.2 Relative Insertion Rates of Alkenes ........................................................................ 13

2.4 Conclusions ..................................................................................................................... 15

2.5 Experimental Section .................................................................................................... 16

2.5.1 Low Temperature: methanol (with 0.03% concentrated HCl) .................................. 17

2.5.2 High Temperature: ethylene glycol (neat) ............................................................... 17

2.5.3 Interpretation of activation parameters ..................................................................... 17

2.5.4 The Eyring Equation ................................................................................................. 18

2.5.5 Application of the Eyring Equation ......................................................................... 18

2.6 References ....................................................................................................................... 19

Chapter 3  THE REACTION OF PALLADIUM(1,5-CYCLOOCTADIENE)-(ALKYL)(CHLORIDE) WITH NORBORNENE DERIVATIVES: RELEVANCE TO METAL-CATALYZED ADDITION POLYMERIZATION OF FUNCTIONALIZED NORBORNENE ........................................ 22

3.1 Introduction ..................................................................................................................... 22

3.2 Results and Discussion ................................................................................................. 24

3.2.1 Reactions of Pd(1,5-cyclooctadiene)(CH₃)(Cl) with Norbornene Derivatives ............. 24
3.2.2 Investigation of Reaction Mechanism ..................................................32
3.3 Conclusion ......................................................................................................36
3.4 Experimental Section ......................................................................................37
  3.4.1 Generation Considerations ..................................................................37
  3.4.2 Synthesis of Complexes .......................................................................38
  3.4.3 General Procedure for NMR Experiments ........................................... 41
  3.4.4 General Procedures for Polymerization Reactions ...............................41
3.5 References .......................................................................................................42

Chapter 4 NEUTRAL PALLADIUM(II) COMPLEXES WITH N-O CHELATE:
SYNTHESSES, CHARACTERIZATION, AND THEIR REACTIVITIES .............44

  4.1 Introduction .....................................................................................................44
  4.2 Results and Discussion ...................................................................................45
    4.2.1 Complex Synthesis ...............................................................................45
    4.2.2 Mechanistic Studies of CO Insertion into Pd-Me Bond using Complex 3c ..........................................................57
    4.2.3 Polymerization of Polar or Nor-polar Vinyl Monomers ......................59
    4.2.4 Reactivities of the complexes toward imine and CO .......................61
  4.3 Conclusions .....................................................................................................66
  4.4 Experimental Section ......................................................................................67
    4.4.1 Generation Considerations ...................................................................67
    4.4.2 Synthesis of Compounds ......................................................................68
    4.4.3 General Procedures for Polymerization Reactions ...............................74
    4.4.4 General Procedure for NMR Experiments ...........................................74
  4.5 References .......................................................................................................75

Chapter 5 NEUTRAL PALLADIUM(II) COMPLEXES WITH P-N-O CHELATE:
SYNTHESSES, CHARACTERIZATION, AND THEIR REACTIVITIES ....................78

  5.1 Introduction .....................................................................................................78
  5.2 Results and Discussion ...................................................................................80
    5.2.1 Ligand Synthesis ..................................................................................80
    5.2.2 Complex Synthesis ...............................................................................81
    5.2.3 Reactivity of the Complexes ................................................................86
  5.3 Experimental Section ......................................................................................94
    5.3.1 General Considerations ........................................................................94
    5.3.2 Synthesis of Compounds ......................................................................96
    5.3.3 General Procedures for Polymerization Reactions ...............................98
  5.4 References .......................................................................................................99

Appendix A .............................................................................................................103

Crystal structure information, compound 6 in Chapter 2 ...............................103
LIST OF FIGURES

Figure 2-1: Generation of Active Species. Selected NMR spectra............6

Figure 2-2: Selected variable temperature NMR spectra..........................8

Figure 2-3: ORTEP view of 6. Hydrogen atoms are not shown for clarity. .................................................................10

Figure 2-4: Hammet plot for migratory insertion of alkenes into palladium(II)-methyl bond. ..................................................12

Figure 3-1: Modes of bonding for functionalized norbornene derivatives (X = coordinating functionality). ...............................23

Figure 3-2: An ORTEP view of 1a, showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. ..............27

Figure 3-3: An ORTEP view of 1b, showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. ..............27

Figure 3-4: An ORTEP view of 1c, showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. ..............28

Figure 3-5: An ORTEP view of 1d, showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. ..............28

Figure 3-6: Molecular weight of norbornene oligomer versus time ..........32
- "Living" system .................................................................................32

Figure 3-7: Plot of ln([NB]/[NB]₀) versus time. Reaction conditions:
1 (3.7x10⁻⁵ mol), norbornenes (7.5x10⁻⁴ mol), CD₂Cl₂ (1 mL), 23°C .................................................................33

Figure 4-1: ORTEP view of complex 3a. Hydrogen atoms are omitted for clarity .................................................................49

Figure 4-2: ORTEP view of complex 3c. Hydrogen atoms are omitted for clarity .................................................................49
Figure 4-3: ORTEP view of complex 3d. Hydrogen atoms are omitted for clarity. ..........................................................................................................50

Figure 4-4: ORTEP view of complex 3e. Hydrogen atoms are omitted for clarity. ..........................................................................................................50

Figure 4-5: ORTEP view of complex 4. Hydrogen atoms are omitted for clarity. ..........................................................................................................53

Figure 4-6: Selected VT $^{13}$C NMR Spectra of the Reaction between 3e and Ph-CH=N-CH$_2$-Ph under $^{13}$CO Atmosphere .........................62

Figure 4-7: ORTEP view of complex 5. Hydrogen atoms are omitted for clarity. ..........................................................................................................63

Figure 4-8: Selected proton coupled $^{13}$C NMR spectrum .......................65

Figure 5-1: ORTEP view of complex 3. Hydrogen atoms are omitted for clarity. ..........................................................................................................83

Figure 5-2: ORTEP view of complex 4. Hydrogen atoms are omitted for clarity. ..........................................................................................................83
LIST OF TABLES

Table 2-1: Kinetic Data for Insertion of Alkenes into Pd(II)-Me bond $^a$ ....................11

Table 3-1: Selected Bond distances (Å) and Angles (°) for 1a ......................................29

Table 3-2: Selected Bond distances (Å) and Angles (°) for 1b ......................................29

Table 3-3: Selected Bond distances (Å) and Angles (°) for 1c .....................................30

Table 3-4: Selected Bond distances (Å) and Angles (°) for 1d .....................................30

Table 3-5: Crystallographic Data and data Collection Parameters for complexes 1a-d .................................................................................................................................31

Table 3-6: Effect of Additives on the Polymerization of Norbornene using (1,5-COD)PdMeCl ..............................................................................................................35

Table 4-1: Selected Bond distances (Å) and Angles (°) for 3a .....................................51

Table 4-2: Selected Bond distances (Å) and Angles (°) for 3c .....................................51

Table 4-3: Selected Bond distances (Å) and Angles (°) for 3d .....................................52

Table 4-4: Selected Bond distances (Å) and Angles (°) for 3e .....................................52

Table 4-5: Selected Bond distances (Å) and Angles (°) for 4 ......................................55

Table 4-6: Crystallographic Data and data Collection Parameters for complexes 3a-e and 4 ..................................................................................................................................56

Table 4-7: Kinetic Data for Insertion of CO into Pd(II)-Me Bond....................................58

Table 4-8: Polymerization of Vinyl Monomers using Complexes 3a-e, and 4 $^a$ ...........59

Table 5-1: Selected Bond distances (Å) and Angles (°) for 3 ........................................84

Table 5-2: Selected Bond distances (Å) and Angles (°) for 4 ........................................84

Table 5-3: Crystallographic Data and data Collection Parameters for complexes 3a-e and 4 ......................................................................................................................86

Table 5-4: Polymerization of vinyl monomers using complexes 3 and 4 with AlEt$_3$$^a$ .......................................................................................................................................88
Table 5-4:  Polymerization of vinyl monomers using complexes 3 and 4 with AlEt$_3^a$ ....................................................................................................................89

Table 5-5:  Polymerization of vinyl monomers using complex 3 with FAL, Al(C$_6$F$_5$)$_3$, as a cocatalyst.................................................................91

Table 5-6:  Polymerization of vinyl monomers using 3 or 4 with MAO as a cocatalyst$^a$ .............................................................................................................92
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Chapter 1

INTRODUCTION

International markets for plastics have greatly expanded. Within the $1,600 billion global chemicals industry, the largest segment, 40%, is the petrochemical industry. Within the petrochemical industry, commodity polymers account for 55%, in terms of volume, of the consumption of basic petrochemicals. According to the industry estimates, global production and consumption of plastics is growing from 125,000 metric tons in 1997 to 210,000 metric tons by 2007, and 380,000 tons by 2020. The overwhelming position of plastics in the petrochemical industry encourages researchers in this scientifically challenging field. High demand for the initiator which can control desired polymer properties underlines the importance of transition metal-catalyzed polymerization systems. The next four chapters are directed to the continued research field which involves developing new catalyst, understanding polymerization mechanisms and making materials with new or improved properties.

The consideration in chapter 2 is the mechanistic studies of the reaction between vinyl bromide and a palladium(II)-based cationic complex, which is relevant to transition metal-catalyzed polymerization of polar vinyl monomers. The Brookhart-type cationic Pd(II)-methyl species, [(ArN=C(Me)C(Me)=NAr)Pd(Me)]⁺ has been employed for this study. In an attempt to gain mechanistic insights, the stepwise coordination and insertion of vinyl bromide were studied using variable temperature NMR spectroscopy. The active species generated in the presence of aluminum trichloride enabled us to investigate the
reaction of vinyl bromide with a late transition metal-based cationic complex, in which 1,2-alkene insertion followed by $\beta$-bromo elimination occurred. The results deduced from the migratory insertion of the polar and nonpolar vinyl monomers and the deactivation pathway observed here directed us to move to a neutral catalytic system for the polymerization of functionalized alkenes.

Chapter 3 describes the reaction of palladium (1,5-cyclooctadiene)(alkyl)-(chloride) with norbornene derivatives. Metal-catalyzed addition polymerization of functionalized alkenes is an area of great current interest in synthetic polymer chemistry because the addition of functionalities to a polymer which is otherwise non-polar can greatly enhance the range of attainable properties. However, a key problem in the development of metal-catalyzed routes to functionalized polyalkenes is the coordination of the functionality present both in the monomer and in the resulting polymer. From the point of view that Ziegler shows in his theoretical calculations, the neutral complex is employed and investigated as a possible initiator for poly(norbornenes). All of the norbornene and norbornene derivatives with pendant exo and endo functionalities insert into the metal-alkyl bonds through the exo face with similar rates. Unlike cationic systems, no coordination of the ester group is observed. The implication of the work with respect to the metal-catalyzed polymerization of polar vinyl monomers is that the key to the efficient polymerization and copolymerization of functionalized norbornene derivatives lies in the use of less electrophilic, neutral metal species.

The syntheses of new neutral Pd(II)-based complexes and their applications have been addressed in chapters 4 and 5. A majority of the work done in those chapters is the syntheses of neutral complexes having [N-N], [N-O], and [P-N-O] chelate ligands and
characterizations of them with various spectroscopic methods including X-ray single-crystal structure analysis. In an attempt to test their possible applications for the polymerization and copolymerization of polar and non-polar monomers, their reactivities toward monomers, such as carbon monoxide, norbornene, and acrylates, have been studied. The main goal of the research in addition insertion polymerization utilizing transition metal-based is better control over the tacticity of the polymer and the possibility of copolymerizations with monomers otherwise inaccessible. Although extensive mechanistic studies need to be done to understand the mechanism involved in the polymerizations employing the new neutral complexes, the complexes have initiated polymerizations of vinyl monomers alone or with the assistance of an activator.

References

1. (a) http://www.americanplasticscouncil.org (b) http://www.bizsites.com
   (c) http://thakur.itgo.com/petro.htm

Chapter 2

TRENDS IN ALKENE INSERTION IN LATE AND EARLY TRANSITION METAL COMPOUNDS: RELEVANCE TO TRANSITION METAL-CATALYZED POLYMERIZATION OF POLAR VINYL MONOMERS

2.1 Introduction

Metal-catalyzed insertion copolymerization of polar vinyl monomers with nonpolar alkenes remains an area of great interest in synthetic polymer chemistry, because the addition of functionalities to a polymer which is otherwise non-polar can greatly enhance the range of attainable properties.\(^1\) For vinyl monomers with pendant coordinating functionalities, such as acrylates, the principal problem has been catalyst poisoning through functional group coordination.\(^{1-3}\) Interestingly, vinyl halides, which do not possess any strongly coordinating functionality, are also not polymerized by any known transition metal-catalyzed systems. Recently, Jordan\(^4\) and Wolczanski\(^5\) have reported the reaction of vinyl halides with rac-(EBI)ZrMe and (t-Bu\(_3\)SiO)\(_3\)TaH\(_2\), respectively. It was demonstrated that, following 1,2-insertion of the alkene, \(\beta\)-halide elimination occurs to generate a metal-halide bond. Since the halophilicity of the transition metal ions tends to decrease on going from left to right in the periodic table, we undertook an examination of the reactivity of vinyl halides towards a late transition metal complex (palladium). Herein we report mechanistic investigations of the reactions of cationic (\(\alpha\)-diimine)Pd-alkyl complexes with alkenes using variable-temperature \(^1\)H NMR spectroscopy.\(^6\)
2.2 Results

2.2.1 Generation of Active Species

The starting point of our investigation was the Brookhart-type cationic Pd(II)-methyl species, 2, generated in our case by the addition of two equivalents of AlCl₃ to the corresponding neutral Pd(II)-methylchloride, 1, (Schemes 2-1 and 2-2). ¹H NMR studies revealed that the active species 2 forms through the intermediate A or B (Scheme 1).⁷ The reaction of 1 and 1 equiv. of AlCl₃ resulted in the generation of A/B and trace amounts of 2 upon stirring for 2 h at room temperature. The addition of a second equiv. of AlCl₃ to the reaction mixture resulted in the formation of the active species 2 (Figure 2-1). The ¹H NMR spectrum of 2 is similar to that of the Brookhart compound [(ArN=C(Me)C(Me)=NAr)Pd(Me)(NCMe)]BAr’F (Ar = 2,6-di-i-Pr-C₆H₃), implying similar structures for both. However, the Brookhart compound was unreactive towards vinyl bromide, presumably because of the failure of the olefin to displace the coordinated MeCN. Reaction of 1 with B(C₆F₅)₃ or NaB(3,5-(CF₃)₂-C₆H₃)₄ generated similar species produced from the reaction of 1 with 1 equiv. of AlCl₃.

![Scheme 2-1](image-url)

Scheme 2-1
**Figure 2-1**

$1 + 1.2$ equiv. NaB(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_3$

$1 + 1$ or $2$ equiv. B(C$_6$F$_5$)$_3$

$1 + 1$ equiv. AlCl$_3$

$1 + 2$ equiv. AlCl$_3$

Brookhart's system

$H_3CCN \quad R_3Pd \quad B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$-$^+$

Brookhart's system

$\text{Figure 2-1: Generation of Active Species. Selected NMR spectra.}$
2.2.2 $^1$H NMR Study of the Reaction of Cationic (α-diimine)Pd-methyl Complex with Vinyl bromide

Several equivalents of vinyl bromide were added to a CD$_2$Cl$_2$ solution of 2 at -90°C and the reaction mixture was monitored by $^1$H NMR spectroscopy as it was gradually warmed up (Figure 2-2 and Scheme 2-2). The coordination of vinyl bromide to the metal center in 2 was observed even at -86°C, resulting in the formation of 3. Warming the reaction mixture to -74°C resulted in the formation of the propene coordinated species, 4, suggesting 1,2-alkene insertion followed by β-bromo elimination. Propene is gradually lost from 4 and is trapped by unreacted 2 to form 7. Formation of complex 7 was confirmed by addition of free propene to the system, which caused the ratio of 7 to 4 to increase. The cationic Pd(II)-halide species arising from 4 by propene loss converts to the chloro-bridged dimer 6. The structure of 6 as a dicationic complex with two aluminum tetrachloride counteranions was established by an X-ray crystal structure determination (Figure 2-3).

Once formed, 7 undergoes 1,2-insertion of propene to form the known β-agostic Pd(II)-tert-butyl compound 8. The complexes 7 and 8 were also independently formed by the addition of propene to a CD$_2$Cl$_2$ solution of 2. The initially formed 7 was found to convert to 8 when the solution was warmed to -36°C. At ambient temperature, the three methyl groups of the tert-butyl complex exchange rapidly on the NMR time scale and appear as a singlet at –0.28 ppm. Upon lowering the temperature to -86°C, a static $^1$H NMR spectrum is observed and the agostic proton appears as a singlet at –8 ppm.
Figure 2-2: Selected variable temperature NMR spectra
where, \( N = \text{structure} \), \( X = \text{Br or Cl} \)

Scheme 2-2. Proposed Reaction Pathway\(^6,7\)
Figure 2-3: ORTEP view of 6. Hydrogen atoms are not shown for clarity.
2.2.3 Kinetics of the Reaction of Cationic (α-diimine)Pd-methyl Complex with Alkenes.

The migratory insertion rates of bound vinyl bromide and propene in 3 and 7, respectively, were directly measured by monitoring the disappearance of the corresponding Pd-CH₃ resonance. For propene our value was in close agreement with that reported by Brookhart.¹⁰ For vinyl bromide, an Arrhenius plot was constructed from rate measurements done between -74 and -37°C. Our values together with those of Brookhart⁹,¹⁰ are reported in Table 2-1.

Table 2-1

<table>
<thead>
<tr>
<th></th>
<th>( k \times 10^3 \text{ s}^{-1} )</th>
<th>( \Delta H^\ddagger \text{ (kcal/mol)} )</th>
<th>( \Delta S^\ddagger \text{ (cal/K•mol)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propene</td>
<td>0.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethene¹⁰</td>
<td>1.9</td>
<td>14.2 ± 0.1</td>
<td>-11.2 ± 0.8</td>
</tr>
<tr>
<td>Vinyl Bromide</td>
<td>22.0</td>
<td>11.9 ± 0.1</td>
<td>-16.8 ± 0.1</td>
</tr>
<tr>
<td>Methyl Acrylate⁹</td>
<td>55.0</td>
<td>12.1 ± 1.4</td>
<td>-14.1 ± 7.0</td>
</tr>
</tbody>
</table>

*Measured or extrapolated to 236.5K
* For kinetic data sources, see appendix N

A Hammett plot²² of the relative insertion rates of substituted alkenes versus \( \sigma_p \)¹⁹ yielded a straight line with a positive \( \rho \) (+3.41) (Figure 2-4). Of note is that the line encompasses values obtained by both Brookhart⁹,¹⁰ and us.
Figure 2-4: Hammet plot for migratory insertion of alkenes into palladium(II)–methyl bond.
2.3 Discussion

2.3.1 Formation of Dimer and Deactivation Pathway.

The identity of the halide ligand in 4 (Scheme 2-2) has not been established but the formation of 6 opens up the possibility of an aluminum-assisted β-bromo abstraction pathway shown in Scheme 2-2. The dimer formation is observed only when vinyl halides, such as vinyl bromide or vinylidene chloride, are utilized as monomers. Surprisingly, the β-bromopropyl-Pd(II) complex was not observed. It is likely that the β-bromoalkyl-metal intermediate rapidly reacts with excess aluminum chloride, followed by Cl/Br exchange, to form the dichloro-bridged palladium-diimine complex 6 which crystallizes out of solution due to its low solubility.

Prolonging the reaction time of 1 with 2 equiv. of AlCl3 in CD2Cl2 also generates 6, which implies another possible pathway for the formation of the dichloro-bridged dimer, 6.

2.3.2 Relative Insertion Rates of Alkenes.

We have observed a linear positive Hammett correlation between the rate of insertion and the increasing electron-withdrawing effect of the substituent on the alkene. Theoretical calculations have also led to a lower insertion barrier for acrylates and vinyl halides compared to ethene.11,12 This can be contrasted with a negative value of ρ obtained by Bercaw for alkene insertion in Cp*2NbH(alkene).13 Additionally, The second-order rate constants obtained by Wolczanski for alkene insertion into Ta(V)-H
bond follow the trend $\text{H} \approx \text{OR} >> \text{halide (F, Cl, Br)}$. The decrease in the rate of insertion with increasing electron withdrawing effect of the substituent on the alkene in the case of early transition metal compounds has been attributed to the development of positive charge on the carbon bearing the substituent either during alkene coordination or the subsequent insertion step. In Wolczanski’s case, it has not been possible to separate the effect of the substituent on binding versus insertion, and the trend for the actual insertion step remains an open question. We ascribe the increase in insertion rate for the palladium-methyl complex to a ground-state effect. An alkene with an electron-withdrawing substituent coordinates less strongly to the electrophilic metal (i.e. donation is more important than back-donation). Thus, a weaker metal-alkene bond has to be broken for the insertion to proceed (i.e., the destabilization of the alkene complex leads to a lower insertion barrier). Another surprising observation is that the observed correlation extends to propene. The slower insertion and polymerization rates of propene, when compared to ethene, are usually attributed to the steric bulk of the methyl group of the former. Our results suggest that, at least for the late transition metal compounds, it is the donating ability of the methyl group, rather than its size, which results in a slower rate for propene insertion and, hence, polymerization. This argument applies even for the sterically encumbered Brookhart-type system. Likewise, for acrylates, the precoordination of the ester group appears to have little effect on its migratory insertion rate.
2.4 Conclusions

What is the implication of our work with respect to the metal-catalyzed polymerization of polar vinyl monomers? First, for the late transition metal compounds, the polar vinyl monomers can clearly outcompete ethene and simple 1-alkenes with respect to insertion. However, the ground-state destabilization of the alkene complex that favors the migratory insertion of the polar vinyl monomers is a two-edged sword because it biases the alkene coordination towards ethene and 1-alkenes. Indeed, we have observed the near quantitative displacement of vinyl bromide by propene to form 7 from 3. Thus, the extent of incorporation of the polar vinyl monomer in the polymer will depend on the opposing trends in alkene coordination and migratory insertion. The above discussion does not take into account the problem of functional group coordination for acrylates or β-halide abstraction for vinyl halides. With respect to the latter, we are currently exploring approaches to suppress this “termination” step, e.g. decreasing the electrophilicity of the metal center.
2.5 Experimental Section

All work involving air and moisture sensitive compounds was carried out under an inert atmosphere of argon or nitrogen by using standard Schlenk or glove-box techniques. Variable-temperature $^1$H NMR experiments were performed on a Brüker DPX 300 NMR spectrometer, using CD$_2$Cl$_2$ as solvent. Actual NMR probe temperatures were measured using anhydrous methanol (with 0.03% concentrated HCl) or ethylene glycol (neat) in a 5 mm NMR tube (see 2.5.1 and 2.5.2).

All solvents were deoxygenated, dried via passage over a column of activated alumina, degassed by repeated freeze-pump-thaw cycles, and stored over 4 Å molecular sieves under nitrogen. The α-diimine ligand, 2,6-C$_6$H$_4$(i-Pr)$_2$-N=C(Me)-C(Me)=N-2,6-C$_6$H$_4$(i-Pr)$_2$, and complex, (2,6-C$_6$H$_4$(i-Pr)$_2$-N=C(Me)-C(Me)=N-2,6-C$_6$H$_4$(i-Pr)$_2$)Pd(Me)(Cl) were prepared as previously reported.$^{20,21}$ AlCl$_3$ (Strem) was stored in a nitrogen-filled drybox and used as received. Vinyl bromide (98%) was purchased from Aldrich and used without further purification.

Rates for migratory insertion of alkenes into the Pd(II)-Me bond were determined by adding 20 equiv. of alkenes to the pre-generated complex 2 solution in CD$_2$Cl$_2$ and monitoring the loss of the Pd(II)-Me resonance over time. The natural logarithm of the methyl integral was plotted versus time (first-order treatment) to obtain kinetic plots. Activation parameters ($\Delta G^\ddagger$, $\Delta H^\ddagger$, and $\Delta S^\ddagger$) were calculated from measured rate constants and temperatures using the Eyring equation.
2.5.1 Low Temperature: methanol (with 0.03% concentrated HCl)\textsuperscript{23}

Temperature range: 175~330K (-100 to 55°C)

\[ T_{\text{meas}}[K] = 403.0 - 29.46(\Delta \delta_M) - 23.83(\Delta \delta_M)^2 \]

where \(\Delta \delta_M\) is the chemical shift difference (in ppm) between the methyl and hydroxyl peaks.

2.5.2 High Temperature: ethylene glycol (neat)\textsuperscript{24}

Temperature range: 310~440K (35 to 165°C)

\[ T_{\text{meas}}[K] = 465.8 - 102.24(\Delta \delta_{\text{EG}}) \]

where \(\Delta \delta_{\text{EG}}\) is the chemical shift difference (in ppm) between the methylene and hydroxyl peaks.

2.5.3 Interpretation of activation parameters

\(\Delta G^\ddagger\), the Gibbs free energy of activation, determines at which rate a certain reaction will run at a given temperature

\(\Delta H^\ddagger\) is a measure for the amount of binding energy that is lost in the transition state relative to the ground state (including solvent effects)

\(\Delta S^\ddagger\) is a measure for the difference in (dis)order between the transition state and the ground state
2.5.4 The Eyring Equation

\[ k_{\text{obs}} = (\kappa T/h) \exp(-\Delta G^\dagger/RT) \]
\[ = (\kappa T/h) \exp(-\Delta H^\dagger/RT) \exp(\Delta S^\dagger/R) \]

where, \( \kappa \) is the Boltzmann Constant, \( h \) is Planck’s constant, \( T \) is the temperature in Kelvin, \( R \) is the universal gas constant, and \( \Delta G^\dagger \) is the free energy of activation.

\[ E_a = \Delta H^\dagger + RT \]
\[ \Delta G^\dagger = \Delta H^\dagger - T \Delta S^\dagger \]

2.5.5 Application of the Eyring Equation

After transforming the latter expression of the Eyring Equation,

\[ k_1/T = (\kappa/h) \exp(-\Delta H^\dagger/RT) \exp(\Delta S^\dagger/R) \]
\[ \ln(k_{\text{obs}}/T) = -(\Delta H/R)(1/T) + (\Delta S/R) + \ln(\kappa/h) \]

one can extract the values for \( \Delta H^\dagger \) and \( \Delta S^\dagger \) from kinetic data by plotting \( \ln(k_{\text{obs}}/T) \) versus \( (1/T) \). Such a plot should provide a straight line of slope \( -\Delta H/R \) and y-intercept \( \Delta S/R + \ln(\kappa/h) \). It is necessary to extrapolate the data to \( 1/T = 0 \) to obtain the latter value.
2.6 References


7. Selected $^1$H NMR data (CD$_2$Cl$_2$, 300MHz, $\delta$ in ppm) (a) $^1$H NMR of A/B (25°C) 2.88 and 2.74 (septet, 2H each, Ar-CHMeMe') 2.06 and 2.02 (s, 3H each, N=C(CH$_3$)-C(CH$_3'$)=N) 1.21, 1.13, 1.08, and 1.00 (d, 6H each, Ar-CHCH$_2$CH$_3'$) 0.39 (s, 3H, Pd-CH$_3$) 0.76 (s, 3H, Pd-CH$_3$) (b) $^1$H NMR of 2 (25°C) 7.42~7.34 (m, 6H, Ar-H) 3.04 (septets, 4H, Ar-CHMeMe') 2.22 and 2.17 (s, 3H each, N=C(CH$_3$)-C(CH$_3'$)=N) 0.76 (s, 3H, Pd-CH$_3$) (c) $^1$H NMR of 3 (-70°C) 5.58 (m, 1H, coordinated CH$_2$=CHBr) 5.0 (m, 2H, coordinated CH$_2$=CHBr) 2.44 and 2.33 (s, 3H each, N=C(CH$_3$)-C(CH$_3'$)=N) 0.65 (s, 3H, Pd-CH$_3$) (d) $^1$H NMR of 4 (-50°C) 5.47 (m, 1H, coordinated CH$_2$=CHCH$_3$) 4.21 (m, 2H, coordinated CH$_2$=CHCH$_3$) 2.00 (m, coordinated CH$_2$=CHCH$_3$) (e) $^1$H NMR of 7 (-40°C) 4.31 (m, 2H, coordinated CH$_2$=CHCH$_3$) CH$_2$=CHCH$_3$ obscured CH$_2$=CHCH$_3$ obscured 0.32 (s, 3H, Pd-CH$_3$) (f) $^1$H NMR of 8a,dynamic (-20°C) –
0.27 (br s, 9H, Pd(C(CH$_3$)$_3$)$_2$) $^1$H NMR of $8_b$, static (-70°C) 0.00 (br s, 6H, Pd(C(CH$_2$-$\mu$-H)-(CH$_3$)$_2$)) –8.00 (br s, 1H, Pd(C(CH$_2$-$\mu$-H)-(CH$_3$)$_2$)) (g) $^1$H NMR of 6 (25°C) 2.33 (s, 12H, N=C(CH$_3$)-C(CH$_3$’)=N) 1.35 and 1.23 (d, 24H each, J = 6.59 and 6.86 Hz)


Chapter 3
THE REACTION OF PALLADIUM(1,5-CYCLOOCTADIENE)(ALKYL)(CHLORIDE) WITH NORBORNENE DERIVATIVES: RELEVANCE TO METAL-CATALYZED ADDITION POLYMERIZATION OF FUNCTIONALIZED NORBORNENE

3.1 Introduction

Metal-catalyzed addition polymerization of functionalized alkenes is an area of great current interest in synthetic polymer chemistry because the addition of functionalities to a polymer which is otherwise non-polar can greatly enhance the range of attainable properties.\(^1\)\(^2\) One particular area of interest has been the addition polymerization of functionalized norbornene derivatives.\(^3\)\(^4\) The resultant polymers exhibit superior etch resistance and thermal stability and are attractive candidates for deep UV photolithography.\(^5\) A key problem in the development of metal-catalyzed routes to functionalized polyalkenes is the coordination of the functionality present both in the monomer and in the resulting polymer. Because they are synthesized by Diels-Alder reaction, functionalized norbornene derivatives sold commercially consist of exo and endo isomers with the latter predominating (approx. molar ratio: 1:3-1:4).\(^6\) Earlier work in other labs,\(^7\)-\(^10\) as well as our own,\(^11\)\(^12\) have shown that the endo-functionalized norbornenes are polymerized more slowly. The slow polymerization rate for commercial functionalized norbornene mixtures has previously been ascribed to the formation of a chelate by coordination of the functionality to the metal center and the C=C bond along the endo face (Figure 3-1).\(^7\)-\(^12\) This has two detrimental effects on polymerization. First,
chelation strengthens metal-alkene interaction, thereby raising the barrier for the insertion step. Second, it forces insertion through the endo face, in sharp contrast to the known propensity for norbornene to insert into metal-carbon bonds through the less hindered exo face.\textsuperscript{13-15} Indeed, we had earlier isolated and characterized a platinum complex formed by the insertion of endo-5-ethylester-2-norbornene into a Pt-H bond through the endo face.\textsuperscript{12}

Figure 3-1

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Modes of bonding for functionalized norbornene derivatives (X = coordinating functionality).}
\end{figure}

The catalyst systems for which the relative exo versus endo reactivity have been reported are cationic. Theoretical calculations by Ziegler show that while the interaction of an oxygen functionality (e.g., ester group) with the metal center is weaker in neutral complexes when compared with the corresponding cationic species, the bonding of the vinyl functionality is not significantly affected because the weaker alkene to metal charge transfer in the neutral complex is compensated by stronger metal to alkene back-bonding.\textsuperscript{16} We have conducted studies encompassing the insertion of norbornene
derivatives into palladium-carbon bonds in a neutral palladium compound, Pd(1,5-cyclooctadiene)(alkyl)(chloride). As described below, we have now succeeded in the first isolation of norbornene and functionalized-norbornene-inserted compounds, as well as the characterization using X-ray crystal structure analysis. The system showed “living”-type polymerization through coordination insertion mechanism.

3.2 Results and Discussion

3.2.1 Reactions of Pd(1,5-cyclooctadiene)(CH₃)(Cl) with Norbornene Derivatives

The result of the NMR scale reaction between (1,5-COD)Pd(CH₃)(Cl) (COD = 1,5-cyclooctadiene) and norbornene, indicating the formation of a norbornene-inserted complex and, consequently, norbornene oligomer, directed us to conduct isolation and characterization process of a desired norbornene-derivative-inserted complex. Four complexes, from norbornene, endo- and exo-5-ester norbornenes, and endo-5-methylacetate norbornene, have been synthesized under similar reaction conditions(Scheme 3-1). All of the compounds have been isolated as a solid by triturating in diethyl ether or diethyl ether/pentane mixture at ambient temperature under the inert atmosphere or at -15°C. For the compound 1a, the apical protons of the norbornene moiety show resonances at 2.1 and 1.04 ppm with a geminal coupling constant of 9.8 Hz. A pair of doublet and multiplet at 1.83 and 1.76 ppm, respectively, are assigned to the two-carbon bridge protons, Pd-CH-CH-CH₃, of the norbornene framework. A coupling of 5.6 Hz was measured between the two protons. Since the vicinal coupling constant of 6 to
7 Hz is a typical value between the endo protons of the norbornene framework, syn addition across the exo face of the norbornene is deduced.

\[
\text{Pd}^+ \left\{ \begin{array}{c} \text{Cl} \\
\text{CH}_3 \\
\text{R} \\
\text{H}_3\text{C} \\
\text{H} \\
\text{H} \\
\text{R} \\
\end{array} \right. \xrightarrow{\text{CH}_2\text{Cl}_2 \ 	ext{RT}} \left\{ \begin{array}{c} \text{Pd} \\
\text{H}_3\text{C} \\
\text{Cl} \\
\text{H} \\
\text{H} \\
\text{R} \\
\text{H}_3\text{C} \\
\text{H} \\
\text{H} \\
\text{R} \\
\end{array} \right. \\
\text{1a-d} \\
\]

where, \( \text{R} = \text{a:} \quad \text{b:} \quad \text{c:} \quad \text{d:} \)

\begin{align*}
\text{a:} & = \end{align*}
\begin{align*}
\text{b:} & = \end{align*}
\begin{align*}
\text{c:} & = \end{align*}
\begin{align*}
\text{d:} & = \end{align*}

**Scheme 3-1**

The products 1a-d of the reaction of \((1,5\text{-COD})\text{Pd}(\text{CH}_3)(\text{Cl})\) with norbornene (NB), endo and exo-5-ethylester-2-norbornene (EtEster-NB, NB-COOCH\(_2\)CH\(_3\)), and endo-5-methylacetate-2-norbornene (MeOAc-NB, NB-CH\(_2\)OC(O)CH\(_3\)) were isolated and their structures were determined by X-ray single-crystal structure analysis. X-ray quality crystals were prepared by slow diffusion of pentane into a concentrated solution of 1a, 1c or 1d in methylene chloride or by slow evaporation of solvent from a solution of 1b in methylene chloride at ambient temperature. The ORTEP plots of 1a-d are shown in
Figures 3-2, 3-3, 3-4, and 3-5. (For crystallographic data, see Table 3-5). The selected bond lengths and angles for 1a-d are given in Tables 3-1, 3-2, 3-3, and 3-4. In the solid state they adopt geometries best described as square planar about each palladium center having slight distortions from idealized geometry. In each case, the insertion of the monomer into the palladium-carbon bond had invariably occurred through the exo face with no evidence for interaction of the ester functionality with the metal (e.g., Figure 3-3). In sharp contrast to the cationic systems, the coordination of alkene is favored over an ester functionality. Interestingly, in the crystals formed from the latter three monomers, the two possible regioisomers with the metal and the ester group in 1,3 and 1,4 relationships, were both present suggesting that the ester functionality exerted minimal steric and electronic effect in the insertion.
Figure 3-2: An ORTEP view of 1a, showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Figure 3-3: An ORTEP view of 1b, showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.
Figure 3-4: An ORTEP view of 1c, showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Figure 3-5: An ORTEP view of 1d, showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.
Table 3-1

<table>
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<th>Bond</th>
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<tr>
<td>Pd1-C1</td>
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<tr>
<td>Pd1-C12</td>
<td>2.160(9)</td>
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<tr>
<td>Pd1-C13</td>
<td>2.188(7)</td>
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<tr>
<td>Pd1-C8</td>
<td>2.364(8)</td>
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<tr>
<td>C1-Pd1-C12</td>
<td>89.2(4)</td>
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<tr>
<td>C1-Pd1-C13</td>
<td>90.9(3)</td>
</tr>
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<td>C1-Pd1-C1</td>
<td>94.5(3)</td>
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<td>C12-Pd1-C13</td>
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<td>C13-Pd1-C13</td>
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<tr>
<td>C1-Pd1-C8</td>
<td>161.2(4)</td>
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<td>C6-C1-Pd1</td>
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<td>C12-Pd1-C8</td>
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<td>C16-C6-C5</td>
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Table 3-2

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<td>C9-Pd1-C5</td>
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<td>C17-C11-C10</td>
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Table 3-3

Table 3-3: Selected Bond distances (Å) and Angles (°) for 1c

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<th>Bond distances (Å)</th>
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<td>Pd1-C8 2.187(3)</td>
<td>Pd1-Cl1 2.3426(7)</td>
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Table 3-4

Table 3-4: Selected Bond distances (Å) and Angles (°) for 1d

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<tr>
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<td>C9-Pd1-C2 160.7(3)</td>
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<tr>
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Table 3-5: Crystallographic Data and data Collection Parameters for complexes 1a-d

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<td>Pți</td>
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<td>a(Å)</td>
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<td>γ(deg)</td>
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<tr>
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<tr>
<td>R(F)</td>
<td>0.0763</td>
<td>0.0250</td>
<td>0.0308</td>
<td>0.0685</td>
</tr>
<tr>
<td>R_w(F)</td>
<td>0.1818</td>
<td>0.0685</td>
<td>0.0765</td>
<td>0.1755</td>
</tr>
<tr>
<td>ρ(calc)(Mg/m³)</td>
<td>1.603</td>
<td>1.569</td>
<td>1.569</td>
<td>1.571</td>
</tr>
</tbody>
</table>
3.2.2 Investigation of Reaction Mechanism

The neutral palladium(II) compound, Pd(1,5-cyclooctadiene)(methyl)(chloride)\textsuperscript{17} was found to be effective for the oligomerization of norbornene. A linear increase in molecular weight was observed with time, with $M_w$ reaching 1,600 (versus polystyrene standard) in approximately 60 min at ambient temperature (Figure 3-6). The behavior suggests that the oligomerization is “living”. The relatively slow reaction rate gave us the opportunity to examine the mechanism of norbornene insertion into the palladium-carbon bond in some detail.

Figure 3-6

![Figure 3-6: Molecular weight of norbornene oligomer versus time](image)

For data sources, see Appendix O
The oligomerization of norbornene by the insertion product 1a derived from Pd(1,5-cyclooctadiene)(methyl)(chloride) and NB was also examined. A linear increase in molecular weight with a slope similar to that seen starting with Pd(1,5-cyclooctadiene)(methyl)(chloride) was observed (Figure 3-6), strongly suggesting that the initial insertion product 1a was an intermediate in norbornene oligomerization by Pd(1,5-cyclooctadiene)(methyl)(chloride).

Figure 3-7

![Graph of ln([NB]/[NB]₀) versus time. Reaction conditions: 1 (3.7x10⁻⁵ mol), norbornenes (7.5x10⁻⁴ mol), CD₂Cl₂ (1 mL), 23°C.](image)

*For kinetic data sources, see Appendix O*

The kinetics of the reaction of Pd(1,5-cyclooctadiene)(methyl)(chloride) with NB, exo- and endo-EtEster-NB was investigated by ¹H NMR spectroscopy. In each case, the reaction was first-order in the monomer (Figure 3-7) with rate constants of 2x10⁻⁵ s⁻¹,
1x10^{-5} \text{s}^{-1}, \text{ and } 5x10^{-6} \text{s}^{-1}, \text{ respectively. This system is the first which exhibits similar insertion rates for norbornene and its } \text{exo- and endo-5-ester derivatives, thereby supporting Ziegler’s calculations}^{16} \text{ and the notion that catalytic polymerization of functionalized monomers will be made more facile by moving from a cationic to a less electrophilic, neutral, metal center. The simplest mechanism that accounts for this observation involves alkene coordination to the fifth-coordination site of the metal, followed by insertion into the } \text{cis metal-carbon bond. The effect of potential coordinating moieties: C=C, chloride, and ester group, on the rate of norbornene polymerization (} = \text{ rate of insertion) was probed by the addition of 1,5-cyclooctadiene, } \text{NR}_4^+\text{Cl}^-, \text{ and ethyl acetate. As shown in Table 3-6, the extent of inhibition clearly decreases in the order C=C > Cl- > RC(=O)OR with the ester group having minimal effect on the polymerization. This observation is in stark contrast to the cationic norbornene polymerization systems whose activities are sharply attenuated by the presence of a coordinating solvent such as ethyl acetate.}^{11,12} \text{ One interesting aspect of the above chemistry is that the insertion of a C=C bond of 1,5-cyclooctadiene is never observed. The reason for this is unclear although the norbornene C=C bond is expected to be more reactive due to greater ring strain.}
Taken together, the twin observations that (a) ethyl acetate does not inhibit norbornene polymerization and (b) norbornene derivatives with pendant *endo* ester functionalities insert into the metal-alkyl bond through the *exo* face with rates similar to that seen with norbornene, clearly demonstrate that there is no coordination of the ester group and suggests that the key to the efficient polymerization and copolymerization of functionalized norbornene derivatives lies in the use of less electrophilic, neutral metal species.

Table 3-6: Effect of Additives on the Polymerization of Norbornene using (1,5-COD)PdMeCl

<table>
<thead>
<tr>
<th>(1,5-COD)PdMeCl (x10⁻⁴ mol)</th>
<th>Additive</th>
<th>Norbornene (equiv.)</th>
<th>Yielda (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.13 None</td>
<td>200</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>1.13 1,5-CODb (20)</td>
<td>200</td>
<td>n.r.</td>
<td></td>
</tr>
<tr>
<td>1.13 1,5-CODb (200)</td>
<td>200</td>
<td>n.r.</td>
<td></td>
</tr>
<tr>
<td>1.13 (Butyl)₄NCl (20)</td>
<td>200</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>1.13 MeCO₂Et (20)</td>
<td>200</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>1.13 MeCO₂Et (200)</td>
<td>200</td>
<td>58</td>
<td></td>
</tr>
</tbody>
</table>

aIsolated solid polymer. Reaction conditions: 60°C, 2 h, PhCl (7 g). b1,5-cyclooctadiene
3.3 Conclusion

We have explored the reactivity of the complex, Pd(1,5-cyclooctadiene)(alkyl)(chloride), encompassing the insertion of norbornene and norbornene derivatives into palladium-carbon bonds in a neutral palladium compound. Norbornene and norbornene derivatives, such as *endo*- and *exo*-5-ester norbornenes, and *endo*-5-methylacetate norbornene, insert into metal-alkyl bond through the *exo* face. Insertion rate of the substituted norbornenes is similar to that seen with unsubstituted norbornene. Norbornene- and substituted-norbornene-inserted complexes are isolated and characterized using NMR spectroscopy as well as X-ray single-crystal structure analysis. Unlike cationic systems, no coordination of the ester group is observed. The plot of molecular weight of norbornene oligomer *versus* time indicates that the polymerization system is “living”. The results that ethyl acetate does not inhibit norbornene polymerization and that there is no coordination of the ester group suggest that the use of less electrophilic, neutral metal species is the key to the efficient polymerization and copolymerization of functionalized norbornene derivatives.
3.4 Experimental Section

3.4.1 Generation Considerations.

All work involving air and moisture sensitive compounds was carried out under an inert atmosphere of argon or nitrogen by using standard Schlenk or glove-box techniques.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX 400 NMR spectrometer and DPX 300 NMR spectrometer. Variable-temperature $^1$H NMR experiments were performed on a Bruker DPX 300 NMR spectrometer, using CD$_2$Cl$_2$, toluene-d$_8$, or chlorobenzene-d$_5$ as solvent. Actual NMR probe temperatures were measured using anhydrous methanol (with 0.03% concentrated HCl) or ethylene glycol (neat) in a 5 mm NMR tube (see 2.5.1 and 2.5.2). NMR analyses of polymers were performed on a Bruker DPX 300 NMR spectrometer at ambient or elevated temperature, using CDCl$_3$ or chlorobenzene-d$_5$ as solvent unless otherwise noted.

Size exclusion chromatography data were obtained on a Shimadzu SEC System using a three-column bank (Styrage 7.8x300 mm columns, 100-5,000 D, 500-30,000 D, 2000-4,000,000 D), a Shimadzu RID-10A Differential Refractometer, and a Shimadzu LC-10AT pump/controller. Size exclusion chromatography was performed in chloroform at ambient temperature and calibrated to polystyrene standards.

Chlorobenzene and dichloromethane was obtained from Aldrich and dried over CaH$_2$ and freeze-thaw degassed three times prior to use. Norbornene was purchased from Acros Organics and used without further purification. Toluene, pentane, and diethyl ether were deoxygenated, dried via passage over a column of activated alumina, degassed by
repeated freeze-pump-thaw cycles, and stored over 4 Å molecular sieves under nitrogen. Palladium(1,5-cyclooctadiene)(methyl)(chloride), was prepared as previously reported\textsuperscript{17}. *Endo*-Ethylester-norbornene, *exo*-ethylester-norbornene, and *endo*-methylacetate-norbornene were supplied by Jeffrey Funk.

### 3.4.2 Synthesis of Complexes

**\((1,5\text{-COD})\text{Pd(CI)(2-Me-norbornanyl)} (1a)\)**. To Pd(1,5-cyclooctadiene)(alkyl)(chloride) (100 mg, 0.38 mmol) in methylene dichloride (5 ml) was added norbornene (36 mg, 0.38 mmol) drop-wise at room temperature. The solution was stirred for 2 h at room temperature. After filtration to remove metallic palladium, removal of solvent in vacuo yielded an oily solid, which is triturated in ether. Upon filtering and washing with diethyl ether followed by pentane, the compound **1a** was obtained as an off-white solid. Recrystallization from methylene dichloride/pentane gave a clear crystalline solid which was suitable for X-ray crystal structure analysis. Yield 0.12 g, 89%. \( ^1H \text{NMR}(CD_2Cl_2): \delta 5.83 (m, 2H, -CH=CH-), 5.01 (m, 2H, -CH=CH^'), 2.85 (s, 1H, bridgehead -CH), 2.73-2.38 (m, 8H, two =CH-CH\_2-CH\_2-CH=), 2.1 (br, 1H, anti apical -CHH and 1H, bridgehead -CH), 1.83 (d, 1H, Pd-CH-), 1.76 (m, 1H, CH\_3-CH-), 1.51 (m, 1H, exo-CHH-), 1.46 (d, 3H, CH\_3-), 1.29 (m, 1H, exo-CHH-), 1.04 (d, syn apical -CHH-), 1.13-0.99 (m, 2H, two endo-CHH-). \( ^1C \text{NMR}(CD_2Cl_2): \delta 125.9 (=CH-CH\_2-CH\_2-CH=), 102.2 (=CH-C'H\_2-C'H\_2-CH=), 64.1 (bridge CH), 49.6 (CH\_3-CH-), 45.7 (Pd-CH-), 44.9 (bridgehead CH), 35.6 (apical CH\_2), 31.7 (CH\_2), 31.6, 31.2 (-CH=CH-), 29.1 (C'H\_2), 27.8, 27.5 (-C'H=C'H-) 22.2 (CH\_3-)
(1,5-COD)Pd(Cl)(2-Me-*endo*-5-ethylester-norbornanyl) \((1b)\). To \(\text{Pd}(\text{1,5}-\text{cyclooctadiene})(\text{alkyl})(\text{chloride})\) (100 mg, 0.38 mmol) in methylene dichloride (5 ml) was added *endo*-5-ethylesternbornene (63 mg, 0.38 mmol) drop-wise at room temperature. The solution was stirred for 2 h at room temperature. After filtration to remove metallic palladium, removal of solvent in vacuo yielded a yellow oil, which is solidified from ether/pentane mixture in freezer. Upon filtering and washing with pentane, the compound \(1b\) was obtained as an yellow solid. Recrystallization from methylene dichloride by slow evaporation gave a yellow crystalline solid which was suitable for X-ray crystal structure analysis. Yield 0.12 g, 74%. \(^1\)H NMR(CD\(_2\)Cl\(_2\)): \(\delta\) 5.87 (m, 2H, \(-\text{CH}=\text{CH}-\)), 5.01 (m, 2H, \(-\text{CH}=\text{CH}^-\)), 4.12 (m, 2H, \(-\text{O}-\text{CH}_2-\text{CH}_3\)), 2.72-2.43 (m, 12H, two \(=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}^-\), two bridgehead \(\text{CH}\), and \(-\text{CH}-\text{C}(=\text{O})\text{O}^-\)), 1.86 (d, 1H, Pd-\(\text{CH}^-\)), 1.75 (m, 1H, \(\text{CH}_3-\text{CH}^-\)), 1.73 (m, 1H, \(\text{exo}-\text{CHH}^-\)), 1.45 (m, 2H, two \(\text{endo}-\text{CHH}^-\)), 1.44 (d, 3H, \(\text{CH}_3-\text{CH}^-\)), 1.31 (t, 3H, \(-\text{O}-\text{CH}_2-\text{CH}_3\)), 1.20 (m, 2H, syn and anti apical \(-\text{CH}^-\) and \(-\text{CHH}^-\)). \(^{13}\)C NMR(CD\(_2\)Cl\(_2\)): 125.8 \((=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}^-\)), 60.4 \((-\text{O}-\text{CH}_2-\text{CH}_3\)), 49.1 \((\text{CH}_3-\text{CH}^-\)), 47.4 \((\text{CH}\)), 45.9 \((\text{Pd}-\text{CH}^-\)), 37.3 \((\text{apical} \text{CH}_2\)), 32.0 \((\text{CH}_2\)), 31.5, 31.4 \((-\text{CH}=\text{CH}^-\)), 27.8, 27.7 \((-\text{CH}^-\text{C}^-\text{CH})\) 22.7 \((\text{CH}_3\)), 14.7 \((-\text{O}-\text{CH}_2-\text{CH}_3\)).

(1,5-COD)Pd(Cl)(2-Me-*exo*-5-ethylester-norbornanyl) \((1c)\). To \(\text{Pd}(\text{1,5}-\text{cyclooctadiene})(\text{alkyl})(\text{chloride})\) (100 mg, 0.38 mmol) in methylene dichloride (5 ml) was added *exo*-5-ethylesternbornene (63 mg, 0.38 mmol) drop-wise at room temperature. The solution was stirred for 2 h at room temperature. After filtration to remove metallic palladium, removal of solvent in vacuo yielded a yellow oil, which is triturated in ether. Upon filtering and washing with ether followed by pentane, the compound \(1c\) was
obtained as an off-white solid. Recrystallization from methylene dichloride/pentane gave a clear crystalline solid which was suitable for X-ray crystal structure analysis. Yield 0.14 g, 86%.

\((\text{1,5-COD})\text{Pd(Cl)(2-Me-end}-\text{o-5-methylacetate-norbornanyl)}\) (1d). To \(\text{Pd(1,5-cyclooctadiene)(alkyl)(chloride)}\) (100 mg, 0.38 mmol) in methylene dichloride (5 ml) was added \(\text{endo-5-methylacetatenorbornene}\) (63 mg, 0.38 mmol) drop-wise at room temperature. The solution was stirred for 2 h at room temperature. After filtration to remove metallic palladium, removal of solvent in vacuo yielded a yellow oil, which is solidified from ether/pentane mixture in freezer. Upon filtering and washing with pentane, the compound 1d was obtained as a yellow solid. Recrystallization from methylene dichloride/pentane gave a clear crystalline solid which was suitable for X-ray crystal structure analysis. Yield 0.13 g, 80%. \(^1\)H NMR(\(\text{CD}_2\text{Cl}_2\)): \(\delta\) 5.83 (m, 2H, \(-\text{CH}=\text{CH}-\)), 5.08 (m, 2H, \(-\text{CH} \cong \text{CH} '-\)), 3.96 (m, 2H, \(-\text{OCH}_2\text{CH} -\)), 2.75-2.42 (m, 8H, two \(=\text{CH-CH}_2\text{-CH}-\)), 2.18 (d, 1H, anti apical \(-\text{CHH} '-\)), 2.04 (s, 3H, \(\text{CH}_3\text{-C(=O)-O-}\)), 1.92 (d, 1H, Pd-\(\text{CH}-\)), 1.80 (m, 1H, \(\text{CH}_3\text{-CH}-\)), 1.61 (m, 1H, exo-\(\text{CHH} '-\)), 1.46 (d, 3H, \(\text{CH}_3\text{-}\)), 1.18 (d, 2H, syn apical \(-\text{CHH} '-\)), 0.58 (m, 1H, \(\text{endo-CHH} '-\)). \(^{13}\)C NMR(\(\text{CD}_2\text{Cl}_2\)): 125.8 (=\(\text{CH-CH}_2\text{-CH}_2\text{-CH} =\)), 101.0 (=\(\text{CH-C} \equiv \text{C}-\text{H}_2\text{-CH}=\)), 66.0 (=\(\text{CH}_2\text{-O-C(=O)-CH}_3\)), 50.0 (\(\text{CH}_3\text{-CH}-\)), 47.5 (CH), 45.8 (\(\text{CH}_3\text{-CH}_2\text{-CH} =\)), 41.0 (Pd-\(\text{CH}_2\)), 37.3 (apical CH\(_2\)), 33.1 (CH\(_2\)), 31.5, 31.3 (=\(\text{CH} =\text{CH} =\)), 27.8, 27.7 (=\(\text{C} \equiv \text{C}-\text{H} =\)) 22.7 (CH\(_3\)), 21.1 (=\(\text{CH}_2\text{-O-C(=O)-CH}_3\)).
3.4.3 General Procedure for NMR Experiments

In a drybox under a nitrogen atmosphere, 1 (10 mg) was weighed into an NMR tube. CD$_2$Cl$_2$ (0.1 mL) was added to the NMR tube. The tube was then capped with a septum, removed from the drybox, and cooled to ca. -90°C using liquid nitrogen/acetone slurry. 10 wt. % norbornene or functionalized norbornene in CD$_2$Cl$_2$ solution(1 mL) was then added to the NMR tube via a gas-tight syringe at that temperature, and the septum was wrapped with Parafilm. The tube was shaken very briefly, and transferred to the NMR probe. For conversion kinetics of norbornene derivatives, NMR spectra were acquired every 15 min at a desired temperature. TMS was employed as an external standard.

3.4.4 General Procedures for Polymerization Reactions

In a 100 mL Schlenk flask, 0.11 mmol of 1 was dissolved in 7 g of chlorobenzene. 22 mmol of norbornene or norbornene derivatives was introduced to the flask. The reaction mixture was stirred at a desired temperature. After the specified reaction time, the reaction was quenched with methanol. The precipitated polymer was filtered and washed with methanol. Volatiles were removed from the polymer in vacuo, and the polymer was dried under vacuum overnight.

To measure the molecular weight of poly(norbornene) versus time, 5 g of norbornene and 40 mL of chlorobenzene were used instead of the amounts listed above. 5 mL of reaction mixture was taken from the flask every 10 min, and quenched with methanol. Each sample was worked up as above.
3.5 References


Chapter 4
NEUTRAL PALLADIUM(II) COMPLEXES WITH N-O CHELATE: SYNTHESES, CHARACTERIZATION, AND THEIR REACTIVITIES

4.1 Introduction

Since the revolution of metallocene-based catalysts for ethylene and $\alpha$-olefin polymerization,\(^1\)\(^2\) many efforts have been made to develop metallocene-\(^3\) and non-metallocene-based\(^4\)\(^7\) complexes for the successful homo- or co-polymerization of vinyl alkenes through a successive coordination insertion mechanism. Utilizing the late-transition-metal-based systems, the majority of the studies for the alkene polymerizations where an insertion mechanism is operative are the systems based on cationic palladium(II) complexes.\(^4\) Although the sensitivity of metallocene-based catalysts to polar functionalities allowed the late-transition metal-based systems to attract considerable attention,\(^6\)\(^8\) the electrophilicity of the cationic palladium compounds still limits their catalytic application to coordination polymerization of monomers having polar functionalities, such as acrylates.

In view of the limited compatibility of the cationic Ni and Pd complexes with a polar functional group of a monomer, considerable attention has been made in developing nickel-based neutral complexes for polymerization of polar- or non-polar vinyl monomers.\(^6\)\(^7\) Recently, several neutral nickel catalysts based on [N,O] chelate ligands following SHOP-type catalysts,\(^9\)\(^-\)\(^13\) where they have [P,O] chelate ligands, have been reported by the DuPont,\(^14\) Grubbs,\(^15\)\(^,\)\(^16\) Brookhart,\(^17\)\(^,\)\(^18\)\(^,\)\(^19\) and other\(^20\)\(^-\)\(^22\) groups. The most
important contribution of the results reported by them to the transition metal based polymerization research area is that they, especially the Grubbs group, showed the unprecedented functional group tolerance of the catalytic system by polymerizing alkenes having polar functionality or by carrying out polymerizations in the presence of polar impurities, which are poisons for cationic catalysts. Palladium-based neutral catalysts have also been reported by the Novak and Sen. Sen and Novak have homo- or co-polymerized methyl acrylate with or without 1-hexene. However, in both cases, a radical mechanism rather than a coordination insertion mechanism was suggested to be operative.

Synthesis of Pd(II)-based neutral complexes having [N,O] and [N,N] chelate ligands and their characterization using NMR spectroscopy as well as X-ray single-crystal analysis are reported in this chapter. The complexes showed reactivity toward carbon monoxide followed by an imine. They also produced norbornene oligomer and poly(methyl acrylate).

4.2 Results and Discussion

4.2.1 Complex Synthesis

A Salicylaldimine ligand was prepared by condensation of 3-tert-butyl-2-hydroxy-benzaldehyde with 2,6-di-isopropyl-aniline in the presence of formic acid as a catalyst (Scheme 4-1).

In situ formation of the sodium salt from 1 upon deprotonation with sodium hydride at room temperature, followed by reaction with the palladium precursor,
cyclooctadienylpalladiummethylchloride, (COD)Pd(Me)Cl, \(^{25}\) in toluene was not satisfactory in our case.\(^{15}\) Only starting ligand was recovered without being deprotonated. However, upon attempted deprotonation of \(\text{I}\) with a slight excess of potassium hydride in THF, potassium salt \(\text{2}\) as the THF adduct with one \textit{equiv.}\ of THF coordinated was successfully isolated as a yellow solid after triturating with pentane. The potassium salt \(\text{2}\) was relatively stable over the course of several months under nitrogen atmosphere.

Neutral palladium complexes of \(\text{3a-3e}\) were first synthesized by combining the potassium salt \(\text{2}\) with (COD)PdMeCl in the presence of slight excess of an appropriate imine in toluene for \textit{ca.} 12h. Potassium chloride was separated by filtration, and the product was isolated by triturating with ether, followed by washing with pentane.
Complexes 3a-3e were obtained as yellow solid in yields of \textit{ca.} 90\% upon recrystallization from pentane or methylene chloride/pentane.

Scheme 4-2. Preparation of the Complexes, 3a-e

For all of complexes, coordination of an imine to the palladium center appears to affect rotation of the 2,6-\textit{di}-isopropylphenyl group about the N-aryl bond, becoming slow on the NMR time scale and thus renders the individual methyl groups of an isopropyl unit inequivalent in the $^1\text{H}$ NMR spectrum. Four doublets, each of which integrates to three protons are observed. For complex 3e, two doublets, each of which integrates to one proton, are observed at 5.61 and 5.10 ppm. As expected, two methylene protons on benzyl group (\text{=N-CH$_2$-Ph}) have different stereochemical environments, which resulted in two sets of doublets. The resonances attributed to the palladium-bound methyl groups are shown at -0.47 to -0.86 ppm, with corresponding $^{13}$C NMR resonances at -4.1 to -6.1 ppm.

The molecular structures of the complexes, 3a and 3c-3e, were determined by single-crystal X-ray structure analysis. X-ray quality crystals of the complexes were
obtained either by slow diffusion of pentane into a concentrated solution of 3e in methylene chloride at room temperature or by cooling a concentrated solution of a complex in pentane down to room temperature(3a and 3d) or to -25°C(3c). The ORTEP plots of 3a and 3c-3e are shown in Figures 4-1, 4-2, 4-3, and 4-4. (For crystallographic data, see Table 4-6). The selected bond lengths and angles for 3a and 3c-3e are given in Tables 4-1, 4-2, 4-3, and 4-4. In the solid state they adopt geometries best described as square planar about each palladium center having slight distortions from idealized geometry. An imine is coordinated through the nitrogen which is in the trans position to a nitrogen of a [N,O] chelate ring as a result of the steric. The planes of C-N-C including palladium-bound nitrogen in imine ligands are roughly perpendicular to the square planes around each palladium. The cis N-Pd-O angles for the complexes 3a-e exceed 90°, due to the formation of six-membered [N,O] chelate rings. Conversely, the cis N-Pd-C, containing nitrogen of an imine and methyl group, angles are in the range of 85.7(3) to 89.28(9), which is smaller than 90°.
Figure 4-1: ORTEP view of complex 3a. Hydrogen atoms are omitted for clarity.

Figure 4-2: ORTEP view of complex 3c. Hydrogen atoms are omitted for clarity.
Figure 4-3: ORTEP view of complex 3d. Hydrogen atoms are omitted for clarity.

Figure 4-4: ORTEP view of complex 3e. Hydrogen atoms are omitted for clarity.
Table 4-1: Selected Bond distances (Å) and Angles (°) for 3a

<table>
<thead>
<tr>
<th>Bond/Stereochemistry</th>
<th>Distance/Angle</th>
</tr>
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<tbody>
<tr>
<td>Pd1-N2</td>
<td>1.989(10)</td>
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<tr>
<td>Pd1-C12</td>
<td>2.035(10)</td>
</tr>
<tr>
<td>Pd1-N1</td>
<td>2.038(9)</td>
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<tr>
<td>Pd1-O2</td>
<td>2.051(7)</td>
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<tr>
<td>O2-C1</td>
<td>1.275(13)</td>
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<tr>
<td>N2-Pd1-C12</td>
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<tr>
<td>N2-Pd1-N1</td>
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<tr>
<td>C12-Pd1-N1</td>
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<tr>
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<td>C12-Pd1-O2</td>
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<tr>
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<tr>
<td>N1-C21</td>
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<tr>
<td>N2-C14</td>
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<td>C14-N2-C13</td>
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<td>C1-O1-Pd1</td>
<td>128.26(15)</td>
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Table 4-2: Selected Bond distances (Å) and Angles (°) for 3c

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<th>Bond/Stereochemistry</th>
<th>Distance/Angle</th>
</tr>
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<tbody>
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<td>Pd1-N1</td>
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<td>Pd1-N2</td>
<td>2.059(2)</td>
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<tr>
<td>Pd1-O1</td>
<td>2.0990(16)</td>
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<tr>
<td>O1-C1</td>
<td>1.285(3)</td>
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<tr>
<td>N2-C25</td>
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<tr>
<td>N2-C92</td>
<td>1.517(3)</td>
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<tr>
<td>N1-C7</td>
<td>1.294(3)</td>
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Table 4-3

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Table 4-4

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<td>N2-Pd1-O1</td>
<td>87.40(7)</td>
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Complex 4 was prepared to compare the coordination ability of an imine to pyridine. The reaction of the potassium salt 2 with (COD)PdMeCl in the presence of tert-butyl-pyridin-2-ylmethylene-amine in toluene afforded the target compound 4 as a yellow solid in good yield after removing the solvent under vacuo following filtration.

![Scheme 4-3. Preparation of the Complex 4](image)

Figure 4-5: ORTEP view of complex 4. Hydrogen atoms are omitted for clarity.
The CH imine protons of the monodentate ligand and [N,O] chelate ring show resonances at 7.71 and 9.94 ppm, respectively. The palladium-bound methyl proton shows its resonance at -0.26 ppm. The molecular structure of complex 4 was confirmed by single crystal X-ray structure analysis. Cooling the concentrated compound 4 solution in pentane down to room temperature produced a yellow crystal which was suitable for the analysis. Figure 4-5 displays the ORTEP diagram of compound 4. Selected bond distances and bond angles are collected in Table 4-5 (see Table 4-6 for crystallographic data). In the solid state it shows square planar coordination geometry about palladium, with bond angles slightly deviating from 90° by virtue of the constraint arisen from the chelate ring. The imine is bound to palladium through the nitrogen of the pyridine ring, indicating that there is a steric reason for the coordination rather than an electronic reason. Nucleophilicity of pyridine is slightly smaller than that of an imine. However, steric forces have been proposed to control the ligand orientation as well as dictating the geometry of the imine ligand. The compound itself assigned the best place for each ligand to ease steric hindrance, in which an imine is positioned trans to the nitrogen of the [N,O] chelate rings, and the plane around the nitrogen in the imine is perpendicular to the square plane around palladium. With the same reason, the ligand is bound to the metal center through the nitrogen on pyridine rather than the nitrogen next to the t-butyl group.
Table 4-5

Table 4-5: Selected Bond distances (Å) and Angles (°) for 4

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<tr>
<td>O1-C1</td>
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<table>
<thead>
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<th>Bond/Angle</th>
<th>Distance/Angle</th>
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<td>C7-N1-Pd1</td>
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Table 4-6

Table 4-6: Crystallographic Data and data Collection Parameters for complexes 3a-e and 4

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<th>3c</th>
<th>3d</th>
<th>3e</th>
<th>4</th>
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<td>C₁₀₅H₁₄₄N₆O₃Pd₃</td>
<td>C₇₄H₈₈N₄O₂Pd₂</td>
<td>C₃₈H₄₆N₂OPd</td>
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<td>98(2)</td>
<td>98(2)</td>
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<td>Triclinic</td>
<td>Triclinic</td>
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<tr>
<td>s. g.</td>
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<td>P2(1)/c</td>
<td>Pī</td>
<td>Pī</td>
<td>Pī</td>
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4.2.2 Mechanistic Studies of CO Insertion into Pd-Me Bond using Complex 3c

The reaction of the complexes 3a-3e with CO was monitored by $^1$H NMR spectroscopy. Treatment of neutral palladium complexes 3a-3e with $^{13}$CO in CD$_2$Cl$_2$ or chlorobenzene-d$_5$ at ambient temperature or 60°C generates the corresponding palladium acyl species. The methyl group of the acyl appears as a doublet resonance at around 2.7 ppm (23°C in CD$_2$Cl$_2$) in the $^1$H NMR spectrum due to the labeled carbon in carbon monoxide. Disappearance of the Pd-methyl resonance and appearance of the acyl resonance indicates a clean insertion of carbon monoxide into Pd(II)-Me bond. The formation of acyl compounds was confirmed by the proton coupled $^{13}$C NMR, in which the labeled acyl carbon appears as a quartet resonance at around 231 ppm (23°C in CD$_2$Cl$_2$). The reaction of the complexes with CO was originally studied as a non-kinetic test for the formation an acyl compound. An intermediate has not been observed. However, in the course of an acyl compound formation, a system utilizing neutral Pd(II) compound may have two possible pathways for the formation of an acyl compound (Scheme 4-4). The first possible pathway is through four-coordinated species – formation of a T-shaped three-coordinate species by releasing the coordinated imine, followed by the coordination of CO, migratory insertion, and the re-coordination of the imine. The other possible pathway is through a five-coordinated species – coordination of CO forming the pyramidal structure, followed by migratory insertion. To investigate the CO insertion pathway, the kinetics of initial carbon monoxide insertion into the palladium methyl bond were directly measured by monitoring the disappearance of the Pd-CH$_3$ resonance or the appearance of corresponding Pd-C(O)-Me resonance in the $^1$H NMR spectrum.
spectrum in CD$_2$Cl$_2$ over time. The first-order rate constants and corresponding enthalpy and entropy of activation for carbon monoxide insertion into the Pd(II)-Me bond for $3c$ in the absence or presence of benzylidene-tert-butylamine are listed in Table 4-7. The table shows that the system having an excess of the corresponding imine does not show any rate difference from the system having no imine at all. On the basis of results for the systems, we propose that carbon monoxide inserts into Pd(II)-Me bond in the neutral complexes $3a$-$e$ through five-coordinate species (Route 2, Scheme 4-4).

![Scheme 4-4. Proposed CO insertion Pathways](image)

Table 4-7

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<tr>
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<th>T(K)</th>
<th>$k$($\times 10^4 s^{-1}$)</th>
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<th>$\Delta S^\ddagger$ (cal/K•mol)</th>
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* For kinetic data sources, see Appendix P
Table 4-8

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<th>yield(g)</th>
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<td>-</td>
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<td>1</td>
<td>0.06</td>
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</table>

⁵⁵Reaction conditions: complex (3.1x10⁻⁵ mol), chlorobenzene (6mL). ⁵in chlorobenzene(30mL). ⁵Molecular weight data were determined by GPC vs polystyrene standards.

4.2.3 Polymerization of Polar or Non-polar Vinyl Monomers

Polymerization of non-polar vinyl monomers, such as ethene, propene, or 1-hexene, using the complexes 3a-e, or 4 gave no polymeric product. It seems that the strongly coordinating donor ligands do not afford a vacant site for an incoming monomer. In this manner, the imine ligands provide inactivity to the title compounds. The reactivity
testing results of the complexes toward CO in this research also proved that the imine ligand is not dissociated during the reaction. NMR scale reactions of vinyl monomers with the complexes showed no reactions of either oligomerization or any other catalytic process occurred, except in the case of the system utilizing norbornene as a monomer. The $^1$H NMR experiment using one of 3a-e and 5 equiv. of norbornene showed resonances corresponding to oligomeric norbornene product at 23°C. By adding ca. 10 equiv. more of norbornene monomer to the system, we obtained increasing resonances in the $^1$H NMR spectrum corresponding to norbornene oligomer or polymer at the same temperature. Upon having the evidence of the polynorbornene formation, we scaled-up the polymerization reaction of norbornene using catalyst 3a-e in chlorobenzene at ambient temperature (entries 8-11, Table 4-8). The yield of polynorbornene isolated as a solid after quenching with methanol did not reach the amount expected, as confirmed by NMR. Removing solvent under vacuum before quenching the reaction mixture with methanol left an oily product. The molecular weight of the oil was less than 500, which is the detection limit of the GPC. Although the exact molecular weight of the oily product could not be measured, the result revealed that most of the reaction product is oligomer, which is soluble in methanol.

Polymerization of methyl acrylate using catalysts 3a-e, or 4 was carried out in chlorobenzene at ambient temperature (entries 1-7, Table 4-8). Low to moderate yields of poly(methyl acrylate) were obtained at the conditions indicated. The polymers produced have high (Mn>211000) to ultrahigh (Mn> 1600000) molecular weight and showed wide polydispersity index. Formation of a sticky polymer started to prevent monomer diffusion to the active catalyst in 1 hr by blocking effective stirring, which seems to cause wide
polydispersity (entries 2-4). Decreasing the monomer concentration by increasing the amount of solvent from 6 mL to 30 mL gave a higher polymer yield with a narrower polydispersity index (entries 4, and 5). Our main interest in this study was the possible application of the palladium-based neutral complexes as a catalyst in the polymerization of polar or non-polar vinyl monomers. Recently, Sen\textsuperscript{24} as well as Novak and co-workers\textsuperscript{23} reported on the homopolymerization of methyl acrylate using neutral palladium compounds where a radical mechanism was invoked. Polycracylates can be achieved through various routes including anionic, radical, or coordination insertion mechanism. We also tested the possible reaction mechanism by using two different monomers, methyl methacrylate and styrene, which are readily polymerized through a radical mechanism, or by using a radical inhibitor, galvinoxyl. Neither methyl methacrylate nor styrene was polymerized by any of the title complexes, 3a-e or 4. The polymerization of methyl acrylate was completely halted when galvinoxyl was utilized. Based on the results of the first experiments, we may rule out traditional free radical or metal based atom transfer radical polymerization mechanism. However, it seems to have a radical pathway for the polymerization of methyl acrylate, which agrees with the results reported by Novak and Sen, although there has been ‘a warning on the use of radical traps as a test for radical mechanisms’.\textsuperscript{26}

4.2.4 Reactivities of the complexes toward imine and CO

Reactions of the title complexes 3a-e with an imine compound under $^{13}$C labeled carbon monoxide atmosphere have been monitored using various NMR techniques.
Several equivalents of an imine were added to a chlorobenzene-\textsubscript{d5} solution of a title complex at ambient temperature and the reaction mixture was monitored by \textsuperscript{1}H NMR, \textsuperscript{13}C{\textsuperscript{1}H}, or proton coupled \textsuperscript{13}C NMR spectroscopy as it was gradually warmed up (Scheme 4-5). The insertion of CO into Pd-Me bond was observed even at room temperature, resulting in the formation of acyl compound (compound 5, Scheme 4-4 and resonance at 231.1 ppm in figure 4-6).

\[ \text{Complex } 3a, 3b, 3c, 3d, \text{ or } 3e + \quad \begin{array}{c}
\text{Phenyl} \\
n-\text{Propyl}
\end{array} 
\quad \text{13CO} \quad \text{NMR Studies} \]

\[ (1 \text{ to } 10 \text{ equiv.}) \quad (50 \text{ psi}) \]

\textit{where}, \( R = \text{Benzyl} \)

\textit{Phenyl}

\textit{n-Propyl}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{scheme4-5.png}
\caption{Reaction Scheme}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4-6.png}
\caption{Selected VT \textsuperscript{13}C NMR Spectra of the Reaction between 3e and Ph-CH=N-CH\textsubscript{2}-Ph under \textsuperscript{13}CO Atmosphere}
\end{figure}
Warming the reaction mixture to 40°C resulted in the formation of a new species which shows resonance at 213.8 ppm. The concentration of this species is gradually increased while an acyl compound slowly disappears as the system warms up to 50°C. All of these species disappears as the system temperature reaches at 60°C, leaving two resonances at 171.0ppm and 168.7ppm. From that point on, it seems no more reaction occurred.

Figure 4-7

To rule out the possibilities of the isomer formation, proton coupled $^{13}$C NMR experiment has been conducted. Since no desired data has been obtained, a new complex 5 having N-benzylbenzylideneimine, Ph-CH=N-CH$_2$-Ph, as a ligand has been prepared and utilized (Figure 4-7). Fortunately, good spectroscopic data has been obtained from the reaction between the complex 5 and N-benzylbenzylideneimine under $^{13}$C labeled
carbon monoxide atmosphere at 50°C (Figure 4-8). As already known, the peak at 231.1 ppm shows the resonance as a quartet indicating the presence of an acyl carbon formed by CO insertion into the Pd-Me bond. This compound undergoes an imine insertion into Pd-acyl bond in two possible pathways. It is generally known that an imine inserts into Pd-acyl bond via *path A* (Scheme 4-6). Although the insertion of an imine through carbon on carbon-nitrogen double bond has never been observed or proposed, the splitting pattern of the peak at 214.4 ppm, which is the resonance as a doublet of quartets suggests that a new insertion pathway of imine into Pd-acyl bond is possible. The acyl carbon on compound 6 formed through *path A* should show the resonance as a quartet instead of doublet of quartets. However, if the imine inserts into Pd-acyl bond via *path B*, the resulting compound 7 would show the resonance as a doublet of quartets for the acyl carbon. The resonance as a quartet at 168.7ppm is assigned as a carbonyl carbon right next to a methyl group, which is not chelated to palladium metal center through oxygen functionality. Based on the results above and the fact that the peaks at 176.8 and 175.0 ppm are the resonance as a singlet and a doublet, respectively, we propose two more possible structures, in which second insertion of carbon monoxide occurred (compound 8 and 9, Scheme 4-6)). Because none of the intermediates and the final compound has been isolated and their structures have not been completely established yet, further research on this topic is in progress.
Figure 4-8: Proposed imine insertion pathways

Scheme 4-6. Proposed imine insertion pathways
4.3 Conclusions

We synthesized a series of neutral salicylaldiminato Pd(II) complexes: Pd(Me)(Ph-CH=N-R')[3-^3^Bu-2-(O)C_6H_3-CH=N-2,6-di-^3^Bu-C_6H_3](R=CH_3, n-Pr, tert-Bu, Ph, Benzyl) (3a-3e), and Pd(Me)[3-(CH=N-t-Bu)-Py][3-^3^Bu-2-(O)C_6H_3-CH=N-2,6-di-^3^Bu-C_6H_3] (4). These complexes have been isolated and characterized spectroscopically, and the solid-state structures of the complexes have also been characterized by X-ray single-crystal structure analysis. According to the results of the NMR studies, the complexes reacted with carbon monoxide to form corresponding acyl complexes through five-coordinated intermediate. These acyl complexes undergo an imine insertion into Pd-acyl bond and two possible insertion pathways are proposed based on the results of NMR experiments. For the investigation of the imine insertion reaction, a neutral N-N chelated complex 5 has been prepared and its structure has been characterized by X-ray single-crystal structure analysis. The neutral complexes, 3a-e and 4, showed the reactivities toward norbornene with the main product of the reactions being norbornene oligomers. They also showed moderate catalytic activity for the polymerization of methyl acrylate at room temperature producing polymers with a high molecular weight but broad polydispersity index. The results of the preliminary polymerization reaction of methyl acrylate using complexes 3a-3e suggest a radical mechanism rather than coordination insertion mechanism.
4.4 Experimental Section

4.4.1 Generation Considerations

All syntheses and manipulations of air- and moisture-sensitive compounds were carried out in flame dried Schlenk-type glassware on a dual-manifold Schlenk line, a high vacuum with argon line, or in a nitrogen-filled glovebox.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX 400 NMR spectrometer, DPX 300 NMR spectrometer, and CDPX 300 NMR spectrometer. Splitting patterns are designated as follows: s, singlet; bs, broad singlet; d, doublet; dd, doublet of doublets; t, triplet; td, triplet of doublets; sept, septet; m, multiplet. All $^1$H NMR spectra are reported in $\delta$ units, parts per million (ppm) downfield from tetramethylsilane. All $^{13}$C NMR spectra are reported in ppm relative to tetramethylsilane using CD$_2$Cl$_2$, toluene-d$_8$, or chlorobenzene-d$_5$ as an internal standard. Variable-temperature $^1$H NMR experiments were performed on a Bruker DPX 300 NMR spectrometer, using CD$_2$Cl$_2$, toluene-d$_8$, or chlorobenzene-d$_5$ as solvent. Actual NMR probe temperatures were measured using anhydrous methanol (with 0.03% concentrated HCl) or ethylene glycol (neat) in a 5 mm NMR tube (see 2.5.1 and 2.5.2). NMR analyses of polymers were performed on a Bruker DPX 300 NMR spectrometer at ambient or elevated temperature, using CDCl$_3$, chlorobenzene-d$_5$, dichlorobenzene-d$_4$, or tetrachloroethane-d$_2$ as solvents unless otherwise noted.

Size exclusion chromatography data were obtained on a Shimadzu SEC System using a three-column bank (Styragel 7.8x300 mm columns, 100-5,000 D, 500-30,000 D, 2000-4,000,000 D), a Shimadzu RID-10A Differential Refractometer, and a Shimadzu
LC-10AT pump/controller. Size exclusion chromatography was performed in chloroform at ambient temperature and calibrated to polystyrene standards.

Chlorobenzene and dichloromethane was obtained from Aldrich and dried via passage over a column of activated alumina (LaRoche A-2). Toluene and diethyl ether were deoxygenated, dried via passage over a column of activated alumina (LaRoche A-2) and columns of Engelhard CU-0226S. Pentane and tetrahydrofuran were distilled under nitrogen from sodium benzophenone ketyl. All solvents were degassed by repeated freeze-pump-thaw cycles, and stored over 4 Å molecular sieves under nitrogen. Norbornene was purchased from Acros Organics and used without further purification. Methyl acrylate and methyl methacrylate were purchased from Aldrich and used after repeated freeze-pump-thaw cycles prior to use. Cyclooctadienyl palladiummethylchloride[(COD)Pd(Me)(Cl)] was prepared as previously reported.

4.4.2 Synthesis of Compounds

3-<sup>1</sup>Bu-2-(OH)C<sub>6</sub>H<sub>3</sub>-CH=N-2,6-di<sup>3</sup>Pr-C<sub>6</sub>H<sub>3</sub> (1). To 3-tert-butyl-2-hydroxybenzaldehyde (1g, 5.6 mmol) in methanol (50 ml) was added 2,6-diisopropylaniline (1.5g, 8.4 mmol), followed catalytic amount of formic acid (2 drops), The solution was stirred at room temperature for 12h. Removal of solvent in Vacuo yielded a yellow oil, which is purified by vacuum distillation. <sup>1</sup>H NMR(CDCl<sub>3</sub>): δ 13.65 (br, 1H, -OH), 8.35 (s, 1H, -CH=N-), 7.49-6.91(m, 6H, Ar-H), 3.06 (sept, 2H, -CH(CH<sub>3</sub>)<sub>2</sub>), 1.52 (s, 9H, -C(CH<sub>3</sub>)<sub>3</sub>), 1.22 (d, 12H, -CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR(CDCl<sub>3</sub>): δ
167.96 (-CH=N-), 160.99, 146.72, 139.31, 137.95, 131.08, 130.78, 125.70, 123.57, 118.96, 118.60 (Ar), 35.22 (-CMe₃), 29.51 (-C(CH₃)₃), 28.49 (-CH(CH₃)₂), 23.73 (-CH(CH₃)₂).

[3-iBu-2-(OK)C₆H₃-CH=N-2,6-di-iPr-C₆H₃]·THF (2). To a stirred suspension of KH (0.19g, 4.68mmol) in THF(30ml) was added ligand 1(0.79g, 2.34mmol) in THF(20mL) at room temperature. The reaction mixture was stirred for 2h and filtered to remove excess KH. After removing solvent under vacuum, small amount of pentane was added to dissolve starting material. Upon filtering and washing with pentane, the potassium salt THF adduct was obtained as a yellow solid. Yield 0.97g, 92%.

Pd(Me)(Ph-CH=N-CH₃)[3-iBu-2-(O)C₆H₃-CH=N-2,6-di-iPr-C₆H₃] (3a) . To a mixture of [3-iBu-2-(OK)C₆H₃-CH=N-2,6-di-iPr-C₆H₃]·THF (0.42g, 0.94mmol) and Ph-CH=N-CH₃ (0.11g, 0.94mmol) in toluene (30mL) was added (COD)PdMeCl (0.25g, 0.94mmol) in toluene (10mL). The reaction mixture was stirred for 12 hours, which was filtered to remove a small quantity of dark insoluble material. The solvent was removed in vacuo to yield a yellow solid. Recrystallization from pentane gave a yellow crystalline solid which was suitable for X-ray crystal structure analysis. Yield 0.49g, 91%. 

1H NMR(CD₂Cl₂): δ 8.36 (s, 1H, Pd-O-Ar-CH=N-), 7.74 (s, 1H, Ph-CH=N-CH₃), 8.98(d), 7.58-7.49(m), 7.28(dd), 7.21-7.16(dd), 7.00(dd), 6.35(t) (11H, Ar-H), 3.99 (s, 3H, Ph-CH=N-CH₃) 3.55, 3.22 (hept each, 2H, Ar-CH(CH₃)₂), 1.29 (s, 9H, Ar-C(CH₃)₃), 1.38, 1.24, 1.18, 1.16 (d each, 12H, Ar-CH(CH₃)₂), -0.49 (s, 3H, Pd-CH₃). 13C NMR(CD₂Cl₂): δ 167.7 (Pd-O-Ar-CH=N-), 166.1 (Ph-CH=N-CH₃), 141.6, 141.5, 134.9, 132.4, 131.3, 130.7, 129.1, 128.9, 128.6, 128.5, 126.4, 123.5, 119.9, 112.0 (Ar), 53.4 (Ph-CH=N-CH₃).
To a mixture of \([3\text{-}tBu-2-(OK)C_6H_3-CH=N-2,6\text{-}di\text{-}Pr-C_6H_3]\cdot THF (0.42g, 0.94mmol) and Ph-CH=N-t-Bu (0.15g, 0.94mmol) in toluene (30mL) was added (COD)PdMeCl (0.25g, 0.94mmol) in toluene (10mL). The reaction mixture was stirred for 12 hours, which was filtered to remove a small quantity of dark insoluble material. The solvent was removed \textit{in vacuo} to yield a yellow solid. Recrystallization from pentane gave a yellow crystalline solid which was suitable for X-ray crystal structure analysis.

Yield 0.51g, 89%. \(^1\)H NMR(CD\(_2\)Cl\(_2\)): \(\delta\) 8.38 (s, 1H, Pd-O-Ar-CH=CH=N-), 7.70 (s, 1H, Ph-CH=N-CH=CH=CH-N), 8.93(d), 7.54-7.43(m), 7.24 (dd), 7.17-7.12(m), 6.96(dd), 6.31(t) (11H, Ar-H), 4.33, 3.68 (m each, 2H, Ph-CH=N-C\(_2\)H\(_2\)-CH\(_3\)), 3.64, 3.39 (hept, 2H, Ar-C(CH\(_3\))\(_3\)), 2.31(sext, 2H, N-CH\(_2\)-CH\(_2\)-CH\(_3\)), 1.25 (s, 3H, Ar-C(CH\(_3\))\(_3\)), 1.02 (Ph-CH=N-CH=CH-CH=CH=CH=CH=CH=N), -0.62 (s, 3H, Pd-CH\(_3\)). \(^1^3\)C NMR(CD\(_2\)Cl\(_2\)): \(\delta\) 167.0 (Pd-O-Ar-CH=CH=N-), 166.0 (Ph-CH=N-CH\(_2\)-CH\(_2\)-CH\(_3\)), 148.7, 141.5, 141.4, 135.0, 134.2, 132.3, 131.4, 130.7, 128.5, 126.3, 124.5, 123.5, 123.4, 120.0, 112.0 (Ar), 68.6 (Ph-CH=N-CH\(_2\)-CH\(_2\)-CH\(_3\)), 35.3 (Ar-C(CH\(_3\))\(_3\)) 29.5 (Ar-C(CH\(_3\))\(_3\)), 28.1, 28.0 (Ar-CH(CH\(_3\))\(_2\)), 25.0 (Ph-CH=N-CH\(_2\)-CH\(_2\)-CH\(_3\)), 25.3, 25.1, 23.1, 22.6 (Ar-CH(CH\(_3\))\(_2\)), 11.8 (Ph-CH=N-CH\(_2\)-CH\(_2\)-CH\(_3\)), -5.0 (Pd-CH\(_3\)).
filtered to remove a small quantity of dark insoluble material. The solvent was removed *in vacuo* to yield a yellow solid. Recrystallization from pentane at -25°C gave a yellow crystalline solid which was suitable for X-ray crystal structure analysis. Yield 0.52g, 90%.

$^1$H NMR(CD$_2$Cl$_2$): $\delta$ 8.51 (s, 1H, Pd-O-Ar-CH=N-), 7.69 (s, 1H, Ph-CH=N-t-Bu), 8.92(d), 7.52-7.43(m), 7.25(dd), 7.15-7.07(m), 6.95(dd), 6.31(t) (11H, Ar-H), 3.69, 3.21 (hept each, 2H, Ar-C(CH$_3$)$_2$), 1.76 (s, 9H, -N-C(CH$_3$)$_3$), 1.29 (s, 9H, Ar-C(CH$_3$)$_3$), 1.24, 1.12, 1.10, 1.03 (d each, 12H, Ar-CH(C$_3$)$_2$), -0.66(s, 3H, Pd-CH$_3$). $^{13}$C NMR(CD$_2$Cl$_2$): $\delta$ 169.1 (Pd-O-Ar=CH=N-), 166.2 (Ph-CH=N-t-Bu), 148.8, 141.6, 141.5, 135.9, 135.1, 131.9, 131.4, 130.4, 128.3, 126.2, 123.5, 123.3, 120.0, 111.8(Ar), 64.7 (-N-C(CH$_3$)$_3$), 35.4(Ar-C(CH$_3$)$_3$), 32.1 (-N-C(CH$_3$)$_3$), 29.7 (Ar-C(CH$_3$)$_3$), 28.0 , 27.9 (Ar-CH(CH$_3$)$_2$), 25.3, 25.1, 23.0, 22.8 (Ar-CH(CH$_3$)$_2$), -6.01 (Pd-CH$_3$).

**Pd(Me)(Ph-CH=N-Ph)[3-^t^B^u^2-(O)C$_6$H$_3$-CH=N-2,6-di^-t^Pr-C$_6$H$_3$]** (3d). To a mixture of [3-^t^B^u^2-(OK)C$_6$H$_3$-CH=N-2,6-di^-t^Pr-C$_6$H$_3$].THF (0.42g, 0.94mmol) and Ph-CH=N-Ph (0.17g, 0.94mmol) in toluene (30mL) was added (COD)PdMeCl (0.25g, 0.94mmol) in toluene (10mL). The reaction mixture was stirred for 12 hours, which was filtered to remove a small quantity of dark insoluble material. The solvent was removed *in vacuo* to yield a yellow solid. Recrystallization from pentane gave a yellow crystalline solid which was suitable for X-ray crystal structure analysis. Yield 0.55g, 92%. $^1$H NMR(CD$_2$Cl$_2$): $\delta$ 8.56 (s, 1H, Pd-O-Ar-CH=N-), 7.70 (s, 1H, Ph-CH=N-Ph), 9.17(d), 7.81(d), 7.61-7.15(m), 6.95(d), 6.30(t) (16H, Ar-H), 3.54, 3.47 (hept each, 2H, Ar-CH(CH$_3$)$_2$), 1.13 (s, 9H, Ar-C(CH$_3$)$_3$), 1.25, 1.24, 1.16, 1.10 (d each, 12H, Ar-CH(CH$_3$)$_2$), -0.47 (s, 3H, Pd-CH$_3$). $^{13}$C NMR(CD$_2$Cl$_2$): $\delta$ 168.1 (Pd-O-Ar-CH=N-), 166.1 (Ph-CH=N-CH$_2$-Ph), 153.0, 148.7, 141.6, 141.4, 134.8, 133.3, 131.4, 131.3, 129.2, 128.7, 128.0,
126.4, 124.1, 123.6, 119.8, 112.0 (Ar), 35.3 (Ar-CH(CH$_3$)$_3$), 29.4 (Ar-C(CH$_3$)$_3$), 28.0 (Ar-CH(CH$_3$)$_2$), 25.3, 25.0, 23.0, 22.6 (Ar-CH(CH$_3$)$_2$), -4.1 (Pd-CH$_3$).

**Pd(Me)(Ph-CH=N-CH$_2$-Ph)[3-$^{t}$Bu-2-(O)C$_6$H$_3$-CH=N-2,6-$^{di}$Pr-C$_6$H$_3$]** (3e). To a mixture of [3-$^{t}$Bu-2-(OK)C$_6$H$_3$-CH=N-2,6-$^{di}$Pr-C$_6$H$_3$]·THF (0.23g, 0.52mmol) and Ph-CH=N-CH$_2$-Ph (0.11g, 0.56mmol) in toluene (30mL) was added (COD)PdMeCl (0.15g, 0.57mmol) in toluene (10mL). The reaction mixture was stirred for 12 hours, which was filtered to remove a small quantity of dark insoluble material. The solvent was removed *in vacuo* to yield a yellow solid. Recrystallization from methylene dichloride and pentane gave a yellow crystalline solid which was suitable for X-ray crystal structure analysis. Yield 0.31g, 92%. $^1$H NMR(CD$_2$Cl$_2$): $\delta$ 8.49 (s, 1H, Pd-O-Ar-CH=N-), 7.71 (s, 1H, Ph-CH=N-CH$_2$-Ph), 5.61 (d, 1H, Ph-CH=N-CH$_2$-Ph), 5.10 (d, 1H, Ph-CH=N-CH$_2$-Ph), 8.94(d), 7.65-6.98(m), 6.37(t) (16H, Ar-H), 3.42 (hept, 2H, Ar-CH(CH$_3$)$_2$), 1.38 (s, 9H, Ar-C(CH$_3$)$_3$), 1.22, 1.19, 1.16, 1.11 (d each, 12H, Ar-CH(CH$_3$)$_2$), -0.86 (s, 3H, Pd-CH$_3$).

$^{13}$C NMR(CD$_2$Cl$_2$): $\delta$ 166.9 (Pd-O-Ar-CH=N-), 166.3 (Ph-CH=N-CH$_2$-Ph), 148.6, 141.6, 136.4, 135.0, 132.5, 131.5, 130.7, 129.1, 129.0, 128.7, 128.5, 126.3, 123.4, 112.1 (Ar), 69.45 (=N-CH$_2$-Ph), 35.4 (Ar-C(CH$_3$)$_3$) 29.7 (Ar-C(CH$_3$)$_3$), 27.9 (Ar-CH(CH$_3$)$_2$), 25.2, 23.2 (Ar-CH(CH$_3$)$_2$), -4.4 (Pd-CH$_3$).

**Pd(Me)[3-(CH=N-$^{t}$Bu)-Py][3-$^{t}$Bu-2-(O)C$_6$H$_3$-CH=N-2,6-$^{di}$Pr-C$_6$H$_3$]** (4). To a mixture of [3-$^{t}$Bu-2-(OK)C$_6$H$_3$-CH=N-2,6-$^{di}$Pr-C$_6$H$_3$]·THF (0.42g, 0.94mmol) and 3-(CH=N-$^{t}$Bu)-Py (0.15g, 0.94mmol) in toluene (30mL) was added (COD)PdMeCl (0.25g, 0.94mmol) in toluene (10mL). The reaction mixture was stirred for 12 hours, which was filtered to remove a small quantity of dark insoluble material. The solvent was removed *in vacuo* to yield a yellow solid. Recrystallization from pentane gave a yellow crystalline
solid which was suitable for X-ray crystal structure analysis. Yield 0.56g, 93%. \(^1\)H NMR(CD\(_2\)Cl\(_2\)): \(\delta\) 9.94 (s, 1H, Pd-O-Ar-CH=N-N), 7.71 (s, 1H, Py-CH=N-t-Bu), 8.97 (d), 8.24 (s), 7.87 (t), 7.36 (dt), 7.26-7.14 (m), 6.95 (dd), 6.30 (t) (10H, Ar-H), 3.69, 3.50 (hept each, 2H, Ar-C(CH\(_3\))\(_2\)), 1.33 (s, 9H, Ar-C(C\(_3\)H\(_3\))), 1.02 (s, 9H, =N-C(CH\(_3\))\(_3\)), 1.35, 1.16, 1.12 (d each, 12H, Ar-CH(C\(_3\)H\(_3\))\(_2\)), -0.26 (s, 3H, Pd-C\(_3\)H). \(^{13}\)C NMR(CD\(_2\)Cl\(_2\)): \(\delta\) 166.4 (Ph-CH=N-t-Bu), 156.9 (Pd-O-Ar-CH=N-N), 168.2, 155.9, 152.3, 141.5, 137.7, 134.7, 131.4, 129.4, 128.6, 126.5, 125.2, 123.7, 123.5, 123.1, 119.8, 112.1 (Ar), 58.7 (=N-CH(CH\(_3\))\(_2\)), 35.1 (Ar-CH(CH\(_3\))\(_2\)), 29.5 (Ar-C(CH\(_3\))\(_3\)), 29.3 (=N-C(CH\(_3\))\(_3\)), 28.3, 28.1 (Ar-CH(CH\(_3\))\(_2\)), 25.0, 22.9 (Ar-CH(CH\(_3\))\(_2\)), -4.0 (Pd-C\(_3\)H).

\[
Pd(Me)(Ph-CH=N-CH\(_2\)-Ph)\mid 2,6-di\(^{3}\)Pr-C\(_6\)H\(_3\)-N-C(Me)-CH-C(Me)-N-2,6-di\(^{3}\)Pr-C\(_6\)H\(_3\)\] (5) .

To a mixture of [2,6-di\(^{3}\)Pr-C\(_6\)H\(_3\)-N=C(Me)-CH=C(Me)-N(H)-2,6-di\(^{3}\)Pr-C\(_6\)H\(_3\)]·Tl (0.50g, 0.8mmol) and Ph-CH=N-CH\(_2\)-Ph (0.15g, 0.8mmol) in toluene (30mL) was added (COD)PdMeCl (0.21g, 0.8mmol) in toluene (10mL). The reaction mixture was stirred for 12 hours, which was filtered to remove a small quantity of dark insoluble material. The solvent was removed in vacuo to yield a yellow solid. Recrystallization from methylene dichloride and pentane gave a yellow crystalline solid which was suitable for X-ray crystal structure analysis. Yield 0.57g, 97%. \(^1\)H NMR(CD\(_2\)Cl\(_2\)): 7.30 (s, 1H, Ph-CH=N-N), 9.05 (d), 7.46-7.32 (m), 7.22-6.86 (m), 6.63 (d) (16H, Ar-H), 4.68 (s, N-C(CH\(_3\))-CH-C(CH\(_3\))\(_3\)-N), 4.57, 3.29 (d each, 2H, Ph-CHH\(_3\)-N), 3.79, 3.66, 3.41, 2.86 (hept each, 4H, Ar-CH(CH\(_3\))\(_2\), Ar-CH\(_2\)(CH\(_3\))\(_2\), Ar-CH\(_3\)'(CH\(_3\))\(_2\), Ar-CH\(_3\)''(CH\(_3\))\(_2\)), 1.56, 1.53 (s each, 6H, N-C(CH\(_3\))-CH-C(CH\(_3\))\(_3\)-N), 1.50, 1.24, 1.20, 1.15, 1.06, 0.84, 1.82, 0.33 (d each, 24H, Ar-CH(CH\(_3\))\(_2\)), -0.74 (s, 3H, Pd-CH\(_3\)). \(^{13}\)C DEPT135 NMR(CD\(_2\)Cl\(_2\)): \(\delta\) 166.3 (-CH=N-N), 132.4, 131.5, 129.2, 128.5, 125.0, 124.6, 124.2, 123.4, 123.2 (Ar), 94.5 (-C(CH\(_3\)))-CH-
C(CH′3)-), 65.9 (Ph-CH2-N), 28.4, 28.1, 27.7, 27.4 (Ar-CH(CH3)2), 26.2 ((-C(CH3)-CH-C(CH′3)-), 25.4, 25.1, 24.9, 24.8, 24.7, 24.2, 24.1, 23.8 (Ar-CH(CH3)2), 4.8 (Pd-CH3).

4.4.3 General Procedures for Polymerization Reactions

In a drybox under a nitrogen atmosphere, a title complex (3.1x10^-5 mol) was dissolved in chlorobenzene (6 mL or 30 mL) in a 100 mL Schlenk flask. Then, a specified amount of methyl acrylate or norbornene was introduced to the flask. The reaction mixture was stirred at a desired temperature. After the specified reaction time, the reaction was quenched with methanol. The precipitated polymer was filtered and washed with methanol. Volatiles were removed from the polymer in vacuo, and the polymer was dried under vacuum overnight.

4.4.4 General Procedure for NMR Experiments

In a drybox under a nitrogen atmosphere, 3c (1.7x10^-5 mol) with or without Ph-C=N-n-Pr(8.3x10^-4 mol) was weighed into a High Pressure NMR tube. CD2Cl2 (1 mL) was added to the NMR tube. The tube was then capped, removed from the drybox, and cooled to ca. -90 °C. After applying vacuum briefly, the mixture was allowed to reach ambient temperature. The NMR tube was then charged with 13C labeled carbon monoxide (50 psi), and cooled again to ca. -90 °C using liquid nitrogen/acetone slurry. The tube was shaken very briefly, and transferred to the NMR probe which is at a preset temperature. NMR spectra were acquired every 10 min at a desired temperature.
4.5 References


Chapter 5

NEUTRAL PALLADIUM(II) COMPLEXES WITH P-N-O CHELATE: SYNTHESSES, CHARACTERIZATION, AND THEIR REACTIVITIES

5.1 Introduction

Since the discovery of metallocene-based catalysts for ethene and α-olefin polymerization, numerous efforts have been directed at the development of non-metallocene-based complexes for the successful homo- or co-polymerization of polar- and nonpolar-alkenes through successive coordination insertion mechanism. The majority of the studies utilizing late transition metal complexes for the alkene polymerizations where an insertion mechanism is operative have been based on the cationic palladium(II) complexes. Although there have been numerous achievements in the area of cationic palladium(II)-initiated addition polymerization, the electrophilicity of the cationic palladium compounds still limits their catalytic application to addition polymerization of monomers having polar functionalities, such as acrylates.

In light of the limited compatibility of the cationic Ni and Pd complexes with polar functional groups on a monomer, considerable attention has been made in developing nickel- or palladium-based neutral complexes for polymerization of polar- or non-polar vinyl monomers. Recently, several neutral nickel catalysts based on [N,O] chelate ligands following SHOP(Shell Higher Olefin Process)-type catalysts have been reported. Furthermore, neutral palladium catalysts based on [N,N] chelate ligand and non-chelate ligand have been reported. On the other hand, there have been alternate
approaches developing overall-charge-neutral zwitterionic complexes based on nickel or palladium for the polymerization of alkenes.23-28

Generation of active SHOP catalyst

In most of the systems utilizing nickel-based neutral or zwitterionic complexes, non-polar alkenes have been tested for the polymerization. There has been only one case reported by Grubbs14 where a neutral transition metal-based complex showed the unprecedented functional group tolerance of the catalytic system by polymerizing alkenes having polar functionality. A zwitterionic palladium complex showed copolymerization activity of carbon monoxide and ethene.28 However, other palladium-based neutral systems produced poly(methyl acrylate) through a radical pathway.21,22

As a part of the aforementioned efforts, we decided to develop a serious of neutral palladium-based complexes to be utilized as catalysts with or without cocatalyst for the polymerization of polar- or non-polar alkenes. We report here the synthesis of neutral palladium complexes based on [P,N,O] chelate ligands, which can be converted to active species, such as a zwitterionic complex, by incorporating a Lewis acid. They are fully characterized in solution by spectroscopic methods and in solid-state by X-ray diffraction.
The complexes in combination with a different Lewis acid show characteristic reactivity toward polar- or non-polar alkenes.

5.2 Results and Discussion

5.2.1 Ligand Synthesis

Hydroxyliminophosphine(P\(^{\text{N,O}}\)) ligands(1 and 2, Scheme 5-1) were prepared by a condensation reaction between an aldehyde and an amine compound in the presence of formic acid as a catalyst. For ligand 1, 2,4-di-tert-butylphenol was transformed by nitration\(^{29}\) to 2-nitro-4,6-di-tert-butylphenol, which was converted to 2-amino-4,6-di-tert-butyl-phenol by hydrogenation over 10% Pd/C in ethanol at ambient temperature. The 2-amino-4,6-di-tert-butyl-phenol purified by recrystallization from methanol was then reacted with 2-(diphenylphosphino)benzaldehyde to afford ligand 1 as a yellow crystalline solid in good yield. The first step in the synthesis of ligand 2 was the preparation of (2-aminophenyl)diphenylphosphine,\(^{30}\) which was condensed with 3,5-di-tert-butyl-2-hydroxybenzaldehyde giving the target compound 2. The CH imine proton of these compounds shows resonances at 9.14 and 8.47 ppm, respectively, with the corresponding \(^{13}\)C NMR resonances at 155.7 and 163.9 ppm, respectively. In the \(^1\)H NMR spectrum of the ligand 1, the imine proton (–N=CH) shows resonance as a doublet with a coupling constant \(J_{P-H} = 4.333\) Hz, indicating that there is a through-space coupling in which the imine proton is directed towards the lone pair electrons on the phosphorus atom.\(^{31,32}\) In the case of complex 2, there is no observed P-H coupling for the
corresponding imine proton. $^{31}$P NMR spectra of 2 show resonances at -10.28 and -13.54 ppm, respectively.

![Scheme 5-1](image)

**Scheme 5-1**

### 5.2.2 Complex Synthesis

Reaction of ligands 1 and 2 with ($N,N,N',N'$-tetramethylethylenediamine) dimethylpalladium(II) [(TMEDA)PdMe$_2$]$^{33}$ in diethyl ether at ambient temperature caused the evolution of methane and generated the corresponding (P$^N$N$^O$)PdMe complexes (Scheme 5-2). Both compounds were obtained in almost quantitative yields as purple 3 or orange 4 solids. Recrystallization from methylene dichloride and pentane gave the analytically pure product. Spectroscopic analysis using 1D and 2D nuclear magnetic resonance (NMR) confirms the structure of the target complexes 3 and 4.
As for the neutral complexes, palladium bound methyl groups in both cases show their $^1$H NMR resonances at 0.60 and 0.72 ppm, with corresponding $^{13}$C NMR resonances at -0.6 to -2.7 ppm, respectively, as a doublet with a coupling constant $^3J_{P-H} = 2.744$ and 2.196 Hz, respectively. This is in the typical range for the methyl group cis to the phosphorus. $^1$H NMR resonances for Ar-CH=N- are at 8.55 and 8.86 ppm with corresponding $^{13}$C NMR resonances at 168.4 and 158.6 ppm, respectively. $^{31}$P NMR spectra show resonances at 39.85 and 40.50 ppm, respectively. A downfield shift of ca. 50 ppm, in $^{31}$P NMR, with respect to the free ligand reflects the coordination of the phosphine group to the palladium metal.

![Scheme 5-2](image-url)
Figure 5-1: ORTEP view of complex 3. Hydrogen atoms are omitted for clarity.

Figure 5-2: ORTEP view of complex 4. Hydrogen atoms are omitted for clarity.
### Table 5-1

<table>
<thead>
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<th>Distance (Å)</th>
<th>Bond</th>
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<td>N1-C7</td>
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<td>C14-P1-C15</td>
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### Table 5-2

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<td>P1-C15</td>
<td>1.815(2)</td>
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<td>1.820(2)</td>
<td>O1-C2</td>
<td>1.300(2)</td>
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<td>N1-C9</td>
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<td>C1-Pd1-N1</td>
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<td>122.41(13)</td>
<td>C9-N1-Pd1</td>
<td>117.27(12)</td>
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</table>
The molecular structures of complexes 3 and 4 were determined by single-crystal X-ray structure analysis. X-ray quality crystals were prepared by slow diffusion of pentane into a concentrated solution of 3 or 4 in methylene chloride at ambient temperature. The ORTEP plots of the complexes are shown in Figures 5-1 and 5-2, respectively. The selected bond lengths and angles are given in Table 5-1 and 5-2. The crystallographic data and the data collection parameters for complexes 3 and 4 are summarized in Table 5-3. The ligand in complex 3 is isomeric with that in complex 4, in that the relative positions of the five- and six-membered [P,N] and [N,O] chelate rings formed on complexation are reversed. As we expected, complex 3 has six-membered [P,N] and five-membered [N,O] chelate rings. Whereas, [P,N] and [N,O] chelate rings form five- and six-membered rings respectively in complex 4.

In the solid state, the complexes adopt geometries about the palladium metal center best described as a distorted square planar arrangement due to the bulk of the phosphine group and the ring strain of the [P,N] chelate (complex 3) or the [N,O] chelate (complex 4) six-membered rings. For complex 3, bond angles substantially deviated from idealized square planar geometry by virtue of the constraint. The bond angle of P(1)-Pd(1)-N(1) in complex 3 is 97.07(6)°, which is similar to that of platinum-based analogue where Pt bound Cl instead of CH₃ and with no t-butyl groups on the aromatic ring. It seems that the large bond length difference between P(1)-C(14) and N(1)-C(8) (1.823(3) and 1.288(3), respectively in the [P,N] six-membered ring in complex 3 caused severe distortion. The substantial decrease in the O(1)-Pd(1)-N(1) angle (81.59(8)°) is observed due to the compensation by in large due to a concomitant increase in the P(1)-
Pd(1)-N(1) angle. On the other hand, in complex 4, the [N,O] six-membered ring is quite symmetrical, thereby resulting in less ring strain than that of complex 3.

Table 5-3

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<td>C$<em>{34}$H$</em>{38}$NOPd</td>
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<td>b(Å)</td>
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<td>c(Å)</td>
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<td>19.005(5)</td>
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<td>β(deg)</td>
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<td>D$_{calc}$ (Mg/m$^3$)</td>
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5.2.3 Reactivity of the Complexes

Catalytic activity of complexes 3 and 4 for polymerization of several vinyl monomers, such as ethene, methyl acrylate, and butylester norbornene, has been tested in dichloromethane at ambient temperature or chlorobenzene at 60°C. None of the tested reactions gave polymeric product. NMR scale experiments of vinyl monomers with one of the complexes showed no reactions of either oligomerization or any other catalytic
process occurred. Activation of the complexes by using a Lewis base, FAB, B(C₆F₅)₃, has been attempted. It was expected that FAB interacts with the complexes through oxygen of the aryloxy group to form a zwitterionic compound affording a vacant site for an incoming monomer. However, no polymeric product has been obtained from the reactions, except in the case of the reaction of methyl acrylate with complex 3, in which a trace amount (ca. 7%) of product was produced. In the NMR scale experiment of the reaction between complex 3 or 4 with FAB in dichloromethane-d₂, we observed the abstraction of the palladium bound methyl group rather than the aryloxy group from 3 or 4 with FAB. Upon addition of the FAB to the purple solution of 3 in dichloromethane-d₂, the color of the solution changed to reddish brown in a few seconds, indicating a reaction occurred. ¹H NMR of the solution shows broad resonance as a singlet at 0.46 ppm, a typical resonance of the non-coordinating MeB(C₆F₅)₃⁻. ¹¹B{¹H} NMR, one of the most notable spectroscopic evidences, shows sharp resonance at -15.29 ppm supporting the formation of the [MeB(C₆F₅)₃]⁻ anion. On the other hand, complex 4 also shows a similar reaction pattern with FAB, having 0.49 ppm in ¹H NMR and -15.29 ppm in ¹¹B{¹H} NMR.

Clear evidence that the complexes cannot be activated by FAB directed us to test several aluminum-based Lewis bases, such as aluminum trichloride, triethyl aluminum, Al(C₆F₅)₃ (FAL) or methyaluminoxane (MAO) for the polymerization of vinyl monomers. The system utilizing aluminum trichloride generated a small amount of polyethylene or no poly(methyl acrylate) in chlorobenzene at 60°C. On the other hand, the polymerization reaction using triethyl aluminum as a cocatalyst showed interesting results (Table 5-4).
Table **5-4**

Table 5-4: Polymerization of vinyl monomers using complexes 3 and 4 with AlEt₃<sup>a</sup>

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<th>Monomer</th>
<th>Yield(g)</th>
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<th>Mₘ/Μₙ&lt;sup&gt;b&lt;/sup&gt;</th>
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<td>(x10⁻⁵mol)</td>
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<td>MMA(g)</td>
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<td>4(3.3)</td>
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* table continued to next page

<sup>a</sup>Carried out in chlorobenzene (5g) at 60°C for 24h.  
<sup>b</sup>Number-average molecular weight (Mₙ) and polydispersity index (PDI) determined by GPC relative to poly(styrene) standards.  
<sup>c</sup>Carried out in CH₂Cl₂ at ambient temperature.  
<sup>d</sup>Repeated reaction.
As mentioned earlier, neutral complex 3 or 4 by itself is inactive for ethene, MA, or MMA polymerization. However, the polymerization by premixing the complex 3 or 4 with 1 equiv. of AlEt$_3$ in chlorobenzene followed by addition of MA or MMA is active, producing PMA or PMMA. The complex 3 mixture with AlEt$_3$ produced PMA or PMMA in relatively low yield (entries 3-5, 20, Table 5-4). The complex 4 with AlEt$_3$ is more

### Table 5-4: Polymerization of vinyl monomers using complexes 3 and 4 with AlEt$_3$\(^a\)

<table>
<thead>
<tr>
<th>entry</th>
<th>Complex (x10$^{-5}$ mol)</th>
<th>AlEt$_3$ (x10$^{-5}$ mol)</th>
<th>Monomer</th>
<th>Yield (g)</th>
<th>$M_n$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>4(0.8)</td>
<td>0.8</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td>0.11</td>
</tr>
<tr>
<td>14</td>
<td>4(0.8)</td>
<td>1.6</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td>0.19</td>
</tr>
<tr>
<td>15</td>
<td>4(0.8)</td>
<td>2.4</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td>0.18</td>
</tr>
<tr>
<td>16</td>
<td>4(0.8)</td>
<td>3.2</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td>0.08</td>
</tr>
<tr>
<td>17</td>
<td>4(0.8)</td>
<td>0.8</td>
<td>-</td>
<td>0.25</td>
<td>-</td>
<td>0.05</td>
</tr>
<tr>
<td>18</td>
<td>4(0.8)</td>
<td>0.8</td>
<td>-</td>
<td>0.75</td>
<td>-</td>
<td>0.25</td>
</tr>
<tr>
<td>19</td>
<td>4(0.8)</td>
<td>0.8</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
<td>0.52</td>
</tr>
<tr>
<td>20</td>
<td>3(3.3)</td>
<td>3.3</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>0.17</td>
</tr>
<tr>
<td>21</td>
<td>4(3.3)</td>
<td>3.3</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>1.01</td>
</tr>
</tbody>
</table>

\(^a\)Carried out in chlorobenzene (5g) at 60°C for 24h. \(^b\)Number-average molecular weight ($M_n$) and polydispersity index (PDI) determined by GPC relative to poly(styrene) standards using chloroform as eluent.
active for the polymerization of MA or MMA (entries 8-10, 21, Table 5-4) than the complex 3 with AlEt$_3$. Although overall running time was 24 hours, polymerization of MA using complex 4 with AlEt$_3$ seems to be almost finished in 2 hours, making the system hard to be stirred. Insolubility of the PMA produced from the reaction condition in chloroform or dichlorobenzene at ambient temperature or at high temperature (up to 150$^o$C) did not allow us to analyze the polymer at all. The PMMA formed by complex 3 or 4 mixture has an extremely narrow polydispersity index of $M_w/M_n=1.0$ to 1.2 with bimodal characters. Polymerization of MA using AlEt$_3$ by itself was carried out (entries 11-12, Table 5-4). It showed similar activity as the mixture of complex 3 and AlEt$_3$. In dilute solutions, polymerizations of MA using the complex 4 and AlEt$_3$ with different molar ratio of complex to AlEt$_3$ or with different molar ratio of complex mixture to monomer were also tested (entries 13-19, Table 5-4). They did not show much difference in molecular weight or molecular weight distribution. Attempted homo- and co-polymerization of ethene with/without MA resulted in trace amount of polymeric product.

![Scheme 5-3](image-url)
Polymerization of various vinyl monomers using premixed complex 3 and FAL, Al(C₆F₅)₃, was carried out in toluene at ambient temperature. Although the mixture did not show any activity for the polymerization of polar monomers (entries 4-6, Table 5-5), poly(norbornene) or poly(n-butyl-nobornene) was produced in good to almost quantitative yield when 3 equiv. of FAL was pre-introduced (entires 1-3, Table 5-5).

Based on the results of the polymerizations using complex 3 or 4 with FAB or FAL and NMR experiments, two different reaction patterns of the Lewis acids, FAB and FAL, toward the title complexes are expected (Scheme 5-3). As already mentioned above, FAB interacts with a palladium bound methyl group to give an ionic pair, in which there is a vacant site for an incoming monomer. However, the resultant compound cannot pursue the next insertion or a subsequent coordination reaction because there is no driving force for further reaction. On the other hand, FAL favors oxygen functionality to form a dative bond with it. In complex 3 or 4, it looks to generate a zwitterionic

<table>
<thead>
<tr>
<th>entry</th>
<th>3×10⁻⁵ mol</th>
<th>FAL (x10⁻⁵ mol)</th>
<th>Monomers(g)</th>
<th>Yield(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.8</td>
<td>0.8</td>
<td>NB(2)</td>
<td>trace</td>
</tr>
<tr>
<td>2b</td>
<td>0.8</td>
<td>2.4</td>
<td>NB(2)</td>
<td>~2</td>
</tr>
<tr>
<td>3</td>
<td>0.8</td>
<td>2.4</td>
<td>Bu-NB(1.5)</td>
<td>1.11</td>
</tr>
<tr>
<td>4</td>
<td>0.8</td>
<td>2.4</td>
<td>Etester-NB(2)</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>0.8</td>
<td>2.4</td>
<td>MA(2)</td>
<td>trace</td>
</tr>
<tr>
<td>6</td>
<td>0.8</td>
<td>2.4</td>
<td>MMA(2)</td>
<td>trace</td>
</tr>
</tbody>
</table>
compound as shown in Scheme 5-3, which can initiate the polymerization reaction of a non-polar vinyl monomer as a cationic complex.\textsuperscript{36}

Table 5-6

<table>
<thead>
<tr>
<th>entry</th>
<th>Complex</th>
<th>Monomers</th>
<th>Yield (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>NB(2g)</td>
<td>n.r.</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>ethene (700psi)</td>
<td>Trace</td>
</tr>
<tr>
<td>3\textsuperscript{b}</td>
<td>-</td>
<td>ethene (700psi)</td>
<td>Trace</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>NB(2g)</td>
<td>1.62</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>NB(2g)</td>
<td>1.58</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>ethene (700psi)</td>
<td>0.35</td>
</tr>
<tr>
<td>7\textsuperscript{b}</td>
<td>3</td>
<td>ethene (700psi)</td>
<td>0.24</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>Bu-NB(2g)</td>
<td>0.38</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>Ester-NB(2g)</td>
<td>n.r.</td>
</tr>
<tr>
<td>10</td>
<td>3</td>
<td>MA(2g)</td>
<td>n.r.</td>
</tr>
<tr>
<td>11</td>
<td>3</td>
<td>MMA(2g)</td>
<td>n.r.</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Carried out in toluene (15mL) at ambient temperature for 3h, complex (3.13x10\textsuperscript{-5} mol), MAO (500mg). \textsuperscript{b}60\degree C.

Polymerization activities of the complex 3 and 4 for vinyl monomers have been tested further with methylaluminoxane, MAO, as a cocatalyst. Both complexes have been activated by MAO, and polymerized non-polar vinyl monomers with no difference between complex 3 and 4 (entries 4 and 5, Table 5-6). In the case of the norbornene
polymerization, the reactions have finished in a few minutes forming a lump of polymer, which blocks effective stirring.

In conclusion, we first synthesized two neutral Pd(II) complexes, [3,5-di-^i^Bu-2-(OH)C_6H_2N=CH-2-PPh_2C_6H_4]PdMe_2 (3) and [3,5-di-^i^Bu-2-(OH)C_6H_2CH=N-2-PPh_2C_6H_4]PdMe_2 (4) in almost quantitative yield from the ligands, 3,5-di-^i^Bu-2-(OH)C_6H_2N=CH-2-PPh_2C_6H_4 (1) and 3,5-di-^i^Bu-2-(OH)C_6H_2CH=N-2-PPh_2C_6H_4 (2), respectively. The title complexes 3 and 4 have been characterized, and their structures have been confirmed by X-ray analysis. In the solid state, the complexes adopt geometries about the palladium metal center best described as a distorted square planar arrangement. The complex 3 showed much more deviation from the idealized square planar geometry by virtue of the constraint caused by the huge bond length difference between P(1)-C(14) and N(1)-C(8) (1.823(3) and 1.288(3), respectively in the [P,N] six-membered ring. Without the assistance of a cocatalyst, complexes 3 and 4 have not shown any catalytic activity for the polymerization or oligomerization of an alkene. In combination with AlEt_3, 3 and 4 produced PMA, where 4 was observed to have a higher activity than 3. The complex 4 with Al(C_6F_5)_3 as a cocatalyst has polymerized norbornene or n-butylnorbornene in excellent yield, but with B(C_6F_5)_3, it has not produced any polymeric product. Different reaction pathways between complexes 3 or 4 and Al(C_6F_5)_3 or B(C_6F_5)_3 have been proposed based on the results of the polymerization and the NMR experiment. The title complexes have been expected to react with Al(C_6F_5)_3 affording a zwitterionic complex, which can initiate the polymerization of a non-polar alkene. The zwitterionic compounds produced have not polymerized polar alkenes due to their cationic character. Utilizing MAO as a co-catalyst, 3 and 4 produced
poly(norbornene) in good yield with no activity difference between 3 and 4. The combination has also not produced any polymer from monomers having polar functionality.

5.3 Experimental Section

5.3.1 General Considerations

All syntheses and manipulations of air- and moisture-sensitive compounds were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, a high vacuum with argon line, or in a nitrogen-filled glovebox.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX 400 NMR spectrometer, DPX 300 NMR spectrometer, and CDPX 300 NMR spectrometer. Splitting patterns are designated as follows: s, singlet; bs, broad singlet; d, doublet; dd, doublet of doublets; t, triplet; td, triplet of doublets; sept, septet; m, multiplet. All $^1$H NMR spectra are reported in $\delta$ units, parts per million (ppm) downfield from tetramethylsilane. All $^{13}$C NMR spectra are reported in ppm relative to tetramethylsilane using CD$_2$Cl$_2$, toluene-d$_8$, or chlorobenzene-d$_5$ as a secondary standard. Variable-temperature $^1$H NMR experiments were performed on a Bruker DPX 300 NMR spectrometer, using CD$_2$Cl$_2$, toluene-d$_8$, or chlorobenzene-d$_5$ as solvent. Actual NMR probe temperatures were measured using anhydrous methanol (with 0.03% concentrated HCl) or ethylene glycol (neat) in a 5 mm NMR tube (see 2.5.1 and 2.5.2). NMR analyses of polymers were performed on a Brüker DPX 300 NMR spectrometer at ambient or elevated temperature, using CDCl$_3$,.
chlorobenzene-\textsubscript{d\textsubscript{5}}, dichlorobenzene-\textsubscript{d\textsubscript{4}}, or tetrachloroethane-\textsubscript{d\textsubscript{2}} as solvent unless otherwise noted.

Size exclusion chromatography data were obtained on a Shimadzu SEC System using a three-column bank (Styragel 7.8x300 mm columns, 100-5,000 D, 500-30,000 D, 2000-4,000,000 D), a Shimadzu RID-10A Differential Refractometer, and a Shimadzu LC-10AT pump/controller. Size exclusion chromatography was performed in chloroform at ambient temperature and calibrated to polystyrene standards.

Chlorobenzene and dichloromethane was obtained from Aldrich and dried via passage over a column of activated alumina (LaRoche A-2).\textsuperscript{37} Toluene and diethyl ether were deoxygenated, dried via passage over a column of activated alumina (LaRoche A-2), and columns of Engelhard CU-0226S\textsuperscript{37}. Pentane and tetrahydrofuran were distilled under nitrogen from sodium benzophenone ketyl. All solvents were degassed by repeated freeze-pump-thaw cycles, and stored over 4 Å molecular sieves under nitrogen. Norbornene was purchased from Acros Organics and used without further purification. Methyl acrylate and methyl methacrylate were purchased from Aldrich and used after repeated freeze-pump-thaw cycles prior to use. Aluminum trichloride and triethyl aluminium were purchased from Aldrich Chemical Co., and used without further purification. MAO, methylaluminoxane, purchased as 10 wt. % solution in toluene from Aldrich Chemical Co. was stored under nitrogen as a solid by removing solvent under vacuum, and prepared as a 20 wt.% solution in toluene before use. Tris(pentafluorophenyl)borane, B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}, was purchased from Strem and used without further purification. Tris(pentafluorophenyl)alane, Al(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}, was prepared as a toluene adduct form of Al(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}(toluene)\textsubscript{1/2} according to a literature procedure.\textsuperscript{38} Extra caution
should be taken for the handling this material because of its thermal and shock sensitivity.\textsuperscript{39}

2-(diphenylphosphino)benzaldehyde, 3,5-di-\textit{tert}-butyl-2-hydroxybenzaldehyde, and 2,4-di-\textit{tert}-butylphenol were purchased from Aldrich and used without further purification. Palladium dichloride(II) was purchased from Strem and used without further purification. 2-nitro-4,6-di-\textit{tert}-butylphenol,\textsuperscript{29} (N,N,N',N'-tetramethylethylenediamine)-dimethylpalladium(II) [(TMEDA)PdMe\textsubscript{2}]\textsuperscript{33} and (2-aminophenyl)diphenylphosphine\textsuperscript{30} were prepared as previously reported.

5.3.2 Synthesis of Compounds

2-Amino-4,6-di-\textit{tert}-butyl-phenol. To 2-nitro-4,6-di-\textit{tert}-butylphenol in ethanol was add 10\% Pd/C. The flask was purged with hydrogen gas, and attached balloon inflated with hydrogen. The reaction mixture was stirred for 2 hours. After removing solvent, the white solid was recrystallized from methanol.

3,5-di-\textit{tBu}-2-(OH)C\textsubscript{6}H\textsubscript{2}N=CH-2-PPh\textsubscript{2}C\textsubscript{6}H\textsubscript{4} (I). To 2-(diphenylphosphino)-benzaldehyde (1.13g, 3.9 mmol) in methanol(50 ml) was added 2-amino-4,6-di-\textit{tert}-butyl-phenol (0.86g, 3.9 mmol), followed by catalytic amount of formic acid (2 drops). The solution was stirred at room temperature for 12h. The resulting yellow-colored precipitate was filtered off and was washed with methanol to provide I as a yellow crystalline solid. Yield 1.7g (86\%). \textsuperscript{1}H NMR(CDCl\textsubscript{3}): $\delta$ 9.14 (d, 1H, Ar-CH=N-), 8.10 (m, 1H), 7.48 (dt, 1H), 7.34 (br, 11H), 7.21 (d, 1H), 6.90 (m, 1H), 6.74 (d, 1H) (ArH), 7.72

(s, 1H, HO-Ar), 1.45 (s, 9H), 1.30 (s, 9H) (-C(CH₃)₃. ¹³C NMR(CDCl₃): δ 155.7 (-CH=N-), 149.0, 141.5 139.4, 139.1, 137.0, 136.9, 135.5, 134.6, 134.5, 134.3, 131.0, 129.4, 129.2, 129.2, 129.1, 123.7, 110.8 (Ar), 35.3, 34.9 (-CMe₃), 32.0, 29.8 (-C(CH₃)₃).

³¹P NMR (CDCl₃) -10.28 (Ph₂P-Ar)

3,5-di-¹Bu-2-(OH)C₆H₂CH=N-2-PPh₂C₆H₄ (2). To 3,5-di-tert-butyl-2-hydroxybenzaldehyde (1g, 4.3 mmol) in methanol(50 ml) was added (2-aminophenyl)diphenylphosphine (1.18g, 4.3 mmol), followed by catalytic amount of formic acid (2 drops). The solution was stirred at room temperature for 12h. Slow concentration of the resulting solution led to precipitation of the product. The yellow precipitate was filtered off and was washed with methanol to provide 1 as a yellow crystalline solid. The compound was recrystallized from methylene dichloride/methanol.

Yield 1.6g (76%). ¹H NMR(CDCl₃): δ 12.91 (s, 1H, HO-Ar) 8.47 (s, 1H, Ar-CH=N-), 7.44-6.94 (m, 16H, ArH), 1.49 (s, 9H), 1.35 (s, 9H) (-C(CH₃)₃. ¹³C NMR(CDCl₃): δ 163.9 (-CH=N-), 158.6, 152.3, 140.6, 137.3, 136.7, 136.5, 134.9, 134.6, 133.7, 133.6, 133.4, 130.3, 129.1, 128.9, 128.8, 128.5, 127.3, 126.9, 118.6, 118.0 (Ar), 35.5, 34.6 (-CMe₃), 31.9, 29.8 (-C(CH₃)₃). ³¹P NMR (CDCl₃) -13.54 (Ph₂P-Ar)

[3,5-di-¹Bu-2-(OH)C₆H₂N=CH-2-PPh₂C₆H₄]PdMe₂ (3) To (TMEDA)PdMe₂ (220mg, 0.87mmol) in diethyl ether (30mL) was added 3,5-di-¹Bu-2-(OH)C₆H₂N=CH-2-PPh₂C₆H₄ (1) (430mg, 0.0.87mmol) in diethyl ether (10mL). The reaction mixture was stirred for 12 hours, which was filtered to remove a small quantity of dark insoluble material. The solvent was removed in vacuo to yield a purple solid. Recrystallization from methylene/pentane gave a purple crystalline solid which was suitable for X-ray crystal structure analysis. Yield >99%. ¹H NMR(CDCl₃): δ 8.55 (s, 1H, Ar-CH=N-), 7.58-
7.41 (m, 14H), 7.20 (m, 2H), (Ar-H), 1.51 (s, 9H, Ar-C(CH$_3$)$_3$), 1.32 (s, 9H, Ar-C(CH$_3$)$_3$), 0.60 (d, 3H, Pd-CH$_3$). $^{13}$C NMR(CD$_2$Cl$_2$): $\delta$ 168.4 (Ar-CH=N-Ar), 149.0, 148.9, 140.7, 137.6, 137.5, 135.9, 135.2, 134.2, 134.1, 132.2, 132.1, 131.7, 131.6, 131.3, 131.2, 129.2, 129.1, 126.4, 124.1, 110.7 (Ar), 35.7, 34.5 (Ar-C(CH$_3$)$_3$), 31.8, 29.5 (Ar-C(CH$_3$)$_3$), -0.6 (Pd-CH$_3$). $^{31}$P NMR (CDCl$_3$) 39.85 (Pd-P-Ar)

[3,5-di-tBu-2-(OH)C$_6$H$_2$CH=N-2-PPh$_2$C$_6$H$_4]$PdMe$_2$ (4) To (TMEDA)PdMe$_2$ (240mg, 0.95mmol) in diethyl ether (30mL) was added 3,5-di-tBu-2-(OH)C$_6$H$_2$CH=N-2-PPh$_2$C$_6$H$_4$ (2) (469mg, 0.95mmol) in diethyl ether (10mL). The reaction mixture was stirred for 12 hours, and then filtered to remove a small quantity of dark insoluble material. The solvent was removed in vacuo to yield an orange solid. Recrystallization from methylene/pentane gave an orange crystalline solid which was suitable for X-ray crystal structure analysis. Yield >99%. $^1$H NMR(CD$_2$Cl$_2$): $\delta$ 8.86 (s, 1H, Ar-CH=N-), 7.79-7.64 (m, 5H), 7.54-7.40 (m, 9H), 7.04 (t, 1H), 6.90 (d, 1H) (Ar-H), 1.52 (s, 9H, Ar-C(CH$_3$)$_3$), 1.33 (s, 9H, Ar-C(CH$_3$)$_3$), 0.72 (d, 3H, Pd-CH$_3$). $^{13}$C NMR(CD$_2$Cl$_2$): $\delta$ 158.6 (-CH=N-), 155.9, 142.4, 135.5, 134.2, 134.0, 133.8, 132.9, 131.9, 131.5, 131.3, 131.3, 131.2, 130.7, 130.3, 129.2, 129.1, 119.8 (Ar), 36.2, 34.2 (-CMe$_3$), 31.7, 30.0 (-C(CH$_3$)$_3$), -2.7 (Pd-CH$_3$). $^{31}$P NMR (CDCl$_3$) 43.50 (Pd-P-Ar)

5.3.3 General Procedures for Polymerization Reactions

In a drybox under a nitrogen atmosphere, a title complex was dissolved in chlorobenzene, dichloromethane, or toluene in a 100 mL Schlenk flask. To the complex solution was introduced a cocatalyst, and the mixture was allowed to generate active
species for 5 min. while stirring at ambient temperature. A desired monomer was introduced to the flask. The reaction mixture was stirred at a desired temperature. After the specified reaction time, the reaction was quenched with aqueous HCl solution (1 N), follow by methanol. The precipitated polymer was filtered and washed with methanol. Volatiles were removed from the polymer in vacuo, and the polymer was dried under vacuum overnight.

5.4 References


   


    2060.


33. De Graaf, W.; Boersma, J.; Smeets, W.J.J.; Spek, A.L.; Van Koten, G. 


Appendix A

Crystal structure information, compound 6 in Chapter 2

Table 1. Crystal data and structure refinement for Complex 6.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
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<td>Empirical formula</td>
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</tr>
<tr>
<td>Formula weight</td>
<td>800.18</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
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</tr>
<tr>
<td></td>
<td>b = 13.3823(7) Å  β = 117.3740(10)°</td>
</tr>
<tr>
<td></td>
<td>c = 13.8935(7) Å  γ = 91.0630(10)°</td>
</tr>
<tr>
<td>Volume</td>
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</tr>
<tr>
<td>Z</td>
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</tr>
<tr>
<td>Density (calculated)</td>
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</tr>
<tr>
<td>Absorption coefficient</td>
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<tr>
<td>F(000)</td>
<td>816</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.30 x 0.10 x 0.05 mm³</td>
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<tr>
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</tr>
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</tr>
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<td>11565</td>
</tr>
<tr>
<td>Independent reflections</td>
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<td>Completeness to theta = 28.27°</td>
<td>90.3 %</td>
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<tr>
<td>Absorption correction</td>
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<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<tr>
<td>Data / restraints / parameters</td>
<td>8060 / 0 / 361</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.034</td>
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<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0338, wR2 = 0.0724</td>
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<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0447, wR2 = 0.0763</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.680 and -0.649 e.Å⁻³</td>
</tr>
</tbody>
</table>

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for 6. U(eq) is defined as one third of the trace of the orthogonalized Uᵢⱼ tensor.

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<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
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<tr>
<td>Atom (1)</td>
<td>Atom (2)</td>
<td>Atom (3)</td>
<td>Atom (4)</td>
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Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1

Table 4. Anisotropic displacement parameters (Å²x 10³) for 6. The anisotropic displacement factor exponent takes the form: -2π²[ h² â²U₁₁ + ... + 2 h k â b̂ U₁₂ ]

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Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for 6

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<td>H(23A)</td>
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<td>H(28B)</td>
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<td>H(28C)</td>
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<td>14411</td>
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Appendix B

Crystal structure information, compound 1a in Chapter 3

Table 1. Sample and crystal data for Complex 1a

<table>
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<tr>
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<td>Temperature</td>
<td>95(2) K</td>
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<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
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<tr>
<td>Crystal size</td>
<td>0.33 x 0.33 x 0.18 mm</td>
</tr>
<tr>
<td>Crystal habit</td>
<td>Clear cuboid</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2(1)/n</td>
</tr>
<tr>
<td>a</td>
<td>10.899(5) Å</td>
</tr>
<tr>
<td>α= 90°</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>12.530(5) Å</td>
</tr>
<tr>
<td>β= 108.150(13)°</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>11.467(5) Å</td>
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<tr>
<td>γ = 90°</td>
<td></td>
</tr>
<tr>
<td>Volume</td>
<td>1488.1(10) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.603 g/cm³</td>
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<tr>
<td>Absorption coefficient</td>
<td>1.408 mm⁻¹</td>
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Table 2. Data collection and structure refinement for Complex 1a

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<tr>
<th>Property</th>
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<tbody>
<tr>
<td>Diffractometer</td>
<td>CCD area detector</td>
</tr>
<tr>
<td>Radiation source</td>
<td>fine-focus sealed tube, MoK</td>
</tr>
<tr>
<td>Generator power</td>
<td>1600 watts (50 kV, 32mA)</td>
</tr>
<tr>
<td>Detector distance</td>
<td>5.8 cm</td>
</tr>
<tr>
<td>Data collection method</td>
<td>omega scans</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.25 to 28.41°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-14 ≤ h ≤ 10, -10 ≤ k ≤ 16, -12 ≤ l ≤ 15</td>
</tr>
</tbody>
</table>
Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å$^2$) for Complex 1a

U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

<table>
<thead>
<tr>
<th></th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd1</td>
<td>0.42167(6)</td>
<td>0.11703(5)</td>
<td>0.25430(5)</td>
<td>0.0283(2)</td>
</tr>
<tr>
<td>Cl3</td>
<td>0.4781(2)</td>
<td>0.23938(16)</td>
<td>0.41588(17)</td>
<td>0.0357(5)</td>
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<tr>
<td>C1</td>
<td>0.5487(11)</td>
<td>0.1788(9)</td>
<td>0.1695(9)</td>
<td>0.057(3)</td>
</tr>
<tr>
<td>C2</td>
<td>0.5441(14)</td>
<td>0.3003(12)</td>
<td>0.1542(13)</td>
<td>0.087(4)</td>
</tr>
<tr>
<td>C11</td>
<td>0.4063(10)</td>
<td>-0.1215(8)</td>
<td>0.2371(9)</td>
<td>0.053(3)</td>
</tr>
<tr>
<td>C10</td>
<td>0.3092(10)</td>
<td>-0.1090(7)</td>
<td>0.3038(9)</td>
<td>0.043(2)</td>
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<tr>
<td>C13</td>
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<td>0.0332(8)</td>
<td>0.0860(7)</td>
<td>0.041(2)</td>
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<tr>
<td>C9</td>
<td>0.3073(7)</td>
<td>0.0002(6)</td>
<td>0.3549(7)</td>
<td>0.0280(17)</td>
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<td>C8</td>
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<td>0.0303(17)</td>
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<td>0.0750(7)</td>
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<td>0.1727(8)</td>
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<tr>
<td>C7</td>
<td>0.6815(13)</td>
<td>0.3216(11)</td>
<td>0.2660(10)</td>
<td>0.074(4)</td>
</tr>
<tr>
<td>C5</td>
<td>0.7534(12)</td>
<td>0.2508(12)</td>
<td>0.2137(12)</td>
<td>0.072(4)</td>
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<tr>
<td>C3</td>
<td>0.5892(12)</td>
<td>0.3311(13)</td>
<td>0.0501(11)</td>
<td>0.076(4)</td>
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<tr>
<td>C6</td>
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<td>0.1510(10)</td>
<td>0.2237(14)</td>
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<tr>
<td>C4</td>
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<td>0.0918(12)</td>
<td>0.097(6)</td>
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<td>0.3424(12)</td>
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Table 4. Bond lengths (Å) for Complex 1a

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<tr>
<td>Pd1-C1</td>
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<td>Pd1-C12</td>
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<td>Pd1-C9</td>
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<td>C1-C6</td>
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<td>C1-C2</td>
<td>1.531(18)</td>
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</tr>
<tr>
<td>C2-C3</td>
<td>1.477(17)</td>
<td>C2-C7</td>
<td>1.662(18)</td>
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<td>C11-C10</td>
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<td>C11-C12</td>
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<td>C10-C9</td>
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<td>C13-C12</td>
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<td>C13-C14</td>
<td>1.500(13)</td>
<td>C9-C8</td>
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<td>C8-C15</td>
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<td>C14-C15</td>
<td>1.513(14)</td>
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<td>C7-C5</td>
<td>1.434(19)</td>
<td>C5-C4</td>
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<td>C3-C4</td>
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<td>C6-C16</td>
<td>1.450(17)</td>
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Table 5. Bond angles (°) for Complex 1a

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<td>C1-Pd1-C12</td>
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<tr>
<td>C12-Pd1-C13</td>
<td>37.3(4)</td>
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<tr>
<td>C12-Pd1-C13</td>
<td>159.6(3)</td>
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<tr>
<td>C1-Pd1-C8</td>
<td>161.2(4)</td>
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<tr>
<td>C13-Pd1-C8</td>
<td>79.8(3)</td>
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<tr>
<td>C1-Pd1-C9</td>
<td>164.2(4)</td>
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<tr>
<td>C13-Pd1-C9</td>
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<tr>
<td>C8-Pd1-C9</td>
<td>32.0(3)</td>
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<tr>
<td>C6-C1-Pd1</td>
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<td>C3-C2-C1</td>
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<td>C1-C2-C7</td>
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<td>C9-C10-C11</td>
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<td>C12-C13-Pd1</td>
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<td>C8-C9-C10</td>
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<td>C10-C9-Pd1</td>
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<td>C9-C8-Pd1</td>
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<tr>
<td>C13-C12-C11</td>
<td>126.4(9)</td>
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<td>C11-C12-Pd1</td>
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<td>C14-C15-C8</td>
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<td>C4-C5-C7</td>
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<td>C7-C5-C6</td>
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<td>C16-C6-C1</td>
<td>117.3(10)</td>
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Appendix C

Crystal structure information, compound 1b in Chapter 3

Table 1. Sample and crystal data for complex 1b.

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<th>Property</th>
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<td>Temperature</td>
<td>95(2) K</td>
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<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
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<tr>
<td>Crystal size</td>
<td>0.26 x 0.24 x 0.12 mm</td>
</tr>
<tr>
<td>Crystal habit</td>
<td>colourless cuboidal</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
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</tr>
<tr>
<td></td>
<td>b = 10.216(2) Å</td>
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<tr>
<td></td>
<td>c = 12.347(3) Å</td>
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<tr>
<td></td>
<td>α = 105.751(3)°</td>
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<td>β = 90.578(4)°</td>
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<tr>
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<td>γ = 109.872(4)°</td>
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<tr>
<td>Density (calculated)</td>
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<td>Absorption coefficient</td>
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Table 2. Data collection and structure refinement for complex 1b.

<table>
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<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Diffractometer</td>
<td>CCD area detector</td>
</tr>
<tr>
<td>Radiation source</td>
<td>fine-focus sealed tube, MoK</td>
</tr>
<tr>
<td>Generator power</td>
<td>1600 watts (50 kV, 32mA)</td>
</tr>
<tr>
<td>Detector distance</td>
<td>5.8 cm</td>
</tr>
<tr>
<td>Data collection method</td>
<td>omega scans</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.72 to 28.32°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-10 ≤ h ≤ 6, -10 ≤ k ≤ 13, -15 ≤ l ≤ 15</td>
</tr>
</tbody>
</table>
Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for complex 1b.

U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

<table>
<thead>
<tr>
<th></th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd1</td>
<td>0.4011(3)</td>
<td>0.7532(9)</td>
<td>0.44967(19)</td>
<td>0.01285(12)</td>
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<td>0.6559(9)</td>
<td>0.0221(19)</td>
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<td>C12</td>
<td>0.1113(3)</td>
<td>0.6760(3)</td>
<td>0.3596(2)</td>
<td>0.0201(5)</td>
</tr>
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<td>C28</td>
<td>0.2849(13)</td>
<td>1.1599(10)</td>
<td>0.7258(9)</td>
<td>0.019(2)</td>
</tr>
<tr>
<td>C9</td>
<td>0.6812(12)</td>
<td>0.8582(12)</td>
<td>0.4554(9)</td>
<td>0.020(2)</td>
</tr>
<tr>
<td>C27</td>
<td>0.1591(10)</td>
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<td>0.6759(8)</td>
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<td>0.5532(8)</td>
<td>0.0211(19)</td>
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<td>C29</td>
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<td>0.6251(7)</td>
<td>0.0191(17)</td>
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<td>C24</td>
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<td>0.6577(8)</td>
<td>0.019(18)</td>
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Table 4. Bond lengths (Å) for complex 1b.

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<td>Pd1-C38</td>
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<td>C32-C29</td>
<td>1.402(13)</td>
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<td>C28-C29</td>
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<td>C27-C33</td>
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<td>C26-C24</td>
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<td>C33-C30</td>
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<td>Bond Angle</td>
<td>Value (°)</td>
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<td>C30-C29-C28</td>
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<td>C30-C25-C26</td>
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<td>C26-C25-Pd1</td>
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## Appendix D

### Crystal structure information, compound 1c in Chapter 3

**Table 1. Sample and crystal data for complex 1c.**

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<th><strong>C38 H58 Cl2 O4 Pd2</strong></th>
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<td><strong>Formula weight</strong></td>
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<tr>
<td><strong>Temperature</strong></td>
<td>96(2) K</td>
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<tr>
<td><strong>Wavelength</strong></td>
<td>0.71073 Å</td>
</tr>
<tr>
<td><strong>Crystal size</strong></td>
<td>0.29 x 0.17 x 0.07 mm</td>
</tr>
<tr>
<td><strong>Crystal habit</strong></td>
<td>light plate</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
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<tr>
<td><strong>Space group</strong></td>
<td>P-1</td>
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<tr>
<td><strong>Unit cell dimensions</strong></td>
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</tr>
<tr>
<td></td>
<td>b = 12.466(2) Å</td>
</tr>
<tr>
<td></td>
<td>c = 13.034(2) Å</td>
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<tr>
<td><strong>Volume</strong></td>
<td>1825.5(5) Å³</td>
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<tr>
<td><strong>Z</strong></td>
<td>2</td>
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<tr>
<td><strong>Density (calculated)</strong></td>
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<tr>
<td><strong>Absorption coefficient</strong></td>
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**Table 2. Data collection and structure refinement for complex 1c.**

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<td>fine-focus sealed tube, MoK</td>
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<tr>
<td><strong>Generator power</strong></td>
<td>1600 watts (50 kV, 32mA)</td>
</tr>
<tr>
<td><strong>Detector distance</strong></td>
<td>5.8 cm</td>
</tr>
<tr>
<td><strong>Data collection method</strong></td>
<td>omega scans</td>
</tr>
<tr>
<td><strong>Theta range for data collection</strong></td>
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</tr>
<tr>
<td><strong>Index ranges</strong></td>
<td>-9 ≤ h ≤ 14, -13 ≤ k ≤ 16, -17 ≤ l ≤ 15</td>
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</table>
Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å$^2$) for complex 1c.
U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

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<th>z/c</th>
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<td>Y</td>
<td>Z</td>
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<td>-----</td>
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<td>-----</td>
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Table 4. Bond lengths (Å) for complex 1c.

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<td>Pd1-C2</td>
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</tr>
<tr>
<td>Pd1-C5</td>
<td>2.388(3)</td>
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<tr>
<td>Pd2-C27</td>
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<tr>
<td>Pd2-C15</td>
<td>2.389(3)</td>
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<tr>
<td>C27-C32</td>
<td>1.534(4)</td>
</tr>
<tr>
<td>C17-C22</td>
<td>1.543(4)</td>
</tr>
<tr>
<td>O4-C34</td>
<td>1.354(4)</td>
</tr>
<tr>
<td>O2-C24</td>
<td>1.347(4)</td>
</tr>
<tr>
<td>C24-O1</td>
<td>1.201(4)</td>
</tr>
<tr>
<td>C34-O3</td>
<td>1.202(4)</td>
</tr>
<tr>
<td>C21-C20</td>
<td>1.546(4)</td>
</tr>
<tr>
<td>C22-C23</td>
<td>1.533(4)</td>
</tr>
<tr>
<td>C31-C32</td>
<td>1.571(4)</td>
</tr>
<tr>
<td>C33-C32</td>
<td>1.533(4)</td>
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<tr>
<td>C18-C19</td>
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</tr>
<tr>
<td>C1-C8</td>
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<tr>
<td>C10-C9</td>
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<td>C14-C15</td>
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<td>C7-C6</td>
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<td>C6-C5</td>
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Table 5. Bond angles (°) for kms22t.

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<th>Bond</th>
<th>Angle (°)</th>
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<td>C17-Pd1-C2</td>
<td>90.15(12)</td>
</tr>
<tr>
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<td>94.79(9)</td>
</tr>
<tr>
<td>C1-Pd1-C11</td>
<td>162.56(9)</td>
<td>C2-Pd1-C11</td>
<td>159.82(9)</td>
</tr>
<tr>
<td>C17-Pd1-C5</td>
<td>162.23(11)</td>
<td>C1-Pd1-C5</td>
<td>93.60(11)</td>
</tr>
<tr>
<td>C2-Pd1-C5</td>
<td>80.10(11)</td>
<td>C17-Pd1-Cl1</td>
<td>89.70(8)</td>
</tr>
<tr>
<td>C17-Pd1-C6</td>
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<td>C1-Pd1-C6</td>
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<tr>
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</tr>
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<tr>
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<td>C32-C27-Pd2</td>
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</tr>
<tr>
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<td>C24-C21-C22</td>
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### Appendix E

**Crystal structure information, compound 1d in Chapter 3**

#### Table 1. Sample and crystal data for complex 1d.

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<td>C19 H29 Cl O2 Pd</td>
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<td>Formula weight</td>
<td>431.27</td>
</tr>
<tr>
<td>Temperature</td>
<td>293(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.41 x 0.21 x 0.1 mm</td>
</tr>
<tr>
<td>Crystal habit</td>
<td>colourless needle</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2(1)/n</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 6.8659(17) Å, α = 90°, b = 23.248(6) Å, β = 96.614(4)°, c = 11.502(3) Å, γ = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>1823.7(8) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.571 g/cm³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
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<tr>
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#### Table 2. Data collection and structure refinement for complex 1d.

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<td>CCD area detector</td>
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<tr>
<td>Radiation source</td>
<td>fine-focus sealed tube, MoK</td>
</tr>
<tr>
<td>Generator power</td>
<td>1600 watts (50 kV, 32mA)</td>
</tr>
<tr>
<td>Detector distance</td>
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</tr>
<tr>
<td>Data collection method</td>
<td>omega scans</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.75 to 28.40°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-9 ≤ h ≤ 8, -30 ≤ k ≤ 21, -15 ≤ l ≤ 15</td>
</tr>
</tbody>
</table>
Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å$^2$) for complex 1d.

U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

<table>
<thead>
<tr>
<th></th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
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<td>0.040(2)</td>
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<td>0.0279(16)</td>
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Table 4. Bond lengths (Å) for complex 1d.

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<td>Pd1-C1</td>
<td>2.391(7)</td>
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<tr>
<td>C2-C1</td>
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<td>C9-C10</td>
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<td>C11-C16</td>
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<td>C3-C4</td>
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Table 5. Bond angles (°) for complex 1d.

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<td>C9-Pd1-C1</td>
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<tr>
<td>C6-Pd1-C2</td>
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</tr>
<tr>
<td>C1-Pd1-Cd</td>
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<tr>
<td>C15-C9-Pd1</td>
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<td>C9-C10-C14</td>
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<td>C14-C10-C11</td>
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<td>C16-C11-C12</td>
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<td>C8-C1-Pd1</td>
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<tr>
<td>C12-C13-C14</td>
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<tr>
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<td>101.3(5)</td>
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<td>C19-C15-C13</td>
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<tr>
<td>C13-C15-C9</td>
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<td>C5-C4-C3</td>
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</tr>
<tr>
<td>C17-O1-C16</td>
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<tr>
<td>C9-Pd1-C6</td>
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<td>C6-Pd1-C2</td>
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<td>C1-Pd1-C2</td>
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<td>Bond Angle (deg)</td>
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<td>------------------</td>
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Appendix F

Crystal structure information, compound 3a in Chapter 4

Table 1. Sample and crystal data for complex 3a.

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<td>C32 H42 N2 O Pd</td>
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<tr>
<td>Formula weight</td>
<td>577.08</td>
</tr>
<tr>
<td>Temperature</td>
<td>98(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.20 x 0.19 x 0.09 mm</td>
</tr>
<tr>
<td>Crystal habit</td>
<td>Yellow-clear Brick</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
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<tr>
<td></td>
<td>b = 11.3688(17) Å</td>
</tr>
<tr>
<td></td>
<td>c = 13.611(2) Å</td>
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<tr>
<td>Volume</td>
<td>1458.3(4) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
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<tr>
<td>Density (calculated)</td>
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</tr>
<tr>
<td>Absorption coefficient</td>
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Table 2. Data collection and structure refinement for complex 3a.

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<td>fine-focus sealed tube, MoK</td>
</tr>
<tr>
<td>Generator power</td>
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</tr>
<tr>
<td>Detector distance</td>
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</tr>
<tr>
<td>Data collection method</td>
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<tr>
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Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å$^2$) for complex 3a.

$U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

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<th>y/b</th>
<th>z/c</th>
<th>U(eq)</th>
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<td>111.8(13)</td>
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### Table 1. Sample and crystal data for complex 3c.

<table>
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<tr>
<th>Property</th>
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<tr>
<td>Empirical formula</td>
<td>C105 H144 N6 O3 Pd3</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1857.46</td>
</tr>
<tr>
<td>Temperature</td>
<td>98(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.45 x 0.15 x 0.15 mm</td>
</tr>
<tr>
<td>Crystal habit</td>
<td>yellow Brick</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2(1)/c</td>
</tr>
</tbody>
</table>
| Unit cell dimensions          | a = 11.4483(11) Å  
β = 90°
|                               | b = 19.4368(19) Å            |
|                               | c = 43.765(4) Å              |
| Volume                        | 9738.5(17) Å³                |
| Z                             | 4                            |
| Density (calculated)          | 1.267 g/cm³                  |
| Absorption coefficient        | 0.599 mm⁻¹                   |
| F(000)                        | 3912                         |

### Table 2. Data collection and structure refinement for complex 3c.

<table>
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<td>CCD area detector</td>
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<tr>
<td>Radiation source</td>
<td>fine-focus sealed tube, MoK</td>
</tr>
<tr>
<td>Generator power</td>
<td>1600 watts (50 kV, 32mA)</td>
</tr>
<tr>
<td>Detector distance</td>
<td>5.8 cm</td>
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<tr>
<td>Data collection method</td>
<td>omega scans</td>
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<tr>
<td>Theta range for data collection</td>
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</tr>
<tr>
<td>Index ranges</td>
<td>-15 ≤ h ≤ 15, -24 ≤ k ≤ 25, -57 ≤ l ≤ 57</td>
</tr>
</tbody>
</table>

### Table 3. Atomic coordinates and equivalent isotropic
**atomic displacement parameters (Å$^2$) for complex 3c.**

$U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

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<th>z/c</th>
<th>$U_{eq}$</th>
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<tr>
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<tr>
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Table 4. Bond lengths (Å) for complex 3c.

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Appendix H

Crystal structure information, compound 3d in Chapter 4

Table 1. Sample and crystal data for complex 3d.

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Table 2. Data collection and structure refinement for complex 3d.

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Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å\(^2\)) for complex 3d.

U(eq) is defined as one third of the trace of the orthogonalized \(U_{ij}\) tensor.

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Table 4. Bond lengths (Å) for complex 3d.

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Table 5. Bond angles (°) for complex 3d.

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### Crystal structure information, compound 3e in Chapter 4

#### Table 1. Sample and crystal data for complex 3e

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<td>Wavelength</td>
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<td>b = 13.0421(6) Å = 81.2500(10)°.</td>
</tr>
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<td>Full-matrix least-squares on F²</td>
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Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3)
for complex 3e.

U(eq) is defined as one third of the trace of the orthogonalized U_ij tensor.

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Table 3. Bond lengths [Å] and angles [°] for complex 3e.

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Table 5. Bond angles (°) for Complex 3e

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Appendix J

Crystal structure information, compound 4 in Chapter 4

Table 1. Sample and crystal data for complex 4.

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<td>Temperature</td>
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</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
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<tr>
<td>Crystal size</td>
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</tr>
<tr>
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<td>Yellow-clear Needle</td>
</tr>
<tr>
<td>Crystal system</td>
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<tr>
<td>Space group</td>
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<tr>
<td>Unit cell dimensions</td>
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</tr>
<tr>
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<td>b = 13.620(3) Å</td>
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<td>c = 13.959(3) Å</td>
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<td></td>
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<td></td>
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Table 2. Data collection and structure refinement for complex 4.

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</tr>
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<td>Detector distance</td>
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<tr>
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<tr>
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Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å$^2$) for complex 4.

U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

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<th>z/c</th>
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## Appendix K

Crystal structure information, compound 5 in Chapter 4

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Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for complex 5. U(eq) is defined as one third of the trace of the orthogonalized U^ij tensor.

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# Appendix L

## Crystal structure information, compound 3 in Chapter 5

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<tr>
<td>Theta range for data collection</td>
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<tr>
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<td>-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -26 ≤ l ≤ 26</td>
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Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å$^2$) for complex 3.

U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

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<th></th>
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<th>y/b</th>
<th>z/c</th>
<th>U(eq)</th>
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<td>0.07066(13)</td>
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<tr>
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<tr>
<td>O1</td>
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<td>0.13621(9)</td>
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<tr>
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Table 4. Bond lengths (Å) for complex 3.

| Bond            | Length  (
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<td>C9-C10</td>
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Table 5. Bond angles (°) for complex 3.

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<td>175.28(5)</td>
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<td>C14-P1-C21</td>
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<td>C22-C21-C26</td>
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<td>C26-C21-P1</td>
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<td>Bond</td>
<td>Angle (°)</td>
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<td>---------------</td>
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<tr>
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<tr>
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<td>C5-C6-C7</td>
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<tr>
<td>C13-C12-C11</td>
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<td>C6-C5-C31</td>
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<td>C11-C10-C9</td>
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<td>C6-C7-N1</td>
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<td>C12-C13-C14</td>
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<td>C32-C31-C33</td>
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<td>C3-C27-C29</td>
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Appendix M

Crystal structure information, compound 4 in Chapter 5

Table 1. Sample and crystal data for complex 4.

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<td>Volume</td>
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<td>Z</td>
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<td>Density (calculated)</td>
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Table 2. Data collection and structure refinement for complex 4.

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<td>Theta range for data collection</td>
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<td>Index ranges</td>
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Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for complex 4.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

<table>
<thead>
<tr>
<th></th>
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<th>z/c</th>
<th>U(eq)</th>
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## Appendix N

Kinetic data sources for Table 2-1 and Figure 2-2

### 199.01 K

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**Gibbs Activation Energy**

63943.577

**63.944 kJ/mol**
205.85 K

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Gibbs Activation Energy

64707.976

64.708 kJ/mol

205.85 K (Pd–CH3)

\[ y = -1.63E-04x - 1.76E-02 \]

\[ R^2 = 9.55E-01 \]
211.96 K

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Gibbs Activation Energy

63786.527

63.787 kJ/mol
211.96 K

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Gibbs Activation Energy

63999.854

64.000 kJ/mol
### 218.28 K

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**Gibbs Activation Energy**

- 65129.297 J/mol
- 65.129 kJ/mol

![Graph](image_url)

**Equation:**

\[ y = -1.18E-03x - 6.25E-02 \]

**R^2:** 9.90E-01
224.25 K

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**Gibbs Activation Energy**

66024.38

**66.024 kJ/mol**

![Graph showing ln([A]t/[A]0) vs. t with the equation y = -1.95E-03x - 6.92E-02 and R² = 9.90E-01]
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\[ E_a = 51.54 \text{ kJ/mol} \]
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Activation enthalpy (J/mol) | Activation Entropy (J/K.mol)
721.01275 | -70.2304
0.721 kJ/mol | -16.7851
172.322047 | -70.230 J/K.mol
0.172 kcal/mol | -16.785 cal/K.mol

Eyring plot (Pd-CH₃), 1st

\[
y = -5994.5x + 15.313 \\
R^2 = 0.9466
\]
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**Activation enthalpy (J/mol)**  
720.254992  
0.720 kJ/mol  
172.140943  
0.172 kcal/mol

**Activation Entropy (J/K.mol)**  
-70.6793  
-70.679 J/K.mol  
-16.8924  
-16.892 cal/K.mol

**Eyring plot (Pd-CH₃), 2nd**

\[ y = -5988.2x + 15.259 \]

\[ R^2 = 0.9615 \]
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\[
y = 3.4104x + 0.0934
\]

\[
R^2 = 0.9721
\]
Appendix O

Data sources for Figure 3-6 and 3-7

1. Scaled-up Reaction: Molecular vs time [using (COD)PdMeCl]

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Molecular Weight of Poly(norbornene) vs time

- Linear (Mw): $y = 14.37x + 736.8$, $R^2 = 0.958$
- Linear (Mn): $y = 5.42x + 550.8$, $R^2 = 0.8809$

![Graph](image_url)
2. Scaled-up Reaction: Molecular vs time [using 1a]

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<th>60</th>
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<tr>
<td>Mw</td>
<td>901</td>
<td>1119</td>
<td>1338</td>
<td>1399</td>
<td>1550</td>
</tr>
<tr>
<td>Mn</td>
<td>552</td>
<td>655</td>
<td>723</td>
<td>733</td>
<td>922</td>
</tr>
</tbody>
</table>

**Molecular Weight of Poly(norbornene) vs time**

\[ y = 15.78x + 630.2 \]
\[ R^2 = 0.9642 \]

\[ y = 8.18x + 389.8 \]
\[ R^2 = 0.9118 \]
<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>Norbornene Conversion</th>
<th>Ethylester-norbornene Conversion</th>
<th>Exo-Ethylester-norbornene Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.94726</td>
<td>0.94726</td>
<td>0.94726</td>
</tr>
<tr>
<td>2700</td>
<td>0.90217</td>
<td>0.93497</td>
<td>0.93824</td>
</tr>
<tr>
<td>5400</td>
<td>0.86584</td>
<td>0.92535</td>
<td>0.93208</td>
</tr>
<tr>
<td>8100</td>
<td>0.82789</td>
<td>0.91752</td>
<td>0.92501</td>
</tr>
<tr>
<td>10800</td>
<td>0.78334</td>
<td>0.9113</td>
<td>0.91974</td>
</tr>
</tbody>
</table>

Conversion of Norbornene vs time

Conversion of Exo-Ethylesternorbornene vs time

Conversion of Endo-Ethylesternorbornene vs time

\( k = 1.5 \times 10^{-5} \text{ M/s} \)

\( R^2 = 0.9985 \)

\( k = 3.3 \times 10^{-6} \text{ M/s} \)

\( R^2 = 0.9828 \)

\( k = 2.5 \times 10^{-6} \text{ M/s} \)

\( R^2 = 0.99188 \)
Appendix P

Kinetic data sources for Table 4-7

<table>
<thead>
<tr>
<th>time</th>
<th>0oC</th>
<th>3c + *CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>-0.024456068</td>
</tr>
<tr>
<td>900</td>
<td>-0.030814613</td>
<td></td>
</tr>
<tr>
<td>1800</td>
<td>-0.04053898</td>
<td></td>
</tr>
<tr>
<td>2700</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3600</td>
<td>-0.0455890</td>
<td></td>
</tr>
<tr>
<td>4500</td>
<td>-0.05178</td>
<td></td>
</tr>
<tr>
<td>5400</td>
<td>-0.06125921</td>
<td></td>
</tr>
<tr>
<td>6300</td>
<td>-0.06348</td>
<td></td>
</tr>
<tr>
<td>7200</td>
<td>-0.07526761</td>
<td></td>
</tr>
<tr>
<td>8100</td>
<td>-0.07981</td>
<td></td>
</tr>
<tr>
<td>9000</td>
<td>-0.08852</td>
<td></td>
</tr>
<tr>
<td>9900</td>
<td>-0.09603</td>
<td></td>
</tr>
<tr>
<td>10800</td>
<td>-0.10032</td>
<td></td>
</tr>
<tr>
<td>11700</td>
<td>-0.10785</td>
<td></td>
</tr>
<tr>
<td>12600</td>
<td>-0.11382</td>
<td></td>
</tr>
<tr>
<td>13500</td>
<td>-0.11905</td>
<td></td>
</tr>
<tr>
<td>14400</td>
<td>-0.127</td>
<td></td>
</tr>
<tr>
<td>15300</td>
<td>-0.13006</td>
<td></td>
</tr>
</tbody>
</table>

\[ y = -7.48954E-06x - 1.90783E-02 \]
\[ R^2 = 9.97233E-01 \]
<table>
<thead>
<tr>
<th>time</th>
<th>0</th>
<th>600</th>
<th>1200</th>
<th>1800</th>
<th>2400</th>
<th>3000</th>
<th>3600</th>
<th>4200</th>
<th>4800</th>
<th>5400</th>
<th>6000</th>
</tr>
</thead>
<tbody>
<tr>
<td>ln([A]_t/[A]_0)</td>
<td>0</td>
<td>-0.012758866</td>
<td>-0.03045737</td>
<td>-0.04629046</td>
<td>-0.06165</td>
<td>-0.07753855</td>
<td>-0.08785</td>
<td>-0.1064788</td>
<td>-0.1179</td>
<td>-0.13748</td>
<td>-0.14677</td>
</tr>
</tbody>
</table>

**Graph:**

- Equation: $y = -2.48732E-05x - 3.95960E-04$
- $R^2 = 9.98240E-01$
<table>
<thead>
<tr>
<th>Time</th>
<th>20°C 3c + *CO</th>
<th>0°C 3c + Imine + *CO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ln([A]_t/[A]_0)</td>
<td>ln([A]_t/[A]_0)</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>300</td>
<td>-0.02056283</td>
<td>-0.03204</td>
</tr>
<tr>
<td>600</td>
<td>-0.05690837</td>
<td>-0.04018</td>
</tr>
<tr>
<td>900</td>
<td>-0.10334</td>
<td>-0.06273</td>
</tr>
<tr>
<td>1200</td>
<td>-0.14927806</td>
<td>-0.08966</td>
</tr>
<tr>
<td>1500</td>
<td>-0.2009</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>-0.14927806</td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>-0.2009</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>-0.14927806</td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>-0.2009</td>
<td></td>
</tr>
</tbody>
</table>

For 20°C 3c + *CO, the linear regression equation is:

\[ y = -1.51015 \times 10^{-4}x + 2.97163 \times 10^{-2} \]

\[ R^2 = 9.96576 \times 10^{-1} \]

For 0°C 3c + Imine + *CO, the linear regression equation is:

\[ y = -7.91689 \times 10^{-6}x - 2.58048 \times 10^{-2} \]

\[ R^2 = 9.99481 \times 10^{-1} \]
<table>
<thead>
<tr>
<th>Temperature</th>
<th>Reaction</th>
<th>time (s)</th>
<th>ln([A]t/[A]₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10°C</td>
<td>3c + Imine + CO</td>
<td>900</td>
<td>-0.071465898</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1800</td>
<td>-0.102683789</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2700</td>
<td>-0.1067224</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3600</td>
<td>-0.13450993</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4500</td>
<td>-0.15938</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5400</td>
<td>-0.16880611</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6300</td>
<td>-0.19135</td>
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<td>7200</td>
<td>-0.21295282</td>
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<td>8100</td>
<td>-0.21279</td>
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<td>9000</td>
<td>-0.24288</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9900</td>
<td>-0.25921</td>
</tr>
</tbody>
</table>

The relationship between time and ln([A]t/[A]₀) is given by the linear equation:

\[ y = -2.02681 \times 10^{-5}x - 0.0598931 \]

The coefficient of determination (R²) is 0.988855. The graph shows the trend line and data points for the given data points.
20°C  3c + Imine +*CO

<table>
<thead>
<tr>
<th>time</th>
<th>300</th>
<th>600</th>
<th>900</th>
<th>1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>ln([A]/[A]₀)</td>
<td>-0.051832773</td>
<td>-0.07799489</td>
<td>-0.09829763</td>
<td>-0.12287</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>time</th>
<th>1500</th>
<th>1800</th>
<th>2100</th>
</tr>
</thead>
<tbody>
<tr>
<td>ln([A]/[A]₀)</td>
<td>-0.1487688</td>
<td>-0.17715</td>
<td>-0.19966078</td>
</tr>
</tbody>
</table>

y = -8.24131E-05x - 2.63290E-02
R² = 9.98626E-01

Temp. Calib. of NMR probe (DPX300)
y = 1.2431x - 65.562
R² = 0.9997

<table>
<thead>
<tr>
<th></th>
<th>1.2431</th>
<th>65.562</th>
</tr>
</thead>
<tbody>
<tr>
<td>273.15</td>
<td>339.552765</td>
<td>273.990765</td>
</tr>
<tr>
<td>283.15</td>
<td>351.983765</td>
<td>286.421765</td>
</tr>
<tr>
<td>293.12</td>
<td>364.377472</td>
<td>298.815472</td>
</tr>
</tbody>
</table>
3c +*CO

<table>
<thead>
<tr>
<th>T</th>
<th>273.9908</th>
<th>286.4218</th>
<th>298.8155</th>
</tr>
</thead>
<tbody>
<tr>
<td>k(s)</td>
<td>7.48954E-06</td>
<td>2.48732E-05</td>
<td>1.51015E-04</td>
</tr>
<tr>
<td>kB(J/K)</td>
<td>1.38E-23</td>
<td>1.38E-23</td>
<td>1.38E-23</td>
</tr>
<tr>
<td>h(J s)</td>
<td>6.63E-34</td>
<td>6.63E-34</td>
<td>6.63E-34</td>
</tr>
<tr>
<td>R(J/K mol)</td>
<td>8.314</td>
<td>8.314</td>
<td>8.314</td>
</tr>
<tr>
<td>DG</td>
<td>9.38E+04</td>
<td>9.53E+04</td>
<td>9.50E+04</td>
</tr>
<tr>
<td>1/T</td>
<td>0.003649758</td>
<td>0.003491354</td>
<td>0.003346547</td>
</tr>
<tr>
<td>ln(k/T)</td>
<td>-17.41509771</td>
<td>-16.25918519</td>
<td>-14.49795771</td>
</tr>
</tbody>
</table>

**DH(kJ/mol)**

| 79686.3644 | 79.686 |

**DS(J/K mol)**

| -52.47167092 | -52.47167092 |

![Eyring Eq.](image-url)
### 3c + Imine +*CO

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>273.9908</th>
<th>286.4218</th>
<th>298.8155</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$ (s$^{-1}$)</td>
<td>7.91689E-06</td>
<td>2.02681E-05</td>
<td>8.24131E-05</td>
</tr>
<tr>
<td>$k_B$ (J/K)</td>
<td>1.38E-23</td>
<td>1.38E-23</td>
<td>1.38E-23</td>
</tr>
<tr>
<td>$h$ (J s)</td>
<td>6.63E-34</td>
<td>6.63E-34</td>
<td>6.63E-34</td>
</tr>
<tr>
<td>$R$ (J/K mol)</td>
<td>8.314</td>
<td>8.314</td>
<td>8.314</td>
</tr>
<tr>
<td>$D_G$ (kJ/mol)</td>
<td>9.37E+04</td>
<td>9.58E+04</td>
<td>9.66E+04</td>
</tr>
<tr>
<td>$1/T$</td>
<td>0.003649758</td>
<td>0.003491354</td>
<td>0.003346547</td>
</tr>
<tr>
<td>ln($k/T$)</td>
<td>-17.35960664</td>
<td>-16.46392789</td>
<td>-15.10359248</td>
</tr>
</tbody>
</table>

| $D_H$ (kJ/mol)  | 61627.525 | 61.628 |
| $D_S$ (J/K mol) | -117.6916753 | -117.6916753 |

**Eyring Eq.**

![Graph showing the Eyring Eq.](image)

$y = -7412.5x + 9.6044$

$R^2 = 0.9793$
VITA

Myeongsoon Kang

Myeongsoon Kang graduated from Inha University, Inchon, S. Korea with a Bachelor’s degree in Chemistry. He got Master’s degree under the guidance of Prof. Dr. Ik-Mo Lee at Inha University. His thesis title was ‘Synthesis of Sterically modified Zirconocenes [(2-R-Ind)₂ZrCl₂ (R=methyl, i-propyl, phenyl and benzyl, Ind=Indenyl)] for polymerization of thermoplastic elastomer’. He joined Prof. Dr. Ayusman Sen’s group in August 1999 to study late transition metal-based catalytic systems for polymerization of polar vinyl monomers. He received the Braucher Research Fellowship, 2003-2004 for his work on the mechanistic study of the reaction between a cationic palladium complex and vinyl halide. He will receive his doctoral degree in August 2004 and will continue working on metal-catalyzed polymerizations.