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Investigating a Catalytic Approach for the Polymerization Reaction of Dichlorophosphinylphosphorimidic Trichloride

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Senior Thesis Project

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ABSTRACT

Polyphosphazenes are a unique class of macromolecules with an inorganic backbone of phosphorus and nitrogen joined by alternating single and double bonds. Polyphosphazenes have a wide array of actual or potential uses due to the wide variation in side groups possible. Many of which are not found in classic organic polymers. The most common method for synthesizing bulk polydichlorophosphazenes, due to the resulting high molecular weight polymer, is via a ring-opening method developed by Allcock and co-workers in 1965.\textsuperscript{1-3} In 1991 De Jaeger developed a synthesis of polydichlorophosphazene from P-trichloro-N-(dichlorophosphoryl) monophosphazene (Cl\textsubscript{3}PNP(O)Cl\textsubscript{2}) (3) that represented an attractive alternative to the Allcock ring-opening polymerization. This synthesis was then further improved upon by Chris Allen, who developed a solvent-free synthesis of polydichlorophosphazene ([PNCl\textsubscript{2}]\textsubscript{n}) (2) and phosphorus oxychloride (POCl\textsubscript{3}) (4) from 3. This work investigated nine catalyst candidates for the melt-phase condensation polymerization of 3 to 2 and 4. Complex 3 was synthesized using the Allen method and purified. Nine catalysts chosen from four main classes of chemicals were then investigated. Five of these catalysts were eliminated due to inactivity, and the remaining four, cyclopentadienyl iron carbonyl dimer, (η\textsuperscript{5}-C\textsubscript{5}H\textsubscript{5})\textsubscript{2}Fe\textsubscript{2}(CO)\textsubscript{4}, tris(pentafluorophenyl)borane, trimethylaluminum, and titanium tetrachloride, were investigated further.
INTRODUCTION

Polyphosphazenes are long chain macromolecules with an inorganic backbone. This inorganic backbone is comprised of phosphorus and nitrogen atoms joined by alternating double and single bonds. The vast majority of polyphosphazenes are represented by Figure 1, where R is most commonly an organic unit such as a phenoxide.

![Figure 1: Structural formula for most polyphosphazenes, where n = 10-15,000](image)

Although the class of organic-inorganic polyphosphazenes is by far the largest, R can also be inorganic or organometallic units. The wide variation in these side groups linked to the skeleton is responsible for an enormous range of physical properties (Figure 2).

![Figure 2: Examples of polyorganophosphazenes, illustrating how changes to side groups changes properties](image)
The extreme range of physical and chemical properties associated with these examples, when applied, results in polyphosphazenes having a wide array of actual or potential uses. Many of these properties found in polyphosphazenes are not found in classic organic polymers.

Polyphosphazenes are used in several industries including environmental cleanup, mineral processing, and in industries such as aerospace and the military.\(^5\) These specific uses range from elastomers, through fire retardants, and coatings, fibers to optical, solid battery electrolytes, fuel cell components, electro-optical, and a variety of membranes.\(^2,4,6\)

What is it about polyphosphazenes that make them so unique in this manner? First, the inorganic backbone of phosphorous and nitrogen gives the polymer properties that are difficult to find in classical organic backbone polymers.\(^4\) These properties include high torsional mobility (flexibility), fire-resistance and resistance to aggressive conditions.\(^4,6\) Second, the side groups are easily variable, resulting in wide structural diversity due to macromolecular substitution chemistry. The polymerization of an organic-substituted small molecule monomer to form the final polymer, the main synthesis route for many organic and silicon polymers, is only used to synthesis a small portion of polyphosphazenes.\(^4\) Instead, a two-step process is utilized in which first a high polymer (10-15,000 repeating units) with two chlorines as the side groups, polydichlorophosphazine ([PNCI\(_2\)]\(_n\)) (2), is synthesized, commonly from a cyclic oligomer. Next, the chlorine side groups are replaced by organic, inorganic, or organometallic side groups using nucleophiles such as sodium alkoxides.\(^6\) This approach allows for a wide array of side groups to be utilized that usually might not survive polymerization or inhibit the process (Scheme 1).\(^6\)
Scheme 1: General route to polyphosphazenes from cyclic oligimer via ring-opening polymerization

The most common method for synthesizing bulk polydichlorophosphazines is a ring-opening method developed by Allcock and co-workers in 1965, which provides a high molecular weight polymer.\textsuperscript{1-2,7} The precursor, hexachlorocyclotriphosphazene ([Cl\textsubscript{2}P\textsubscript{N}]\textsubscript{3}) (1) is synthesized from phosphorus pentachloride (PCl\textsubscript{5}) and ammonium chloride (NH\textsubscript{4}Cl) and then polymerized to 2 via thermal ring-opening. The De Jaeger synthesis of polydichlorophosphazene from P-trichloro-N-(dichlorophosphoryl) monophosphazene (Cl\textsubscript{3}PNP(O)Cl\textsubscript{2}) (3) reported in 1991\textsuperscript{8} represents an attractive alternative to the Allcock ring-opening polymerization. This is due to the inherently more stable reaction pathway, that in turn results in better control of molecular weight.\textsuperscript{9} De Jaeger utilized Emsley’s solution-based reaction of phosphorous tetrachloride (PCl\textsubscript{3}) and ammonium sulfate ((NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}) to make 3 (Scheme 2).\textsuperscript{9} Unfortunately, this reaction takes place at extremely high temperatures of 240 °C, and at the end requires extraction of 3 from the
solvent. Despite these disadvantages, there are also many advantages to this method including ease of preparation, purification and handling of 3.\(^{10}\)

\[
\begin{align*}
\text{Scheme 2: Synthesis of P-trichloro-N-(dichlorophosphoryl) monophosphazene (Cl}_3\text{PNP(O)Cl}_2) \\
\text{(3) from phosphorus pentachloride and ammonium sulfate}
\end{align*}
\]

Allen’s development of the melt-phase polymerization of 3 to form 2 eliminated the need for a solvent and also maintained all of the advantages of the De Jaeger method.\(^5\) The only major downfall of this method is that the polymerization still requires a high temperature to be completed and also to distill phosphorus oxychloride (POCl\(_3\)) (4) (Scheme 3).

\[
\begin{align*}
\text{Scheme 3: Condensation polymerization of 3 to yield polydichlorophosphazene ([PNCl}_2]_n) (2) \\
\text{and phosphorus oxychloride (POCl}_3\) (4)
\end{align*}
\]

A catalyst may allow this reaction to proceed at a lower temperature, which would be of great significance for commercial use of 2 as a precursor to making polyorganophosphazenes. Additionally, the other product of the Allen method, phosphorus oxychloride (POCl\(_3\)) (4), is used as a key ingredient for making a variety of products that have wide uses in pharmaceutical, textile, and the agricultural industries. Currently, there is no report of a catalyst for this reaction.
However, if a catalyst is discovered, it could greatly improve the efficiency of the melt phase reaction and increase convenience of synthesizing polyphosphazenes for use in the laboratory setting. It would also contribute to the knowledge of phosphazene compounds’ reactivity in the field of materials science.

**EXPERIMENTAL**

**Materials**

Materials used in the following experimental were obtained from either Alfa Aesar (Ward Hill, MA, USA) or Sigma-Aldrich (St. Louis, MO, USA) and used without further purification unless explicitly stated. All air-sensitive manipulations were performed under a positive pressure of nitrogen using standard Schlenk techniques or in an M. Braun glovebox. Solvents were dried on the MBraun solvent purification system. Tetrahydrofuran and diethyl ether were dried by stirring with sodium followed by distillation. All solvents were tested for dryness using benzophenone.

**Measurements**

NMR spectra were collected on a Bruker AXR 500 MHz spectrometer (Bruker, Billerica, MA, USA) and are reported with reference to an external standard of 50 mM Ph₃PO (δ 24.50) for $^{31}$P NMR spectra.

**Synthesis and Purification of Cl₃PNP(O)Cl₂ (3)**

The synthesis of 3 was performed according to the Allen method.$^{5,10}$ In the glovebox, a 500 mL schlenk flask was charged with 50.02 g (0.240 mol) of PCl₅ and 7.12 g (0.054 mol) of (NH₄)₂SO₄ (a 9:2 ratio). On the Schlenk line, the flask was then fitted with a condenser and 180° adaptor attached to tubing leading to a water bath. The apparatus was then heated at 160 °C for 1 hour, during which gas evolution was evident. After the system had cooled, the light yellow liquid with white precipitate was cannula filtered. The yellow liquid was distilled at 110 °C to
remove impurities via short path vacuum distillation for 3 hours or until small crystals were observed in the receiving flask. Once cooled, the remaining liquid in the distilling flask was purified via recrystallization until determined pure via $^{31}\text{P}$ NMR spectroscopy: $^{31}\text{P}$ NMR (202 MHz, Toluene) $\delta$ -2.85 (d, $J$ = 17.2 Hz), -13.20 (d, $J$ = 16.2 Hz).

**Catalysis Trials**

In the glovebox, a J-Young type NMR tube was charged with 0.25 mL of a stock solution of toluene and pure 3, and with a catalyst loading of 10 mol %. The samples were then monitored over the next 24 hours at room temperature for reactivity. If none or little was observed, then the sample would be placed in a 60 °C hot bath and once again monitored over the next 24 hours or so. If once again little or no reactivity was observed, then the temperature would be increased to 110 °C and the reaction monitored until no observable reaction occurred. Each trial differed based on the catalyst being tested. As such, a compilation of the samples tested, and times at each temperature are found in the appendix.

**Stoichiometric Trial of Titanium Tetrachloride**

A J-Young type NMR tube was charged with 0.25 mL of 0.05 M 3 in toluene, and 0.25 mL of 0.05 M TiCl$_4$ in toluene. The reaction was monitored over the next 24 hours at room temperature until seemed to show completion.

**Stoichiometric Trial of Tris(pentafluorophenyl)borane**

A J-Young type NMR tube was charged with 0.25 mL of 0.05 M 3 in toluene, and 0.25 mL of 0.05 M B(C$_6$F$_5$)$_3$ in toluene. The reaction was monitored over the next 24 hours at room temperature, then at 60 °C over a weekend at which point completion was observed.
Investigation of Reactivity of Titanium Tetrachloride and Phosphorus Oxychloride

A J-Young type NMR tube was charged with 0.25 mL of 0.25 M POCl₃ in toluene, and 0.25 mL of 0.25 M TiCl₄ in toluene. The reaction was monitored over the next week at room temperature, at which point completion was observed.

RESULTS AND DISCUSSION

P-trichloro-N-(dichlorophosphoryl) monophosphazene (Cl₃PNP(O)Cl₂) (3) was successfully synthesized using the Allen method,⁵,¹¹ and purified via distillation followed by recrystallization from pentane. Purity was determined by phosphorus (³¹P) NMR (Figure 3).

![NMR Spectrum](image)

Figure 3: A representative ³¹P NMR spectrum of pure 3 with the internal standard triphenylphosphine oxide (Ph₃OP) at 24.50 ppm.

Over the course of this study, nine potential catalyst candidates were screened using ³¹P NMR for the condensation polymerization of 3. The catalysts screened are listed in Table 1 by general classification.
Each catalyst category and catalyst were chosen for a few reasons. The organometallic category, chloro(1,5-cyclooctadiene)rhodium(I) dimer [(η^2-C_8H_12)_2RhCl_2] and cyclopentadienyl iron carbonyl dimer, (η^5-C_5H_5)_2Fe_2(CO)_4 (Fp_2), were chosen due to that each catalyst are relatively active. In addition, (η^2-C_8H_12)_2RhCl_2 is known to catalyze other polymerizations\(^1\), while Fp_2 has shown interesting reactivity with phosphines that is still being investigated, and has been shown to polymerize arsine – boranes.\(^2\) Lewis acids were chosen as a category to be investigated due to Lewis acids being known catalysts for the ring opening polymerization of 3.\(^4\) Also, upon investigation of the monomer, there is a Lewis basic site at nitrogen, where Lewis acids could react and conceivably cleave the nitrogen-phosphorus bond. There is evidence to support that this is the first step in the condensation of 3.\(^7\) Similarly, the phosphorus of the trichlorophosphazene group can be considered slightly Lewis acidic, so it is conceivable for a Lewis base to attack there, remove a chlorine and initiate polymerization. The radicals chosen are ones that are often used to initiate radical polymerization of organic polymers.\(^14\) In this context, it was thought that the radical in question could initiate formation of a chlorine radical on the trichlorophosphazene group which would sever the P – Cl bond, resulting in a free chlorine radical that could attack the dichlorophosphoryl to form phosphorous oxychloride.

\(^1\) 2,2′-Azobis(2-methylpropionitrile) (AIBN) – A free radical initiator used in radical polymerization.
\(^2\) 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) – A free radical initiator also used in radical polymerization.
For each catalyst screening, a J-Young type NMR tube was charged with 0.25 mL of pure 3 in toluene, and 10 mol % of the catalyst. Although the intention is to investigate a catalyst for the solvent-free polymerization, the screening trials were conducted in solvent for convenience and ease of observations. Each sample was monitored initially at room temperature over several hours, then at elevated temperatures depending on the reactivity. Each $^{31}$P NMR was monitored initially for loss of monomer (3), which has resonances at -2.85 ppm (d) and -13.20 ppm (d), and production of 4, which has a resonance at 5.90 ppm. However, as the investigation progressed, it became evident that although loss of monomer is relatively straightforward to observe, production of 4 is more difficult to observe as after production, it likely continues to react with either the catalyst, or with various oligomers produced. Regardless, with only looking at consumption of the monomer, five candidates were eliminated. The candidates that were
eliminated due to no changes in monomer concentration are triphenylphosphine, pyridine, 2,2,6,6-tetramethyl-1-piperidinyloxy or TEMPO ([(CH₂)₃(CMe₂)₂NO), 2,2′-Azobis(2-methylpropionitrile) or AIBN ([(CH₃)₂C(CN)]₂N₂) and (η²-C₈H₁₂)₂Rh₂Cl₂. All NMR spectra for these trials are shown in the Appendix.

Of the remaining four catalyst candidates, Fp₂ showed interesting chemistry when the solvent used was toluene, where a single broad resonance was observed, starting at -2.49 ppm. As time went on, precipitate was observed in the J-Young NMR tube accompanied by a loss in intensity of the only phosphorus resonance besides the internal standard, which had also shifted upfield. This is interesting because polymer resonances are often observed broad in NMR spectra, due to the many different chemical environments of a polymer. However, when the solvent was removed, and a NMR spectra obtained for the precipitate which was soluble in THF, only two small relatively sharp resonances were observed, -0.56 ppm and -14.29 ppm. These are not indicative of polymers, however, this catalyst could not yet be ruled out. Therefore, the polymerization reaction was run again, this time with a more polar solvent. The solvent chosen was cyclopentalmethyl ether, due to its relatively high boiling point of 106 °C. Additionally, this reaction was run side by side with a control, due to a control having not been run with this solvent before. However, over the course of 24 hours, the main resonance observed at 8.03 ppm was similar as in the control (Table 2). Therefore, it was determined that Fp₂ is most likely not acting as a catalyst for this reaction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Major Resonances</th>
<th>2 hr</th>
<th>6 hr</th>
<th>24 hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalytic</td>
<td>none</td>
<td>8.20</td>
<td>8.03</td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>7.84, -8.07</td>
<td>7.95</td>
<td>8.06</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Summary of results from Fp₂ catalyst trial in cyclopentalmethyl ether
The final three catalyst candidates are all of the same class, Lewis acids, and all demonstrated similar reactivity. All three reactions, as monitored via NMR, showed a shift in monomer peaks upfield, followed by precipitation, or conversion to other products in the case of trimethylaluminum. Although, it is important to note that 4 is never observed in any of these trials. Of the three Lewis acids, titanium tetrachloride showed seemingly the cleanest and fastest reactivity, with tris(pentafluorophenyl)borane following according to $^{31}\text{P}$ NMR. Trimethylaluminum showed some reactivity; However, it seemed to form several different products. Therefore, it was decided to continue the investigation of tris(pentafluorophenyl)borane and titanium tetrachloride as catalyst options.

The next step was to investigate how the catalytic reactivity compared with a 1:1 stoichiometric ratio. The reasoning for this is that even though the initial reactions were run with catalytic amounts of tris(pentafluorophenyl)borane and titanium tetrachloride, the reaction that occurred is not necessarily a catalyzed condensation polymerization reaction. In order to investigate the other possibilities, the first step is to investigate if the catalyst and 3 are reacting in a stoichiometric manner to make a new product that is not polymer. In order to investigate this, the reactions were run with a 1:1 stoichiometric ratio. If the products resulting were the same as the catalytic, that would indicate that the reaction occurring is indeed a reaction between 3 and the catalyst candidate. What was actually found was that both stoichiometric investigations of tris(pentafluorophenyl)borane and titanium tetrachloride demonstrated different reactivity compared to the catalytic investigations (Figures 5 and 6). Neither investigation resulted in the same product being made. Additionally, the catalytic trials consumed the monophosphazene completely in a similar time frame as the stoichiometric. This indicates that the previously observed reactivity is most likely due to catalysis.
**Figure 5**: Comparison of the stoichiometric investigation of $\text{B}(\text{C}_6\text{F}_5)_3$ and the catalytic investigation.

**Figure 6**: Comparison of the stoichiometric investigation of $\text{TiCl}_4$ and the catalytic investigation.
With the catalytic scale reactivity confirmed to be due to catalysis as opposed to a reaction between 3 and the catalyst candidate, the investigation turned towards identifying the products of the catalyst reactions. To this end, an attempt was made to determine what products would be produced if a catalyst reacted with any 4 that is typically a byproduct of this condensation polymerization. This was only tested with titanium tetrachloride, and the only product made had a resonance at 15.02 ppm (Figure 7).

![Figure 7: Stoichiometric 4 and TiCl₄ to investigate products](image)

This resonance was not observed in any titanium tetrachloride catalyzed reactions, therefore it was concluded that 4 is most likely not being produced with TiCl₄ as a catalyst. In an attempt to obtain a larger amount of product to be isolated and characterized via ³¹P NMR spectroscopy and solid state characterization methods, larger scale reactions were run using both tris(pentafluorophenyl)borane and titanium tetrachloride. Additionally, in an attempt to make
characterization easier, if the product of the reactions is indeed polydichlorophosphazene, then it is simple to convert it to poly(bisphenoxy)phosphazene. This polymer is much easier and better characterized than polydichlorophosphazene, and would also provide conclusive evidence that the product of the reaction is indeed polydichlorophosphazene. Unfortunately, despite multiple attempts to isolate the products of both catalysis reactions, isolation and purification of the products has yet to be achieved.

Of the categories investigated, Lewis acids showed the greatest reactivity. As such, a mechanism has been proposed using titanium tetrachloride as the representative Lewis acid (Scheme 4). This mechanism is very similar to the one proposed by De Jaeger in 1992\textsuperscript{7} for the condensation polymerization of 3 to 2, with the exception of titanium tetrachloride initiating the N-dichlorophosphoryl bond cleavage as opposed to a nitrogen of another equivalent of monomer initiating the cleavage.

![Scheme 4: Proposed mechanism for TiCl\textsubscript{4} catalyzed condensation polymerization of P-trichloro-N-dichlorophosphoryl monophosphazene](image)

CONCLUSIONS

P-trichloro-N-dichlorophosphoryl monophosphazene (Cl\textsubscript{3}PNP(O)Cl\textsubscript{2}) (3) was successfully synthesized and purified via the Allen method. A selection of catalyst candidates,
from the broad categories of organometallic, Lewis acid, Lewis base, and radicals were tested. From these nine candidates, the three Lewis acids, titanium tetrachloride, tris(pentafluorophenyl)borane and trimethylaluminum showed the greatest reactivity. Further investigations of these three Lewis acids showed titanium tetrachloride having the greatest reactivity, and tris(pentafluorophenyl)borane showing the second most. Additionally, it was confirmed via stoichiometric trials, that the reactions are indeed proceeding via a catalytic pathway. Investigations into the products of these reactions were begun in the form of larger scale reactions and attempted isolation, but with little success. Further research should consider continuing to attempt the isolation and purification of the products to characterize them as well as investigating the reactivity solventless. In addition, there are a few more catalyst categories that should be investigated including protons acids and electrophiles.
References:

APPENDIX

I. Catalytic Screening Conditions

I-A. Table of Catalytic Screening Conditions

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>mol %</th>
<th>Solvent</th>
<th>Temperature</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>--</td>
<td>Neat</td>
<td>220 °C</td>
<td>1 hour</td>
</tr>
<tr>
<td>Fp₂</td>
<td>10</td>
<td>Toluene</td>
<td>110 °C</td>
<td>&gt;24 hr</td>
</tr>
<tr>
<td>Fp₂</td>
<td>10</td>
<td>CPME</td>
<td>110 °C</td>
<td>24 hr</td>
</tr>
<tr>
<td>[Rh(COD)Cl]₂</td>
<td>10</td>
<td>Toluene</td>
<td>RT, 65 °C</td>
<td>1 week</td>
</tr>
<tr>
<td>AlMe₃</td>
<td>10</td>
<td>Toluene</td>
<td>RT, 110 °C</td>
<td>6 days</td>
</tr>
<tr>
<td>TiCl₄</td>
<td>10</td>
<td>Toluene</td>
<td>RT, 60 °C, 100 °C</td>
<td>5 days</td>
</tr>
<tr>
<td>B(C₆F₅)₃</td>
<td>10</td>
<td>Toluene</td>
<td>RT, 65 °C</td>
<td>6 days</td>
</tr>
<tr>
<td>TEMPO</td>
<td>10</td>
<td>Toluene</td>
<td>RT, 60 °C</td>
<td>1 week</td>
</tr>
<tr>
<td>AIBN</td>
<td>10</td>
<td>Toluene</td>
<td>RT, 65 °C</td>
<td>~ 1 week</td>
</tr>
<tr>
<td>Ph₃P</td>
<td>10</td>
<td>Toluene</td>
<td>RT, 60 °C</td>
<td>3 days</td>
</tr>
<tr>
<td>Pyridine</td>
<td>1</td>
<td>Toluene</td>
<td>60 °C, 110 °C</td>
<td>1 week</td>
</tr>
</tbody>
</table>

II. NMR Spectra for Catalytic Screenings

II-A. ³¹P NMR spectrum of Fp₂ Trial After 1 hour at 110 °C
II-B. $^{31}$P NMR spectrum of Fp$_2$ Trial After 2 hours at 110 °C

II-C. $^{31}$P NMR spectrum of Fp$_2$ Trial After 3 hours at 110 °C
II-D. $^{31}\text{P}$ NMR spectrum of Fp$_2$ Trial After Running Overnight at 110 °C

II-E. $^{31}\text{P}$ NMR spectrum of Fp$_2$ Trial After Running More than 24 hours at 110 °C
II-F. $^{31}$P NMR spectrum of Fp$_2$ Trial Product in THF

II-G. $^{31}$P NMR spectrum of Fp$_2$ Trial in Cyclopentalmethyl Ether after 2 hours at 110 °C
II-H. $^{31}$P NMR spectrum of Fp$_2$ Trial in Cyclopentalmethyl Ether after 6 hours at 110 °C

II-I. $^{31}$P NMR spectrum of Fp$_2$ Trial in Cyclopentalmethyl Ether after 24 hours at 110 °C
II-J. $^{31}$P NMR spectrum of [Rh(COD)Cl]$_2$ Trial in Toluene Initial

II-K. $^{31}$P NMR spectrum of [Rh(COD)Cl]$_2$ Trial in Toluene Overnight at Room Temperature
II-L. $^{31}$P NMR spectrum of [Rh(COD)Cl]$_2$ Trial in Toluene 24 hours at Room Temperature

II-M. $^{31}$P NMR spectrum of [Rh(COD)Cl]$_2$ Trial in Toluene after 24 hours at 65 °C
II-N. $^{31}\text{P}$ NMR spectrum of $\left[\text{Rh}($COD$)\text{Cl}\right]_2$ Trial in Toluene after 2 days at 65 °C

II-O. $^{31}\text{P}$ NMR spectrum of $\left[\text{Rh}($COD$)\text{Cl}\right]_2$ Trial in Toluene after 1 week at 65 °C
II-P. $^{31}$P NMR spectrum of AlMe$_3$ Trial in Toluene Initial

II-Q. $^{31}$P NMR spectrum of AlMe$_3$ Trial in Toluene After 1 hour at Room Temperature
II-R. $^{31}$P NMR spectrum of AlMe$_3$ Trial in Toluene After 2 hours at Room Temperature

II-S. $^{31}$P NMR spectrum of AlMe$_3$ Trial in Toluene After 3 hours at Room Temperature
II-T. $^{31}$P NMR spectrum of AlMe$_3$ Trial in Toluene After 4 hours at Room Temperature

II-U. $^{31}$P NMR spectrum of AlMe$_3$ Trial in Toluene After Overnight at Room Temperature
II-V. $^{31}$P NMR spectrum of AlMe$_3$ Trial in Toluene After 6 hours at 60 °C

II-W. $^{31}$P NMR spectrum of AlMe$_3$ Trial in Toluene After 12 hours at 60 °C
II-X. $^{31}$P NMR spectrum of AlMe$_3$ Trial in Toluene After 6 hours at 100 °C

II-Y. $^{31}$P NMR spectrum of AlMe$_3$ Trial in Toluene After 12 hours at 100 °C
II-Z. $^{31}$P NMR spectrum of AlMe$_3$ Trial in Toluene After 18 hours at 100 °C

II-AA. $^{31}$P NMR spectrum of AlMe$_3$ Trial in Toluene After 24 hours at 100 °C
II-AB. $^{31}$P NMR spectrum of AlMe$_3$ Trial in Toluene After 30 hours at 100 °C

II-AC. $^{31}$P NMR spectrum of AlMe$_3$ Trial in Toluene After 4 days at 100 °C
II-AD. $^{31}$P NMR spectrum of TiCl$_4$ Trial in Toluene Initial

II-AE. $^{31}$P NMR spectrum of TiCl$_4$ Trial in Toluene after 6 hours at Room Temperature
II-AF. $^{31}$P NMR spectrum of TiCl$_4$ Trial in Toluene after 6 hours at 60 °C

II-AG. $^{31}$P NMR spectrum of TiCl$_4$ Trial in Toluene after 18 hours at 60 °C
II-AH. $^{31}$P NMR spectrum of TiCl₄ Trial in Toluene after 24 hours at 60 °C

II-Al. $^{31}$P NMR spectrum of TiCl₄ Trial in Toluene after Weekend at 100 °C
II-AJ. $^{31}$P NMR spectrum of TiCl$_4$ Trial in Toluene after 3 hours at 150 °C

II-AK. $^{31}$P NMR spectrum of B(C$_6$F$_5$)$_3$ Trial in Toluene Initial
II-AL. $^{31}$P NMR spectrum of $\text{B(C}_6\text{F}_5)_3$ Trial in Toluene Overnight at Room Temperature

II-AM. $^{31}$P NMR spectrum of $\text{B(C}_6\text{F}_5)_3$ Trial in Toluene Overnight at 65 °C
II-AN. $^{31}$P NMR spectrum of B(C$_6$F$_5$)$_3$ Trial in Toluene Weekend at 65 °C

II-AO. $^{31}$P NMR spectrum of TEMPO Trial in Toluene for 1 hour at Room Temperature
II-AP. $^{31}$P NMR spectrum of TEMPO Trial in Toluene for 18 hours at Room Temperature

II-AQ. $^{31}$P NMR spectrum of TEMPO Trial in Toluene for more than 24 hours at Room Temperature
II-AR. $^{31}\text{P}$ NMR spectrum of TEMPO Trial in Toluene Overnight at 60 °C

II-AS. $^{31}\text{P}$ NMR spectrum of TEMPO Trial in Toluene Over the weekend at 65 °C
II-AT. $^{31}$P NMR spectrum of AIBN Trial in Toluene Initial

II-AU. $^{31}$P NMR spectrum of AIBN Trial in Toluene Overnight at Room Temperature
II-AV. $^{31}$P NMR spectrum of AIBN Trial in Toluene for 24 hours at Room Temperature

II-AW. $^{31}$P NMR spectrum of AIBN Trial in Toluene for 24 hours at 65 °C
II-AX. $^{31}$P NMR spectrum of AIBN Trial in Toluene for 2 days at 65 °C

II-AY. $^{31}$P NMR spectrum of AIBN Trial in Toluene for 1 week at 65 °C
II-AZ. $^{31}$P NMR spectrum of Ph$_3$P Trial in Toluene Initial

II-BA. $^{31}$P NMR spectrum of Ph$_3$P Trial in Toluene Overnight at Room Temperature
II-BB. $^{31}$P NMR spectrum of Ph$_3$P Trial in Toluene for 2 hours at 60 °C

II-BC. $^{31}$P NMR spectrum of Ph$_3$P Trial in Toluene Overnight at 60 °C
II-BD. $^{31}$P NMR spectrum of Pyridine Trial in Toluene Initial

II-BC. $^{31}$P NMR spectrum of Pyridine Trial in Toluene Overnight at Room Temperature
II-BD. $^{31}$P NMR spectrum of Pyridine Trial in Toluene for 2 hours at 60 °C

II-BE. $^{31}$P NMR spectrum of Pyridine Trial in Toluene Overnight at 60 °C
II-BF. $^{31}$P NMR spectrum of Pyridine Trial in Toluene for 2 days at 60 °C

II-BG. $^{31}$P NMR spectrum of Pyridine Trial in Toluene for 6 hours at 110 °C
II-BH. $^{31}$P NMR spectrum of Pyridine Trial in Toluene for a weekend at 110 °C

III. NMR Spectra for Stoichiometric Trials of B(C$_6$F$_5$)$_3$ and TiCl$_4$

III-A. $^{31}$P NMR spectrum of Stoichiometric B(C$_6$F$_5$)$_3$ and 3 Initial
III-B. $^{31}$P NMR spectrum of Stoichiometric B(C₆F₅)₃ and 3 After 18 hours at Room Temperature

III-C. $^{31}$P NMR spectrum of Stoichiometric B(C₆F₅)₃ and 3 After >25 hours at Room Temperature
III-D. $^{31}$P NMR spectrum of Stoichiometric B(C₆F₅)₃ and 3 Overnight at 60 °C

III-E. $^{31}$P NMR spectrum of Stoichiometric B(C₆F₅)₃ and 3 Over the weekend at 60 °C
III-F. $^{31}$P NMR spectrum of Stoichiometric TiCl$_4$ and 3 Initial

III-G. $^{31}$P NMR spectrum of Stoichiometric TiCl$_4$ and 3 6 hours at Room Temperature
III-H. $^{31}$P NMR spectrum of Stoichiometric TiCl$_4$ and 3 12 hours at Room Temperature

III-I. $^{31}$P NMR spectrum of Stoichiometric TiCl$_4$ and 3 >24 hours at Room Temperature
IV. NMR Spectra of stoichiometric POCl$_3$ and TiCl$_4$

IV-A. $^{31}$P NMR spectrum of POCl$_3$ with TiCl$_4$ Initial

IV-B. $^{31}$P NMR spectrum of POCl$_3$ with TiCl$_4$ Over the weekend at Room Temperature
IV-C. $^{31}$P NMR spectrum of POCl$_3$ with TiCl$_4$ for 1 week at Room Temperature