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KINETIC ANALYSIS AND MECHANOChemICAL SYNTHESSES OF PALLADIUM COMPLEXES

Jonathon Zachary

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KINETIC ANALYSIS AND MECHANOCHEMICAL SYNTHESES OF PALLADIUM COMPLEXES

A Thesis
Presented to
The Faculty of the Department of Chemistry
Jesse D. Jones Hall
Murray State University
Murray, Kentucky

In Partial Fulfillment
of the Requirements for the Degree
of Masters of Chemistry

By: Jonathon R. Zachary
July 2017
ACKNOWLEDGEMENTS

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Further, the author must acknowledge all the people who have made this work possible, beginning with Dr. Rachel Allenbaugh, for her time and patience in mentoring this budding scientist. Without your help, the development of this material and the knowledge and skills that the author has accumulated would not have been possible. Additionally, to all his fellow researchers of the Allenbaugh research group, who either helped carry out experiments or helped to lay the groundwork for this material, the author is eternally grateful. It is “individual commitment to a group effort—that is what makes a team work, a company work, a society work, a civilization work.” -Vince Lombardi.
Mechanochemical synthesis is a rapidly developing, more environmentally friendly alternative to traditional solution based syntheses. Mechanochemical methods often result in higher overall yields, minimize undesirable side reactions, and present cleaner more concise methods for compound preparation. This work will address the syntheses of three dialkyl 2,2′-bipyridyl-4,4′-dicarboxylate complexes of palladium(II) iodide and the kinetics of these reactions, and this work will address the improved synthesis and purification of 1,3-dimethyl-1H-benzimidazolium iodide and the synthesis of diiodo-bis(1,3-dimethyl benzimidazol-2-ylidene) palladium(II).

The successful synthesis of dialkyl 2,2′-bipyridyl-4,4′-dicarboxylate complexes of palladium(II) iodide was carried out under solvent free ball milling conditions and the kinetic analysis was carried out utilizing $^1$H NMR spectroscopy. The kinetics of these reactions were analysed by comparison to several mathematical models. These reactions were found to best fit the nonlinear form of the Johnson-Mehl-Avrami-Yerofeev-Kolmogrov (JMAYK) equation. Based on this model, the reactions demonstrated pre-existing nucleation sites and discernible dimensionality of crystal growth. The JMAYK model gave coefficients of determination between 0.9702-0.9880, 0.9681-0.9811, and 0.9739-0.9825 for diiodo di-2-decyl 2,2′-bipyridyl-4,4′-dicarboxyl palladium(II), diiodo di-2-hexadecyl 2,2′-bipyridyl-4,4′-dicarboxyl palladium(II), and diiodo dihexadecyl 2,2′-bipyridyl-4,4′-dicarboxyl palladium(II), respectively.

Finally, the mechanochemical synthesis of diiodo-bis(1,3-dimethyl benzimidazol-2-ylidene) palladium(II) began to be analyzed under similar ball
milling conditions as the bipyridyl complexes. This synthesis began with synthesis and purification of the ligand precursor, 1,3-dimethyl-1H-
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CHAPTER 1: INTRODUCTION

Mechanochemical syntheses, those reactions that are induced by the input of mechanical energy, are becoming increasingly popular due to the environmental and cost benefits of these preparations. These benefits are realized mainly through the decreased or eliminated use of solvents in mechanochemical reactions; although, decreased reaction times are also realized for many systems. These benefits have been well reviewed. A wide variety of processes and mechanochemical energy sources are implicated under the heading of mechanochemistry, as evidenced by the breath of a recent *Faraday Discussion* on the topic. Given the wide range of these topics, it is perhaps no surprise that despite the increasing interest in the field, relatively little research has been carried out in “molecular” mechanochemistry, the mechanochemical preparation of discrete molecules and complexes rather than extended network materials.

Initially, this work will address the syntheses of dialkyl 2,2′-bipyridyl-4,4′-dicarboxylate complexes of palladium(II) iodide (1,2, and 3, Figure 1) and the kinetics of these reactions. Secondly, the improved synthesis of diiodo-bis(1,3-dimethyl benzimidazol-2-ylidene) palladium(II) (4a and 4b, Figure 2), began with the synthesis and purification of 1,3-dimethyl-1H-benzimidazolium iodide (5, Figure 3), and. In light of the fact that this work is largely the culmination of two distinct projects, this material will be treated separately, initially addressing the bipyridyl complex synthesis and kinetic analysis, before turning to the carbene complexes.
Figure 1. The structures of 1, 2, and 3.

Figure 2. Compounds 4a and 4b, showing both the cis and trans form of diiodo-bis(1,3-dimethyl benzimidazol-2-ylidene) palladium(II), respectively.

Figure 3. The structure of 1,3-dimethyl-1H-benzimidazolium iodide, 5.
1.1 Bipyridyl complexes

Throughout this work, two types of syntheses will be discussed, traditional synthesis and mechanochemical synthesis. An illustration outlining a few differences in these two methodologies is given in Scheme 1. Traditional chemical reactions are usually carried out under solvent heavy conditions, where all the reacting species are dissolved then driven to react (Scheme 1, blue arrows). These reactions are usually driven by the input of external energy, typically in the form of heat. Often, these reactions have to be carried out under inert atmosphere. Traditional synthesis also may require specialized apparatus, as well as personnel with special training and skills. All too often, these reactions generate a mixture of unreacted starting materials, by-products, decomposition products, and desired products which must be further purified.

**Scheme 1.** The traditional preparation of the complexes (blue arrows) requires extensive use of solvents because the conversion is not complete, and purification by column chromatography is required. The mechanochemical synthesis (green arrows) gives complete conversion in the absence of solvent.
Mechanochemical synthesis is an alternative methodology to traditional synthesis. Processes from solid-solid phase changes and the formation of co-crystals to the breaking and forming of new covalent bonds can all be considered within the realm of mechanochemical synthesis.\textsuperscript{1-2, 4, 14} The fundamental difference between mechanochemical synthesis and the traditional syntheses that will be considered in this work are the reaction conditions themselves. In this work, reactions are carried out in as little solvent as possible and reactions are ground or milled in a vibrational ball mill. This solvent-free or solvent-limited grinding is what will be meant by “mechanochemical synthesis” from this point forward.

Historically, the use of mechanochemical methods to chemical synthesis have been somewhat limited.\textsuperscript{15-16} However, according to Takacs,\textsuperscript{4} mechanochemistry may have been used as early as the 4\textsuperscript{th} century B.C. to produce elemental mercury by grinding cinnabar with acetic acid in a copper vessel. This and similar types of reactions that resulted in the production of metals, metal oxides, and alloys seem to have been most extensively applied in the field.\textsuperscript{1}

Some of the modern applications of mechanochemical methods range from the Baeyer–Villiger oxidations of ketones, as shown in the work by Toda,\textsuperscript{17} where these types of oxidations demonstrate a much faster reaction rate in the solid state than in solution, to the production of drug cocrystals for application in the pharmaceutical industry, as shown in the work by Li.\textsuperscript{18} In Li’s work, it was
asserted that mechanochemical co-crystallization might provide an efficient route to specifically tailored drug development. Furthermore, co-crystallization by liquid assisted mechanochemistry was studied by Nemec.19

While the previously mentioned co-crystallization and metal reactions do not involve organic bond formation, reactions like the Baeyer-Villager oxidation of ketones in the work by Toda17 demonstrate that such areas of organic synthesis should not neglect the applications of mechanochemistry. In fact, in the works by Stolle,15-16 several methodologies where mechanochemistry can be applied to organic synthesis are discussed. Because many organic materials are not in a physical phase that would readily lead researchers to consider the mechanical input of energy to drive reactions; microwave, sonication, and the use of ionic liquids are somewhat more known to organic chemists, than is vibrational ball milling. Stolle15 remarks that vibrational ball milling as is utilized in this work is more woefully “underrepresented in the knowledge of organic chemists” despite being an applicable methodology.

The formation of carbon-carbon bonds is another synthetic area where mechanochemistry has been utilized by Kaupp and coworkers20 for Knoevenagel condensations. In Kaupp’s work, 23 examples were all found to be quantitative, atom economical, and waste free. Their work exemplifies several of the many potential advantages of mechanochemistry.

An additional attribute to some mechanochemical methods that makes them of great interest in many synthetic fields is that mechanochemical methods can be selective as to the products of the reaction. For example, methods can be
sterically selective to certain products, making only one product or favoring one isomer of the synthesized product. For example, in the work of Rightmire et al.,\textsuperscript{21} organometallic complexes of arsenic, antimony, and bismuth were all shown to demonstrate some symmetric preference based on the reaction method and conditions. These organometallic systems, which are all found in two diastereometric forms of $C_1$ and $C_3$ symmetry, demonstrate an increase in the ratio of $C_1$ to $C_3$ up to 330%, when synthesized mechanochemically rather than by traditional methods.

Mechanochemistry has been applied, albeit limedly, to the area of transition metal complex formations.\textsuperscript{1, 3-4, 6-14} The discussion of these transition metal complexes will be restricted to complexes that require formation of metal-nitrogen bonds, because this is the type of bond formed in complexes 1, 2, and 3. This area includes the synthesis of coordination polymers and ligand addition reactions. Furthermore, because this area can be somewhat broad, only specific examples will be chosen for discussion.

Mechanochemical formation of coordination polymers involves the use of poly-functional ligand materials and metal centers. Some of these reactions can form new products that are different from those obtained from the same reactants in traditional solution chemistry. Examples are shown in the work by Bourne et al.\textsuperscript{22} where one and two-dimensional polymer networks of zinc bromide and pyrazine were formed. Such materials were shown to exhibit either a 1-D zigzag chain (Figure 4), or a 2-D square-grid network (Figure 5). In their work, it was
shown that solid state synthesis produced the 2-D grid type network, making this synthetic method both selective and environmentally friendly.

**Figure 4.** The structure of the 1-D zigzag form of the coordination polymer of zinc(II) bromide and pyrazine from the work by Bourne.

**Figure 5.** The structure of 2-D grid type form of the coordination polymer of zinc(II) bromide and pyrazine from the work by Bourne.
Additionally, pyridine ligands have been used in the work by Trobs et al.\textsuperscript{23} In their synthesis, bismuth(III) nitrate pentahydrate was ground with pyridine dicarboxylic acid in the presence of potassium hydroxide to form the compound shown in Figure 6. This material formed not only the nitrogen metal bond but also an oxygen metal bond as a result of the deprotonation of the carboxylic acid.

\textbf{Figure 6.} The structure of the coordination complex of bismuth(III) nitrate and pyridine dicarboxylic acid studied in the work by Trobs.\textsuperscript{23}

This thesis is a direct extension of the work by Hyatt et al.,\textsuperscript{24} where he demonstrated that the formation of bipyridyl metal complexes was possible mechanochemically. In their study, the platinum compound 6 (Figure 7) was synthesized mechanochemically for the study of its liquid crystalline properties. The work this study progresses from there to study palladium iodide bipyridyl complexes, including the study of their synthesis kinetics, with a comparison across different ligand precursors.
Figure 7. The structure of compound 6, the platinum chloride bipyridyl compound studied in the work by Hyatt et al.\textsuperscript{24}

1.2 Kinetic models

As with any synthesis, one of the major areas of concern is reaction time. To that end, this study not only addresses the synthesis of compounds 1, 2, and 3, but also the kinetics of these reactions. This study focused on the time to conversion and the rate at which these reactions attained conversion, through generation of $\alpha$-curves, plotted as $\alpha$ vs time, for the reaction of each synthesized complex. Conversion fraction, $\alpha$, or mole abundance of products to compared to total theoretical moles of product, of the reaction at a given time point is defined in Equation 1 where $M(p)$ is the moles of synthesized product and $M(ty)$ is theoretical yield in moles.

$$\alpha = \frac{M(p)}{M(ty)}$$

The understanding and exploration of the kinetics governing mechanochemical reactions is vital to maximizing the benefits of these more
sustainable reaction methods, and trying to understand the processes that drive these syntheses. The review by Khawam and Flanagan\textsuperscript{25} presented several mathematical models that will be applied in this study. These models are shown in Table 1 and are presented in the same order as found in the work by Khawam and Flanagan.
Table 1. Kinetic models in their differential, \( f(\alpha) \), and linear integral, \( g(\alpha) \), forms. The generic forms of the JMAYK\(^a\) model, where \( n \) is fitted rather than fixed, are also included.

<table>
<thead>
<tr>
<th>Model</th>
<th>Abbrev.</th>
<th>( f(\alpha) = \frac{1}{k} \frac{d\alpha}{dt} )</th>
<th>( g(\alpha) = kt )</th>
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<tr>
<td>Power Law</td>
<td>P2</td>
<td>( 2\alpha^{1/2} )</td>
<td>( \alpha^{1/2} )</td>
</tr>
<tr>
<td></td>
<td>P3</td>
<td>( 3\alpha^{2/3} )</td>
<td>( \alpha^{1/3} )</td>
</tr>
<tr>
<td></td>
<td>P4</td>
<td>( 4\alpha^{3/4} )</td>
<td>( \alpha^{1/4} )</td>
</tr>
<tr>
<td>JMAYK(^a)</td>
<td>A2</td>
<td>( 2(1 - \alpha)[-\ln(1 - \alpha)]^{1/2} )</td>
<td>( [-\ln(1 - \alpha)]^{1/2} )</td>
</tr>
<tr>
<td></td>
<td>A3</td>
<td>( 3(1 - \alpha)[-\ln(1 - \alpha)]^{2/3} )</td>
<td>( [-\ln(1 - \alpha)]^{1/3} )</td>
</tr>
<tr>
<td></td>
<td>A4</td>
<td>( 4(1 - \alpha)[-\ln(1 - \alpha)]^{3/4} )</td>
<td>( [-\ln(1 - \alpha)]^{1/4} )</td>
</tr>
<tr>
<td>Prout-Tompkins</td>
<td>B1</td>
<td>( \alpha(1 - \alpha)^{1/2} )</td>
<td>( \ln\left(\frac{\alpha}{(1 - \alpha)}\right) + c )</td>
</tr>
<tr>
<td>Contracting Area</td>
<td>R2</td>
<td>( 2(1 - \alpha)^{1/2} )</td>
<td>( 1 - (1 - \alpha)^{1/2} )</td>
</tr>
<tr>
<td>Contracting Volume</td>
<td>R3</td>
<td>( 3(1 - \alpha)^{2/3} )</td>
<td>( 1 - (1 - \alpha)^{1/3} )</td>
</tr>
<tr>
<td>1-D Diffusion</td>
<td>D1</td>
<td>( \frac{1}{2} \alpha )</td>
<td>( \alpha^2 )</td>
</tr>
<tr>
<td>2-D Diffusion</td>
<td>D2</td>
<td>( -\frac{1}{\ln(1 - \alpha)} )</td>
<td>( [(1 - \alpha) \ln(1 - \alpha)] + \alpha )</td>
</tr>
<tr>
<td>3-D Diffusion, Jander</td>
<td>D3</td>
<td>( \frac{3}{2}(1 - \alpha)^{2/3} )</td>
<td>( [1 - (1 - \alpha)^{1/3}]^2 )</td>
</tr>
<tr>
<td>Ginstling-Brounshtein</td>
<td>D4</td>
<td>( \frac{3}{2}[1 - (1 - \alpha)^{1/3}]^{-1/3} )</td>
<td>( 1 - \frac{2}{3} \alpha - (1 - \alpha)^{2/3} )</td>
</tr>
<tr>
<td>Zero-Order</td>
<td>F0</td>
<td>( \frac{1}{(1 - \alpha)^{1/2}} )</td>
<td>( \frac{\alpha}{(1 - \alpha)^{2/3}} )</td>
</tr>
<tr>
<td>First-Order</td>
<td>F1</td>
<td>( (1 - \alpha) )</td>
<td>( -\ln(1 - \alpha) )</td>
</tr>
<tr>
<td>Second-Order</td>
<td>F2</td>
<td>( (1 - \alpha)^2 )</td>
<td>( \frac{1}{(1 - \alpha)^{2/3}} - 1 )</td>
</tr>
<tr>
<td>Third-Order</td>
<td>F3</td>
<td>( (1 - \alpha)^3 )</td>
<td>( \frac{1}{2}[(1 - \alpha)^{2/3} - 1] )</td>
</tr>
<tr>
<td>JMAYK(^a)</td>
<td>An</td>
<td>( \alpha = 1 - e^{-(kt)^n} )</td>
<td>( \ln[-\ln(1 - \alpha)] = n\ln(k) + n\ln(t) )</td>
</tr>
</tbody>
</table>

\(^a\)Johnson-Mehl-Avrami-Yerofeev-Kolmogrov model
Traditionally, mechanochemical reaction models have fallen into one of four classes as outlined by Khawam and Flanagan in their review: (1) nucleation, including power laws (P2-4, Table 1), Johnson-Mehl-Avrami-Yerofeev-Kolmogrov (JMAYK) (A2-4, and An), and Prout-Tompkins models (B1); (2) geometrical contraction, including contracting volume and contracting area models (R2 and R3); (3) diffusion, including one-, two-, and three-dimensional diffusion models (D1-4), where three-dimensional diffusion models include both Jander and Ginsling-Brounshtein types, and (4) reaction order models (F0-3), which follow the typical models observed for solution reactions. Each of these models will be addressed in more detail later.

These kinetic models have been applied to several solid-state reactions and transitions. These reactions and transitions include crystal formation, recrystallization, crystal transition, decomposition, and adsorption. It is in this broad application that the robustness of these models becomes apparent.

These models can be further categorized into accelerating, decelerating, and sigmoidal models. Accelerating models (power law models) feature slow initial rates that become more rapid as conversion begins. Conversely, decelerating models (diffusion, order and contracting geometries) have very rapid initial rates then slow down as conversion proceeds. The exception to this is the F0 model which is constant. Alternatively, sigmoidal models feature both an accelerating and decelerating period as in the JMAYK models and Prout-Tompkins.
For the crystal studied in this thesis, nucleation site growth is one type of product growth that might be expected. A few models fall within this nucleation-type category. These include power law, JMAYK, and Prout-Tompkins models. Crystal lattices have fluctuating local energies from imperfections in the lattice which may be due to impurities, surface edges, or point defects. These imperfections are often sites for reaction through nucleation of product growth, since the reaction activation energy is minimized at these points. These imperfect spots are known as nucleation sites.

1.2.1 Power law models

Some nucleation models assume that nucleation and nuclei, or product, growth occur in a single step. In the power law models, potential nucleation sites, assuming that all sites have equal probability for growth once the nuclei form, grow outward and the rate of growth is a far simpler process than site formation. When the rate of nucleation is very high, it indicates that all active sites are rapidly nucleated, resulting in an observed instantaneous rate of nucleation.

The power law models assume constant nuclei growth without consideration to growth restrictions. These models are usually applied to the analysis of the acceleratory period of a reaction curve. Some of these ignored restrictions include the blocking of adjacent reactive sites by formed product, and the rate and efficacy of the mixing of reactants. These types of models can be thought of as having no nucleation growth term, only a nuclei formation term.
1.2.2 JMAYK models

Unlike the power law models, the JMAYK (A2, A3, and A4, Table 1) models do not ignore restrictions on nuclei growth. In these models, it is asserted that in any solid-state, there are certain restrictions on nuclei growth. One such restriction is ingestion. Ingestion is the elimination of a nucleation site by the growth of an existing nucleus. Ingested nuclei are referred to as “phantom” nuclei. Another such restriction is coalescence, the loss of reactant/product interface when reaction zones of two or more growing nuclei merge. The $\alpha$-curves for the JMAYK models are characterized by sigmoidal behavior and have further implications that will be discussed later.

1.2.3 Prout-Tompkins model

The Prout-Tompkins model is another model of interest. The Prout-Tompkins model is an autocatalytic model. Autocatalysis occurs when the generation of products catalyze the generation of further products of the reaction. This can occur when the reactants are regenerated during a reaction or when the presence of products lowers the activation energy of reactants. Inevitably, the reactants will be consumed and the reaction will go into a termination state where reaction will cease. In solid state kinetics, autocatalysis occurs when nuclei growth promotes continued reaction due to the formation of imperfections faster than their consumption. Termination occurs when the reaction begins to spread into areas where material has reacted already. Prout and Tompkins derived the autocatalysis model (B1, Table 1) for the thermal decomposition of potassium permanganate which produced considerable crystal cracking during
decomposition. The reaction rate is related to the number of nuclei and the rate of new nuclei formation. This model predicts a definite change in the observed reaction rate, as evident by its sigmoidal behavior. This apparent change in rate would be due to the change in the number of active sites in the material. Early in the reaction the rate is slow because of the limited number of sites and increases until reactive material begins to be exhausted and the declining number of available unreacted molecules begins to dwindle.

1.2.4 Geometrical contraction models

Geometrical contraction, including contracting volume and contracting area models have been developed (R2-R3, Table 1). These models assume that reaction takes place on the surface of shaped particles like a contracting cylinder (R2) and or a contracting sphere (R3). These models address the reaction of materials at a surface and the resulting transformation of products into reactants. As the surface size of unreacted material decreases then the resulting number of exposed active sites decreases. This decrease in active sites results in the decrease of rate exhibited by these models.

1.2.5 Diffusion models

One of the major differences between homogeneous and heterogeneous kinetics is the mobility of the material in the reaction. While reactant molecules are usually readily available to one another in homogeneous “traditional synthesis” systems, solid-state reactions occur many times between crystal lattices where movement of any single molecule is limited because of its
incorporation within the lattice. Alternatively, one reactant could be forced to permeate into lattices of another. In these lattices motion is restricted and many times often depend on lattice defects to produce active sites.\textsuperscript{38}

Diffusion usually plays a role in the rates of reaction between two solids, most often when reactants are in separate crystal lattices.\textsuperscript{39,40} Diffusion takes place through the material and the shapes that the material diffuses through or into must be brought into consideration. Thus, several diffusion based models (D1-4, Table 1) can be brought into consideration. The D1 model simulates diffusion through a two dimensional flat lattices during reaction. Similarly, the reacting particles may take a cylindrical shape as in D2 where these particles react around the sides of the materials. Finally, both the D3 and D4 models model spherical diffusion of materials with the latter doing so at much faster rates.

1.2.6 Order models

The last models of consideration are those of reaction order models, which follow the typical models observed for solution reactions. The application of these reaction models is perhaps surprising given that they were developed to model more traditional reaction conditions. Nevertheless, the work by Ma and co-workers,\textsuperscript{41} which will be discussed later, showed that these models can be applicable. The order models require the treatment of reactants in the same manner as that of traditional reactions, where the problems with mass transfer within the reaction mixture are typically found to not be an issue. These models suggest that all particles have the same ability to react with any other particle.
1.2.7 Other models

The JMAYK models A2-4 presented in Table 1 all fix the Avrami exponent ($n$) to set values the importance and implications of the Avrami exponent will be covered in the discussion. However, the nonlinear version of the JMAYK (An, Table 1) model was also considered and fitting of this model has difficulties that will be discussed later. This model unlike the linear approximations, A2-A4, exhibits a sigmoidal behavior and allows for some inferences to be drawn by not fixing $n$ to a more common value as is demonstrated in the work by Khanna.\textsuperscript{36} Additionally, the Finke-Watzky model was also examined,\textsuperscript{42} as those authors had demonstrated that the kinetics of many reactions was more accurately modelled. Both models examine solid-state kinetics in terms of nucleation and growth. However, while the JMAYK equation results in a single, rate constant ($k$) for both steps as shown in Table 1, the Finke-Watzky model gives separate $k$ values for nucleation ($k_1$) and autocatalytic growth ($k_2'$, where $k_2'=k_2[A_0]$) as shown in Equation 2. It is important to note that both of these models were derived for simple decompositions as shown in Equations 3 and 4.

$$\alpha = 1 - \frac{k_1 + k_2'}{k_2' + k_1 e^{(k_1 + k_2')t}} \quad \text{(2)}$$

$$A \xrightarrow{k_1} B \quad \text{(3)}$$

$$A + B \xrightarrow{k_2} 2B \quad \text{(4)}$$
1.3 Carbene Complexes

In addition to the kinetic studies of compounds 1-3, some time was spent in the consideration of further areas where mechanochemistry could be applied. The area of research that was ultimately chosen was that of palladium carbene formation. Thus, the mechanochemical synthesis of 4a and 4b, (Figure 2) starting with the ligand precursor, 1-3 dimethyl-2H-benzimidizolium iodide 5 (Figure 3) will be discussed. The interest in this material initially stemmed from its use as a catalyst for coupling reactions. Some of the reactions which these materials act as a catalyst for include Suzuki–Miyaura and Ullmann coupling reactions, acylation of anilines, and acylation of alcohols. Also, 5 has properties that make its synthesis a point of significant interest, most notably that this family of molecules has been shown to be antimicrobial.

It was initially believed that that 5 could be synthesized mechanochemically in light of the fact that similar materials (Scheme 2) had already been prepared that way in the work by Beillard and colleagues. Such a solvent free synthesis would be considered a superior method to the traditional synthesis of 5, as shown in Scheme 3. The traditional synthesis of 5 requires a large excess of methyl iodide as well as heating the reaction mixture in a pressure tube. The solvent-free synthesis of 5 had not been demonstrated prior to this work, nor, had the traditional synthesis been carried out as a “single step” reaction.
Scheme 2. The mechanochemical synthesis of some benzimidazolium species.

Scheme 3. The traditional synthesis of 5.

After the synthesis of the ligand starting materials, the mechanochemical synthesis of 4a and 4b was attempted based on the work by Beillard et al.\textsuperscript{3} who showed that a similar imidazolium based material (Scheme 4) could be made mechanochemically. In their work, the silver imidazolium carbenes were synthesized by vibrational ball milling, and the palladium carbene species was produced via a transmetalation approach. Traditional synthesis of 4a and 4b does not require the transmetalation step as demonstrated by Huynh (Scheme 5).\textsuperscript{49}
Scheme 4. Mechanochemical synthesis of palladium-imidazolium carbenes by solvent free ball milling and transmetalation found in the work by Beillard.³

\[
\begin{align*}
2 \text{imidazolium carbenes} + AgO & \rightarrow \text{PdI}_2(\text{NCMe})_2 \\
Y = \text{Me, iPr} & \\
R = \text{Ph, Py}
\end{align*}
\]

Scheme 5. The traditional solution synthesis of 4a and 4b from the work by Huynh.⁴⁹
2.1 Bipyridyl complexes

2.1.1 General Procedures.

The $^1$H and $^{13}$C NMR spectra were recorded on a JEOL-ECS 400 MHz spectrometer at room temperature in CDCl$_3$ solution. The CDCl$_3$ was stored over activated alumina to remove trace acid in the solution. Trace acid can result in protonation of the complexes below. Elemental analyses were performed at Atlantic Microlabs, Norcross VA. The lack of liquid crystalline behavior for these complexes was determined via polarized optical microscopy at room temperature using a model A1530 USB camera and Scope Image Plus image capture. Differential scanning calorimetry (DSC) measurements using a TA Instruments DSC Q200 were performed at a ramp rate of 10 °C min$^{-1}$. Two heating/cooling cycles were performed for each sample. Data discussed in this thesis was taken from the second heating/cooling cycle. Thermogravimetric analysis (TGA) was performed using a TA Instruments TGA Q500 at a ramp rate of 10 °C min$^{-1}$ using a platinum pan. Decomposition temperatures are reported for the inflection of the first mass loss.

2.1.2 Synthetic Procedures.

Various alcohols, and PdI$_2$ were obtained from Sigma-Aldrich. Ark Pharm was the source of 2,2'-bipyridine-4,4'-dicarboxylic acid. All reagents were utilized without further purification. Dialkyl 2,2'-bipyridine-4,4'-dicarboxylate ligands were synthesized according to the general synthetic method of Pucci et al.$^{50}$ and were purified by triple recrystallization from hot ethanol. Characterization
information for all ligands has been reported previously. Mechanochemical reactions were performed in a SPEX 5100 Mixer Miller at 3000 cycles per minute (back-and-forth motions of the sample vial) using a 2.5 mL stainless steel grinding jar with a 6.35 mm diameter stainless steel ball. The mechanochemical syntheses discussed below are quantitative as determined by $^1$H NMR spectroscopy.

Throughout the discussion, the so-called “standard conditions” for syntheses will be 1.1-1.3 equivalents of PdI$_2$ per equivalent of ligand and total reagent masses of 0.36-0.38 g. The compound diiodo dihexadecyl 2,2′-bipyridyl-4,4′-dicarboxyl palladium(II), 3, was prepared and handled in the same manner as 1 and 2. The $^1$H NMR spectroscopy agreed with that previously established.$^{51}$

_Diiodo di-2-decyl 2,2′-bipyridyl-4,4′-dicarboxyl palladium(II), 1._ In a steel vial, PdI$_2$ (174.0 mg, 0.4830 mmol) and ligand (204.6 mg, 0.3898 mmol) were mixed before being milled. The reaction mixture was dissolved in 5 mL of chloroform and filtered to remove excess PdI$_2$. The solvent was then evaporated to yield a dark red, paste-like material. The material is hygroscopic, but water is readily lost upon drying under vacuum. Yield: 294.0 mg, 94.6%. $^1$H NMR (400 MHz, CDCl$_3$, δ): 10.19 (d, $J$ = 6.0 Hz, 2H, ArH$_{6,6′}$), 8.65 (s, 2H, ArH$_{3,3′}$), 8.11 (dd, $J$ = 0.8, 5.6 Hz, 2H, ArH$_{5,5′}$), 5.26 (sex, $J$ = 6.0 Hz, 2H, β-H), 1.80 (m, 2H, γ-Ha), 1.68 (m, 2H, γ-Hb), 1.41 (d, $J$ = 6.4 Hz, 6H, α-H), 1.4-1.2 (br m, 24H, -OCHCH$_2$C$_6$H$_{12}$CH$_3$), 0.85 (t, $J$ = 6.0 Hz, 6H,-CH$_3$). $^{13}$C NMR (CDCl$_3$, δ): 162.56 (C=O), 156.29 (ArC$_{2,2}$), 155.01 (ArC$_{6,6}$), 140.85 (ArC$_{4,4}$), 126.84 (ArC$_{5,5}$), 122.68 (ArC$_{3,3}$), 74.94 (β-C), 35.80 (γ-CH$_2$), 31.81 (CH$_2$), 29.45 (CH$_2$), 29.38 (CH$_2$),
29.21 (CH₂), 25.45 (CH₂), 22.63 (CH₂), 19.95 (α-C), 14.09 (CH₃). Anal. Calcd.
for C₃₂H₄₈N₂O₄PdI₂: C, 43.42; H, 5.48; N, 3.17. Found: C, 43.61; H, 5.55; N, 3.23.

_Diiodo di-2-hexadecyl 2,2′-bipyridyl-4,4′-dicarboxylate palladium(II), 2._ In a steel vial, PdI₂ (205.1 mg, 0.5694 mmol) and ligand (171.9 mg, 0.2480 mmol) were premixed before milling. The reaction mixture was dissolved in 5 mL of chloroform and filtered to remove excess PdI₂. The solvent was then evaporated to yield a voluminous dark red powder. The material is hygroscopic, but water is readily lost upon drying under vacuum. Yield: 183.3 mg, 97.7%. ¹H NMR (400 MHz, CDCl₃, δ): 10.15 (d, J = 5.2 Hz, 2H, ArH₆,₆′), 8.65 (s, 2H, ArH₃,₃′), 8.10 (dd, J = 2.0, 6.0 Hz, 2H, ArH₅,₅′), 5.26 (sex, J = 6.8 Hz, 2H, β-H), 1.80 (m, 2H, γ-Ha), 1.67 (m, 2H, γ-Hb), 1.41 (d, J = 6.4 Hz, 6H, α-H), 1.4-1.2 (br m, 48H, -OCHCH₂C₁₂H₂₄CH₃), 0.85 (t, J = 7.2 Hz, 6H, -CH₃). ¹³C NMR (CDCl₃, δ): 162.79 (C=O), 156.29 (ArC²,²’), 155.30 (ArC₆,₆’), 141.08 (ArC⁴,⁴’), 127.08 (ArC⁵,⁵’), 122.84 (ArC³,³’), 75.19 (β-C), 36.04 (γ-CH₂), 32.14 (CH₂), 29.91 (CH₂), 29.89 (CH₂), 29.81 (CH₂), 29.79 (CH₂), 29.64 (CH₂), 29.59 (CH₂), 25.70 (CH₂), 22.91 (CH₂), 20.18 (α-C), 14.36 (CH₃). Anal. Calcd. for C₄₄H₇₂N₂O₄PdI₂: C, 50.17; H, 6.90; N, 2.66. Found: C, 50.45; H, 6.77; N, 2.62.

2.1.3 Kinetic Sampling.

Reactions prepared similar to those discussed above in ratios appropriate to the experiment. The reaction mixture was typically sampled at 1, 2, 3, 5, and 10 minute intervals and then every 10 minutes thereafter. Samples were dissolved in CDCl₃ that had been treated to remove trace acid (see above) and filtered to remove unreacted PdI₂ prior to ¹H NMR spectroscopic analysis.
2.2 Carbene complexes

2.2.1 General Procedures.

The \(^1\)H spectra were recorded on a JEOL-ECS 400 MHz spectrometer at room temperature in DMSO-\(d_6\) or CDCl\(_3\) solution. The CDCl\(_3\) solution was stored over activated alumina to remove trace acid in the solution. Trace acid can result in protonation of the complexes below.

2.2.2 Synthetic Procedures.

Starting materials were obtained from Sigma-Aldrich. All reagents were utilized without further purification. Mechanochemical reactions were performed in a SPEX 5100 Mixer Mill at 3000 cycles per minute using a 2.5 mL stainless steel grinding jar with a 6.35 mm diameter stainless steel ball or a 5 mL Teflon\(^\circledR\) grinding jar with a 6.35 mm diameter stainless steel ball. Also a SPEX 8000m Mixer Mill at 1740 cycles per minute, was utilized using a 2.5 mL stainless steel grinding jar with a 6.35 mm diameter stainless steel ball or a 5 mL Teflon\(^\circledR\) grinding jar with a 6.35 mm diameter stainless steel ball. The mechanochemical syntheses discussed below are quantitative as determined by \(^1\)H NMR spectroscopy.

*1,3-dimethyl-1H-benzimidazolium iodide, 5.* In a Teflon\(^\circledR\) vial, benzimidazole (204.5 mg, 1.73 mmol) sodium carbonate (187.3 mg, 1.76 mmol) and methyl iodide (615 µL, 9.87 mmol) were premixed before milling for 900 min in a SPEX 8000m mill. The reaction mixture was placed in hot ethanol, and hot filtered to remove sodium bicarbonate. The desired product was crystallized from the ethanol. The product was recovered by filtration and allowed to dry in a desiccator. Yield: 444.6 mg, 93.7%. The \(^1\)H NMR spectrum was collected then
compared the literature\textsuperscript{48,53} and purchased reagent, and indicated complete conversion from benzimidazole to 1,3-dimethyl benzimidazolium iodide.

\textit{1,3-dimethyl-1H-benzimidazolium iodide, 5.} In a 20-mL glass vial, benzimidazole (410.5 mg, 3.774 mmol) sodium carbonate (341.4 mg, 3.22 mmol) and methyl iodide (725 µL, 14.38 mmol) were premixed before and allowed to sit in a dark cabinet overnight. The reaction mixture was placed in hot ethanol, and hot filtered to remove sodium bicarbonate. The desired product was then crystallized from the ethanol. The product was recovered by filtration and allowed to dry in a desiccator. Yield: 779.0 mg, 81.7\%. The \textsuperscript{1}H NMR spectrum was collected, then compared to the literature\textsuperscript{48,53} and purchased reagent, and indicated complete conversion from benzimidazole to 1,3-dimethyl benzimidazolium iodide.

\textit{Cis- and trans- diiodo-bis(1,3-dimethyl benzimidazol-2-ylidene) palladium(II), 4a and 4b.} In a steel vial, 1,3-dimethyl-1H-benzimidazolium iodide (207.6 mg, 0.757 mmol), sodium carbonate (223.4 mg, 2.11 mmol), and palladium acetate (86.2 mg, 0.383 mmol) were premixed before milling for 1550 min in a SPEX 5100 mill. The reaction mixture was placed in hot ethanol, and hot filtered to remove sodium bicarbonate. The desired product was washed from the crude reaction mixture with cold ethanol then the ethanol was removed under vacuum. The product was allowed to dry in a desiccator. Yield: 230.8 mg, 92.1\%. The \textsuperscript{1}H NMR spectrum was collected, and shown to agree with the literature.\textsuperscript{49}
CHAPTER 3: RESULTS AND DISCUSSION

This work will now address the syntheses of dialkyl 2,2’-bipyridyl-4,4’-dicarboxylate complexes of palladium(II) iodide (1, 2, and 3, Figure 1) and the kinetics of these reactions. Later, the improved synthesis and purification of 1,3-dimethyl-1H-benzimidazolium iodide (5, Figure 3) will be discussed. Finally, the synthesis of cis and trans diiodo-bis(1,3-dimethyl benzimidazol-2-ylidene) palladium(II) (4a and 4b, Figure 2) will be discussed.

3.1 Bipyridyl complexes

3.1.1 Synthesis

The syntheses of 1, 2, and 3 began with the ligand syntheses already established in literature. The synthesis of these ligands 7-8, Figure 8 began with the traditional ligand synthesis that can be seen illustrated in Scheme 6. At this time, there has not been found a method by which to synthesize these ligands mechanochemically. The traditional synthesis however begins with the reaction of bipyridine dicarboxylic acid with thionyl chloride to produce the acid chloride. This step is necessary to overcome solubility and reactivity problems with the appropriate alcohol to produce a desired ligand. In fact, if it were not for these limiting issues, this reaction could be carried out via Fischer esterification without suffering poor yields.
Figure 8. The structures of the ligand starting materials for the syntheses of 1-3, referred to as 7-8, respectively.

Scheme 6. The traditional synthesis of bipyridine ligands (7-8).

The work presented herein was a continuation of the foundations laid out by Hyatt et al.\textsuperscript{24} and Hughes,\textsuperscript{54} who were attempting to discover liquid crystalline materials with improved properties, and explore more efficient and cleaner ways to achieve conversion to product without decomposing the precious metal salts. The use of mechanochemical methods resulted in the elimination of solvent during synthesis and a more efficient synthesis, attaining complete conversion of the ligand to product. It was shown that mechanochemical synthesis eliminates
the use of solvents during preparation and achieves complete conversion. This removed the need for column chromatographic purification as required in the traditional preparation.

It will be shown how, after successfully establishing that conversion could be tracked reliably with $^1$H-NMR analysis, the kinetic data from these reactions were analyzed and compared to several previously established models.\textsuperscript{25, 36, 55} Initially, the models considered ranged from the traditional order based models\textsuperscript{25} to the Johnson-Mehl-Avrami-Yerofeev-Kolmogorov (JMAYK) kinetic model.\textsuperscript{55} This work will further discuss the results of the study as published in \textit{Liquid Crystals}\textsuperscript{56} showing that the non-linear JMAYK model was the model of best fit for these reactions. Using the JMAYK model, where conversion fraction ($\alpha$) is modeled as a function of time ($t$), the Avrami exponent ($n$), and a kinetic parameter ($k$) (see Table 1), several assertions about the mechanisms that give rise to these syntheses will be discussed, as well as some considerations on the conceptualization of the growth of these complexes.

Although molecular mechanochemical syntheses of transition metal complexes are rare, as discussed above, Ma and coworkers\textsuperscript{41} established that the mechanochemical synthesis of Zn(im)$_2$ (Him = imidazole) followed a reaction order model similar to that expected for solution-phase models. In their work, they point to the scarcity of kinetic and mechanistic models for molecular mechanochemistry. This is not surprising, given the difficulty in monitoring reactions in heterogeneous systems, and the other inherent difficulties in solid-state chemistry. Indeed, in their own work, the traditional method for determining
reaction order, varying the relative concentrations of reactants, could not be utilized because such variation resulted in different products. However, synthesis of the Pd derivatives 1-3 shown in Figure 1 can be studied under a variety of reaction conditions and metal to ligand ratios, (ligands used herein are shown in Figure 8) because a single product is produced regardless of the starting material ratio. Additionally, rapid syntheses could be accomplished, so the effects of substitution on the mesomorphic potential of 1 and 2 derivatives could be investigated. This research was initiated based on the results from similar Pt compounds.\textsuperscript{24} When the ligand substitution of Pt derivatives, was altered form improved liquid crystalline properties including widened and increased stable temperature ranges for the liquid crystalline phases was obtained.\textsuperscript{24, 52}

Complexes 1 and 2 have not previously been synthesized, even though 3 is well known.\textsuperscript{51} The solid-state synthesis of the Pd compounds discussed herein proceeds very similarly to the preparation of the Pt compounds,\textsuperscript{24} with the exception that 1 takes much longer to reach complete conversion than platinum chloride derivative. Throughout the discussion, the so-called “standard conditions” for syntheses will be 1.1-1.3 equivalents of Pdl\textsubscript{2} per equivalent of ligand and total reagent masses of 0.36-0.38 g, because stoichiometric ratios cannot be varied across all the compounds synthesized without also varying the reagent volumes and masses, both important factors in mechanochemical reactions, a baseline for comparison needed to be established.
3.1.2 Thermal Characterization

Compound 3 has been characterized previously\textsuperscript{51} and demonstrates a lamellar liquid crystalline phase. As shown in Table 2, 2 is not liquid crystalline. It transitions from a crystalline solid to an isotropic liquid at 150.7 °C. This behavior is contrary to that observed for the Pt derivative, where changes in substitution gave a more thermally stable liquid crystalline phase at a lower temperature than did α-substitution.\textsuperscript{52} The shorter alkyl chain of 1 eliminated the crystal-crystal transition observed for 2, making the likely source of this transition the rearrangement of the alkyl chains – a supposition supported by the temperature of the transition.
Table 2. Thermal properties of 1, 2, and 3.<sup>a</sup>

<table>
<thead>
<tr>
<th>Species (decomp., °C)</th>
<th>Transition</th>
<th>Temp. (°C)</th>
<th>ΔH (kJ/mol)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cr-I</td>
<td>181.1</td>
<td>25.5</td>
<td></td>
</tr>
<tr>
<td>(299.7)</td>
<td>I-Cr</td>
<td>156.7</td>
<td>24.0</td>
<td>b</td>
</tr>
<tr>
<td>2</td>
<td>Cr′-Cr</td>
<td>24.7</td>
<td>29.7</td>
<td></td>
</tr>
<tr>
<td>(289.1)</td>
<td>Cr-I</td>
<td>168.8</td>
<td>27.7</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>I-Cr</td>
<td>150.7</td>
<td>26.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cr-Cr′</td>
<td>16.8</td>
<td>32.3</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>LC-I</td>
<td>170.1</td>
<td>13.0</td>
<td>50</td>
</tr>
<tr>
<td>(337.0)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>I-LC</td>
<td>172.0</td>
<td>12.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LC-Cr</td>
<td>59.4</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cr-Cr′</td>
<td>33.8</td>
<td>26.4</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Transition temperatures for compounds from DSC maxima/minima during second heat/cool, melting temperatures determined by melting point apparatus, decomposition temperatures from TGA first mass loss inflection points; crystalline phase (Cr), liquid crystalline phase (LC), isotropic liquid (I).

<sup>b</sup>This work
3.1.3 Kinetic Studies

The concern of this study was less a mechanistic understanding of the reactions of these complexes than a simple desire to understand how long reactions had to be milled to reach complete conversion and further to avoid reaction conditions that would lead to incomplete conversion. Incomplete reactions, while successful in producing product, are unsatisfactory because purification by column-chromatography essentially eliminates all of the green chemistry benefits derived from ball milling.

Initial studies of these mechanochemical reactions focused on an observation from the analysis of the synthesis of 6, Figure 7. The preparation of 6 requires an excess of PtCl₂ to be present for complete conversion of all available ligand to product. Without this excess, conversion will “level-off” and increased milling time does not significantly improve conversion. When 2 was prepared, even in the presence of 0.2 equivalents excess PdI₂, conversion reached approximately 55% and stopped. Syntheses of 2 could be made to reach complete conversion, if the PdI₂ excess was increased to 1.3 equivalents. Interestingly, sub-stoichiometric amounts of PdI₂ (0.8-0.9 equivalents based on ligand) were as effective in giving complete conversion as increasing the amount of PdI₂ present; however, this required much longer times as shown in Table 3. Compound 3 displays similar behavior; although sub-stoichiometric amounts of PdI₂ appear to inhibit complete conversion. The syntheses of 1 will reach complete conversion even if sub-stoichiometric amounts of PdI₂ are utilized, and these syntheses all exhibit reduced time to complete conversion when increased equivalents of PdI₂ are utilized. It is worth noting that these trends do not
correlate with a reaction order type mechanism, as will be further supported by the analysis of the kinetic curves discussed below.

**Table 3.** Typical time (min) for complete conversion based on the molar ratio of PdI$_2$ to ligand used in the reaction. Conversion was determined by $^1$H NMR spectroscopy sampling at 1, 2, 3, 5, and 10 minutes and then every 10 minutes thereafter until conversion reached 100% or reached a maximum for that reaction.

<table>
<thead>
<tr>
<th>Product</th>
<th>2.2-2.4 Mol. equiv.</th>
<th>1.1-1.3 Mol. equiv.</th>
<th>0.89-0.93 Mol. equiv.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>60</td>
<td>220</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>130</td>
<td>incomplete</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>incomplete</td>
<td>90</td>
</tr>
</tbody>
</table>

Traditionally, there are two methods by which kinetic data can be fitted to determine reaction models. If $\alpha$ is plotted as a function of time, the data are fitted to a function, here termed $f(\alpha)$, which corresponds to the differential form of the rate equation for the reaction model. Because these functions are non-linear for all reaction models except the zero-order reaction kinetics, it is common to utilize an integrated version ($g(\alpha)$, Equation 5) of each model instead. In this method of fitting, values of $g(\alpha)$ are calculated from $\alpha$ and are plotted versus time ($t$) such that, for each model:

$$g(\alpha) = Ae^{\frac{E_a}{RT} t} = kt$$  \hspace{1cm} (5)

While plotting $g(\alpha)$ vs. $t$ can be convenient because linear correlations are obtained when the data is correctly modelled, difficulties may result from functions which are not well defined at the start of the reaction ($t=0$). Both $f(\alpha)$ and $g(\alpha)$ expressions for the models examined in this study were given in Table 1. In this table, models are abbreviated according to Khawam’s and Flanagan’s comprehensive review of solid-state reaction models.$^{25}$
The appearance of the $\alpha$ vs $t$ curves can be utilized to give a general description of the type of reaction as being linear, accelerating, decelerating, or sigmoidal as discussed previously. Figure 9 shows the sigmoidal behavior of the reaction kinetics of the complexes studied. The general behavior of this reaction had significance when choosing the ideal models to fit the data, which will be discussed later.

![Figure 9: Conversion fraction over time for the syntheses of 1 (blue ▲), 2 (purple ×) and 3 (red ■). These reactions were carried out under the standard conditions discussed in the section on syntheses, and all data were fitted to the JMAYK model. Determination of which model best fit the data was made using the equations given in Table 1. Early impetus for the analysis of the reaction kinetics of this system was engendered by the work of James and coworkers.\textsuperscript{1} Therefore, special examination was made to assure that the reaction kinetics...](image-url)
were not a simple reaction order model. Their work on the synthesis of Zn(im)$_2$
complexes (Him = imidazole) established that the reaction followed simple
second-order reaction kinetics, and the solid-state reaction mixture acted as a
pseudo-fluid under the milling conditions.\textsuperscript{41}

Determination of $\alpha$ was made from the $^1$H NMR spectroscopic analysis of
small sample aliquots of the reaction mixture taken at various times throughout
the reaction. Coefficients of determination, the so-called $R^2$ values that indicate
how well the data fit a given model, were calculated after plotting $g(\alpha)$ as a
function of time. This analysis was then performed for multiple trials. In Figure
10, an example of this analysis is shown for the reaction order models (F1-F3,
Table 1). The zero-order model is not shown in the figure as this corresponds to
the $\alpha$ vs $t$ plot already shown in Figure 9. Care should be taken in utilizing only
$R^2$ values for determination of best fit as the data may appear linear for a single
trial/complex, but will not fit the model over all experiments. An example of such
behavior is shown in Figure 10. Although the first-order modeling achieves
excellent linear correlation in this particular case, $R^2 = 0.9940$, repeated trials
gave much lower $R^2$ values and varying the ligand demonstrated a lack of linear
correlation. As shown in Table 4, none of the models gave acceptable linear fits
across all ligands and trials. Table 4 shows the minimum and maximum $R^2$
values achieved for each model.
Figure 10. Attempts to fit the kinetics of 2 to the F1-F3 models, F1 (blue ▲), F2 (red ■), and F3 (purple ×).
Table 4. Coefficients of determination ($R^2$) values for fitting of linear models to kinetic data. The data from individual reactions was fitted to each model. Over all the resulting fits, the maximum and minimum $R^2$ values for each model were determined to give the range of $R^2$ values presented here. Model fittings designated with * include a point at $t=0$, where defined.

<table>
<thead>
<tr>
<th>Model</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2</td>
<td>0.6185-0.8407</td>
<td>0.7065-0.9628</td>
<td>0.9102-0.9551</td>
</tr>
<tr>
<td>P3</td>
<td>0.5897-0.8314</td>
<td>0.6740-0.9482</td>
<td>0.8760-0.9319</td>
</tr>
<tr>
<td>P4</td>
<td>0.5754-0.8266</td>
<td>0.6573-0.9396</td>
<td>0.8569-0.9326</td>
</tr>
<tr>
<td>A2</td>
<td>0.7882-0.9851</td>
<td>0.7683-0.9679</td>
<td>0.9279-0.9916</td>
</tr>
<tr>
<td>A3</td>
<td>0.7462-0.9778</td>
<td>0.7305-0.9542</td>
<td>0.8810-0.9940</td>
</tr>
<tr>
<td>A4</td>
<td>0.7243-0.9692</td>
<td>0.7106-0.9459</td>
<td>0.8430-0.9902</td>
</tr>
<tr>
<td>B1</td>
<td>0.7649-0.9744</td>
<td>0.6875-0.9212</td>
<td>0.9006-0.9891</td>
</tr>
<tr>
<td>R2</td>
<td>0.8952-0.9880</td>
<td>0.8264-0.9868</td>
<td>0.9464-0.9869</td>
</tr>
<tr>
<td>R3</td>
<td>0.8987-0.9900</td>
<td>0.8375-0.9870</td>
<td>0.8606-0.9724</td>
</tr>
<tr>
<td>D1</td>
<td>0.8445-0.9654</td>
<td>0.8949-0.9698</td>
<td>0.8953-0.9708</td>
</tr>
<tr>
<td>D2</td>
<td>0.8687-0.9924</td>
<td>0.9064-0.9676</td>
<td>0.8923-0.9464</td>
</tr>
<tr>
<td>D3</td>
<td>0.8952-0.9880</td>
<td>0.8264-0.9686</td>
<td>0.9464-0.9869</td>
</tr>
<tr>
<td>D4</td>
<td>0.9339-0.9864</td>
<td>0.9065-0.9668</td>
<td>0.8359-0.9321</td>
</tr>
<tr>
<td>F0/R1</td>
<td>0.7038-0.9035</td>
<td>0.7915-0.9861</td>
<td>0.9526-0.9899</td>
</tr>
<tr>
<td>F1</td>
<td>0.8914-0.9935</td>
<td>0.8589-0.9872</td>
<td>0.7612-0.9721</td>
</tr>
<tr>
<td>F2</td>
<td>0.6154-0.9965</td>
<td>0.8975-0.9874</td>
<td>0.4881-0.9709</td>
</tr>
<tr>
<td>F3</td>
<td>0.4751-0.9676</td>
<td>0.8972-0.9867</td>
<td>0.2988-0.9691</td>
</tr>
<tr>
<td>P2*</td>
<td>0.5466-0.6855</td>
<td>0.5723-0.6022</td>
<td>0.7983-0.9179</td>
</tr>
<tr>
<td>P3*</td>
<td>0.4200-0.5375</td>
<td>0.4397-0.4565</td>
<td>0.7055-0.8813</td>
</tr>
<tr>
<td>P4*</td>
<td>0.3393-0.5224</td>
<td>0.3606-0.4635</td>
<td>0.6375-0.8644</td>
</tr>
<tr>
<td>A2*</td>
<td>0.7488-0.9445</td>
<td>0.6616-0.6899</td>
<td>0.8821-0.9834</td>
</tr>
<tr>
<td>A3*</td>
<td>0.6360-0.8353</td>
<td>0.5218-0.5384</td>
<td>0.8871-0.9431</td>
</tr>
<tr>
<td>A4*</td>
<td>0.5571-0.7185</td>
<td>0.4264-0.4368</td>
<td>0.8505-0.8799</td>
</tr>
<tr>
<td>B1*</td>
<td>0.7649-0.9744</td>
<td>0.7152-0.8245</td>
<td>0.8283-0.9891</td>
</tr>
<tr>
<td>R2*</td>
<td>0.8945-0.9813</td>
<td>0.8125-0.8429</td>
<td>0.9302-0.9879</td>
</tr>
<tr>
<td>R3*</td>
<td>0.9167-0.9896</td>
<td>0.8239-0.8514</td>
<td>0.9043-0.9558</td>
</tr>
<tr>
<td>D1*</td>
<td>0.8656-0.9679</td>
<td>0.8976-0.9074</td>
<td>0.8987-0.9701</td>
</tr>
<tr>
<td>D2*</td>
<td>0.8971-0.9930</td>
<td>0.9115-0.9120</td>
<td>0.8915-0.9455</td>
</tr>
<tr>
<td>D3*</td>
<td>0.8945-0.9813</td>
<td>0.8125-0.8429</td>
<td>0.9302-0.9879</td>
</tr>
<tr>
<td>D4*</td>
<td>0.9397-0.9861</td>
<td>0.9121-0.9161</td>
<td>0.8524-0.9306</td>
</tr>
<tr>
<td>F0/R1*</td>
<td>0.7109-0.8779</td>
<td>0.7758-0.8141</td>
<td>0.8816-0.9895</td>
</tr>
<tr>
<td>F1*</td>
<td>0.9055-0.9940</td>
<td>0.8452-0.8663</td>
<td>0.7623-0.9396</td>
</tr>
<tr>
<td>F2*</td>
<td>0.6140-0.9956</td>
<td>0.8924-0.8967</td>
<td>0.4873-0.6601</td>
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<tr>
<td>F3*</td>
<td>0.4686-0.9506</td>
<td>0.9016-0.9283</td>
<td>0.2966-0.4989</td>
</tr>
</tbody>
</table>
In addition to the $R^2$ values, the rate related parameter, $k$, can be utilized in helping to ascertain the correct reaction model. For a given temperature, the correct model should give a constant value of $k$ across all experimental trials. Once a model with high coefficients of determinations is found, examination of $k$ can help determine if the behavior is linear. None of the models provided adequate linear fits as shown in Table 5.
Table 5. Rate related parameters ($k$) values for fitting of linear models to kinetic data. The data from individual reactions was fitted to each model. Over all the resulting fits, the minimum and maximum $k$ values for each model were determined to give the range of $k$ values presented here. Model fittings designated with * include a point at $t=0$, where defined.

<table>
<thead>
<tr>
<th>Model</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2</td>
<td>0.0033-0.0105</td>
<td>0.0031-0.0032</td>
<td>0.0027-0.0065</td>
</tr>
<tr>
<td>P3</td>
<td>0.0023-0.0077</td>
<td>0.0025-0.0026</td>
<td>0.0039-0.0054</td>
</tr>
<tr>
<td>P4</td>
<td>0.0018-0.0060</td>
<td>0.0021-0.0022</td>
<td>0.0037-0.0050</td>
</tr>
<tr>
<td>A2</td>
<td>0.0142-0.0327</td>
<td>0.0044-0.0044</td>
<td>0.0040-0.0185</td>
</tr>
<tr>
<td>A3</td>
<td>0.0086-0.0216</td>
<td>0.0034-0.0035</td>
<td>0.0028-0.0121</td>
</tr>
<tr>
<td>A4</td>
<td>0.0062-0.0162</td>
<td>0.0027-0.0028</td>
<td>0.0048-0.0093</td>
</tr>
<tr>
<td>B1</td>
<td>0.0475-0.1131</td>
<td>0.0167-0.0178</td>
<td>0.0174-0.0697</td>
</tr>
<tr>
<td>R2</td>
<td>0.0073-0.0194</td>
<td>0.0023-0.0023</td>
<td>0.0005-0.0074</td>
</tr>
<tr>
<td>R3</td>
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<td>0.0016-0.0017</td>
<td>0.0003-0.0071</td>
</tr>
<tr>
<td>D1</td>
<td>0.0077-0.0216</td>
<td>0.0025-0.0027</td>
<td>0.0001-0.0081</td>
</tr>
<tr>
<td>D2</td>
<td>0.0096-0.0223</td>
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<td>0.0001-0.0087</td>
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<tr>
<td>D3</td>
<td>0.0070-0.0194</td>
<td>0.0023-0.0023</td>
<td>0.0005-0.0074</td>
</tr>
<tr>
<td>D4</td>
<td>0.0030-0.0076</td>
<td>0.0004-0.0004</td>
<td>0.00001-0.0026</td>
</tr>
<tr>
<td>F0/R1</td>
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<td>0.0036-0.0036</td>
<td>0.0009-0.0078</td>
</tr>
<tr>
<td>F1</td>
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<td>0.0057-0.0059</td>
<td>0.0010-0.0625</td>
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<tr>
<td>F2</td>
<td>0.3375-1.2832</td>
<td>0.0092-0.0100</td>
<td>0.0010-0.7392</td>
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<tr>
<td>F3</td>
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<td>0.0153-0.0175</td>
<td>0.0011-33.5830</td>
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<tr>
<td>P2*</td>
<td>0.0060-0.0177</td>
<td>0.0040-0.0041</td>
<td>0.0027-0.0072</td>
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<tr>
<td>P3*</td>
<td>0.0054-0.0160</td>
<td>0.0037-0.0038</td>
<td>0.0039-0.0057</td>
</tr>
<tr>
<td>P4*</td>
<td>0.0050-0.0150</td>
<td>0.0034-0.0053</td>
<td>0.0035-0.0048</td>
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<tr>
<td>A2*</td>
<td>0.0169-0.0442</td>
<td>0.0053-0.0055</td>
<td>0.0028-0.0225</td>
</tr>
<tr>
<td>A3*</td>
<td>0.0121-0.0347</td>
<td>0.0046-0.0047</td>
<td>0.0040-0.0141</td>
</tr>
<tr>
<td>A4*</td>
<td>0.0099-0.0301</td>
<td>0.0041-0.0042</td>
<td>0.0048-0.0105</td>
</tr>
<tr>
<td>B1*</td>
<td>0.0475-0.1131</td>
<td>0.0167-0.0178</td>
<td>0.0174-0.0899</td>
</tr>
<tr>
<td>R2*</td>
<td>0.0080-0.0217</td>
<td>0.0025-0.0026</td>
<td>0.0005-0.0093</td>
</tr>
<tr>
<td>R3*</td>
<td>0.0076-0.0212</td>
<td>0.0018-0.0018</td>
<td>0.0003-0.0085</td>
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<tr>
<td>D1*</td>
<td>0.0084-0.0239</td>
<td>0.0026-0.0028</td>
<td>0.0001-0.0106</td>
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<tr>
<td>D2*</td>
<td>0.0097-0.0237</td>
<td>0.0016-0.0018</td>
<td>0.0001-0.0102</td>
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<tr>
<td>D3*</td>
<td>0.0077-0.0217</td>
<td>0.0025-0.0026</td>
<td>0.0005-0.0093</td>
</tr>
<tr>
<td>D4*</td>
<td>0.0029-0.0076</td>
<td>0.0004-0.0004</td>
<td>0.00001-0.0032</td>
</tr>
<tr>
<td>F0/R1*</td>
<td>0.0067-0.0211</td>
<td>0.0040-0.0041</td>
<td>0.0009-0.0096</td>
</tr>
<tr>
<td>F1*</td>
<td>0.0385-0.0801</td>
<td>0.0061-0.0065</td>
<td>0.0001-0.0646</td>
</tr>
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<td>0.0097-0.0106</td>
<td>0.0001-0.7766</td>
</tr>
<tr>
<td>F3*</td>
<td>1.8772-50.7320</td>
<td>0.0158-0.0181</td>
<td>0.0011-35.4480</td>
</tr>
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</table>
Based on the $R^2$ values shown in Table 4 with the variation of $k$ in Table 5, none of the linear kinetic models correlated well with the data; however, inspection of the $\alpha$ versus $t$ curves shown in Figure 9 demonstrates sigmoidal behavior. This led to explorations of JMAYK models where $n$, the so-called Avrami exponent, was fitted rather than simply fixing its value to some of the more common options as in models A2-A4. The data can be fit in two ways. First, there is a linear form of the JMAYK equation as shown in Table 1. One difficulty in using this equation is that the model is not defined at $t=0$. Secondly, following the suggestion of Finney and Finke\textsuperscript{42} given modern computing capabilities, the sigmoidal version of the JMAYK equation was fitted using PSI-plot\textsuperscript{TM} software.

In addition to the JMAYK model, the so-called Finke-Watzky model was also examined,\textsuperscript{42} as those authors had demonstrated that the kinetics of many reactions was more accurately modelled by the Finke-Watzky model and that model gives physically meaningful rate information. Both models examine solid-state kinetics in terms of nucleation and growth steps; however, the JMAYK equation results in a single, combined rate related parameter ($k$) for both steps as shown in Table 1. This form of the JMAYK equation was that originally developed by Khanna and Taylor\textsuperscript{36} and previously used by Finney and Finke.\textsuperscript{42} This model is preferred because it results in $k$ values with physically relevant s\textsuperscript{-1} units. The Finke-Watzky models gives separate $k$ values for nucleation ($k_1$) and autocatalytic growth ($k_2'$, where $k_2'=k_2[A_0]$) as shown in Equation 2.
Fitting the data for the syntheses to the Finke-Watzky model gave consistently low values for $k_2'$, and, in the case of 1 and 2 syntheses, frequent negative values. Restricting the model to positive values of $k_2'$ returned a zero value for that constant, pointing to a lack of autocatalytic growth in these systems. In that case, the Finke-Watzky model is reduced to a JMAYK model in which $n=1$. The Finke-Watzky model gives reasonable fits for 1 and 3 kinetics, but does not effectively model 2 kinetics, as shown in Table 6.

<table>
<thead>
<tr>
<th>Model/parameter</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>JMAYK/R²</td>
<td>0.9702-0.9880</td>
<td>0.9681-0.9811</td>
<td>0.9739-0.9825</td>
</tr>
<tr>
<td>JMAYK/k</td>
<td>0.08±0.03</td>
<td>0.0051±0.0005</td>
<td>0.017±0.003</td>
</tr>
<tr>
<td>JMAYK/n</td>
<td>0.8±0.1</td>
<td>0.38±0.01</td>
<td>1.5±0.1</td>
</tr>
<tr>
<td>Finke-Watzky, unrestricted/R²</td>
<td>0.9651-0.9838</td>
<td>0.8842-0.9021</td>
<td>0.9795-0.9869</td>
</tr>
<tr>
<td>Finke-Watzky, unrestricted/k₁</td>
<td>0.10±0.04</td>
<td>0.045±0.004</td>
<td>0.007±0.001</td>
</tr>
<tr>
<td>Finke-Watzky, unrestricted/k₂'</td>
<td>-0.06±0.03</td>
<td>-0.09±0.01</td>
<td>0.03±0.01</td>
</tr>
<tr>
<td>Finke-Watzky, k₂'≥0/R²</td>
<td>0.9479-0.9757</td>
<td>0.5463-0.5563</td>
<td>0.9795-0.9868</td>
</tr>
<tr>
<td>Finke-Watzky, k₂'≥0/k₁</td>
<td>0.2±0.3</td>
<td>0.010±0.001</td>
<td>0.007±0.001</td>
</tr>
<tr>
<td>Finke-Watzky, k₂'≥0/ k₂'</td>
<td>0</td>
<td>0</td>
<td>0.03±0.01</td>
</tr>
</tbody>
</table>

Although the JMAYK equation is most frequently applied to decomposition or phase-change processes, it has also been applied to heterogeneous reactions and to solid-state combination reactions. In some studies, the linear form of the JMAYK equation was utilized; however, because this form of the equation is undefined at zero, it cannot model the initial period of a reaction well. Utilizing the JMAYK equation for modelling the reaction kinetics in the syntheses of these systems seems well supported.
The JMAYK equation models systems where linear growth occurs, in addition to systems of diffusion controlled growth during early stages.\textsuperscript{55} Ham’s work has clearly demonstrated that the JMAYK equation has no fundamental significance in diffusion limited circumstances.\textsuperscript{60} However, the focus of the present study is to model the reaction curves for information useful to the practical considerations of synthesis (e.g. reaction time, expected conversion) rather than to prove one-or-another reaction mechanism through modelling. With this in mind, a few practical conclusions can be drawn from the available data.

The JMAYK equation treats nucleation and growth under a single so-called Avrami exponent, $n$; however, this value has been subdivided into three components: $a$, the term for nucleation rate which is 0 for existing nuclei and 1 for a constant nucleation rate; $b$, the dimensionality of the growing phase, and $p$, a term for the growth mechanism, which is $\frac{1}{2}$ for parabolic, diffusion controlled growth and 1 for interfacial growth.\textsuperscript{55} Equation 6 shows the breakdown of the Avrami exponent into these parameters.

\begin{equation}
\begin{aligned}
n &= a + bp
\end{aligned}
\end{equation}

Lower values of $n$ are generally consistent with diffusion controlled growth.\textsuperscript{55} Given that $n$ is 0.38±0.01 for the synthesis of 2, according to the above equation all nucleation sites would need to be pre-existing in the system, and the reaction kinetics are therefore limited by the ability of material to diffuse into, and out of, these nucleation sites. Further support for those nucleation sites existing on the surface of the PdI$_2$ can is provided in pre-milling experiments. Pre-milling the PdI$_2$, that is milling the PdI$_2$ sample in the absence of ligand, for
30 minutes, reduces 1 synthesis conversion at 110 minutes from 90-100%, depending on exact PdI<sub>2</sub>/ligand ratio, to 13.4%. Pre-milling appears to destroy existing nucleation sites, and additional sites do not appear to be generated during the course of the reaction. Pre-milling the ligand material for 1, however, does not lead to a decrease in conversion.

Based on the above parameters, the differences in Avrami exponent among the three complexes could then be explained in terms of the dimensionality of the growing product phase. In 3, three-dimensional growth occurs ($b \approx 3$), while in 1, the growth is essentially two-dimensional ($b \approx 2$). The relatively slow synthesis of 2, would then be a result of one-dimensional growth ($b \approx 1$).

Interestingly, although pre-milling would typically cause a decrease in particle size and a corresponding increase in rate in a diffusion limited process, no rate enhancement was observed. This is likely a result of the very soft nature of both the ligands and the resulting metal complexes. This softness is most apparent in the synthesis of 3. A creamy paste is present for the vast majority of the reaction process. Indeed, as shown in Table 2, 3 is liquid crystalline between 59.4 and 172.0°C. While external temperature monitoring, measured via a thermocouple just outside the milling vial, gives temperatures no higher than 36 °C, localized heating is expected to bring the complex into its liquid crystalline phase during synthesis. Thus, this is the first time that mechanochemical synthesis in a liquid crystalline phase has been demonstrated to give a rate enhancement.
The rate enhancement is further supported by analysis of the 2 reactions. The isomeric nature of the ligands makes reaction masses and mole ratios identical for comparison to the 3 derivative. The isomer 2 does not evidence liquid crystalline behavior and its clearing point (168.8 °C) is high. Thus, the 2 synthesis is expected to be truly solid-state. Moreover, unlike 3, 2 is a voluminous powder, rather than a compact paste. Indeed, care must be taken when selecting reagent masses for 2 syntheses, as the volume of solid produced can result in the milling ball becoming immobilized. This variation appears to result in the change in Avrami exponent for the reactions.

As a final exploration of the utility of the JMAYK model for the studied syntheses, the model was fitted to reaction profiles where the equivalents of PdI2 present in the reaction had been varied. Table 7 gives coefficients of determination and JMAYK parameters for reactions under a variety of PdI2/ligand molar ratios. These data are for the same reactions as those presented in Table 6. Increasing the amount of PdI2 present in the reaction mixture leads to an increase in the Avrami exponent, except for the case of 3 where it had already reached the maximum (n=1.5) for a diffusion controlled process occurring at a pre-existing number of nucleation sites. In the case of 3, the large excess of PdI2 presumably acted to harden otherwise soft reaction mixture, limiting diffusion to the nucleation sites. Optimizing these mechanochemical reactions therefore requires a determination of the PdI2/ligand ratio necessary to achieve the maximum Avrami exponent, but additional equivalents are likely to impede reaction speed.
Table 7. JMAKY parameters and coefficients of determination ($R^2$) for the studied syntheses using different starting material ratios. Equivalents are based on moles of PdI$_2$ per mole of ligand, and reactions correspond to the examples given in Table 6.

<table>
<thead>
<tr>
<th>Product/parameter</th>
<th>2.2-2.4 equiv.</th>
<th>1.1-1.3 equiv.</th>
<th>0.89-0.93 equiv.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/R$^2$</td>
<td>0.9985</td>
<td>0.9880</td>
<td>0.9985</td>
</tr>
<tr>
<td>2/R$^2$</td>
<td>0.9104</td>
<td>0.9811</td>
<td>0.9718</td>
</tr>
<tr>
<td>3/R$^2$</td>
<td>0.9755</td>
<td>0.9825</td>
<td>0.9830</td>
</tr>
<tr>
<td>1/k</td>
<td>0.41</td>
<td>0.066</td>
<td>0.41</td>
</tr>
<tr>
<td>2/k</td>
<td>0.033</td>
<td>0.0056</td>
<td>0.038</td>
</tr>
<tr>
<td>3/k</td>
<td>0.079</td>
<td>0.016</td>
<td>0.0074</td>
</tr>
<tr>
<td>1/n</td>
<td>1.2</td>
<td>0.81</td>
<td>0.38</td>
</tr>
<tr>
<td>2/n</td>
<td>1.1</td>
<td>0.37</td>
<td>0.71</td>
</tr>
<tr>
<td>3/n</td>
<td>0.79</td>
<td>1.5</td>
<td>0.45</td>
</tr>
</tbody>
</table>

3.2 Carbene complexes

The second area that will be discussed in this thesis is the synthesis of 4a and 4b, beginning with the synthesis of the ligand precursor, 5. The relevant literature synthesis$^{48}$ of 5 has several drawbacks which were able to be significantly improved upon in this research. Specifically, the literature synthesis requires extensive use of solvents and heat. It also necessitates significant excess of costly, toxic, starting reagents.$^{3, 48}$ However, the developed method for 5 requires no solvent, takes place at room temperature and, aside from the initial mixing of reagents, requires no mechanical energy input.

Despite the improvements to the synthesis of 5, the goal of this research is to improve the synthesis of compounds 4a and 4b. To that end several improvements were made to the previous literature$^{3, 49}$ syntheses of 4a and 4b in both the areas of reaction conditions as well as the overall environmental impact of these reactions. This work will illustrate these improved syntheses and show
how utilizing mechanochemical methods synthesis can be made both more efficient and more environmentally friendly.

The traditional synthesis of 5 is shown in Scheme 3 where 5.5 equivalents of methyl iodide are reacted with methyl-benzimidazole, and 4.5 equivalents are wasted in the end. The traditional synthesis lacks in the area of sustainability methyl iodide is very volatile and requires specialized handling and disposal. This coupled with its intrinsic toxicity makes this overall a very undesirable situation. A few similar compounds have been generated using mechanochemical methods (see Scheme 2) however 5 has not been synthesized mechanochemically

Ultimately, a method was developed that was both solvent free and did not use an abundant excess of any reagent as shown in Scheme 7. Both the mechanochemical ball milling synthesis and the “sit and develop” method are effective preparations. Both methods achieve complete conversion to desired product as determined by $^1$H NMR spectroscopy.

Scheme 7. Newly developed synthesis of 1,3-dimethyl-1H-benzimidazolium iodide, 5.
The synthesis of 5 was carried out two ways: (1) as a “sit and develop” method where the starting materials were allowed to react overnight in a scintillation vial, and (2) as a ball milling experiment where the reagents in the same stoichiometry as Scheme 6 were ground in a vibrational ball mill. Both methods produce the same final product. Both syntheses were analyzed using $^1$H NMR spectroscopy. Figure 11 shows the $^1$H-NMR analysis of the sit and develop method. The $^1$H NMR spectrum is color coded to show unreacted starting material middle (purple), the mono substituted intermediate right (green), and the final desired product far left (red). Due to the overlapping aromatic signals of in the progress reaction mixture, it is difficult to analyze the in-progress spectrum based on the aromatic protons. However, each of the anticipated species present possess a different resonance for the proton located on the acidic carbon-2 position of the imidazole portion of the molecule. The differences of the expected shift of this proton make the analysis of the ligand synthesis a far simpler matter.
The synthesis of 4a and 4b was carried out in a vibrational ball mill via two different routes. First, the material was synthesized directly from palladium acetate and 5 (Scheme 8), and later via a one-pot method (Scheme 9) where the ligand and carbene were prepared simultaneously. The aromatic region of the $^1$H NMR spectrum of the first method (Scheme 8) is shown in Figure 12, and that of the attempted one-pot synthesis is shown in Figure 13.
Scheme 8. The mechanochemical preparation of 4a and 4b from 5.

Scheme 9. The mechanochemical preparation of 4a and 4b via a one pot synthesis.
Figure 12. The aromatic region of the $^1$H NMR spectrum of the final product of the preparation of 4a and 4b. A higher resolution image can be found in the appendix.
The preliminary work on what appeared to be stereochemical selective one-pot synthesis of the *cis* isomer 4a should be mentioned; although, it was not fully realized at the conclusion of this work. The potential significance of this improved synthesis being that the *cis* isomer is the catalytically active isomer, it is usually introduced into reactions by isomerization of the *trans* isomer. As such, direct preparation of the *cis* isomer will result in less wasted time on the isomerization from *trans* to *cis* conformation. Similarly to the ligand synthesis, during the course of milling, this reaction becomes very hard to analyze in the aromatic region. However, once higher conversions are attained this region clears up and can be easily compared to the literature spectra.
For synthesis of the selected carbene species 4a and 4b as well as ligand precursors 5, all reactions were carried out in the absence of heat or solvent. It is also noteworthy that both syntheses are greatly benefited by the addition of sodium carbonate. This benefit is believed to be a result of neutralizing acetic acid and HI in their respective reactions, thus further pushing the reactions to completion. The addition of sodium carbonate is still considered a green alternative due to its non-toxicity and availability in living systems.
CHAPTER 4: CONCLUSIONS

4.1 Bipyridyl complexes

The reaction profiles for the syntheses of complexes 1, 2, and 3 have been modeled using a variety of systems. While the Finke-Watzky model gave good fits for the syntheses of 1 and 3, the best modeling was obtained utilizing a JMAYK model. While this model is empirical, it appears that the reaction is occurring by a diffusion limited process occurring at a limited number of nucleation sites on the surface of PdI₂. The synthesis of 3, in comparison to 2, demonstrated that there was a rate enhancement when the product was in the liquid-crystalline phase. This work may allow for future rate improvements by taking advantage of liquid crystalline mechanochemistry.

The JMAYK model gave coefficients of determination between 0.9702-0.9880, 0.9681-0.9811, and 0.9739-0.9825 for 1, 2, and 3, respectively. Similarly, the Avrami exponent was found to be 0.8±0.1, 0.38±0.01, and 1.5±0.1 for each of 1, 2, and 3 respectively. This discovery led to some considerations of the expansion of the Avrami exponent into its subsequent terms. It was determined that for all three complexes the active sites were pre-existing and that they all experienced parabolic growth, all culminating in the assertion that the differences in rate of these reactions can be attributed to the dimensionality of each type of crystal growth.

4.2 Carbene complexes

It was discovered also that palladium carbenes, as well as their ligand precursors, can be efficiently synthesized mechanochemically. While there are a few materialistic considerations to take into account, these methods are simpler
can use less excess materials, do not require heat and produce the same final material at an equal or higher overall yield to more traditional approaches. The simplification of these types of syntheses will serve to push the future of chemical synthesis by allowing for more sustainable chemical practices.
REFERENCES


54. Hughes, C. Investigation of the conversion over time in the mechanochemical synthesis of bis(2-hexadecyl) 2,2'-bipyridine-4,4'-dicarboxylate complexes of platinum and cadmium. CHE 495, Murray State University, Murray, KY, 2014.
Figure A1. DSC trace for 1 over two cycles with initial heating from the as purified product.
Figure A2. DSC trace for 2 over two cycles with initial heating from the as purified product.
Figure A3. The full resolution $^1$H-NMR spectrum of 1.
Figure A4. The full resolution $^{13}$C-NMR spectrum of 1.
Figure A5. The full resolution $^1$H-NMR spectrum of 2.
Figure A6. The full resolution $^{13}$C-NMR spectrum of 2.
Figure A7. The full resolution $^1$H-NMR spectrum of 3.
Figure A8. The full resolution spectrum $^1$H-NMR of 5.
Figure A9. The full resolution $^1$H-NMR spectrum of 4a and 4b.