DEVELOPMENT OF NOVEL MAGNESIUM, ZINC, AND ALUMINUM ORGANOMETALLIC CATALYSTS FOR THE COPOLYMERIZATION OF CO₂ AND EPOXIDES

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by

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Abstract

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The aim of this dissertation is to describe the synthesis, characterization, and catalytic performance in the copolymerization of CO₂ and cyclohexene oxide of various homogeneous metal complexes containing magnesium, zinc, and aluminum metal centers.

The introduction provides historical context for this work, including discussion of heterogeneous and homogeneous catalysis using zinc as the choice metal. Also included is a mechanistic discussion leading to the development of dinuclear metal complexes as catalysts.

Chapter 2 describes the synthesis and characterization of a bis(pyrazolyl)methylphenol “heteroscorpionate” ligand and the corresponding zinc and magnesium complexes.

Chapter 3 focuses on the synthesis of five “salen-type” ligands and the corresponding magnesium, zinc, and aluminum metal complexes.
Chapter 4 focuses on the synthesis and characterization of heterobimetallic dinuclear macrocyclic metal complexes containing lithium and magnesium, or lithium and zinc centers.

Chapter 5 focuses on the synthesis of three novel $m$-phenylene-bridged (phosphinimino/phosphorano)methane ligands. The coordination chemistry of the phosphine oxide derivative with magnesium, zinc, and aluminum metal centers is discussed.
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and my late father, Raymond Edwin Eberle, Jr.
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CHAPTER 1:
GENERAL INTRODUCTION

1.1 Utilization of CO\textsubscript{2} as C\textsubscript{1} Feedstock

The use of carbon dioxide (CO\textsubscript{2}) as a C\textsubscript{1} chemical feedstock has garnered much attention the past several decades\textsuperscript{[1-5]} Not only is it non-toxic and relatively inexpensive, it is also a problematic greenhouse gas. As a waste product of industrial processes such as power generation, fermentation, and manufacturing, utilizing CO\textsubscript{2} as a C\textsubscript{1} feedstock for fuels and materials is being realized. However, as CO\textsubscript{2} is one of the most thermodynamically stable forms of carbon,\textsuperscript{[4]} there is a need to develop catalysts that are effective at activation and facilitating chemical transformations. Indeed, CO\textsubscript{2} can be transformed into carbon monoxide, methane, methanol, formate, carbonates, ureas, etc. by homogeneous and heterogeneous catalysis, electrochemical and photochemical methods, both industrially and academically.\textsuperscript{[6]}

Of interest to us is utilizing CO\textsubscript{2} to form polymers, such as polycarbonates. Reaction of CO\textsubscript{2} with epoxides leads to the formation of either polycarbonate (which could be used in engineering applications such as thermoplastics or packaging)\textsuperscript{[2]} and cyclic carbonates (solvents with high boiling points used as electrolytes in batteries).\textsuperscript{[6]} By using CO\textsubscript{2} and epoxides to produce polycarbonates, this could provide a more
sustainable and less toxic route to these useful materials which are typically formed by
the polycondensation reaction of phosgene with bisphenol-A.

By reacting epoxides, such as propylene oxide (PO) or cyclohexene oxide (CHO),
in the presence of a metal catalyst under a CO\textsubscript{2} atmosphere, the formation of three
major products can result: alternating copolymer resulting in polycarbonates,
polyethers, and cyclic carbonates as shown in Scheme 1.1.

![Scheme 1.1. General reaction of epoxides with CO\textsubscript{2}. Formed
products are polycarbonate, polyether, and cyclic carbonate.](image)

1.2 Previous Work in the Literature

1.2.1 Discovery of Copolymerization of CO\textsubscript{2} and Epoxides

In 1969, Inoue et al. showed that CO\textsubscript{2} could be copolymerized with propylene
oxide (PO) in the presence of catalytic amounts of diethylzinc (ZnEt\textsubscript{2}) and water to form
a small amount of poly(propylene carbonate) (PPC).\cite{7} At atmospheric pressure of CO\textsubscript{2},
the resulting copolymer was formed in poor yield with 88% selectivity for carbonate
linkages in the polymer backbone, as determined by elemental analysis and NMR
spectroscopy. By increasing the pressure of CO\textsubscript{2} to 50-60 atm, the yield of copolymer
formed increases, as does the selectivity for carbonate linkages. The use of
triethylaluminum (AlEt\textsubscript{3}) led to the exclusive formation of the polyether, poly(propylene
oxide) (PPO). Other epoxides such as ethylene oxide (EO), epichlorohydrin (ECH), and styrene oxide (SO) can also be copolymerized with CO₂ using ZnEt₂·H₂O (1:0.9) at room temperature.⁸

1.2.2 Other Heterogeneous Zinc Catalyst Systems

Following this discovery, exploration with the use of various di- and trihydric molecules, such as dicarboxylic acids, primary amines, and dihydroxyphenol, in combination with ZnEt₂ has been applied to the copolymerization of PO and CO₂. Kuran and coworkers developed new heterogeneous zinc phenoxides utilizing pyrogallol and resorcinol. These were capable of producing PPC with turn over frequencies (TOFs) up to 0.3 h⁻¹ at 35 °C and 60 atm CO₂.

In general, heterogeneous zinc catalysts produced from reaction of ZnEt₂ with monoprotic sources such as alcohols and secondary amines produced the cyclic carbonate propylene carbonate (PC), while di- or triprotic sources gave the alternating PPC copolymer.⁹

For the formation of PPC from PO and CO₂, there are several limitations to catalyst development. First, the polymer poly(propylene carbonate) is thermodynamically less stable than PC, as well as it is less stable than propylene glycols, which is produced by homopolymerizing PO. Second, the activity of the best catalysts used for formation of PPC is below 1000 kg per kg of metal in the catalysts on an industrial scale. For example, using zinc glutarate in the preparation of PPC affords 350 kg polymer per kg of zinc. Third, the catalytic action of the heterogeneous catalysts at a
molecular level is not well understood. Finally, some catalysts that are active in the formation of PPC, are not active in the formation of copolymers of CO$_2$ and other epoxides, such as CHO, and vice versa. Thus, the preparation of homogeneous catalysts was pursued by several groups to shed some light on the mechanism to improved catalytic performance.

1.2.3 Homogeneous Catalysis

1.2.3.1 Zinc Phenoxides

A switch to homogeneous catalysis to improve selectivity and understand mechanistic details was initiated in the mid-1990s by Darensbourg and coworkers$^{[11]}$ using one of the first examples of a well-characterized, mononuclear zinc catalyst. Inspired by work from Caulton’s group in preparing the first soluble 2,6-disubstituted zinc bis(aryloxides),$^{[12]}$ zinc bis(2,6-diphenylphenoxide) (Figure 1.1) could be prepared in high yield by reaction of 2 equivalents of the phenol with 1 equivalent of zinc bis(bis(trimethylsilyl)amide) in tetrahydrofuran (THF) or diethyl ether. By using zinc bis(2,6-diphenylphenoxide) as a catalyst, shown in Figure 1.1, poly(cyclohexene carbonate) (PCHC) could be formed in a yield of 366 g polycarbonate/g Zn with a polydispersity index (PDI) of 4.5 at 80 °C for 69 h and 800 psi CO$_2$. 

4
By varying the ortho-position substituents, the effect on catalytic activity was substantial. Darensbourg attributes this to electronic effects and steric hindrance around the metal center. For example, when \( R_1 \) increases in steric bulk, (\( iPr < Ph < tBu \)) (Figure 1.2), the yield of copolymer increases to 477, 602, and 677 g polymer/g Zn, respectively, over 69 h at 80 °C and 750 psi \( CO_2 \). The polymers prepared with these catalysts exhibited greater than 90% selectivity for carbonate linkages over ether linkages.[13]

When \( R_1 = F, Cl, \) or \( Br \), dimeric zinc complexes can be prepared from THF solution, due to the lack of steric bulk of the di-halophenoxide moieties (Figure 1.3).[14]

At 80 °C and 55 bar \( CO_2 \), the catalytic activity of this series decreases as electron density at the zinc center increases, that is \( F > Cl > Br (R_2 = Me) \) with 790, 539, and 329 g
polymer/g Zn, respectively. The authors note that the resulting decreased Lewis acidity at the metal center inhibits binding ability to the epoxide substrate. The copolymer formed from CO$_2$ and CHO with these catalysts exhibit a completely alternating nature with essentially no polyether linkages.

1.2.3.2 Zinc β-diimimates

Shortly thereafter, beginning in 1998, Coates published work on a series of zinc β-diiminate (BDI) complexes (Scheme 1.2),$^{15-18}$ the first of which was active in the formation of PCHC at 100 psi CO$_2$. In subsequent work, a series of BDI-ZnX complexes were prepared by reacting the ligand with $n$-butyllithium and subsequent transmetallation with an appropriate zinc salt (halide or acetate). Alternatively, reaction with a zinc base such as ZnEt$_2$ or Zn[N(SiMe$_3$)$_2$]$_2$ affords the ethyl and amido zinc complexes, respectively. Protonolysis of the ethyl or amido zinc complexes with acids or alcohols afford the BDI-ZnX (X = halide, alkoxide, carboxylate) complexes. The desired alkoxide or carboxylate complexes formed by protonolysis of the BDI-ZnEt complexes.
often resulted in poor yields after recrystallization due to the protonation of the ligand by the acid or alcohol.

![Image of scheme 1.2 showing synthesis of zinc BDI complexes.](image)

**Scheme 1.2 Synthesis of zinc BDI complexes.**

By varying substituents at the *ortho*-position of the *N*-aryl imine arm of the BDI ligand, the electronic and steric properties of the ligand can be tuned. Variations in steric and electronic bulk of the BDI ligand demonstrated profound changes in activity of the catalysts. Also of note, the use of alkyl, hydroxide, or halide groups as the bridging ligand showed no catalytic activity, however the utilization of carboxylates, alkoxides, or amides were generally shown to be active. Reaction of CO$_2$ and CHO using [(BDI-1)ZnOAc] (Scheme 1.2, R$_1$, R$_2$ = iPr, R$_3$ = H, X = OAc) as a catalyst (0.1 mol% loading) at 50 °C and 100 psi (6.89 bar) resulted in a turn over number (TON) of 494, TOF of 247 h$^{-1}$, and PDI of 1.11 (Table 1.1, Entry 1). For this system, it was found that mixed ethyl and isopropyl *ortho*-N-aryl substituents on the β-diketiminate ligand was the optimal geometry for catalysis, resulting in TON of 515, TOF of 257 h$^{-1}$, and PDI of 1.14 (Table 1.1, Entry 2).

[^17]: By including an electron-withdrawing group (Scheme 1.2, R$_3$ = CN) into...
the backbone of the ligand, activities of the catalysts increased to over 2200 h\(^{-1}\) at 7 atm CO\(_2\).\(^{[19]}\)

To investigate the mechanism of copolymerization, Coates also performed some rate studies. It was found that the overall rate law was first order with respect to epoxide, zeroth order for CO\(_2\) and almost second order (1.73 for [(BDI-1)ZnOAc]) with respect to zinc, suggesting a bimetallic transition state.\(^{[17]}\) By modifying the steric bulk of the N-aryl ortho positions, zinc β-diiminates could be isolated as monomeric or dimeric. X-ray crystallography revealed that [(BDI-1)ZnX] (Figure 1.4, R\(_1\), R\(_2\) = iPr, R\(_3\) = H, X = OAc, OiPr, or OMe) as a dimer. \(^1\)H NMR spectroscopy indicated that steric effects play a role in monomer/dimer equilibria.\(^{[9]}\)

![Figure 1.4](image)

**Figure 1.4.** Monomer/dimer equilibrium of BDI-ZnX complexes.

Rieger *et al.* reported the synthesis of BDI-Zn ethylsulfinate complexes in quantitative yields by reaction of dry SO\(_2\) with BDI-ZnEt.\(^{[18]}\) This provides a synthesis route to a new series of BDI-Zn(II) complexes that are plagued by side reactions through protonolysis of the BDI-ZnEt complexes reported by Coates.\(^{[16]}\) By exchanging the initiating ligand from alkoxides, carboxylates, or amides to ethylsulfinate (Figure 1.4,
R₁=R₂=Et, X=O₂SEt, Rieger and coworkers were able to achieve TON of 651 and TOF of 217 under 10 bar pressure CO₂ at 60 °C and a catalyst loading of 0.1 mol% (Table 1.1, Entry 3).[18]

1.2.3.3 Dinuclear Ligand Frameworks

After the mechanistic studies by Coates,[17] it became apparent that preparing dinuclear metal catalysts would be beneficial. Indeed, by utilizing a dinuclear framework, the entropically unfavorable requirement for dimerization of mononuclear complexes in high dilution is circumvented. An advantage is to have two multidentate units far enough away to allow for coordination of two metal centers, yet not so far where the two centers cannot interact synergistically.

In 2005, Lee and coworkers synthesized a dinuclear ligand system featured o-terphenylene-bridged anilido-aldimine units[20,21] (Figure 1.5). It was found that a zinc methylsulfinate complex (Figure, R₁ = Me, R₂ = iPr) could produce PCHC with TON = 1560, TOF = 312 h⁻¹, and PDI = 1.7 with 0.01 mol% loading at 80 °C for 5 h and 12 bar CO₂. As reported early by Coates,[19] increasing the Lewis acidity at the zinc centers by introducing electron-withdrawing groups in the ancillary ligand would increase activity. When using a perfluorinated ligand (Figure 1.5),[21] the zinc methylsulfinate complex where R₁ = Me, R₂ = iPr provided the polycarbonate with TON = 9930, TOF = 2860 h⁻¹, and PDI = 1.4 at 50 °C for 4 h and 14 bar CO₂. However, the increased activity resulted in a decrease in selectivity for polycarbonate over polyether formation in the resulting polymer (from 94% to 78% carbonate linkages).
Figure 1.5. Anilido-aldimine Zn complexes.

A different approach utilizing a smaller, albeit wider-angled bridge, such as meta- or para-phenylene or pyridylene units, was explored by Harder and coworkers. Attached to the bridge were either β-diketimine\(^{[22]}\) or salicylaldimine\(^{[23]}\) (salen) moieties which provided a wide range of metal-metal distances (2.5-8 Å for the meta-phenylene and meta-pyridylene-bridged species, 5.5-8.5 Å for the para-phenylene-bridged species).

The salicylaldimine metal complexes, namely magnesium, were inactive in the copolymerization of CHO and CO\(_2\), however were active in the ROP of rac-lactide. Difficulties in forming stable heteroleptic calcium and zinc complexes with amide ligands in solution prevented further investigation for catalytic activity.\(^{[23]}\) However, successful preparation of heteroleptic calcium and zinc amide reagents could be isolated with the β-diketiiminate ligands. Unfortunately, it was shown that only some of the zinc complexes were active in the copolymerization of CHO and CO\(_2\).\(^{[22]}\) The most active Zn
complex, META-[ZnOS(O)Et]₂ (Figure 1.6) showed good activity (up to TON 1196, TOF 199 h⁻¹) under low catalyst loadings of 0.033 mol% and 10 bar pressure CO₂.

![Figure 1.6. m-phenylene-bridged BDI Zn complexes.](image)

More recently, Williams used a reduced Robson-type macrocyclic ligand framework.[24-28] Unlike other catalysts which require higher pressures (> 6 bar) of CO₂, the dizinc[25] and dimagnesium[26] diacetate complexes (Figure 1.7) can efficiently form poly(cyclohexene carbonate) with >99% carbonate linkages at 1 atm CO₂ at 80 °C for 6h with TON of 220 and 522 and TOF of 9.2 h⁻¹ and 35 h⁻¹, respectively.

![Figure 1.7 Reduced-form Robson-type macrocycle for dinuclear metal complexes.](image)
Table 1.1 presents a summary of the homogeneous catalysts described above.
### TABLE 1.1.

**SUMMARY OF HOMOGENEOUS CATALYSTS USED IN THE COPOLYMERIZATION OF CYCLOHEXENE OXIDE AND CO\textsubscript{2}**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Loading</th>
<th>t (h)</th>
<th>T (°C)</th>
<th>P (bar)</th>
<th>TON\textsuperscript{a}</th>
<th>TOF\textsuperscript{b}</th>
<th>M\textsubscript{n} (x10\textsuperscript{-3})/PDI</th>
<th>Carbonate Linkages (%)\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[(BDI-1)ZnOAc]\textsuperscript{[24]}</td>
<td>1:1000</td>
<td>2</td>
<td>50</td>
<td>6.89</td>
<td>494</td>
<td>247</td>
<td>31.0/1.11</td>
<td>96</td>
</tr>
<tr>
<td>2</td>
<td>[(BDI-5)ZnOMe]\textsuperscript{[16]}</td>
<td>1:1000</td>
<td>2</td>
<td>50</td>
<td>6.89</td>
<td>515</td>
<td>257</td>
<td>32.1/1.14</td>
<td>99</td>
</tr>
<tr>
<td>3</td>
<td>[(BDI-2)ZnOSOEt]\textsuperscript{[18]}</td>
<td>1:1000</td>
<td>3</td>
<td>60</td>
<td>10</td>
<td>651</td>
<td>217</td>
<td>49.6/1.13</td>
<td>96</td>
</tr>
<tr>
<td>4</td>
<td>AN-(ZnOS(O)Me)\textsubscript{[20]}</td>
<td>1:5600</td>
<td>5</td>
<td>80</td>
<td>12</td>
<td>1560</td>
<td>312</td>
<td>225/1.7</td>
<td>94</td>
</tr>
<tr>
<td>5</td>
<td>AN-(ZnOS(O)Me)\textsubscript{[20]}</td>
<td>1:16800</td>
<td>15</td>
<td>80</td>
<td>12</td>
<td>2980</td>
<td>200</td>
<td>284/1.7</td>
<td>91</td>
</tr>
<tr>
<td>6</td>
<td>F-AN-(ZnOS(O)Me)\textsubscript{[21]}</td>
<td>1:5600</td>
<td>2</td>
<td>80</td>
<td>14</td>
<td>1570</td>
<td>785</td>
<td>118/2.1</td>
<td>65</td>
</tr>
<tr>
<td>7</td>
<td>F-AN-(ZnOS(O)Me)\textsubscript{[21]}</td>
<td>1:22400</td>
<td>3</td>
<td>80</td>
<td>14</td>
<td>4860</td>
<td>1620</td>
<td>179/1.7</td>
<td>69</td>
</tr>
<tr>
<td>8</td>
<td>F-AN-(ZnOS(O)Me)\textsubscript{[21]}</td>
<td>1:50000</td>
<td>4</td>
<td>50</td>
<td>14</td>
<td>9930</td>
<td>2860</td>
<td>245/1.2</td>
<td>79</td>
</tr>
<tr>
<td>9</td>
<td>META-[Zn[SiMe\textsubscript{3}]]\textsuperscript{[22]}</td>
<td>1:1000</td>
<td>2</td>
<td>60</td>
<td>10</td>
<td>346</td>
<td>173</td>
<td>74.1/1.33</td>
<td>97</td>
</tr>
<tr>
<td>10</td>
<td>META-[Zn[SiMe\textsubscript{3}]]\textsuperscript{[22]}</td>
<td>1:1000\textsuperscript{d}</td>
<td>5</td>
<td>60</td>
<td>10</td>
<td>748</td>
<td>150</td>
<td>97.7/1.39</td>
<td>&gt;99</td>
</tr>
<tr>
<td>11</td>
<td>META-[ZnOS(O)Et]\textsuperscript{[22]}</td>
<td>1:1000</td>
<td>2</td>
<td>60</td>
<td>10</td>
<td>363</td>
<td>181</td>
<td>39.4/1.28</td>
<td>96</td>
</tr>
<tr>
<td>12</td>
<td>META-[Zn OS(O)Et]\textsuperscript{[22]}</td>
<td>1:3000</td>
<td>6</td>
<td>60</td>
<td>10</td>
<td>1196</td>
<td>199</td>
<td>110/1.33</td>
<td>&gt;99</td>
</tr>
<tr>
<td>13</td>
<td>[Zn\textsubscript{2}OAc\textsubscript{4}]\textsuperscript{[22]}</td>
<td>1:1000</td>
<td>6</td>
<td>80</td>
<td>1</td>
<td>220</td>
<td>9.2</td>
<td>6.2/1.19</td>
<td>&gt;99</td>
</tr>
<tr>
<td>14</td>
<td>[MgZnOAc\textsubscript{4}]\textsuperscript{[22]}</td>
<td>1:1000</td>
<td>6</td>
<td>80</td>
<td>1</td>
<td>522</td>
<td>35</td>
<td>6.5/1.03</td>
<td>&gt;99</td>
</tr>
<tr>
<td>15</td>
<td>[MgZnOAc\textsubscript{4}]\textsuperscript{[22]}</td>
<td>1:1000</td>
<td>6</td>
<td>80</td>
<td>1</td>
<td>476</td>
<td>79</td>
<td>5.2/1.12</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The turn over number (TON) is the average number of CHO/CO\textsubscript{2} insertions per metal center. \textsuperscript{b}The turn over frequency (TOF) is TON/time. \textsuperscript{c}The % carbonate linkages as determined by \textsuperscript{1}H NMR by integration of methine region protons. \textsuperscript{d}Metal/CHO/toluene = 1/1000/2000.
1.2.4 Proposed Bimetallic Mechanism

Both the Coates\cite{17} and Williams\cite{29,30} groups have investigated mechanistic details of this reaction with the zinc BDI and macrocyclic complexes, respectively. These studies showed a first order dependence on epoxide, as well as a second order dependence on the metal center (1.7 for the mononuclear Zn-BDI and 1 for the dinuclear zinc macrocycle). Williams proposed a “shuttling” mechanism, where the propagating chain cooperatively switches between two metal centers (Scheme 1.3). In the proposed mechanism, initiation starts with the dissociation of one of the κ²-coordinated acetate groups to create an empty coordination site at one of the zinc centers. This is followed by coordination of the epoxide. Formation of a metal alkoxide bond results from nucleophilic attack of the acetate to the coordinated epoxide. Epoxide ring-opening was determined to be the rate-determining step in both the Zn-BDI and Zn₂-macrocyclic systems. Next, rapid insertion of CO₂, which coordinates to the other zinc center, into the Zn alkoxide bond occurs, forming a new metal carbonate bond. This alternating coordination-insertion pair leads to propagation of the growing polycarbonate chain. Other products, as shown in [figure], can be formed through alternative mechanisms. For instance, polyether formation is the result of subsequent epoxide enchainment, whereas cyclic carbonate is formed through a “back-biting” mechanism, where the metal alkoxide acts as a nucleophile at the carbonyl carbon of a neighboring carbonate unit, forming a stable five-membered ring (Scheme 1.3).
Scheme 1.3 Proposed mechanism of the copolymerization of CO$_2$ and CHO. Figure adapted from references 29 and 30. Also shown are pathways to produce cyclic carbonate through a “back-biting” mechanism and polyether through consecutive epoxide enchainment.
1.3 Dissertation Summary

The overall goal of the project is to investigate a series of metal complexes that could potentially act as efficient catalysts for the copolymerization of CO\textsubscript{2} and epoxides at low pressures (~1 atm) of CO\textsubscript{2}.

\[ \text{O} \xrightarrow{\text{cat.}} \text{1 atm CO}_2 \rightarrow \left( \begin{array}{c} \text{O} \\ \text{O} \end{array} \right) \]

In line with the aim of developing a more environmentally benign synthetic route to obtain polycarbonates, we chose to investigate catalysts containing biocompatible and nontoxic metals, starting with magnesium, zinc, and aluminum. Additionally, magnesium and zinc have demonstrated activity as copolymerization catalysts.\textsuperscript{[16,25-27]} Aluminum has not been widely used in this type of catalysis, although it was Inoue who first developed a homogeneous Al-porphyrin system capable of copolymerizing CO\textsubscript{2} and CHO into poly(cyclohexene carbonate) with narrow weight distributions (PDI 1.06) at 50 atm pressure CO\textsubscript{2}.\textsuperscript{[31]} It was our thinking that by including aluminum to our arsenal, we may develop catalyst systems where tuning of the Lewis acidity of the catalyst can include cationic species, as seen in polyolefin catalysis.\textsuperscript{[32]}

Design requirements for the ancillary ligand include being multidentate, monovalent (for divalent metal systems) and to also provide relative ease in tuning steric and electronic properties. Overall, frameworks that provide access to an open coordination site at the metal center are preferable. Also, it needs to be kept in mind that an anion is required to act as an initiator. Previous studies have found that amides,
alkoxides, carboxylates, and sulfinates\textsuperscript{18} act as good initiators in the catalysis, whereas alkyl and halide ligands are poor initiators.\textsuperscript{16} The utility of the initiating groups `O\textsubscript{2}CR, `OR', or `NR\textsubscript{2}` is thought to come from similar propagating species,\textsuperscript{16} following initiation, perhaps due to their similarity to putative intermediates formed, namely metal alkoxide or carbonate species.

This dissertation summarizes our work in the preparation, characterization, and, if applicable, catalytic performance of various magnesium, zinc, and aluminum metal complexes synthesized in our laboratory. Chapter 2 focuses on the preparation of metal complexes containing a heteroscorpionate ligand. Chapter 3 contains details on the preparation of metal complexes with a class of salen ligands. Work on attempts at isolating a heterobimetallic complex based on an ancillary macrocyclic ligand is detailed in Chapter 4. Chapter 5 highlights the design and synthesis of a new ligand family built around (phosphinimino/phosphorano)methane units containing a phenylene bridge, as well as the preparation and isolation of various metal complexes containing magnesium, zinc, and aluminum.

1.4 References


CHAPTER 2:
ZINC AND MAGNESIUM HETEROSCORPIONATE COMPLEXES

2.1 Introduction

One particularly interesting class of nitrogen-donor ligands are the scorpionates, such as the poly(azolyl)borates and poly(azolyl)alkanes. First introduced in 1967 by Trofimenko,[1] the tris(pyrazolyl)hydroborates, \([\text{HB(pz)}_3]\)\(^{-}\) (pz = pyrazole), have been used to form complexes with most metals on the periodic table, and has thus become one of the most widely exploited class of ligands in coordination chemistry.[2] Similarly, by replacing the \([\text{BH}]^{-}\) anionic moiety with an isoelectronic CR group, the tris(pyrazolyl)methanes, and corresponding anionic methanides, have also been widely explored. These ligand classes have been referred to as scorpionates (or homoscorpionates, as each coordinating moiety is the same).

By replacing one coordinating moiety for another, the heteroscorpionates, having the general formula of \([\text{RR'}B(pz)_2]^{-}\) or \([\text{RR'C(pz)}_2]\), have become a widely-studied ligand class. In particular, the heteroscorpionate ligands derived from bis(pyrazol-1-yl)methane, \([\text{RR'C(pz)}_2]\), have found application in both transition and main group metal coordination chemistry.[3] These ligands can be sterically and electronically tuned and can bear a wide variety of anionic donor groups, such as, alkoxides, aryloxides, carboxylates, and cyclopentadienyl, just to name a few. Metal complexes containing this
ligand class are, in general, facially capped by the tridentate ligand in a $\kappa^3-N,N',X$ fashion (where $X = C, N, O, S,$ etc).

Bis(pyrazolyl)methanes have been prepared through various routes. One route involves preparing $N,N'$-methylenebis(pyrazolyl) systems and then subsequent introduction of a third donor moiety at the methylene bridge. Another route uses a bis(pyrazolyl)ketone intermediate, obtained by reaction of phosgene and pyrazolate, which is reacted with a compound containing the third coordinating moiety.$^4$ Finally, an alternative route using thionyl chloride provides a strategy for one-pot syntheses of bis(pyrazolyl)methane heteroscorpionates, where a wide scope of these ligands can be prepared by reaction of substituted pyrazoles and choice of aldehyde in high yields. This method involves reaction of pyrazolate, formed by deprotonation of the parent pyrazole with a base, such as NaH, and SOCl$_2$, forming a sulfoxide intermediate. This intermediate is then reacted with an aldehyde in the present of a catalytic amount of cobalt(II) chloride, forming the desired heteroscorpionate ligands in yields up to 90% (Scheme 2.1).$^5$

![Scheme 2.1. General synthesis of bis(pyrazolyl)methane heteroscorpionate ligands using SOCl$_2$.](image)

My work began by exploring the use of heteroscorpionate-based metal complexes, specifically the (bis(pyrazol-1-yl)methyl)phenolates (Figure 2.1). Magnesium
and zinc complexes utilizing this ligand framework have shown to be catalytically active in the ring-opening polymerization of cyclic esters, but have not been reported to be used in the copolymerization of CO₂ and epoxides. Other complexes utilizing Cr³⁺, Sc³⁺, Y³⁺, Ti⁴⁺, and Zr⁴⁺ centers have been successfully used in ethylene polymerization reactions. Our initial thinking was that this heteroscorpinate framework could possibly provide a hemilabile donor group in the phenoxide moiety to provide an open coordination face. This is due to the formation of a 7-membered ring between the metal and the ligand through the phenoxide oxygen, unlike the tris(pyrazolyl)methanes and boranes, which form three 6-membered rings upon coordination with the metal center.

We considered this ligand framework as a good place to start in making mononuclear metal complexes with magnesium and zinc. Systematic variation of the substituents on the pyrazole and phenol rings should be straightforward from a synthetic standpoint and would provide a handle on studying how steric bulk affects metal binding, as well as catalytic activity.

![Figure 2.1. Heteroscorpionate ligand based on 2-(bis(3,5-disubstitutedpyrazolyl)methyl)phenol.](image-url)
2.2 Synthesis of HOPz ligand

We initially began this work with looking at a simple heteroscorpionate ligand based on 3,5-dimethylpyrazole and salicylaldehyde. The ligand 2-(bis(3,5-dimethyl-1H-pyrazol-1-yl)methyl)phenol (HOPz) was synthesized via a modified literature procedure[6] (Scheme 2.2) in moderate yield (63%).

![Scheme 2.2. Synthesis of HOPz.](image)

2.3 Synthesis of M(OPz)X Complexes

With the simple HOPz ligand in hand, we began metalation experiments by two different methods high throughput of metal complex preparation by combining the ligand, choice of divalent metal salt and a base, such as sodium methoxide, or by using a strong magnesium or zinc base. Both approaches are described below.
2.3.1 Complex Formation via High Throughput Methods

Scheme 2.3. High throughput synthesis of OPz metal complexes.

Metallation of HOPz was attempted using a variety of metal salts, bases, and solvents. For example, in a 1:1:1 stoichiometric ratio, 0.2 mmol HOPz, sodium methoxide, and a divalent metal salt (CoCl$_2$·6H$_2$O, MgCl$_2$, MgOAc$_2$·4H$_2$O, ZnCl$_2$, ZnOAc$_2$, CaOAc$_2$·H$_2$O) were heated in 10 mL methanol in an oven at 70 °C for 3 days. The formation of insoluble solid precipitates precluded characterization by NMR spectroscopy. The same metallation reactions were repeated by replacing sodium methoxide with triethylamine. This resulted in the formation of unidentifiable products. Next, the solvent was altered, utilizing ethanol or acetonitrile instead. Again, the resulting solid precipitates were insoluble in common NMR solvents.

By heating the reaction mixtures in an oil bath, instead of in an oven, microcrystalline products formed from methanol solutions that were insoluble in common NMR solvents. However, two zinc complexes, [Zn(OPz)$_2$]ZnCl$_2$ and [Zn(OPz)Br], shown in Scheme 2.4, were isolated as crystalline solids and were thus characterized by single crystal X-ray diffraction.
Scheme 2.4. Preparation of [Zn(OPz)₂]ZnCl₂ and [Zn(OPz)Br] complexes via solvothermal methods.

[Zn(OPz)₂]ZnCl₂ crystallizes as a dinuclear complex in which two zinc centers exhibit octahedral and tetrahedral coordination environments, respectively (Figure 2.2 and Figure 2.3). One zinc center, Zn₁, is bisligated in an octahedral fashion, each tridentate ligand facially coordinated through the pyrazole nitrogens and phenolate oxygen in a κ³-N,N',O fashion. The Zn₁-O₁ bond length is 2.1041(11) Å, Zn₁-N₁ being 2.1233(13) Å, and Zn₁-N₄ 2.1685(13) Å. Bond angles around the zinc center show a distorted octahedron with the O₁-Zn₁-O₁' angle at 76.56(6)°. Other angles in the same N₁,O₁,O₁',N₁' plane are ~91°. The angle of N₄-Zn₁-N₄' is 167.37(4)°. The second zinc center, Zn₂, is tetrahedrally coordinated to the phenolate oxygen atoms (Zn₂-O₁: 1.9736(10) Å) and two chloride atoms (Zn₂-Cl₁: 2.2243(5) Å). Zn₂ is a distorted tetrahedron with the following bond angles, in degrees: O₁-Zn₂-Cl₁: 117.15(3), O₁-Zn₂-O₁': 82.67(6), O₁-Zn₂-Cl₁': 110.78(3), Cl₁-Zn₂-Cl₁':114.62(3). The two zinc centers sit near one another with a distance of 3.1336(4) Å. There is one molecule of methanol that is disordered across a 2-fold rotation axis. After difficulty modelling the disorder, the solvent electron density was removed by using the SQUEEZE[7] routine in PLATON[8].
overall structure is isostructural to a cobalt(II) complex reported by Grassi and coworkers in 2011.[9]

Figure 2.2. Structure of [Zn(OPz)$_2$]ZnCl$_2$ (top). Atomic displacement ellipsoids drawn at 50% probability level. Solvent and most H atoms omitted for clarity. Zn (light grey), O (red), N (blue), C (dark grey), and Cl (green).
Figure 2.3. Coordination environment of [Zn(OPz)₂]ZnCl₂ (top). Atomic displacement ellipsoids drawn at 50% probability level. Solvent, most H atoms, and ring moieties omitted for clarity. Zn (light grey), O (red), N (blue), C (dark grey), and Cl (green).

Zn(OPz)Br crystallizes as a tetrahedral zinc center coordinated by the OPz ligand in a κ³-N,N',O fashion (Zn1-O1: 1.919(2) Å, Zn1-N2: 2.0151(16) Å) with a Br atom (Zn1-Br1: 2.3093(7) Å) completing the coordination sphere (Figure 2.4). Bond angles around Zn1 show a distorted tetrahedron with O1-Zn1-Br1: 115.48(6)°, O1-Zn1-N2: 100.46(6)°, N2-Zn1-Br1: 122.45(5)°, N2-Zn1-N2': 90.40(9)°.
2.3.2 via Alkyl Metal Reagents

Alternatively, by using alkyl metal reagents, other zinc and magnesium complexes were prepared. Reaction of one equivalent of ZnEt₂ with HOPz in toluene or THF at room temperature afforded Zn(OPz)Et as an off-white solid in 75% isolated yield. The ¹H NMR spectrum in CDCl₃ shows an upfield shift of the methine and aromatic proton signals. The ethyl moiety can be seen with a triplet centered at δ 1.37 ppm and a quartet at δ 0.45 ppm, integrating to 3H and 2H, respectively.
Scheme 2.5. Reaction of HOPz with one equivalent of ZnEt$_2$ in toluene affords Zn(OPz)Et.

Crystals suitable for single crystal X-ray diffraction were grown by diffusion of hexane into a toluene solution. The asymmetric contains two molecules of Zn(OPz)Et, which are conformational isomers. One molecule shows the ethyl group as *anti* to the phenoxide O, while the other *gauche*.

In the *anti* isomer (Figure 2.6, top), a tetrahedral zinc center, Zn1, is coordinated by the OPz ligand in a $\kappa^3$-N,N',O fashion (Zn1-O1: 1.958(2) Å, Zn1-N2: 2.065(2) Å, Zn1-N4: 2.064(2) Å) and an ethyl group (Zn1-C18 1.973(3) Å). The ethyl group is *anti* to the phenoxide O at 178.82(1) degrees. Bond angles (in degrees) around Zn1 show a distorted tetrahedron with N2-Zn1-N4 87.99(9), O1-Zn1-N2 95.60(9), O1-Zn1-N4 95.84(9), O1-Zn1-C18 122.69(10), C18-Zn1-N2 124.14(11), and C18-Zn1-N4 122.00(11).

In the *gauche* isomer (Figure 2.6, bottom), a tetrahedral zinc center, Zn2, is coordinated by the OPz ligand in a $\kappa^3$-N,N',O fashion (Zn2-O2: 1.9527(19) Å, Zn2-N6: 2.077(2) Å, Zn2-N8: 2.060(2) Å) and an ethyl group (Zn2-C37 1.974(3) Å). The ethyl group is *gauche* to the phenoxide O at -37.77(1) degrees. Bond angles (in degrees) around Zn1
show a distorted tetrahedron with N6-Zn2-N8 85.48(9), O2-Zn2-N6 94.80(9), O2-Zn2-N8 98.28(9), O2-Zn2-C37 119.07(10), C37-Zn2-N6 125.29(12), and C37-Zn2-N8 125.40(11).

Figure 2.5. Asymmetric unit of Zn(OPz)Et. Atomic displacement ellipsoids drawn at 50% probability level. Zn (light grey), O (red), N (blue), and C (dark grey). Most H atoms omitted for clarity. One molecule shows the ethyl group as *anti* to the phenoxide O, while the other *gauche*. 
Protonolysis of Zn(OPz)Et with 1 equivalent of acetic acid affords the zinc acetate complex, Zn(OPz)OAc as a yellow solid in 64% yield. Most notably in the $^1H$ NMR spectrum is the disappearance of the ethyl signals and the appearance of a new singlet integrating to 3H at $\delta$ 2.18 ppm. Attempts at growing quality crystals for X-ray
diffraction experiments have thus far failed. Also, subsequent attempts to replicate these results have failed.

![Scheme 2.6. Synthesis of Zn(OPz)OAc via protonolysis of Zn(OPz)Et with one equivalent of acetic acid.]

By reacting HOPz with 1 equivalent of \(^n^\text{Bu}_2\text{Mg}\) in toluene, followed by addition of 1 equivalent acetic acid affords a homoleptic bisligated species, Mg(OPz)$_2$ (Scheme 2.7).

![Scheme 2.7. Synthesis of bisligated Mg complex, Mg(OPz)$_2$.]

Crystals suitable for XRD analysis were grown from slow evaporation of a dichloromethane solution. The crystal structure shows an octahedral homoleptic magnesium center bisligated by two OPz$^-$ ligands, coordinated in a $\kappa^3$-N,N',O fashion, as shown in Figure 2.7. A truncated view of the coordination environment of the
magnesium center is offered in Figure 2.8 for clarity. The Mg1-O1 bond is 1.9755(19) Å.
Both Mg1-N2 and Mg1-N4 bonds are 2.206(2) Å. Bond angles around Mg1 are listed as follows (in degrees): O1-Mg1-O1’: 180.00(15), O1-Mg1-N2: 89.61(8), O1-Mg1-N4: 89.57(8), N2-Mg1-N4: 81.27(8). Also in the asymmetric unit are one molecule of dichloromethane and one molecule of THF.

Figure 2.7. Structure of Mg(OPz)$_2$. Atomic displacement ellipsoids drawn at 50% probability level. Mg (light green), O (red), N (blue), C (dark grey), and Cl (green) Solvent and most H atoms omitted for clarity.
An alternate route to the bisligated Mg complex involves reacting one equivalent of Mg\([\text{N(TMS)}_2]\)\_2 with the sodium salt, NaOPz, formed in situ by deprotonation of the ligand by sodium hydride in THF solution. Attempts at isolating the heteroleptic magnesium bis(trimethylsilyl)amide complex have failed thus far. Even reaction of one equivalent of Mg\([\text{N(SiMe}_3]_2\)\_2 with HOPz affords the homoleptic bisligated Mg heteroscorpionate complex.
Scheme 2.8. Reaction of Mg[N(TMS)₂]₂ with NaOPz in THF solution affords bisligated Mg(OPz)₂.

2.4 Copolymerization of CO₂ and cyclohexene oxide

[Zn(OPz)₂]ZnCl₂ and Zn(OPz)Br were tested for their catalytic activity. By reacting the metal complex (1 mol% catalyst loading) in neat cyclohexene oxide in a Schlenk tube under 1 atm CO₂ at 80 °C (Scheme 2.9), some polymer was formed.

Scheme 2.9. Copolymerization of CHO and CO₂ under 1 atm CO₂ at 80 °C.

Unfortunately, these complexes proved to be poor catalysts in the copolymerization of CO₂ and CHO with low conversion of epoxide (~5%) to a 2:1:1 ratio of polyether/cyclic carbonate/polycarbonate, as determined by ¹H NMR spectroscopy.

On reflection, the coordination geometry of the OPz complexes provides a facially capped metal center through κ³-N,N',O donors. This does not provide an open face, nor does the phenoxide appear to be hemilabile as we had initially envisioned.
Additionally, as noted in the \([\text{Zn(OPz)}_2]\text{ZnCl}_2\) crystal structure, bisligation of the Zn center with two \(~\text{OPz}~\) ligands to form the homoleptic six-coordinate sandwich complex is quite facile, even when steric bulk is added at the \textit{ortho}- position (such as \textit{tert}-butyl groups) of the phenolate ring,\(^3\) leaving the metal center coordinatively saturated and inaccessible for substrate binding. Additionally, Coates and coworkers found that halide ligands are poor initiators in the copolymerization of CO\(_2\) and epoxides.\(^{10}\)

2.5 Conclusions

By using the tridentate HOPz ligand, one magnesium and four zinc complexes have been prepared. Bisligated magnesium and zinc centers readily form due to the lack of steric bulk about the HOPz ligand. Other groups have also had little success in forming heteroleptic magnesium heteroscorpionates, even with bulky substituents on the phenol ring, often isolating the bisligated magnesium complex, with the heteroleptic complex as a minor product.\(^6\)

\([\text{Zn(OPz)}_2]\text{ZnCl}_2\) and \(\text{Zn(OPz)Br}\) were screened for catalytic activity in the copolymerization of CO\(_2\) and CHO at 1 atm CO\(_2\) and 1 mol\% catalyst loading. Both behaved as poor catalysts for polycarbonate formation. This may be due to several factors as mentioned above. Thus, we abandoned the heteroscorpionate complexes in search of a more suitable system.
2.6 Experimental

2.6.1 General Procedures

All manipulations were carried out using either standard Schlenk techniques under a nitrogen atmosphere or in an argon-filled glovebox. All glassware was flame-/oven-dried prior to use. Toluene, tetrahydrofuran (THF), hexane, and diethyl ether were degassed and purified by passage through a solvent purification system (Innovative Technology). Thionyl chloride (Alfa Aesar) and salicylaldehyde (Acros) were used as received. Cyclohexene oxide (CHO, Alfa Aesar) was distilled from CaH₂ under reduced pressure prior to use. Sodium hydride (60% dispersion in oil) was washed with hexane three times and dried under vacuum prior to use. n-Butyllithium (nBuLi, 2.5 M in hexanes), di-n-butylmagnesium (nBu₂Mg, 1.0 M in heptane), and diethylzinc (ZnEt₂, 1.0 M in hexanes) were purchased from Sigma-Aldrich and were standardized by titration against salicylaldehyde phenylhydrazone in dry THF prior to use.¹¹ 3,5-dimethylpyrazole and 3,5-diphenylpyrazole were synthesized according to modified literature procedures.¹² Chloroform-d (CDCl₃) was purchased from Cambridge Isotope Laboratories (CIL, Tewksbury, MA) and were degassed via several freeze-pump-thaw cycles and dried by storing over 4 Å molecular sieves. ¹H and ¹³C spectra were recorded on a Bruker AVANCE III HD 400 or Bruker AVANCE III HD 500 spectrometer at 293K and were referenced internally to the residual signals of the deuterated solvent.
2.6.2 X-ray crystallography

Single crystals were examined under Paratone-N oil. The datum crystals were affixed to a Mitegen mounting loop and transferred to a 120K nitrogen stream of a Bruker Kappa or Bruker APEX-II diffractometer, equipped with an Oxford Cryostream 700 series low-temperature apparatus. Cell parameters were refined using reflections harvested from data collection with I ≥ 10σ(I). All data were corrected for Lorentz and polarization effects, and runs were scaled using SADABS. Structure solution was by either direct or Patterson methods and refined by full-matrix least-squares analysis of $F^2$ against all reflections. Olex2 was used for structure visualization. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen atoms on carbons were placed at calculated geometries and allowed to ride on the position of the parent atom. Hydrogen thermal parameters were set to 1.2 (1.5 for methyl) times the equivalent isotropic $U$ of the parent atom. Where warranted, reflection intensities were corrected for solvent contribution through the SQUEEZE routine in PLATON. Mercury was used for structure visualization and analysis, as well as creation of figures.

2.6.3 Ligand Synthesis

2.6.3.1 Synthesis of HOPz

Modified from a literature procedure: A Schlenk flask was charged with a solution of 3,5-dimethylpyrazole (4.8g, 50 mmol) in THF (200 mL) under N$_2$ atmosphere. The clear, colorless solution was cooled to 0 °C where n-butyllithium (22.0 mL, 2.5M, 55
mmol) was added slowly, resulting in evolution of butane. The pale yellow solution was allowed to stir at 0 °C for 30 minutes before dropwise addition of thionyl chloride, followed by an additional hour of stirring at 0 °C. The dark yellow solution was slowly warmed to room temperature, turning clear orange. Salicylaldehyde (2.7 mL, 25 mmol) and CoCl$_2$ (0.325 g, 2.5 mmol) was added, and the solution was refluxed overnight. Once the blue-green solution had cooled to room temperature, 150 mL water and 50 mL ether were added and the biphasic solution was stirred for 1 h. The layers were separated and the aqueous layer was extracted with ether (2 x 50 mL), the organic layers were combined and washed with water (2 x 50 mL), saturated brine (50 mL), and then dried over MgSO$_4$. Volatiles were removed via rotary evaporation, yielding an off-white solid. Yield: 4.7 g, 63%. $^1$H NMR (400 MHz, CDCl$_3$) δ 10.20 (bs, 1H), 7.33 (s, 1H), 7.21 (m, J = 2.8 Hz, 1H), 6.99 (dd, J = 1.5, 7.7 Hz, 1H), 6.88 (d, J = 8.1 Hz, 1H), 6.82 (dt, J = 1.0, 7.5 Hz, 1H), 5.84 (s, 2H), 2.18 (s, 6H), 2.12 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 155.82, 148.53, 140.64, 131.09, 130.17, 122.24, 119.86, 119.03, 107.27, 73.73, 13.87, 11.44.

2.6.4 Metalation of HOPz

2.6.4.1 Synthesis of [Zn(OPz)$_2$]ZnCl$_2$

In a 20 mL scintillation vial, 10 mL methanol was added to HOPz (60 mg, 0.2 mmol), NaOMe (11 mg, 0.2 mmol), and ZnCl$_2$ (27 mg, 0.2 mmol). The vial was sealed with a Teflon-lined cap and placed in an oil bath at 70 °C for 1 day. Colorless needles. 68 mg, 86% yield.
2.6.4.2 Synthesis of Zn(OPz)Br

In a 20 mL scintillation vial, 10 mL methanol was added to HOPz (60 mg, 0.2 mmol), NaOMe (11 mg, 0.2 mmol), and ZnBr₂ (45 mg, 0.2 mmol). The vial was sealed with a Teflon-lined cap and placed in an oil bath at 70 °C for 1 day. Colorless needles formed. 82 mg, 93% yield.

2.6.4.3 Synthesis of Zn(OPz)Et

HOPz (148.2 mg, 0.5 mmol) was suspended in 10 mL toluene. ZnEt₂ (0.55 mL, 0.55 mmol) was added dropwise via syringe at room temperature and the yellow solution was stirred for 3 h, after which an off-white solid precipitated. The solid was isolated by filtration, washed with hexanes, and dried under vacuum. 147 mg, 75% yield.

\(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.13 (m, 1H), 6.99 (d, \(J = 7.5\) Hz, 1H), 6.98 (d, \(J = 7.5\) Hz, 1H), 6.87 (s, 2H), 6.82 (dd, \(J = 1.3, 8.3\) Hz, 1H), 6.39 (m, 1H), 5.91 (s, 1H), 2.45 (s, 6H), 2.33 (s, 6H), 1.37 (t, \(J = 8.1\) Hz, 3H), 0.45 (q, \(J = 8.1\) Hz, 2H). \(^1\)C NMR (101 MHz, CDCl₃) \(\delta\) 166.65, 150.18, 140.05, 132.33, 130.82, 124.71, 120.86, 112.78, 106.71, 73.15, 13.32, 12.98, 11.73, -2.27. HRMS (ESI-MS) m/z calc. for C\(_{19}\)H\(_{25}\)N\(_4\)OZn M+H 389.1314, found 389.1329.

2.6.4.4 Synthesis of Zn(OPz)OAc

HOPz (148.2 mg, 0.5 mmol) was suspended in 10 mL toluene. ZnEt₂ (0.55 mL, 0.55 mmol) was added dropwise via syringe at room temperature and the yellow solution was stirred for 3 h, after which an off-white solid precipitated. Acetic acid (30 μL, 0.55 mmol) was added and the solution was stirred at reflux for 2 h. Upon cooling to
room temperature, a yellow solid precipitated out. The solid was isolated by filtration and dried under vacuum. 135 mg, 64% yield. $^1$H NMR (500 MHz, CDCl$_3$) δ ppm 7.16 (t, $J$=7.58 Hz, 1 H) 6.98 (d, $J$=7.09 Hz, 1 H) 6.94 (s, 1 H) 6.90 (d, $J$=8.07 Hz, 1 H) 6.44 (t, $J$=6.97 Hz, 1 H) 5.95 (s, 1 H) 2.47 (s, 6 H) 2.34 (s, 6 H) 2.18 (s, OAc, 3 H).

2.6.4.5 Synthesis of Mg(OPz)$_2$

HOPz (148.2 mg, 0.5 mmol) was suspended in 10 mL toluene $^8$Bu$_2$Mg (0.55 mL, 0.55 mmol) was added dropwise via syringe at room temperature. After 2 h, acetic acid (30 μL, 0.55 mmol) was added to the clear yellow solution. The solution was stirred at reflux for 2 h. Upon cooling to room temperature, a yellow solid precipitates out. The supernatant was removed via cannula and the solid was dried under vacuum. 136 mg, 88% yield (based on OPz$^-$). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.13 (dd, $J$= 3.0 Hz, 1H), 7.09 (m, $J$ = 4.3 Hz, 1H), 6.98 (s, 1H), 6.60 (d, $J$ = 8.1 Hz, 1H), 6.32 (t, $J$ = 6.7 Hz, 1H), 5.80 (s, 2H), 2.45 (s, 6H), 1.96 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 167.53, 150.08, 139.37, 131.70, 130.28, 123.46, 122.60, 110.22, 106.56, 73.41, 13.40, 12.08.

2.6.4.6 Representative procedure for copolymerization reactions

Cyclohexene oxide (5 mL, 50 mmol) and catalyst (0.05 mmol) were placed in a Schlenk tube. The reaction mixture was degassed, placed under 1 atm CO$_2$ pressure, and heated to 80 °C with vigorous stirring. After 6 h, the reaction was quenched by exposing the reaction mixture to air. Conversion of CHO to polymer was determined by recording a $^1$H NMR spectrum of the crude reaction mixture. Unreacted CHO was removed under
vacuum. The residue was extracted with CH$_2$Cl$_2$ and precipitated out by addition of methanol.

2.7 References


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CHAPTER 3:

MAGNESIUM, ZINC, AND ALUMINUM COMPLEXES BASED ON SALEN LIGANDS

3.1 Introduction

One of the most investigated homogenous systems for the copolymerization of CO₂ and epoxides is the salen system.[1] "Salen" is the collective term used in the literature for salicylaldimine type ligands, with the parent salen ligand as the Schiff based formed by condensation of salicylaldehyde (sal) and ethylenediamine (en).[2]

![Figure 3.1 "Jacobsen's catalyst" used by Darensbourg and coworkers in the copolymerization of CO₂ and epoxides.](image)

Work with using chromium(III) salen complexes began in 2000 by Darensbourg and coworkers, after inspiration by Jacobsen and coworkers’ use of chiral Cr(III) catalysts for the asymmetric ring opening of meso epoxides.[3] By using “Jacobsen’s catalyst”, shown in Figure 3.1, in the presence of N-methylimidazole (N-MeIm), CO₂ and cyclohexene oxide (CHO) could be copolymerized to form poly(cyclohexene carbonate). Without cocatalyst, (salen)CrCl forms poly(cyclohexene carbonate) at 80 °C and 58.5 bar
pressure CO₂ with a TON of 683 and TOF of 28.5 h⁻¹. Addition of N-Melm increased the activity up to TOFs of 88.2 h⁻¹ with 5 equivalents of cocatalyst.⁴ Around the same time, Nguyen and coworkers prepared other (salen)CrCl complexes, employing different diamines in the backbone of the ligand, to efficiently prepare cyclic carbonates from CO₂ and epoxides in the presence of (4-dimethylamino)pyridine (DMAP).⁵

Using the same (salen)CrCl catalyst, Daresnbourg also investigated the copolymerization of CO₂ and propylene oxide (PO) to form poly(propylene carbonate) (PPC). In the presence of various phosphine or bis(triphenylphosphine)iminium chloride (PPNCl) cocatalysts, TOFs of around 200 h⁻¹ could be reached.⁶

Switching the metal center to Co(III), Coates and coworkers found that (salen)CoOAc (Figure 3.1, M = CoOAc) copolymerized CO₂ and PO to form PPC at 25 °C and 55 bar pressure CO₂ with TOFs up to 59 h⁻¹.⁷

Aluminum-based salen metal complexes (Figure 3.2) prepared by Lu and coworkers in 2004 coupled CO₂ with various epoxides to form cyclic carbonates at 25 °C and 0.6 MPa pressure CO₂ in the presence of a quaternary ammonium halide cocatalyst.⁸

![Figure 3.2 Aluminum-based salen complexes used by Lu and coworkers to prepare cyclic carbonates.](image-url)
Darensbourg performed mechanistic studies using in situ IR spectroscopy, to examine how (salen)CrCl complexes form polycarbonates from CO$_2$ and epoxides. These studies indicated in the presence of a cocatalyst, the chain propagation step (copolymer formation) was first-order in metal catalyst and epoxide concentrations with 2 equivalents of cocatalyst, relative to catalyst loading. Without cocatalyst, the copolymer is still formed with a first-order dependence on catalyst concentration, however at a reduced rate as mentioned above.$^{[4]}$ The mechanism proposed by Darensbourg is shown in Scheme 3.1.

Where transition metal salen complexes have been investigated in this field, our work began by investigating the effect magnesium and zinc metal centers would have on the copolymerization of CO$_2$ and cyclohexene oxide using salen ligand class as a framework.
Scheme 3.1 Proposed mechanism of copolymerization of CO$_2$ and epoxides by (salen)CrCl complexes. Adapted from ref 4.
3.2 Ligand synthesis

The salen-type ligand systems are attractive since a wide range of ligands can easily and efficiently prepared and their coordination chemistry can be modified to meet the requirements for catalysis.\cite{5} Catalyst steric and electronic properties can be tuned by the choice of diamine or salicylaldehyde derivatives used in the construction of the ligands.

During this work, we utilized five known salen-type ligands using a variety of salicylaldehyde derivatives and two diamines. The details of their syntheses are described below.

Scheme 3.2. General synthesis of ligands 3.1-5.
3.2.1 Synthesis of 3.1

![Scheme 3.3 Synthesis of 3.1.](image)

3.1 was synthesized using a modified literature procedure by reacting two equivalents of salicyaldehyde with one equivalent o-phenylenediamine in a methanol solution heated at reflux for 30 minutes. An orange solid precipitated and was isolated by filtration, with a yield of 94%. The $^1$H NMR spectrum agrees with reported literature values.$^9$

3.2.2 Synthesis of 3.2

![Scheme 3.4 Synthesis of 3.2.](image)
3.2 was synthesized using a modified literature procedure by reacting two equivalents of 2-hydroxybenzaldehyde (o-vanillin) with one equivalent o-phenylenediamine in a methanol solution heated at reflux for 30 minutes. An orange-red solid precipitated and was isolated by filtration, with a yield of 90%. The $^1$H NMR spectrum agrees with reported literature values.\cite{10}

3.2.3 Synthesis of 3.3

$\text{3.3}$ was synthesized using a modified literature procedure by reacting two equivalents of 3,5-di-tert-butyl-2-hydroxybenzaldehyde with one equivalent o-phenylenediamine in a methanol solution heated at reflux for two hours. A yellow solid precipitated and was isolated by filtration, with a yield of 85%. NMR data matches literature values.\cite{11}

Scheme 3.5 Synthesis of 3.3.
3.2.4 Synthesis of 3.4

3.4 was synthesized using a modified literature procedure by reacting two equivalents of salicylaldehyde with one equivalent 2,2-dimethyl-1,3-propanediamine in a methanol solution. A yellow solid precipitated and was isolated by filtration, with a yield of 81%. In the $^1$H NMR spectrum in CDCl$_3$, the phenolic protons appear as a singlet at 13.55 ppm. The imine protons come in at 8.34 ppm as a singlet, integrating to two protons. The methylene protons appear as a singlet at 3.49 ppm and the methyl groups appear as a singlet 1.08 ppm.
3.2.5 Synthesis of 3.5

![Scheme 3.7 Synthesis of 3.5.](image)

3.5 was synthesized using a modified literature procedure by reacting two equivalents of 3,5-di-tert-butyl-2-hydroxybenzaldehyde with one equivalent 2,2-dimethyl-1,3-propanediamine in a methanol solution heated at reflux for two hours. A yellow solid precipitated and was isolated by filtration, with a yield of 81%. In the $^1$H NMR spectrum in CDCl$_3$, the phenolic protons appear at 13.85 ppm. The imine protons appear at 8.37 ppm. The methylene protons appear at 3.48 ppm and the methyl groups appear as a singlet at 1.10 ppm. Two tert-butyl environments are noted, with singlets appearing at 1.47 and 1.10 ppm.

3.3 Preparation of Mg, Zn, and Al-R (R = Me or Et) complexes

With five ligands in hand, the corresponding magnesium, zinc, and alkylaluminum (alkyl = methyl or ethyl) complexes were prepared.
3.3.1 Metal complexes of 3.1

3.3.1.1 Synthesis of 3.1-Mg

One equivalent of di-n-butylmagnesium was reacted with one equivalent of 3.1 in toluene at room temperature. After two hours, volatiles were removed under reduced pressure, affording 3.1-Mg as an orange solid in 91% yield. In the $^1$H NMR spectrum in DMSO-$d_6$, deprotonation of the ligand is apparent by the disappearance of the phenolic OH protons. The imine protons appear at 8.72 ppm. The aromatic protons appear in the range of 7.76 to 6.37 ppm with six separate sets of signals.
3.3.1.2 Synthesis of 3.1-Zn

One equivalent of diethyl zinc was reacted with one equivalent of 3.1 in toluene at room temperature. After two hours, volatiles were removed under reduced pressure, affording 3.1-Zn as a yellow solid in 85% yield. In the $^1$H NMR spectrum in DMSO-$d_6$, the imine protons appear at 9.01 ppm. Like 3.1-Mg, there are six sets of signals for the aromatic protons – two sets overlap – ranging from 7.90 to 6.51 ppm.
3.3.1.3 Synthesis of 3.1-AlEt

One equivalent of triethylaluminum was reacted with one equivalent of 3.1 in toluene at room temperature. After two hours, volatiles were removed under reduced pressure, affording 3.1-AlEt as a yellow solid in 60% isolated yield. In the $^1$H NMR spectrum in CDCl$_3$, the ethyl group signals for the AlCH$_2$CH$_3$ moiety appear as a quartet at -0.40 ppm (AlCH$_2$CH$_3$, $J = 8.26$ Hz) and a triplet (AlCH$_2$CH$_3$, $J = 8.06$ Hz). The imine protons appear as a singlet at 8.79 ppm. The aromatic protons appear in the range of 7.70-6.76 ppm and show symmetry equivalence, suggesting a 5-coordinate Al center with the ethyl group as an apical ligand. This agrees with literature.$^{[12]}$
3.3.2 Metal complexes of 3.2

3.3.2.1 Synthesis of 3.2-Mg

One equivalent of di-n-butylmagnesium was reacted with one equivalent of 3.2 in toluene at room temperature. After two hours, volatiles were removed under reduced pressure, affording 3.2-Mg as an orange solid in 93% yield. In the $^1$H NMR spectrum in DMSO-$d_6$, there appears to be two-fold symmetry. The imine protons appear at 8.71 ppm. The methoxy protons appear as a singlet at 3.74 ppm.
3.3.2.2 Synthesis of 3.2-Zn

One equivalent of diethyl zinc was reacted with one equivalent of 3.2 in toluene at room temperature. After two hours, volatiles were removed under reduced pressure, affording 3.2-Zn as an orange solid in 85% yield. In the $^1$H NMR spectrum in DMSO-$d_6$, like 3.2-Mg, there appears to be two-fold symmetry in the metal complex. The imine protons appear at 8.99 ppm and the methoxy protons appear as a singlet at 3.74 ppm.

3.3.2.3 Synthesis of 3.2-AlEt

Scheme 3.13 Synthesis of 3.2-AlEt.
One equivalent of triethylaluminum was reacted with one equivalent of 3.2 in toluene at room temperature. After two hours, volatiles were removed under reduced pressure, affording 3.2-AlEt as a yellow solid 95% yield. In the $^1$H NMR spectrum in CDCl$_3$, the ethyl group signals for the AlCH$_2$CH$_3$ moiety appear as a quartet at -0.36 ppm (AlCH$_2$CH$_3$, $J = 8.1$ Hz) and a triplet (AlCH$_2$CH$_3$, $J = 8.07$ Hz). The imine protons appear as a singlet at 8.79 ppm. The aromatic protons appear in the range of 7.66–6.71 ppm and show symmetry equivalence, suggesting a 5-coordinate Al center with the ethyl group as an apical ligand.

3.3.3 Metal complexes of 3.3

3.3.3.1 Synthesis of 3.3-Mg

Scheme 3.14 Synthesis of 3.3-Mg.

One equivalent of di-$n$-butylmagnesium was reacted with one equivalent of 3.3 in toluene at room temperature. After two hours, volatiles were removed under
reduced pressure, affording 3.3-Mg as a yellow solid in 83% yield. In the $^1$H NMR spectrum in DMSO-$d_6$, there appears to be two-fold symmetry. The imine protons appear at 8.84 ppm as a singlet. There are two tert-butyl environments, each appearing as singlets at 1.47 and 1.26 ppm, respectively.

3.3.3.2 Synthesis of 3.3-Zn

Scheme 3.15 Synthesis of 3.3-Zn.

One equivalent of diethyl zinc was reacted with one equivalent of 3.3 in toluene at room temperature. After two hours, volatiles were removed under reduced pressure, affording 3.3-Zn as a yellow solid in 86% yield. In the $^1$H NMR spectrum in DMSO-$d_6$, there appears to be two-fold symmetry. The imine protons appear at 9.03 ppm as a singlet. There are two tert-butyl environments, each appearing as singlets at 1.48 and 1.28 ppm, respectively. Other preparations of this complex are known in the literature,$^{[13]}$ including using a one-pot condensation-metalation that involves 3,5-di-tert-butylsalicylaldehyde, 1,2-phenylenediamine, and zinc acetate in methanol.$^{[14]}$
3.3.3.3 Synthesis of 3.3-AlMe

Scheme 3.16 Synthesis of 3.3-AlMe.

One equivalent of trimethylaluminum was reacted with one equivalent of 3.3 in toluene at room temperature. After two hours, volatiles were removed under reduced pressure, affording 3.3-AlMe as a yellow solid in 78% yield. In the $^1$H NMR spectrum in CDCl$_3$, the methylaluminum group appears as a singlet at -0.64 ppm. The salen ligand shows symmetric equivalence, with the imine protons appearing as a singlet at 8.82 ppm and four aromatic signals ranging from 7.71 to 7.17 ppm. This suggests the methyl group is the apical ligand of a five-coordinate aluminum center.
3.3.4 Metal complexes of 3.4

3.3.4.1 Synthesis of 3.4-Mg

One equivalent of di-n-butylmagnesium was reacted with one equivalent of 3.4 in toluene at room temperature. After two hours, volatiles were removed under reduced pressure, affording 3.4-Mg as a yellow solid in 80% yield. In the $^1$H NMR spectrum in DMSO-$d_6$, there appears to be two-fold symmetry. Most notably is the appearance of a singlet for the methylene protons at 3.46 ppm, integrating to four protons. The methyl group in the backbone appears as a singlet at 0.89 ppm, integrating to six protons.
3.3.4.2 Synthesis of 3.4-Zn

Scheme 3.18 Synthesis of 3.4-Zn.

One equivalent of diethyl zinc was reacted with one equivalent of 3.4 in toluene at room temperature. After two hours, volatiles were removed under reduced pressure, affording 3.4-Zn as a yellow solid in 84% yield. In the $^1$H NMR spectrum in DMSO-$d_6$, there appears to be two-fold symmetry. Most notably is the appearance of a singlet for the methylene protons at 3.48 ppm, integrating to four protons. The methyl group in the backbone appears as a singlet at 0.91 ppm, integrating to six protons.
3.3.4.3 Synthesis of 3.4-AlMe

Scheme 3.19 Synthesis of 3.4-AlMe.

One equivalent of trimethylaluminum was reacted with one equivalent of 3.4 in toluene at room temperature. After two hours, volatiles were removed under reduced pressure, affording 3.4-AlMe as an off-white solid in 98% yield. In the $^1$H NMR spectrum in CDCl$_3$, the methyl group bound to the aluminum center appears as a singlet at -0.80 ppm. The ligand shows symmetrically equivalent signals in the imine and aromatic protons. The methylene protons in the ligand backbone are diasterotopic, appearing as a doublet of doublets at 3.56 ppm ($J$=12, 242.8 Hz). The two methyl groups in the ligand backbone are also inequivalent, appearing each as singlets at 1.16 and 1.00 ppm. This is likely due to one methyl group being locked in position axial, and the other equatorial, to the Al-N-CH$_2$-C(Me)$_2$-CH$_2$-N ring.
3.3.5 Metal complexes of 3.5

3.3.5.1 Synthesis of 3.5-Mg

One equivalent of di-\textit{n}-butylmagnesium was reacted with one equivalent of 3.5 in toluene at room temperature. After two hours, volatiles were removed under reduced pressure, affording 3.5-Mg as a yellow solid in 81% yield. In the \textsuperscript{1}H NMR spectrum in DMSO-\textit{d}$_6$, there appears to be two-fold symmetry. Most notably is the appearance of a singlet for the methylene protons at 3.47 ppm, integrating to four protons. The methyl group in the backbone appears as a singlet at 0.93 ppm, integrating to six protons. Two tert-butyl environments appear as singlets at 1.43 and 1.22 ppm, each integrating to 18 protons.
Scheme 3.21 Synthesis of 3.5-Zn.

One equivalent of diethyl zinc was reacted with one equivalent of 3.5 in toluene at room temperature. After two hours, volatiles were removed under reduced pressure, affording 3.5-Zn as a yellow solid in 85% yield. In the \(^1\)H NMR spectrum in DMSO-\(d_6\), there appears to be two-fold symmetry. Most notably is the appearance of a singlet for the methylene protons at 3.45 ppm, integrating to four protons. The methyl group in the backbone appears as a singlet at 1.07 ppm, integrating to six protons. Two tert-butyl environments appear as singlets at 1.42 and 1.31 ppm, each integrating to 18 protons.
One equivalent of triethylaluminum was reacted with one equivalent of 3.5 in toluene at room temperature. After two hours, volatiles were removed under reduced pressure, affording 3.5-AlEt as a yellow solid in 77% yield. This compound is also known in the literature.\textsuperscript{[15-17]}

3.4 Copolymerization of CO\textsubscript{2} and cyclohexene oxide

These metal complexes were then tested for their catalytic activity. At 1 mol\% catalyst loading in neat epoxide at 80 °C for 6h under 1 atm CO\textsubscript{2}, CHO was converted to the polyether in low yield with scant amounts of polycarbonate formation, as determined by \textsuperscript{1}H NMR spectroscopy. Upon reflection, this may be considered unsurprising, due to the absence of a cocatalyst. Other salen systems utilizing Cr\textsuperscript{3+}, Co\textsuperscript{3+}, or Al\textsuperscript{3+} centers need the addition of a cocatalyst such as bis(triphenylphosphine)iminium chloride, [PPN]Cl in order to form polycarbonate.\textsuperscript{[18]}

Scheme 3.22 Synthesis of 3.5-AlEt.
Using [PPN]Cl with complex **3.3-Mg** at 1 mol% catalyst loading in neat CHO resulted in the formation of exclusively poly(cyclohexene carbonate) (as determined by $^1$H NMR spectroscopy), however, with only 0.15% conversion of the epoxide after 6 hours.

3.5 Conclusions

In this work, five salen ligands and their corresponding magnesium, zinc, and alkylaluminum complexes (alkyl = methyl or ethyl) were prepared. The $^1$H NMR spectra of the magnesium and zinc complexes show signals that suggest two-fold symmetry. The $^1$H NMR spectra of the aluminum complexes suggest five-coordinate aluminum centers, with the alkyl group as an apical ligand.

Screening the metal complexes for catalytic activity in the copolymerization of CO$_2$ and CHO resulted in low yields of polyether and scant amounts of polycarbonate formation. The lack of activity is perhaps due to slow initiation of epoxide ring opening, especially in the absence of a cocatalyst. Other salen systems utilizing Cr$^{3+}$, Co$^{3+}$, or Al$^{3+}$ centers need the addition of a cocatalyst such as bis(triphenylphosphine)iminium chloride [PPN]Cl, in order to form polycarbonate.$^{[18]}$ Addition of cocatalyst [PPN]Cl resulted in exclusive formation of polycarbonate, however, at very low conversion.
3.6 Experimental

3.6.1 General Procedures

All manipulations were carried out using either standard Schlenk techniques under a nitrogen atmosphere or in an argon-filled glovebox. All glassware was flame-/oven-dried prior to use. Toluene, tetrahydrofuran (thf), hexane, and diethyl ether were degassed and purified by passage through a solvent purification system (Innovative Technology). Di-n-butylmagnesium (\(n\)Bu\(_2\)Mg, 1.0 M in heptane), diethylzinc (ZnEt\(_2\), 1.0 M in hexanes) were purchased from Sigma-Aldrich and were standardized by titration against salicylaldehyde phenylhydrazone in dry THF prior to use.\(^{[19]}\) Triethylaluminum (AlEt\(_3\), 2.0 M in toluene) was purchased from Sigma-Aldrich and used as received. Salicylaldehyde (Alfa Aesar), o-vanillin (Alfa Aesar), o-phenylenediamine (Alfa Aesar), and 2,2-dimethyl-1,3-propanediamine (TCI) were used as received. 3,5-di-tert-butyl-2-hydroxybenzaldehyde was synthesized according to literature procedures.\(^{[20]}\) Deuterated solvents (chloroform-\(d\), methylene chloride-\(d_2\), benzene-\(d_6\), DMSO-\(d_6\)) were purchased from Cambridge Isotope Laboratories (CIL, Tewksbury, MA) and were degassed via several freeze-pump-thaw cycles and dried by storing over 4 Å molecular sieves. \(^1\)H and \(^{13}\)C spectra were recorded on a Bruker AVANCE III HD 400, Bruker AVANCE III HD 500, or Varian DirectDrive 600 spectrometer at 293K and were referenced internally to the residual signals of the deuterated solvent. Electrospray ionization (ESI) mass spectra were obtained using a Bruker microTOF-II mass spectrometer and the peaks reported are the mono-isotopic mass.
3.6.2 Ligand Synthesis

3.6.2.1 Synthesis of $\text{H}_2\text{L}^1$ (3.1)

Modified from a literature procedure\cite{9}: In a 50 mL Schlenk tube, o-phenylenediamine (20 mmol, 2.16 g) was dissolved in methanol (20 mL). Salicylaldehyde (40 mmol, 4.26 mL) was added and the yellow solution was heated to reflux for 30 min. An orange solid formed. The reaction mixture was cooled to room temperature and the precipitate was filtered, washed with diethyl ether, and dried in air. Yield: 5.95g (94%).

$^1\text{H}$ NMR (400 MHz, CDCl$_3$) $\delta$ 13.04 (bs, 2H), 8.64 (s, 2H), 7.36 (m, 6H), 7.24 (m, 2H), 7.05 (d, $J = 8.0$ Hz, 2H), 6.92 (m, $J = 3.2$ Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 163.87, 161.49, 142.71, 133.51, 132.47, 127.83, 119.88, 119.36, 119.11, 117.70.

3.6.2.2 Synthesis of $\text{H}_2\text{L}^2$ (3.2)

Modified from a literature procedure\cite{10}: In a 50 mL Schlenk tube, o-phenylenediamine (20 mmol, 2.16 g) was dissolved in methanol (20 mL). o-Vanillin (2-hydroxybenzaldehyde) (40 mmol, 4.26 mL) was added and the yellow solution was heated to reflux for 2 h. An orange-red solid formed. The reaction mixture was cooled to room temperature and the red-orange precipitate was filtered, washed with diethyl ether, and dried in air. Yield: 6.78g (90%). $^1\text{H}$ NMR (400 MHz, CDCl$_3$) $\delta$ 13.14 (s, 2H), 8.62 (s, 2H), 7.33 (m, 2H), 7.19 (m, 2H), 6.99 (m, 4H), 6.86 (t, $J = 7.9$ Hz, 2H), 3.90 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 164.37, 151.62, 148.57, 142.53, 127.57, 123.95, 120.42, 119.20, 118.49, 115.13, 56.18.
3.6.2.3 Synthesis of $\text{H}_2\text{L}^3 (3.3)$

In a 50 mL Schlenk tube, o-phenylenediamine (5 mmol, 0.54 g) was dissolved in methanol (20 mL). 3,5-di-tert-butyl-2-hydroxybenzaldehyde (10 mmol, 2.34 g) was added and the golden yellow solution was heated to reflux for 2 h. A yellow solid formed. The reaction mixture was cooled to room temperature and the precipitate was filtered, washed with diethyl ether, and dried in air. Yield: 2.30 g (85%). $^1\text{H}$ NMR (400 MHz, CDCl$_3$) $\delta$ 13.53 (s, 2H), 8.66 (s, 2H), 7.44 (d, $J = 2.2$ Hz, 2H), 7.32 (m, 2H), 7.23 (m, 4H), 1.44 (s, 18H), 1.32 (s, 18H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 164.72, 158.58, 142.77, 140.32, 137.20, 128.18, 127.30, 126.77, 119.81, 118.36, 35.12, 34.17, 31.47, 29.43.

3.6.2.4 Synthesis of $\text{H}_2\text{L}^7 (3.4)$

In a 50 mL Schlenk tube, salicylaldehyde (4.25 mL, 40 mmol) was dissolved in 20 mL methanol. 2,2-dimethyl-1,3-propanediamine (2.4 mL, 20 mmol) was added dropwise via syringe. After 5 minutes, a lemon-yellow solid precipitated, which was isolated by filtration. Yield: 5.03 g (81 %) $^1\text{H}$ NMR (400 MHz, CDCl$_3$) $\delta$ 13.55 (s, 2H), 8.34 (s, 2H), 7.32 (m, $J = 2.5$ Hz, 2H), 7.26 (q, $J = 3.1$ Hz, 2H), 6.97 (d, $J = 8.1$ Hz, 2H), 6.89 (m, $J = 3.2$ Hz, 2H), 3.49 (s, 4H), 1.08 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 165.75, 161.22, 132.33, 131.37, 118.74, 118.64, 116.98, 68.18, 36.27, 24.40.

3.6.2.5 Synthesis of $\text{H}_2\text{L}^4 (3.5)$

In a 50 mL Schlenk tube, 2,2-dimethyl-1,3-propanediamine (5 mmol, 0.6 mL) was dissolved in methanol (20 mL). 3,5-di-tert-butyl-2-hydroxybenzaldehyde (10 mmol, 2.34
g) was added and the yellow solution was heated to reflux for 2 h. A yellow solid formed. The reaction mixture was cooled to room temperature and the precipitate was filtered, washed with diethyl ether, and dried in air. Yield: 2.17 g (81%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 13.85 (s, 2H), 8.37 (s, 2H), 7.39 (d, \(J = 2.4\) Hz, 2H), 7.11 (d, \(J = 2.5\) Hz, 2H), 3.48 (d, \(J = 0.8\) Hz, 4H), 1.47 (s, 18H), 1.31 (s, 18H), 1.10 (s, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 166.76, 158.20, 139.99, 136.67, 126.90, 125.93, 117.87, 68.29, 36.34, 35.08, 34.14, 31.51, 29.45, 24.58.

3.6.3 Synthesis of metal complexes

3.6.3.1 Representative synthesis of metal complexes

3.n (n = 1-5) (1 mmol) was dissolved in 10 mL THF or toluene. Metal alkyl (\(n^\text{Bu}_2\)Mg, ZnEt\(_2\), AlMe\(_3\) or AlEt\(_3\)) (1.1 mmol) was added dropwise via syringe at room temperature. The solution was stirred for 2 h. Solvent was removed under reduced pressure and the solid residue was dried under vacuum overnight.

3.6.3.2 Synthesis of 3.1-Zn

Prepared following the representative synthesis procedure using 3.1 and ZnEt\(_2\). Yellow solid. Yield: 311 mg (82%). \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) ppm 9.01 (s, 2 H) 7.90 (dd, \(J=6.29, 3.54\) Hz, 1 H) 7.41-7.35 (m, 4H) 7.23 (m, 2H) 6.70 (d, \(J=8.26\) Hz, 1 H) 6.51 (t, \(J=7.08 \text{ Hz}, 1 \text{ H}\)). \(^{13}\)C NMR (101 MHz, DMSO) \(\delta\) 172.95, 163.53, 140.06, 136.93, 135.02, 127.94, 123.78, 120.12, 117.18, 113.65.
3.6.3.3 Synthesis of 3.1-Mg

Prepared following the representative synthesis procedure using 3.1 and n-Bu₂Mg. Orange solid. Yield: 310 mg (91%). ¹H NMR (400 MHz, DMSO-≤d₆) δ ppm 8.72 (s, 2 H) 7.76 (dd, J=5.90, 3.54 Hz, 2 H) 7.34 (dd, J=7.87, 1.97 Hz, 2 H) 7.29 (dq, J=6.29, 3.54 Hz, 2 H) 7.16 (ddd, J=8.65, 7.08, 1.97 Hz, 2 H) 6.56 (d, J=7.47 Hz, 2 H) 6.37 (ddd, J=7.87, 6.69, 1.18 Hz, 2 H). ¹³C NMR (101 MHz, DMSO) δ 171.84, 162.18, 142.95, 137.06, 134.52, 127.39, 123.53, 122.41, 117.22, 112.03.

3.6.3.4 Synthesis of 3.1-AlEt

Prepared following the representative synthesis procedure using 3.1 and AlEt₃. Yellow solid. Yield: 220 mg (59%). ¹H NMR (400 MHz, CDCl₃) δ ppm 8.79 (s, 2 H) 7.70 (dd, J=6.29, 3.54 Hz, 2 H) 7.42 - 7.50 (m, 4 H) 7.35 (dd, J=7.87, 1.97 Hz, 2 H) 7.16 (d, J=8.65 Hz, 2 H) 6.76 - 6.83 (m, 2 H) 0.61 (t, J=8.06 Hz, 3 H) -0.40 (q, J=8.26 Hz, 2 H). ¹³C NMR (101 MHz, CDCl₃) δ 167.28, 161.88, 139.07, 137.25, 134.18, 128.97, 123.22, 119.15, 117.32, 116.30, 10.12 (Could not locate Al-C signal with extended acquisition with T1 delay of 8.5s) HRMS (ESI-MS) m/z calc. for C₂₂H₂₀AlN₂O₂ M+H 371.1335, found 371.1328.

3.6.3.5 Synthesis of 3.2-Zn

Prepared following the representative synthesis procedure using 3.2 and ZnEt₂. Orange solid. Yield: 375 mg (85%). ¹H NMR (500 MHz, DMSO-≤d₆) δ ppm 8.99 (s, 2 H) 7.87 (dd, J=6.11, 3.42 Hz, 1 H) 7.36 (dd, J=6.11, 3.42 Hz, 1 H) 7.02 (dd, J=8.31, 1.71 Hz, 1 H) 6.86 (dd, J=7.58, 1.71 Hz, 1 H) 6.44 (t, J=7.58 Hz, 1 H) 3.74 (s, 3 H). ¹³C NMR (101 MHz,
DMSO) δ 164.33, 163.50, 153.20, 140.08, 128.09, 127.80, 119.36, 117.07, 114.48, 112.49, 55.83.

3.6.3.6 Synthesis of 3.2-Mg

Prepared following the representative synthesis procedure using 3.2 and nBu_2Mg. Orange solid. Yield: 309 mg (78%). ^1H NMR (400 MHz, DMSO-d_6) δ ppm 8.71 (s, 2 H) 7.72 - 7.77 (m, 2 H) 7.24 - 7.30 (m, 2 H) 6.97 (dd, J=8.26, 1.57 Hz, 2 H) 6.78 (dd, J=7.47, 1.57 Hz, 2 H) 6.29 (t, J=7.67 Hz, 2 H) 3.74 (s, 6 H). ^13C NMR (126 MHz, DMSO) δ 163.41, 161.93, 153.44, 142.99, 128.50, 127.19, 121.47, 117.10, 114.21, 110.66, 55.86 (s, OCH_3).

3.6.3.7 Synthesis of 3.2-AlEt

Prepared following the representative synthesis procedure using 3.2 and AlEt_3. Yellow solid. Yield: 95%. ^1H NMR (500 MHz, CDCl_3) δ 8.82 (s, 2 H) 7.66 - 7.76 (m, 2 H) 7.40 - 7.50 (m, 2 H) 6.98 (t, J=8.25, 4 H) 6.71 (t, J=7.70 Hz, 2 H) 3.94 (s, 6 H) 0.57 (t, J=8.07 Hz, 3 H) -0.36 (q, J=8.1 Hz, 2 H). ^13C NMR (101 MHz, CDCl_3) δ 161.72, 158.73, 152.39, 139.11, 128.81, 125.29, 118.94, 117.42, 116.46, 116.21, 56.38, 10.18.

3.6.3.8 Synthesis of 3.3-Zn

Prepared following the representative synthesis procedure using 3.3 and ZnEt_2. Yellow solid. Yield: 86%. ^1H NMR (500 MHz, DMSO-d_6) δ ppm 9.03 (s, 2 H) 7.90 - 7.96 (m, 2 H) 7.20 - 7.36 (m, 6 H) 1.48 (s, 18 H) 1.28 (s, 18 H). ^13C NMR (101 MHz, DMSO-d_6) δ
3.6.3.9 Synthesis of 3.3-Mg

Prepared following the representative synthesis procedure using 3.3 and \( \text{\textsuperscript{6}}\text{Bu}_2\text{Mg} \). Yellow solid. Yield: 83%. \(^1\text{H}\) NMR (500 MHz, DMSO-\(d_6\)) \( \delta \) ppm 8.84 (s, 2 H) 7.82 (dd, \( J=6.11, 3.42 \) Hz, 2 H) 7.16 - 7.31 (m, 6 H) 1.47 (s, 18 H) 1.26 (s, 18 H). \(^{13}\text{C}\) NMR (101 MHz, DMSO) \( \delta \) 169.56, 163.45, 143.05, 140.69, 133.04, 130.22, 128.74, 127.07, 120.76, 117.05, 35.79, 34.21, 32.70, 32.18, 30.28. HRMS (ESI-MS) \( m/z \) calc. for C\(_{36}\)H\(_{46}\)MgN\(_2\)O\(_2\) M\(^+\) 563.3482, found 563.3586.

3.6.3.10 Synthesis of 3.3-AlMe

Prepared following the representative synthesis procedure using 3.3 and AlMe\(_3\). Yellow solid. \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \( \delta \) ppm 8.82 (s, 2H), 7.71 (dd, \( J=3.4, 6.1 \) Hz, 2H), 7.61 (d, \( J=2.6 \) Hz, 2H), 7.40 (dd, \( J=3.3, 6.1 \) Hz, 2H), 7.17 (d, \( J=2.5 \) Hz, 2H), 1.58 (s, 18H), 1.36 (s, 18H), -0.64 (s, 3H). \(^{13}\text{C}\) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 165.17, 162.09, 139.15, 132.22, 128.15, 128.04, 118.81, 115.89, 35.87, 34.26, 31.54, 30.03. (Could not locate ipso C or Al-C signal with extended acquisition with T1 delay of 10.0 s)

3.6.3.11 Synthesis of 3.4-Zn

Prepared following the representative synthesis procedure using 3.4 and ZnEt\(_2\). Yellow solid. Yield: 313 mg (84%). \(^1\text{H}\) NMR (500 MHz, DMSO-\(d_6\)) \( \delta \) ppm 8.14 (s, 2 H) 7.07
- 7.12 (m, 4 H) 6.53 (dd, J=9.05, 0.98 Hz, 2 H) 6.36 (ddd, J=8.07, 7.09, 0.98 Hz, 2 H) 3.48 (s, 4 H) 0.91 (s, 6 H). $^{13}$C NMR (126 MHz, DMSO) δ 171.74, 170.15, 135.72, 133.74, 122.93, 119.45, 112.81, 72.56, 35.99, 25.43.

3.6.3.12 Synthesis of 3.4-Mg

Prepared following the representative synthesis procedure using 3.4 and $^{n}$Bu$_2$Mg. Yellow solid. Yield: 184 mg (55%). $^1$H NMR (400 MHz, DMSO-$d_6$) δ ppm 7.89 (s, 2 H) 7.00 - 7.08 (m, 4 H) 6.49 (d, $J$=8.26 Hz, 2 H) 6.26 (t, $J$=7.28 Hz, 2 H) 3.46 (br. s., 4 H) 0.89 (s, 6 H).

3.6.3.13 Synthesis of 3.4-AlMe

Prepared following the representative synthesis procedure using 3.4 and AlMe$_3$. Off-white solid. Yield: 77%. $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 8.09 (s, 2H), 7.37 (m, 2H), 7.20 (dd, $J$=1.9, 7.7 Hz, 2H), 7.02 (m, 2H), 6.72 (m, 2H), 3.56 (dd, $J$=12, 242.8 Hz, 4H), 1.16 (s, 3H), 1.00 (s, 3H), -0.80 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 169.24, 166.10, 135.79, 133.03, 122.68, 119.12, 116.64, 70.26, 26.01, 23.98. (Could not locate Al-C signal with extended acquisition with T1 delay of 8.5s)

3.6.3.14 Synthesis of 3.5-Zn

Prepared following the representative synthesis procedure using 3.5 and ZnEt$_2$. Yellow solid. Yield: 84%. $^1$H NMR (500 MHz, CDCl$_3$) δ ppm 8.20 (s, 2 H) 7.45 (d, $J$=2.69 Hz, 2 H) 6.98 (d, $J$=2.69 Hz, 2 H) 3.45 (s, 4 H) 1.42 (s, 18 H) 1.31 (s, 18 H) 1.07 (s, 6 H). $^{13}$C
NMR (126 MHz, CDCl$_3$) $\delta$ 170.79, 168.69, 142.11, 135.58, 129.55, 128.98, 117.45, 68.24, 37.66, 35.84, 34.08, 31.62, 29.58, 26.52.

3.6.3.15 Synthesis of 3.5-Mg

Prepared following the representative synthesis procedure using 3.5 and $^6$Bu$_2$Mg. Yellow solid. Yield: 80%. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.99 (s, 2H), 7.16 (d, $J = 2.7$ Hz, 2H), 6.88 (d, $J = 2.7$ Hz, 2H), 3.47 (s, 4H), 1.43 (s, 18H), 1.22 (s, 18H), 0.93 (s, 6H).

$^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 169.53, 167.57, 139.05, 131.12, 128.60, 126.39, 119.46, 74.26, 35.16, 35.00, 33.28, 31.52, 29.93, 24.86.

3.6.3.16 Synthesis of 3.5-AlEt

Prepared following the representative synthesis procedure using 3.5 and AlEt$_3$. Yellow solid. 77% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ ppm 8.10 (s, 2 H) 7.47 (d, $J = 2.45$ Hz, 2 H) 7.00 (d, $J = 2.45$ Hz, 2 H) 3.24 - 3.49 (m, 4 H) 1.45 - 1.53 (m, 18 H) 1.26 - 1.33 (m, 18 H) 1.16 (s, 3 H) 1.04 (s, 3 H) 0.71 - 0.78 (m, 3 H) -0.29 (q, $J = 8.07$ Hz, 2 H).

3.6.4 Representative procedure for copolymerization reactions

Cyclohexene oxide (5 mL, 50 mmol) and catalyst (0.05 mmol) were placed in a Schlenk tube. The reaction mixture was degassed, placed under 1 atm CO$_2$ pressure, and heated to 80 °C with vigorous stirring. After 6 h, the reaction was quenched by exposing the reaction mixture to air. Conversion of CHO to polymer was determined by recording a $^1$H NMR spectrum of the crude reaction mixture. Unreacted CHO was removed under
vacuum. The residue was extracted with CH$_2$Cl$_2$ and precipitated out by addition of methanol.

3.7 References


4.1 Introduction

An interest in bimetallic catalysts for the copolymerization of CO₂ and epoxides has led to the development of a variety of dinculeating ligand systems. One such system was exploited by the Williams group, in which dizinc\textsuperscript{[1]} and dimagnesium\textsuperscript{[2]} complexes were prepared by using a reduced form of a Robson macrocycle. A general representation of these metal complexes is shown in Figure 4.1

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{general_representation.png}
\caption{General representation of dinuclear macrocyclic complexes developed by the Williams group. M = Mg, Zn.}
\end{figure}
Using the dizinc macrocyclic metal complex, [Zn₂(OAc)₂Mac], shown in Figure 4.2, Williams and coworkers could achieve “very high activity” for the copolymerization of CHO and CO₂ under mild pressures. Under 1 atm CO₂ at 80 °C at 0.1 mol% loading, poly(cyclohexene carbonate) was produced with 96% selectivity for polycarbonate over cyclic carbonate or polyether formation. Turnover numbers (TONs) and turnover frequencies (TOFs) were in the range of 430-530 and 18-25 h⁻¹, respectively. Compared to other known zinc catalysts, such as the β-diiminate zinc or bis(phenoxide)zinc catalysts mentioned in Chapter 1, the activity of [Mg₂(OAc)₂Mac] is comparable at a fraction of the pressure of CO₂ (about 1/7 and 1/55, respectively).

Subsequently, Williams and coworkers tested the dinuclear magnesium analog, [Mg₂(OAc)₂Mac] under similar conditions. Under 1 atm CO₂ at 80 °C at 0.1 mol% loading,
poly(cyclohexene carbonate) was produced with >99% selectivity for polycarbonate over cyclic carbonate or polyether formation. The TON and TOF were 522 and 35 h\(^{-1}\), respectively. The TOF is twice that of the zinc analog. By performing the copolymerization at 100 °C, the TOF increases to 152 h\(^{-1}\), with no change in the fidelity of the polycarbonate backbone with >99% selectivity. Williams and coworkers attribute the increased activity of [Mg\(_2\)(OAc)\(_2\)Mac], as compared to [Zn\(_2\)(OAc)\(_2\)Mac], to the Lewis acidity and decreased electronegativity of magnesium.\(^2\)

These findings by Williams and coworkers on homometallic dinuclear zinc\(^1\) and magnesium\(^2\) macrocyclic metal complexes, as well as the proposed mechanism\(^3,4\) depicted in Scheme 4.1, inspired us to look at attempting to prepare heterobimetallic complexes. The rationale being that in the mechanism, it is suggested each metal center plays a different role. One metal center coordinates an epoxide, while the other coordinates CO\(_2\), allowing for insertion of CO\(_2\) into a metal alkoxide bond by a “shuttling” mechanism. By changing the identity of each metal center by preparing mixed metal complexes, we envisioned that by tuning the Lewis acidity of each center, we could make more efficient catalysts.
Scheme 4.1 Proposed mechanism of the copolymerization of CO$_2$ and CHO. Figure adapted from references 3 and 4. Also shown are pathways to produce cyclic carbonate through a “back-biting” mechanism and polyether through consecutive epoxide enchainment.
4.2 Ligand Synthesis

This class of ligands require few synthetic steps and can be readily modified by choice of starting phenol or diamine. For example, starting with a para-substituted phenol, the corresponding 2,6-diformylphenol could be prepared by the Duff reaction using hexamethylenetetramine in trifluoracetic acid heated to reflux, followed by hydrolysis. The corresponding Robson macrocycle, [H₄Mac⁸](ClO₄)₂, could be formed reacting the 4-substituted-2,6-diformylphenol with a diamine in the presence of sodium perchlorate and acetic acid in methanol, as shown in Scheme 4.2. Sodium borohydride can then be employed to reduce the imine arms to afford the amine based macrocyclic ligand, H₂Mac⁸ (Scheme 4.3).

Scheme 4.2 Synthesis of [H₄Mac⁸](ClO₄)₂. i) hexamethylenetetramine, TFA, 125 °C, 16 h, ii) 3M HCl, 100 °C. iii) acetic acid, NaClO₄, MeOH, 25 °C, 16 h.
Our work began using the same reduced Robson-type macrocycle used by the Williams group. Following literature procedures, 2,6-diformyl-4-tert-butylphenol was prepared from 4-tert-butylphenol. This was then reacted with one equivalent 2,2-dimethyl-1,3-propanediamine in the presence of sodium perchlorate to afford the macrocycle $[\text{H}_4\text{Mac}](\text{ClO}_4)_2$ (Scheme 4.2, $R = \text{tBu}$). Reduction of the imine moieties with sodium borohydride in methanol provided the ligand $\text{H}_2\text{Mac}$ (Scheme 4.3, $R = \text{tBu}$).

4.3 Preparation of Heterobimetallic Macroyclic Complexes

Homobimetallic metal complexes, such as $\text{Zn}^{2+}$ and $\text{Mg}^{2+}$, were formed by deprotonation of the pro-ligand with KH, followed by reaction with two equivalents of the metal acetate (Scheme 4.4).
To prepare mixed metal complexes, our approach involved stepwise addition of various metal reagents to try to cleanly afford the targeted heterobimetallic complexes. A general reaction scheme illustrating our approach is shown in Scheme 4.5. Since our group has previously prepared mixed lithium/magnesium complexes,[8-10] we targeted complexes mixing Li with Mg and Zn.
4.3.1 Li/Mg Mixed Metal Complex

Preparation of a new heterobimetallic Li/Mg macrocyclic complex was attempted by deprotonation of the pro-ligand using \(n\)BuLi, followed by addition of one equivalent of \(n\)Bu\(_2\)Mg. This was subsequently reacted with one equivalent acetic acid to afford the Li/Mg acetate macrocyclic complex (Scheme 4.6).

![Scheme 4.6 Synthesis of [LiMgOAcMac].](image)

Crystals of [LiMgOAcMac] were grown from acetonitrile solution. The crystal structure of the Li/Mg complex, shown in Figure 4.3, shows both Li and Mg in the coordination pocket of the macrocycle with a bridging acetate ligand. The Li center has a square pyramidal geometry and is coordinated by the O,N,N’,O’ donor motif of the macrocycle as the base of the square pyramid and the acetate ligand at the apical position. Some key bond lengths (Å) and angles (°) about the Li center are as follows: Li1-O1 2.354(4), Li1-O2 2.191(4), Li1-O3 1.989(4), Li1-N1 2.130(4), Li1-N2 2.166(4); O1-Li1-O2 77.24(14), O1-Li1-O3 96.52(17), O2-Li1-O3 111.82(19), O3-Li1-N1 89.21(17), O3-
Li1-N2 108.83(19). The Mg center has an octahedral geometry, coordinated by a water molecule trans to the acetate ligand. Some key bond lengths (Å) and angles (°) about the Mg center are as follows: Mg1-O1 2.0523(17), Mg1-O2 2.0448(17), Mg1-O4 2.0625(18), Mg1-O5 2.0946(17), Mg1-N3 2.207(2), Mg1-N4 2.199(2); O1-Mg1-O2 87.74(7), O1-Mg1-O4 94.37(7), O1-Mg-O5 91.75(7), O4-Mg1-N3 81.85(7). In the expanded structure, the complex is a dimer with hydrogen bonding from the water molecule to both phenolic oxygens on a neighboring macrocycle (O5-H···O1 1.90(4) and O5-H···O2 2.02(5) Å).

Figure 4.3 Atomic displacement ellipsoids of [LiMgOAcMac·H2O] drawn at 50% probability level. Most H omitted for clarity. C (dark grey), N (blue), O (red), Li (pink), and Mg (light grey).

Analysis of the bulk material by NMR spectroscopy proved to be difficult. At room temperature in non-coordinating deuterated solvents, such as chloroform-\(d\),
1,1,2,2-tetrachloroethane-$d_2$, signals are broad in the obtained $^1$H NMR spectra. The use of pyridine-$d_5$ as the solvent at -15 °C resolves some of the broad features into separate signals attributed to the aromatic protons (7.25 and 7.28 ppm), benzylic (4.56 and 3.27 ppm) and methylene (2.93 and 2.45 ppm), protons. There are also two separate tert-butyl environments at 1.36 and 1.19 ppm and two acetate environments at 2.07 and 1.16 ppm, as determined by HMBC. However, by integration of the signals and correlation experiments, it is difficult to determine if there are one or more species present in solution. A representative $^1$H NMR spectra is shown in Figure 4.4.

Figure 4.4 $^1$H NMR spectra of [LiMgOAcMac] in pyridine-$d_5$ at -15 °C.
Williams and coworkers describe conformational isomers in zinc- or magnesium-metalated complexes where the macrocyclic ligand can adopt a “bowl” or “S-shaped” conformation. The two conformations appear to be isoenergetic, as shown by DFT calculations.\[3\] Upon warming the solution to 50 °C, two distinct aromatic environments are still present, however one peak overlaps one of the solvent peaks. The two distinct tert-butyl environments appear at 1.41 and 1.26 ppm. Two acetate environments appear at 2.13 and 1.22 ppm. A minor low-symmetry species is still present above the baseline even while raising the temperature. This suggests there are at least two species in solution and not just a set of conformational isomers.

Figure 4.5 $^1$H NMR spectra of [LiMgOAcMac] in pyridine-$d_5$ at 50 °C.
Additional synthetic routes to isolate [LiMgOAcMac] were attempted, as shown in Scheme 4.7. Unfortunately, none of these routes led to isolation of the pure target mixed-metal complex.

Scheme 4.7 Synthetic routes attempted to isolate [LiMgOAcMac].

4.3.2 Li/Zn Mixed Metal Complex

Similarly, attempts at isolating the zinc analog were made, as shown in Scheme 4.8. The macrocyclic pro-ligand was deprotonated with nBuLi, followed by addition of one equivalent of ZnEt₂. This was subsequently reacted with one equivalent of acetic acid.
Crystals grown from dichloromethane solution revealed not the [LiZnOAcMac] complex, but rather a lithium acetate adduct of the dizinc diacetate macrocyclic complex. Shown in Figure 4.6, the crystal structure of the Li/Zn species shows a trinuclear complex with two octahedral zinc atoms coordinated by the macrocycle’s O,N,N’,O’ donor motif. Select bond lengths (Å) and angles (°) for the Zn centers are as follows: Zn1-O1 2.1547(11), Zn1-O2 2.1018(12), Zn1-O3 2.1872(12), Zn1-O5 2.0824(12), Zn1-N1 2.1370(14), Zn1-N2 2.1487(14), Zn2-O1 2.1733(11), Zn2-O2 2.1018(12), Zn2-O4 2.1318(13), Zn2-O8 2.0625(13), Zn2-N3 2.1342(14), Zn2-N4 2.1517(14)° O1-Zn1-O2 82.92(4), O1-Zn1-O3 94.70(4), O2-Zn1-O3 89.51(5), O3-Zn1-N1 81.92(5), O1-Zn2-O5 97.29(5), O2-Zn2-O4 95.03(5), O2-Zn2-N3 173.55(5), N3-Zn2-O4 83.43(5). On the bottom face of the “bowl” formed by the macrocycle is a bridging AcO-Li-OAc moiety, where the Li atom is a distorted tetrahedral. Select bond lengths (Å) and angles (°) for the Li center are as follows: Li1-O1 1.995(3), Li1-O6 1.899(3), Li1-O7 1.936(3); O1-Li1-O6
109.23(15), O6-Li1-O7 113.70(16), O1-Li1-O8 120.39(15), O1-Li1-O7* 119.39(16)

(symmetry transformations generated by -x, -y+1, -z+1). The grown structure features a dimer bridged by the LiOAc moiety, shown in Figure 4.7.

Crystals obtained from diffusion of pentane into chloroform solution were identified as the dizinc dichloride macrocyclic complex, Zn$_2$Cl$_2$Mac (Figure 4.8), analogous to the Zn$_2$Br$_2$Mac complex characterized by Williams and coworkers$^{[11]}$. 
Figure 4.6 Top: Atomic displacement ellipsoids of [LiZn₂OAc₃Mac]₂ drawn at 50% probability level. Most hydrogen atoms omitted, and ligand partially drawn in wireframe for clarity. Bottom: Labelling of atoms the asymmetric unit of [LiZn₂OAc₃Mac]₂. Macrocyclic ligand partially drawn in wireframe or truncated for clarity. C (dark grey), N (blue), O (red), Li (pink), and Zn (steel grey).
Figure 4.7 Grown structure of [LiZn$_2$OAc$_3$Mac]$_2$. Bottom: Ligand omitted for clarity to illustrate core of dimer. C (dark grey), N (blue), O (red), Li (pink), and Zn (steel grey).
Figure 4.8 Left: Atomic displacement ellipsoids of [Zn$_2$Cl$_2$Mac] drawn at 50% probability level. Most hydrogen atoms omitted for clarity C (dark grey), N (blue), O (red), Cl (green), and Zn (steel grey). Right: ChemDraw representation of [Zn$_2$Cl$_2$Mac].

Analysis of the bulk material by NMR spectroscopy at room temperature in DMSO-$d_6$, shown in Figure 4.9, notably displays a single tert-butyl environment at 1.21 ppm, integrating to 18 protons and one acetate environment integrating to approximately 6 protons. This, along with information obtained from the crystal structures, suggests the targeted Li/Zn mixed-metal complex is not formed. The Li atom is perhaps preferentially displaced by Zn from the coordination environment of the macrocyclic ligand. Other synthetic routes were attempted to isolate [LiZnOAcMac], as shown in Scheme 4.9. Attempts to isolate the 1:1 Li/Zn species have been unsuccessful to date.
Figure 4.9 $^1$H NMR spectra in DMSO-$d_6$ at 20 °C of [Zn$_2$OAc$_2$Mac].
Scheme 4.9 Synthetic routes attempted to isolate [LiZnOAcMac].

Since isolation of pure Li/Mg or Li/Zn mixed-metal complexes proved to be difficult, our attention then shifted to preparing mixed Mg/Zn complexes. The synthetic route we envisioned involved reacting the proligand with one equivalent diethylzinc in THF solution, followed by reaction with one equivalent magnesium acetate, as shown in Scheme 4.10. However, also during this time, Williams and coworkers published work on a mixed Mg/Zn diacetate complex.\(^{[12]}\) Unfortunately, they were unable to obtain a pure, isolated compound. Rather, their route afforded a statistical mixture of 1:2:1 of the Mg\(_2\):Mg/Zn:Zn\(_2\) diacetate complexes. It was not until later in 2015 where their group isolated the pure dibromo Mg/Zn complex, prepared by reaction of ZnEt\(_2\) with the proligand, followed by addition of MgBr\(_2\).\(^{[11]}\)
Scheme 4.10 Proposed synthetic route for [ZnMg(OAc)$_2$Mac].

4.4 Conclusions

Two new heterobimetallic complexes have been prepared utilizing a reduced form Robson macrocycle. [LiMgOAcMac] was prepared by sequential addition of lithium and magnesium alkyl bases to the ligand, followed by protonolysis of acetic acid. The crystal structure shows both Li and Mg metal centers housed in the coordination pocket of the macrocyclic ligand. The Li center adopting a square pyramidal geometry, coordinated by the ligand in a ($\kappa^4$-O,N,N',O') fashion, forming the base of the pyramid, and an acetate ligand in the apical position. The Mg center is octahedral, coordinated by the ligand in a ($\kappa^4$-O,N,N',O') fashion, with an acetate ligand and a water molecule occupying the axial positions.

Following a similar route to form the analogous Li/Zn complex afforded a complex mixture where a trinuclear heterobimetallic complex was isolated. Two octahedral zinc centers are located in the coordination pocket of ligand, each bound to
the ligand in a ($\kappa^4$-O,N,N',O') fashion. One acetate ligand bridges the two Zn centers.

Below the “bowl” of the ligand, an acetate ligand from each Zn center is coordinated to a Li atom. Several alternative synthetic routes were attempted to isolate the 1:1 Li/Zn complex, however isolation of this species has failed to date.

Attempts at synthesizing a Mg/Zn heterobimetallic complex was abandoned, as Williams and coworkers published a route\textsuperscript{[11]} similar to what we proposed while this work was being performed.

4.5 Experimental

4.5.1 General Procedures

All manipulations were carried out using either standard Schlenk techniques under a nitrogen atmosphere or in an argon-filled glovebox. All glassware was flame-oven-dried prior to use. Tetrahydrofuran (THF) was degassed and purified by passage through a solvent purification system (Innovative Technology). 4-tert-butylphenol (Lancaster), hexamethylenetetramine (Alfa Aesar), acetic acid (Sigma-Aldrich) trifluoroacetic acid (Alfa Aesar), 2,2-dimethyl-1,3-propanediamine (TCI), sodium perchlorate (Alfa Aesar), and sodium borohydride (Aldrich) were used as received. $n$-Butyllithium ($n$BuLi, 2.5 M in hexanes), di-$n$-butylmagnesium ($^{6}$Bu$_2$Mg, 1.0 M in heptane), and diethylzinc (ZnEt$_2$, 1.0 M in hexanes) were purchased from Sigma-Aldrich and were standardized by titration against salicylaldehyde phenylhydrazone in dry THF prior to use.\textsuperscript{[13]} Cyclohexene oxide (CHO, Alfa Aesar) was distilled from CaH$_2$ under reduced pressure prior to use. Deuterated solvents (chloroform-d, tetrachloroethane-d$_2$, DMSO-
were purchased from Cambridge Isotope Laboratories (CIL, Tewksbury, MA) and were degassed via several freeze-pump-thaw cycles, dried over CaH₂, and stored over 4 Å molecular sieves. ¹H and ¹³C spectra were recorded on a Bruker AVANCE III HD 400, Bruker AVANCE III HD 500, or Varian DirectDrive 600 spectrometer at 293K and were referenced internally to the residual signals of the deuterated solvent.

4.5.1.1 Synthesis of 2,6-diformyl-4-tert-butylphenol

Modified from a literature procedure:[⁵] 4-tert-butylphenol (5.26 g, 35 mmol) and hexamethylenetetramine (9.81 g, 70 mmol) were dissolved in 50 mL trifluoracetic acid and brought to reflux under a nitrogen atmosphere for 24 h. The reaction mixture was cooled to room temperature and then poured over 300 mL 2 M aqueous HCl. The product was extracted with methylene chloride (3 x 75 mL). The combined organic phases were washed with 2M aqueous HCl (2 x 150 mL), water (200 mL), and brine (200 mL), dried over MgSO₄. Volatiles were removed by rotary evaporation, affording a yellow solid. 6.1825 g, 86% yield. NMR values match the literature.[⁵]

4.5.1.2 Synthesis of [H₄Mac](ClO₄)₂

Prepared by literature procedure:[¹] A 250 mL round-bottomed flask was charged with 2,6-diformyl-4-tert-butylphenol (1.44 g, 7 mmol) NaClO₄ (3.42 g, 28 mmol), acetic acid (0.8 mL, 14 mmol), and 50 mL methanol. The solution was heated to 70 °C. When the solution began to boil, 2,2-dimethyl-1,3-propanediamine (0.84 mL, 7 mmol) in 30 mL methanol was added slowly. The yellow solution turned orange as the reaction mixture
was allowed to cool to room temperature. A bright orange precipitate settles, which was isolated by filtration and washed with cold methanol. 95 % yield. NMR values match the literature.[1]

4.5.1.3 Synthesis of H₂Mac

   Prepared by literature procedure:[1] In a 250 mL round-bottomed flask, [H₄Mac](ClO₄)₂ (1.59 g, 2.14 mmol) was suspended in 160 mL methanol and cooled to 0 °C. NaBH₄ (2.02 g, 53.4 mmol) was added slowly in portions. The red-orange suspension turns to a clear solution. Water was slowly added to the solution, forming a white precipitate. The white solid was filtered and dried in air. 1.03 g, 87% yield. NMR values match the literature.[1]

4.5.1.4 Synthesis of [LiMgOAcMac]

   In a 50 mL Schlenk tube, H₂Mac (276 mg, 0.5 mmol) was dissolved in 10 mL THF and cooled to -78 °C. nBuLi (2.5 M, 0.2 mL, 0.5 mmol) was added dropwise. The solution was stirred at -78 °C for 1 h. nBu₂Mg (1 M, 0.5 mL, 0.5 mmol) was added. The solution was allowed to warm to room temperature and was stirred overnight. Acetic acid (29 μL, 0.5 mmol) was added. The solution was stirred at room temperature for 2 h. Volatiles were removed under reduced pressure, affording a white solid.
4.5.1.5 Attempt at Preparing [LiZnOAcMac]

In a 50 mL Schlenk tube, $\text{H}_2\text{Mac}$ (276 mg, 0.5 mmol) was dissolved in 10 mL THF and cooled to -78 °C. nBuLi (2.5 M, 0.2 mL, 0.5 mmol) was added dropwise. The solution was stirred at -78 °C for 1 h. ZnEt$_2$ (1 M, 0.5 mL, 0.5 mmol) was added. The solution was allowed to warm to room temperature and was stirred overnight. Acetic acid (29 μL, 0.5 mmol) was added. The solution was stirred at room temperature for 2 h. Volatiles were removed under reduced pressure, affording a white solid.

4.5.2 X-ray crystallography

Single crystals were examined under Paratone-N oil. The datum crystals were affixed to a Mitegen mounting loop and transferred to a 120K nitrogen stream of a Bruker Kappa or Bruker APEX-II diffractometer, equipped with an Oxford Cryostream 700 series low-temperature apparatus. Cell parameters were refined using reflections harvested from data collection with $I \geq 10\sigma(I)$. All data were corrected for Lorentz and polarization effects, and runs were scaled using SADABS.$^{[14]}$ Structure solution was by either direct or Patterson methods$^{[15]}$ and refined by full-matrix least-squares analysis of $F^2$ against all reflections.$^{[16]}$ Olex2 was used for structure visualization.$^{[17]}$ All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen atoms on carbons were placed at calculated geometries and allowed to ride on the position of the parent atom. Hydrogen thermal parameters were set to 1.2 (1.5 for methyl) times the equivalent isotropic $U$ of the parent atom. Mercury was used for structure visualization and analysis, as well as the creation of figures.$^{[18]}$
4.6 References


CHAPTER 5:

COORDINATION CHEMISTRY OF NEW TETRADENTATE \( M \)-PHENYLENE-BRIDGED

(PHOSPHINIMINO/PHOSPHORANO)METHANES

5.1 Introduction

First reported in 1919 by Staudinger and Meyer, phosphinimines display interesting chemistries, much like the analogous carbon-based ylides, featuring a four-coordinate phosphorus atom with a formal double bond to nitrogen.\(^1\) These compounds are also referred to as iminophosphoranes or phosphazenes. Described here are their direct preparation, following two different approaches. The first involves the Staudinger oxidation of a tertiary phosphine with an azide, whereas the second approach utilizes the reaction of an amine with a tertiary phosphine dibromide species, referred to as the Kirsanov reaction.

The Staudinger reaction involves nucleophilic addition of the azide to a phosphine (or other \( P^{\text{III}} \) center) and subsequent dinitrogen elimination, as represented in Scheme 5.1. One advantage of this route is the only side product produced is dinitrogen, thus further purification of the phosphinimine product is unnecessary. Also, a variety of \( P^{\text{III}} \) centers with different substituents can be utilized. The main drawback for this approach is the azide. The thermal and shock sensitivity associated with most azide derivatives presents an explosion risk. Additionally, the commercial availability or
feasible synthesis of azides with a wide range of N-substituents is limiting. These azides are usually obtained by displacement of a halide using sodium azide.\[^1\]

\[
\begin{align*}
R_3P & + R'N_3 \rightarrow R_3P=NR' \\
& - N_2
\end{align*}
\]

Scheme 5.1 Representation of a Staudinger oxidation by reaction of an azide with a tertiary phosphine.

Discovered in 1950 by Kirsanov, reaction of PCl\(_5\) with benzenesulfonylamide produced N-benzenesulfonylimino-P,P,P-trichlorophosphorane. This could subsequently be converted to the triarylphosphinimine N-benzenesulfonyliminotriphenylphosphorane by reaction with phenylmagnesium bromide, as shown in Scheme 5.2.\[^1,2\] Later, Horner and Oediger synthesized N-arylphosphinimines by reaction of dibromotriphenylphosphorane with primary arylamines, followed by deprotonation of the aminophosphonium salt by triethylamine.\[^1\] Additionally, Zimmer and Singh prepared N-alkylphosphinimines using the same method above, however when using triethylamine, the reaction stopped at the formation of the aminophosphonium salt. A stronger base, such as sodium amide, was necessary to produce the neutral N-alkylphosphinimine.\[^3\]

\[
\begin{align*}
PCl_5 & + ArSO_2NH_2 \rightarrow ArSO_2N=PCl_3 \\
& + PhMgBr \rightarrow ArSO_2N=PPh_3
\end{align*}
\]

Scheme 5.2 Preparation of N-benzenesulfonyliminotriphenylphosphorane by the Kirsanov reaction.
Using the Kirsanov approach provides advantages over the Staudinger oxidation to produce phosphinimines. A wide variety of commercially available primary alky- and arylamines can be used, and as a result, options for steric and electronic modifications to the ligand are not dependent on the commercial availability or synthesis of azides. One drawback to this approach is the need for bromine, which is toxic.

Previous work by our group,[4,5] as well as others,[6-11] have utilized bis(phosphorano and/or sulfonylmethylene)ligands to access monoanionic and geminal dianionic metal complexes. This is possible due to the acidity of the protons at the methylene position. The monoanionic and geminal dianionic alkali metal complexes of these types of ligands have been used to access transition metal and rare earth metal methanide complexes via salt metathesis.[12,13]

5.2 Design of $H_4NPPY$ Ligands

Whereas the chemistry of bidentate methylene(phosphorano/phosphorane) ligands has been well developed, utilization of this motif in a tetradentate ligand framework has only recently been realized. Le Floch and coworkers developed an unusual $X_2N_2$ (X = P, O, S)[14,15] ligand framework by connecting two methylene(phosphorano/phosphorane) units with an ethylene bridge (Figure 5.1).

![Figure 5.1. Ligand framework used by LeFloch and coworkers. Y = lone pair, O, or S.](image)
Their group has used these ligands as neutral donors to coordinate Pd$^{2+}$, Ni$^{2+}$, Fe$^{2+}$ (Figure 5.2), and Rh$^{1+/3+}$ to explore Suzuki-Miyaura coupling$^{[14]}$ and transfer hydrogenation reactions.$^{[15,16]}

![Figure 5.2. Example of an iron(II) complex of the O$_2$N$_2$ ligand prepared by Le Floch’s group.$^{[15]}$](image)

Inspired by this framework and the work of Harder with phenylene-bridged β-diiminate (BDI) units,$^{[17]}$ we wished to design and develop a 1,3-phenylene-bridged framework incorporating two methylene(phosphinimino/phosphorano) units, as shown in Figure 5.3.

![Figure 5.3. Proposed H$_4$NPPY ligands.](image)

By using this (phosphinimino/phosphorano)methane moiety in our framework, the potential tunability of the ligand’s anionic valency (neutral to tetravalent) could be explored with various metal centers, such as di- and trivalent metals. One attractive feature of the methylene(phosphorano/phosphorane) ligand framework is the ability to tune the donor atoms available for chelation, as well as the electronic and steric
properties. Oxidation of P(III) to P(V) is relatively straightforward through conventional methods to make phosphine oxides, thiophosphines, selenophosphines, and phosphinimines. Additionally, the installation of phosphinimine units on the outer arms of the ligand provides wide scope to tune steric bulk around the metal center. And unlike the classical imine systems, like the BDI ligand framework, the (phosphinimino)methanes exhibit much different electronic and steric properties, namely due to the absence of an extended π-system.

With the m-phenylene bridge separating the two chelating moieties, the coordination environment is set up to form dinuclear metal complexes. The development of dinuclear homo- and heterobimetallic catalysts is attractive, as bimetallic catalysts can promote a variety of reactions such as hydroformylation,[18,19] carbonylation,[20-22] hydrogenation,[18,23] azide-alkyne cycloaddition,[24] alkynylation,[25] aldol addition,[26,27] and polymerization.[28] In particular, Coates[29] and Williams[30,31] have proposed that a bimetallic mechanism is involved in the copolymerization of epoxides and CO₂ to form polycarbonates.

Building on this knowledge, we set out to prepare three ligands of this class with phosphine, phosphine oxide, and thiophosphine donors on the outer arms. Synthetic and characterization details will be presented below. Attempts at metalation of these ligands will also be discussed.
5.2.1 Synthesis of H₄NPP

Following a similar procedure employed by Le Floch and coworkers,[16] mono-oxidation of bis(diphenylphosphino)methane (dppm) was carried out with one equivalent of bromine in dichloromethane at -78 °C. After stirring for 20 minutes at -78 °C, the orange suspension was slowly warmed to room temperature and stirred for one hour, becoming a clear, pale yellow solution. This was again cooled to -78 °C, where one equivalent of m-phenylenediamine (m-Ph(NH₂)₂) was added as a solid, with half an equivalent acting as a nucleophile to displace bromide from phosphorus, and the other half equivalent acting as an HBr mop. The reaction mixture was warmed to room temperature, forming a white solid. After aqueous workup, the bis(hydrobromide)aminophosphonium salt was isolated in good yield (90%) as a white solid (Scheme 5.3).

Attempts were made with using tertiary amines as the HBr mop. Using one equivalent of triethylamine and Hünig’s base provided a mixture of products. However, using 0.5 equivalent 1,4-diazabicyclo[2.2.2]octane (DABCO) afforded H₄NPP-(HBr)₂ in excellent isolated yields (>95%). Additionally, it was also discovered that thoroughly
degassing the dichloromethane prior to synthesis was necessary to prevent side product formation. One of these side products was isolated and identified as methylenebis(diphenylphosphine oxide).

Multinuclear NMR spectra were taken of H₄NPP-(HBr)₂ in CDCl₃. The ¹H NMR spectrum notably shows NH protons appearing at 10.21 ppm as a broad doublet. The four methylene protons come in at 4.21 ppm as a doublet with J = 16.0 Hz coupling. The ³¹P NMR spectrum shows two inequivalent phosphorous atoms, with P⁵⁻N at δ 25.8 ppm as a doublet, and P⁷⁻ at -40.4 ppm as a doublet, both doublets with J = 76 Hz coupling.

![Figure 5.4. Crystal structure of H₄NPP-(HBr)₂. Atomic displacement ellipsoids drawn at 50% probability level. Most H atoms omitted for clarity. C (dark grey), N (blue), P (purple) and Br (orange).](image)

Crystals suitable for single crystal X-ray diffraction experiments were grown from a concentrated acetonitrile solution. H₄NPP-(HBr)₂ crystallizes in the orthorhombic
space group $P2_12_12_1$ with four molecules in the unit cell and $H_4NPP-(HBr)_2$ as the asymmetric unit, shown in Figure 5.4. The P-N bond lengths are 1.633(6) Å for P1-N1 and 1.639(6) Å for P3-N2. The hydrogens bound to the nitrogen atoms were located within the electron density map and show close contacts with the bromide anions, at 2.405 Å for N1-H···Br1 and 2.347 Å for N2-H···Br2, respectively. The methylene C-P bonds are C7-P1 as 1.772(7) Å and C7-P2 as 1.846(7) Å.

The bis(hydrochloride)amino phosphonium salt, $H_4NPP-(HCl)_2$ was also prepared in excellent isolated yields as a white solid by an analogous procedure, but by adding a wash step with saturated aqueous sodium chloride solution to the aqueous work up (Scheme 5.4).

![Scheme 5.4. Synthesis of $H_4NPP-(HCl)_2$.](image)

Multinuclear NMR spectra were taken of $H_4NPP-(HCl)_2$ in CDCl$_3$. The $^1$H NMR spectrum notably shows the NH protons appearing at 11.08 ppm as a broad doublet, shifted downfield from $H_4NPP-(HBr)_2$. The four methylene protons come in at 4.18 ppm as a doublet with $J = 16.3$ Hz coupling. The $^{31}$P NMR spectrum shows two inequivalent phosphorous atoms, with $P^V-N$ at δ 25.09 ppm as a doublet, and $P^{III}$ at -40.38 ppm as a doublet, both doublets with $J = 76.2$ and 76.5 Hz coupling, respectively.
Single crystals suitable for single crystal X-ray diffraction experiments were grown from saturated acetonitrile solution. Isostructural to \( \text{H}_4 \text{NPP}\)\-(HBr)\(_2\), \( \text{H}_4 \text{NPP}\)\-(HCl)\(_2\) crystallizes in the orthorhombic space group \( P2_12_12_1 \) with four molecules in the unit cell and \( \text{H}_4 \text{NPP}\)\-(HCl)\(_2\) as the asymmetric unit, shown in Figure 5.5. P-N bond lengths are \( 1.639(3) \) Å for P1-N1 and \( 1.635(3) \) Å for P3-N2, respectively. The hydrogens bound to the nitrogen atoms show close contact to the chloride anions at \( 2.275 \) Å for N1-H···Cl1 and \( 2.267 \) Å for N2-H···Cl2. The methylene C-P bonds are C7-P1 as \( 1.795(4) \) Å and C7-P2 as \( 1.865(4) \) Å.

![Figure 5.5. Crystal structure of \( \text{H}_4 \text{NPP}\)\-(HCl)\(_2\). Atomic displacement ellipsoids drawn at 50% probability level. Most H atoms omitted for clarity. C (dark grey), N (blue), P (purple) and Cl (green).](image)

The neutral phosphine, \( \text{H}_4 \text{NPP} \), could be prepared by deprotonation of either \( \text{H}_4 \text{NPP}\)\-(HBr)\(_2\) or \( \text{H}_4 \text{NPP}\)\-(HCl)\(_2\) with two equivalents of \( n \text{BuLi} \) in toluene or THF in excellent yields as a yellow solid (Scheme 5.5).

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Scheme 5.5. Synthesis of $H_4NPP$.

Multinuclear NMR spectra were taken of $H_4NPP$ in CDCl$_3$. The $^1H$ NMR spectrum of $H_4NPP$ in CDCl$_3$ shows the four methylene protons come in at 2.62 ppm as a doublet with $J = 12.5$ Hz coupling, shifting almost 1.5 ppm upfield from the HX adducts. The $^{31}P$ NMR spectrum shows two inequivalent phosphorous atoms, with $P^{V}$-$N$ at $\delta -7.49$ ppm as a doublet, and $P^{III}$ at $-36.54$ ppm as a doublet, both doublets with $J = 39.6$ and 52.8 Hz coupling, respectively.

Crystals suitable for single crystal X-ray diffraction experiments were grown by vapor diffusion of pentane into chloroform solution of $H_4NPP$. $H_4NPP$ crystallizes in the orthorhombic space group, Pbcn. In the asymmetric unit is one half molecule of $H_4NPP$ and two chloroform molecules. Most notably, the $P$-$N$ bond length contracts to 1.5786(17) Å for $P1$-$N1$, as compared to $\sim1.64$ Å for the HX adducts mentioned above. The methylene C-P bond lengths are 1.8150(19) Å for $P1$-$C7$ and 1.8775(19) Å for $P2$-$C7$. There is an elongation of $P1$-$C7$ from the HX case of 0.043 and 0.020 Å for the HBr and HCl adducts, respectively.
5.2.2 Synthesis of $\text{H}_4\text{NPPO}$

Oxidation of the phosphine arm with hydrogen peroxide in dichloromethane at room temperature affords the corresponding phosphine oxide aminophosphonium halide in excellent yields. Multinuclear NMR spectra were taken of $\text{H}_4\text{NPPO} \cdot (\text{HBr})_2$ and $\text{H}_4\text{NPPO} \cdot (\text{HCl})_2$. For $\text{H}_4\text{NPPO} \cdot (\text{HCl})_2$ in CDCl$_3$, the $^1\text{H}$ NMR spectrum shows the methylene protons as a double of doublets at 4.99 ppm. In the $^{31}\text{P}$ NMR spectrum, two inequivalent phosphorous atoms have signals at 31.72 (s) and 23.36 (d, $J = 7.2$ Hz) ppm.
Scheme 5.6. Synthesis of $H_4$NPPO-$(HX)_2$.

Crystals suitable for single crystal X-ray diffraction experiments of $H_4$NPPO-$(HCl)_2$ were from concentrated acetonitrile solution. $H_4$NPPO-$(HCl)_2$ crystallizes in the monoclinic space group $P12_{1}/n$, with one molecule of $H_4$NPPO-$(HCl)_2$, one molecule of acetonitrile, and one water molecule in the asymmetric unit. Only $H_4$NPPO-$(HCl)_2$ is shown in Figure 5.7, for clarity. P-N bond lengths are 1.629(2) Å for P1-N1 and 1.6236(19) Å for P3-N2, respectively. The hydrogens bound to the nitrogen atoms show close contact to the chloride anions at 2.273 Å for N1-H···Cl1 and 2.251 Å for N2-H···Cl2. The methylene C-P bonds are C7-P1 as 1.806(2) Å and C7-P2 as 1.809(2) Å. The P=O bond lengths are 1.4779(19) Å for P2-O1 and 1.4807(18) Å for P4-O2.
Figure 5.7. Crystal structure of H₄NPPO-(HCl)₂. Atomic displacement ellipsoids drawn at 50% probability level. Most H atoms and solvent omitted for clarity. C (dark grey), N (blue), O (red), P (purple) and Cl (green).

Deprotonation of the H₄NPPO-(HX)₂ with a variety of bases was carried out. Reactions with nBuLi and tBuLi resulted in mixtures of products which were difficult to separate. However, deprotonation using NaNH₂ as a base in toluene or THF cleanly afforded the neutral phosphine oxide H₄NPPO in excellent yields (Scheme 5.7).

Scheme 5.7. Synthesis of H₄NPPO.

Multinuclear NMR spectra were taken of H₄NPPO in CDCl₃. The ¹H NMR spectrum shows the disappearance of the NH protons. The methylene CH₂ protons
come at 3.13 ppm as a triplet with $J = 13.7$ Hz coupling. In the $^{31}$P NMR spectrum, two sets of doublets are observed at 13.72 ppm ($J = 15.2$ Hz), and -13.46 ppm ($J = 15.0$ Hz).

Crystals suitable for single crystal X-ray diffraction experiments of H$_4$NPPO were grown by diffusion of hexane into a dichloromethane solution. H$_4$NPPO crystallizes in the orthorhombic space group Pna2$_1$, with one molecule of H$_4$NPPO as the asymmetric unit. Most notably, the P-N bond length contracts to 1.590(2) Å for P1-N1 and 1.565(3) Å, as compared to ~1.62 Å for the HCl adduct mentioned above. The methylene C-P bond lengths are 1.850(2) Å for P1-C7 and 1.824(2) Å for P2-C7.

Figure 5.8. Crystal structure of H$_4$NPPO. Atomic displacement ellipsoids drawn at 50% probability level. Only ipso C of phenyl rings bound to P shown for clarity. Most H atoms omitted for clarity. C (dark grey), N (blue), O (red), and P (purple).
5.2.3 Synthesis of H₄NPPS

Oxidation of the phosphine arm with elemental sulfur in dichloromethane for several hours at reflux affords the corresponding thiophosphine aminophosphonium halide in excellent yields after removal of solvent. Multinuclear NMR spectra were taken of H₄NPPS-(HBr)₂ in CDCl₃. Notably, the ¹H NMR spectrum shows a broad singlet at δ 10.61 ppm for the NH protons and the methylene protons as a double of doublets at 5.26 ppm. In the ³¹P NMR spectrum, 2 phosphorous signals appear as singlets at δ 32.24 ppm and 32.04 ppm.

For H₄NPPS-(HCl)₂, the NH protons appear at 10.96 ppm as a broad doublet. The four methylene protons appear as a double of doublets at 5.29 ppm in the ¹H NMR spectrum. In the ³¹P NMR spectrum, two singlets appear at 32.24 and 32.04 ppm.

Scheme 5.8. Synthesis of H₄NPPS-(HX)₂.

Crystals suitable for single crystal X-ray diffraction experiments were grown by diffusion of diethyl ether into a dichloromethane solution of H₄NPPS-(HCl)₂. H₄NPPS-(HCl)₂ crystallizes in the triclinic space group P-1 with one molecule of H₄NPPS-(HCl)₂ and four disordered dichloromethane molecules. Only H₄NPPS-(HCl)₂ is shown in Figure 5.9. P-N bond lengths are 1.6238(17) and 1.6326(16) Å for P1-N1 and P3-N2, respectively.
The S=P bond lengths are 1.9410(7) and 1.9463(8) Å for S1-P2 and S2-P4, respectively. The methylene C-P bonds are 1.7952(18) and 1.8167(19) Å for C7-P1 and C7-P2. The N1-H···Cl1 and N2-H···Cl2 contacts are 2.25 Å.

Figure 5.9. Crystal structure of $\text{H}_4\text{NPPS}-(\text{HCl})_2$. Atomic displacement ellipsoids drawn at 50% probability level. Most H atoms and solvent omitted for clarity. C (dark grey), N (blue), P (purple), S (yellow), and Cl (green).

The neutral thiophosphine, $\text{H}_4\text{NPPS}$, could be prepared by deprotonation of either $\text{H}_4\text{NPPS}-(\text{HBr})_2$ or $\text{H}_4\text{NPPS}-(\text{HCl})_2$ with two equivalents of nBuLi in toluene or THF in excellent yields as a yellow solid (Scheme 5.9). In the $^1\text{H}$ NMR spectrum, the disappearance of the NH protons is apparent, along with an upfield shift of the methylene protons, appearing as a triplet at 3.45 ppm. In the $^{31}\text{P}$ NMR spectrum, two inequivalent phosphorus atoms appear as doublets at 26.61 ($d, J = 17.6$ Hz, P=S) and -14.95 ($d, J = 17.6$ Hz, P=N) ppm.
Scheme 5.9. Synthesis of H₄NPPS.

Figure 5.10. Crystal structure of H₄NPPS. Atomic displacement ellipsoids drawn at 50% probability level. Only ipso C of phenyl rings bound to P shown for clarity. Most H atoms and solvent omitted for clarity. C (dark grey), N (blue), P (purple), and S (yellow).

Crystals suitable for single crystal X-ray diffraction experiments were grown by diffusion of pentane into a toluene solution. H₄NPPS crystallizes in the monoclinic space group C12/c1 with one molecule of H₄NPPS and one toluene molecule in the
asymmetric unit. The P-N bond lengths are 1.556(3) Å for P1-N1 and 1.569(3) Å for P3-N2. P=S bond lengths are 1.9321(16) Å for S1-P2 and 1.9426(15) Å for S2-P4, respectively. The methylene C-P bond lengths are 1.835(3) Å for P1-C7 and 1.820(3) Å for P2-C7.

5.3 Metalation Reactions

With H₄NPP, H₄NPPO, and H₄NPP, along with their HCl and HBr salts in hand, we began our studies of their coordination chemistry as bis(monoanionic) ligands – overall ligand charge being -2. Initially, we thought that the phosphine oxide would provide the most interesting chemistry, provided that the hard O donor would be a preferable match to hard metal centers like Mg and Al. By reacting the ligands with a variety of magnesium, zinc, and aluminum bases and salts, our attempts at isolating metal complexes are discussed below.

5.3.1 H₄NPPO

5.3.1.1 Synthesis of Mg-based complexes

Reacting one equivalent of H₄NPPO with two equivalents tBuMgCl in THF solution resulted in the formation of a colorless crystalline solid which displayed limited solubility, which made characterization difficult. However, if the reaction mixture was allowed to stand shortly after addition of tBuMgCl, colorless block crystals would form within 1 h at room temperature. Single crystal X-ray diffraction experiments demonstrated that the reaction conditions did not afford the anticipated heteroleptic
magnesium halide dimer complex as shown in Scheme 5.10. Instead, a bisligated homoleptic magnesium dimer was characterized, shown in Figure 5.11.

\[ \text{Scheme 5.10. Attempted preparation of heteroleptic magnesium chloride dimer.} \]

The crystal structure shows two magnesium atoms are each tetrahedrally coordinated to two H$_2$NPPO$^2$- ligands in a ($\kappa^2$-N,O) ($\kappa^2$-N',O'). Bond lengths of the O and N donors to the Mg center are as follows: Mg1-O1 1.9611(11), Mg1-O2i 1.9751(11), Mg1-N1 2.0647(12), Mg1-N2i 2.0374(12). Each Mg center is a distorted tetrahedron with bond angles O1-Mg1-O2i 102.74(4), O1-Mg1-N2i 113.82(5), O1-Mg1-N1 106.24(5), N1-Mg1-O2i 121.01(5). There is elongation of the P1-N1 bond to 1.6276(12) Å from 1.590(2) Å in the neutral ligand. Each methylene bridge has been deprotonated to give the corresponding methanide which is almost trigonal planar with bond angles P1-C7-P2 at 127.59(11), P1-C7-H7 115.3(15), and P2-C7-H7 at 116.5(15) degrees. The P1-C7 bond has contracted to 1.7178(14), as well as P2-C7 at 1.7011(14) Å from the neutral ligand having P1-C7 and P2-C7 bond lengths of 1.850(2) and 1.824(2) Å, respectively.
Figure 5.11. Crystal structure of [H$_2$NPPO-Mg]$_2$ (top) with truncated view to show coordination (bottom). Atomic displacement ellipsoids drawn at 50% probability level. Only ipso C of phenyl rings bound to P shown for clarity. Most H atoms and solvent omitted for clarity. C (dark grey), N (blue), O (red), P (purple), and Mg (light grey).
Other attempts at making the heteroleptic magnesium complexes were attempted using di-\textit{n}-butylmagnesium, other Grignard reagents, and Mg[N(SiMe$_3$)$_2$]$_2$—all resulting in the isolation of the homoleptic bisligated magnesium dimer.

![Scheme 5.11](image)

**Scheme 5.11.** Formation of [H$_2$NPPO-Mg]$_2$ can be achieved by various magnesium bases in THF solution, where $X =$ alkyl, amide, and $Y =$ alkyl, amide, or halide.

### 5.3.1.2 Synthesis of Zn-based complexes

Reacting one equivalent of H$_4$NPPO with two equivalents ZnEt$_2$ in THF solution resulted in the formation of a colorless crystalline solid which displayed limited solubility, which made characterization difficult. However, if the reaction mixture was allowed to stand shortly after addition of ZnEt$_2$, colorless block crystals formed within one hour at room temperature. Single crystal X-ray diffraction experiments demonstrated that the reaction conditions did not afford the anticipated heteroleptic alkyl zinc dimer complex as shown in Scheme 5.12, however the formation of the homoleptic bisligated zinc dimer was observed.
The crystal structure, shown in Figure 5.12, shows the bisligated zinc dimer where two zinc atoms are each tetrahedrally coordinated to two $\text{H}_2\text{NPPO}^{2-}$ ligands in a ($\kappa^2$-N,O) ($\kappa^2$-N,O'). Bond lengths of the O and N donors to the Zn center are as follows: 

\[
\text{Zn1-O1} \ 2.0021(14) \ \text{Å}, \ \text{Zn1-O2i} \ 1.9979(13) \ \text{Å}, \ \text{Zn1-N1} \ 1.9772(15) \ \text{Å}, \ \text{Zn1-N2i} \ 1.9860(15) \ \text{Å}.
\]

Each zinc center is a distorted tetrahedron with bond angles (in degrees, °): O2i-Zn1-O1 99.73(6), N1-Zn1-O1 100.53(6), Zn1-Zn1-O2i 112.34(6), N1-Zn1-N2i 114.52(6). There is elongation of the P1-N1 bond to 1.6118(16) from 1.590(2) Å in the neutral ligand. Each methylene bridge has been deprotonated to give the corresponding methanide which is almost trigonal planar with bond angles P1-C7-P2 at 127.59(11), P1-C7-H7 115.3(15), and P2-C7-H7 at 116.5(15) degrees. The P1-C7 bond has contracted to 1.704(2), as well as P2-C7 at 1.710(2) Å from the neutral ligand having P1-C7 and P2-C7 bond lengths of 1.850(2) and 1.824(2) Å, respectively. This structure is isostructural to the homoleptic magnesium dimer.
Figure 5.12. Crystal structure of $\text{[H}_2\text{NPPO-Zn]}_2$ (top) with truncated view to show coordination (bottom). Atomic displacement ellipsoids drawn at 50% probability level. Only ipso C of phenyl rings bound to P shown for clarity. Most H atoms and solvent omitted for clarity. C (dark grey), N (blue), O (red), P (purple), and Zn (light blue-grey).
One attempt at an NMR-scale reaction of H₄NPPO with Zn[N(SiMe₃)₂]₂ in benzene resulted in the eventual formation of the homoleptic bisligated zinc dimer after heating at 60 °C for several days.

To date, the isolation of the heteroleptic metal complexes have eluded us. Thus, it appears that formation of the homoleptic dimer is thermodynamically favorable for magnesium and zinc centers.

5.3.1.3 Synthesis of Al-based complexes

On one attempt, reaction of one equivalent of H₄NPPO with two equivalents AlMe₃ in toluene afforded the bis(dimethyl)aluminum heteroleptic complex (Scheme 5.14). Small colorless crystals formed upon diffusion of pentane into a concentrated solution.
toluene solution of the reaction mixture. The crystals were of poor quality and displayed weak diffraction, which fortunately resulted in data sufficient enough for connectivity information, shown in Figure 5.13. The bis(monoanionic) ligand supports two aluminum centers which are four-coordinate, binding to the ligand in a (κ²-N,O) fashion, as well as two methyl groups.

![Crystal structure of [H₂NPPO-(AlMe₂)₂].](image)

Figure 5.13 Crystal structure of [H₂NPPO-(AlMe₂)₂]. Only ipso C of phenyl rings bound to P are shown for clarity. H atoms omitted for clarity. C (dark grey), N (blue), O (red), P (purple), and Al (light pink).

Unfortunately, several attempts to replicate these results have failed thus far.

5.4 DFT Calculations

To investigate the apparent thermodynamic stability of [H₂NPPO-Mg]₂ and [H₂NPPO-Zn]₂, DFT calculations were carried out. As our model system, we chose to explore the ligand distribution of the heteroleptic [H₂NPPO-{MgCl(THF)}₂] complex to homoleptic dimer, [H₂NPPO-Mg]₂ and MgCl₂(THF)₄, as the molecular structure of tetrakis-(tetrahydrofuran)magnesium dichloride is established via X-ray crystallography.
The crystal structure of $[\text{H}_2\text{NPPO-Mg}]_2$ was used as a starting point for the homoleptic dimer, $[\text{H}_2\text{NPPO}^*-\text{Mg}]_2$. To reduce calculation expenditure, the phenyl rings in the ligand backbone were replace with methyl groups, shown in Figure 5.14. The heteroleptic complex was built by replacing one of the $\text{H}_2\text{NPPO}^2\text{-}$ ligands with chloride anion and a molecule of THF for each Mg center.

![Simplified model of $[\text{H}_2\text{NPPO-Mg}]_2$ with methyl groups replacing the phenyl substituents on P. Most H atoms and solvent omitted for clarity. C (dark grey), N (blue), O (red), P (purple), and Mg (light grey).](image)

Figure 5.14 Simplified model of $[\text{H}_2\text{NPPO-Mg}]_2$ with methyl groups replacing the phenyl substituents on P. Most H atoms and solvent omitted for clarity. C (dark grey), N (blue), O (red), P (purple), and Mg (light grey).

The geometry of each structure was optimized at the B3LYP/6-31G* level of theory. Reasonable agreement was found between calculated and experimentally determined structures with $[\text{H}_2\text{NPPO}^*-\text{Mg}]_2$ and $\text{MgCl}_2(\text{THF})_4$. Frequency and stability calculations for all structures at the same level of theory showed that each optimized structure was at an energy minimum.
In the gas phase, the energy of formation for the homoleptic dimer, \([\text{H}_2\text{NPPO}*-\text{Mg}]_2\) is unfavorable by 27 kcal/mol, as compared to the formation of the heteroleptic dimer, \([\text{H}_2\text{NPPO}*-\{\text{MgCl(thf)}\}_2]\), shown in Scheme 5.15. Since the major product isolated experimentally is the homoleptic dimer, calculations with an implicit THF solvent model were carried out.\(^{[32]}\) The individual components become more stable in energy. Most notably, the heteroleptic dimer, \([\text{H}_2\text{NPPO}*-\{\text{MgCl(THF)}\}_2]\), is stabilized by 21.6 kcal/mol, as compared to the 17.1 kcal/mol stabilization experienced by the homoleptic dimer. As a result, the formation of the homoleptic dimer becomes 40 kcal mol\(^{-1}\) less favorable.

This proves to be an interesting result since products isolated from metalation reactions using magnesium and zinc bases are identified as the bisligated homoleptic dimers. One explanation for this is the homoleptic dimers are insoluble in tetrahydrofuran or arene solvent, and thus precipitation drives the equilibrium towards the formation of the ligand redistributed product.

\[ \begin{align*}
\text{THF} & \quad \text{THF} \\
\text{Mg} & \quad \text{Mg} \\
\text{Me} & \quad \text{Me} \\
\text{N} & \quad \text{N} \\
\text{P} & \quad \text{P} \\
\text{Me} & \quad \text{Me} \\
\text{H} & \quad \text{H} \\
\end{align*} \]

\[ \Delta E = 27 \text{ kcal mol}^{-1} \]

\[ \begin{align*}
\text{2 MgCl}_2(\text{THF})_4 & \\
\end{align*} \]

Scheme 5.15 Ligand redistribution of \([\text{H}_2\text{NPPO}*-\{\text{MgCl(THF)}\}_2]\) to form the homoleptic bisligated dimer, \([\text{H}_2\text{NPPO}*-\text{Mg}]_2\), is thermodynamically unfavorable, as suggested by calculations performed at the B3LYP/6-31G* level of theory.
5.5 Conclusions

Three novel tetradeionate \textit{m-}phenylene-bridged methylene(phosphinimino/phosphorane) ligands have been synthesized utilizing an approach based on the Kirsanov reaction. Attempts to study the coordination chemistry of these ligands to magnesium, zinc, and aluminum centers as bis(monoanionic) donors have been initiated through this work.

Magnesium and zinc complexes of the deprotonated phosphine oxide ligand \(H_2\text{NPPO}^2\) experience disproportionation in THF and arene solution. The resulting isolated homoleptic bisligated metal complexes feature two tetrahedral metal centers, coordinated to the ligands in a \((\kappa^2\text{-N,O})\ (\kappa^2\text{-N’,O’})\) fashion. Without steric bulk on the outer phosphorane arm, bisligation to divalent metals seems favorable to form homoleptic dimers. However, calculations suggest that the formation of the homoleptic dimer is thermodynamically favorable. The isolation of the homoleptic dimer as the major product could indicate that once the homoleptic dimer forms, it precipitates from solution, driving the equilibrium towards the formation of homoleptic dimer.

Meanwhile, reaction of \(H_4\text{NPPO}\) with two equivalents of \(\text{AlMe}_3\) affords a heteroleptic dimethylaluminum dimer with each aluminum center tetrahedrally coordinated by two methyl groups and the ligand in a \((\kappa^2\text{-N,O})\) fashion.

The coordination chemistry of \(H_4\text{NPP},\ H_4\text{NPPO},\) and \(H_4\text{NPPS}\) as neutral and bis(monoanionic) ligands needs to be further explored. In particular, not much is known about the coordination behavior of either the phosphine or thiophosphine ligand with magnesium, zinc, or aluminum.
5.6 Future Work

The three ligands described vide supra are a new class of ligands capable of forming dinuclear metal complexes. In this work, we have attempted metalation of the phosphine oxide, H₄NPPO, with magnesium, zinc, and aluminum bases. However, as mentioned previously, with the (phosphinimino/phosphorano)methane moieties and their ability to form methanide and methandiide complexes, it would be interesting to see this new class of ligands exhibit similar behavior. Synthesizing the alkali salts of the ligand (from monoanionic to tetraanionic) would open the doors to interesting chemistries, particularly with transmetalation to transition or rare earth metals. The preparation of heterobimetallic complexes may also be of interest.

To prevent bisligation, synthesizing additional ligand derivatives with sterically bulky outer phosphorane arms would be beneficial. For instance, the installation of bulky N-aryl substitutents or the formation of a phosphine-borane adduct on the outer arms of the ligand may prove interesting and allow for the isolation of heteroleptic magnesium or zinc complexes.

5.7 Experimental

5.7.1 General Procedures

All manipulations were carried out using either standard Schlenk techniques under a nitrogen atmosphere or in an argon-filled glovebox, unless otherwise indicated. All glassware was flame- or oven-dried prior to use. Toluene, tetrahydrofuran (THF), hexane, and diethyl ether were degassed and purified by passage through a solvent
purification system (Innovative Technology). Pentane and dichloromethane were distilled from CaH₂ and stored over 4 Å molecular sieves. Bis(diphenylphosphino)methane (dppm, Acros), bromine (Sigma-Aldrich), H₂O₂ (30% w/w, Sigma-Aldrich), sulfur (Alfa Aesar), and sodium amide (NaNH₂, Alfa Aesar) were used as received. m-Phenylenediamine (m-Ph(NH₂)₂) (Acros) was recrystallized from ethanol and sublimed prior to use. DABCO (Acros) was recrystallized from petroleum ether and then sublimed prior to use. n-Butyllithium (nBuLi, 2.5 M in hexanes), di-n-butylmagnesium (nBu₂Mg, 1.0 M in heptane), tert-butylmagnesium chloride (tBuMgCl, 2.0 M in diethyl ether), diethylzinc (ZnEt₂, 1.0 M in hexanes) trimethylaluminum (AlMe₃, 2.0 M in toluene) were purchased from Sigma-Aldrich and were standardized by titration against salicylaldehyde phenylhydrazone in dry THF prior to use. Deuterated solvents (chloroform-d, methylene chloride-d₂, benzene-d₆) were purchased from Cambridge Isotope Laboratories (CIL, Tewksbury, MA) and were degassed via several freeze-pump-thaw cycles, dried over CaH₂, and stored over 4 Å molecular sieves. ¹H and ¹³C spectra were recorded on a Bruker AVANCE III HD 400, Bruker AVANCE III HD 500, or Varian DirectDrive 600 spectrometer at 293K and were referenced internally to the residual signals of the deuterated solvent. ³¹P NMR spectra were recorded on the same instruments and externally referenced relative to 85% H₃PO₄. Electrospray ionization (ESI) mass spectra were obtained using a Bruker microTOF-II mass spectrometer and the peaks reported are the mono-isotopic mass.
5.7.2 Ligand Synthesis

5.7.2.1 Synthesis of H₄NPP-(HBr)₂

Dppm (1.88 g, 4.88 mmol) in 50 mL CH₂Cl₂ was cooled to -78 °C. Bromine (250 μL, 4.88 mmol) was added dropwise. The orange solution was warmed to room temperature with a color change to clear, pale yellow upon warming. After cooling the solution to -78 °C, m-Ph(NH₂)₂ (528 mg, 4.88 mmol) was added as a solid, and the solution was warmed to room temperature. After stirring 1 h at room temperature, 20 mL water were added. The layers were separated and the organic phase was washed with water (2 x 20 mL) and dried over Na₂SO₄. Volatiles were removed via rotary evaporation, yielding a white solid residue, which was washed with diethyl ether. Yield: 2.37 g, 94%. ¹H NMR (400 MHz; CDCl₃): δ 10.21 (s, 2H), 7.88 (dd, J = 13.1, 7.6 Hz, 8H), 7.68-7.64 (m, 4H), 7.49 (td, J = 7.7, 3.6 Hz, 8H), 7.36 (td, J = 8.2, 1.3 Hz, 10H), 7.27-7.19 (m, 12H), 6.96 (s, 1H), 6.72-6.64 (m, 1H), 6.59-6.57 (m, 2H), 4.21 (d, J = 16.0 Hz, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 139.55 (s), 135.30 (dd, J = 12.0, 8.9 Hz), 135.01 (d, J = 2.7 Hz), 133.76 (dd, J = 10.9, 3.1 Hz), 133.22 (d, J = 21.6 Hz), 132.99 (d, J = 12.0 Hz), 130.24 – 129.50 (m), 128.99 (d, J = 7.9 Hz), 119.74 (s), 118.95 (s), 115.14 (d, J = 7.6 Hz), 110.73 (s), 25.41 (dd, J = 65.6, 33.7 Hz). ³¹P NMR (162 MHz; CDCl₃): δ 35.13 (d, J = 76.9 Hz, 2P), - 30.94 (d, J = 76.7 Hz, 2P). Crystals suitable for X-ray analysis were obtained from slow evaporation of acetonitrile solution of H₄NPP-(HBr)₂.
5.7.2.2 Synthesis of H₄NPP-(HCl)₂

Similar procedure to H₄NPP-(HBr)₂, however during the aqueous workup, the organic phase was also washed with a saturated aqueous NaCl solution (2 x 25 mL).

Yield: 95%. ¹H NMR (500 MHz; CDCl₃): δ 11.08 (s, 2H), 7.86 (dd, J = 12.8, 7.8 Hz, 8H), 7.65 (t, J = 7.2 Hz, 4H), 7.49-7.45 (m, 8H), 7.35-7.31 (m, 8H), 7.26-7.20 (m, 10H), 6.96 (s, 1H), 6.68 (t, J = 8.1 Hz, 1H), 6.57 (d, J = 7.1 Hz, 2H), 4.18 (d, J = 16.3 Hz, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 139.91 (s), 135.67 – 135.05 (m), 134.86 (s), 133.77 (dd, J = 10.8, 3.2 Hz), 133.14 (dd, J = 21.4, 9.7 Hz), 129.82 (dd, J = 19.0, 13.9 Hz), 129.02 (t, J = 10.4 Hz), 119.97 (s), 119.20 (s), 114.98 (s), 110.94 (s), 25.50 (dd, J = 66.0, 33.0 Hz). ³¹P NMR (202 MHz; CDCl₃): δ 25.09 (d, J = 76.2 Hz, 2P), -40.38 (d, J = 76.5 Hz, 2P). Crystals suitable for X-ray analysis were obtained from slow evaporation of acetonitrile solution of H₄NPP-(HCl)₂.

5.7.2.3 Synthesis of H₄NPP

H₄NPP-(HX)₂ (0.588 mmol) was suspended in 10mL toluene and cooled to -78 °C. nBuLi (2.5 M, 0.25 mL) was added slowly via syringe. The solution immediately turned yellow. The solution was allowed to warm to room temperature and stirred for 1 h. The solution was filtered to remove insoluble lithium salts and the solvent was removed under reduced pressure, yielding a yellow solid. Yield: 490 mg, 95%. ¹H NMR (500MHz, CDCl₃) δ = 7.58 (dd, J = 7.9, 11.1 Hz, 9 H), 7.34 - 7.27 (m, 4 H), 7.25 - 7.11 (m, J = 7.1, 7.1, 14.2 Hz, 30 H), 6.34 (d, J = 7.6 Hz, 2 H), 5.91 (br. s., 1 H), 2.92 (d, J = 12.5 Hz, 4 H). ³¹P NMR (202MHz, CDCl₃) δ = -7.49 (d, J = 39.6 Hz, 2 P), -36.54 (d, J = 52.8 Hz, 2 P). HRMS
(ESI-MS) m/z calc. for C_{56}H_{49}N_{2}P_{4} M^+ 873.2841, found 873.2829. Crystals suitable for X-ray analysis were obtained by pentane diffusion into chloroform solution of H_{4}NPP.

5.7.2.4 Synthesis of H_{4}NPPO-{(HBr)}_{2}

H_{2}O_{2} (170 μL, 1.5 mmol) was added to H_{4}NPP-{(HBr)}_{2} (1.035 g, 1 mmol) in 25 mL CH_{2}Cl_{2} and stirred at room temperature for 1 h. 20 mL water was added and the layers were separated. The organic phase was washed with water (2 x 20 mL) and dried over Na_{2}SO_{4}. Volatiles were removed via rotary evaporation, affording a cream-colored solid residue, which was redissolved in 5 mL CH_{2}Cl_{2} and precipitated by addition of diethyl ether. The resulting white solid was isolated via filtration. Yield: 997 mg, 93%.

5.7.2.5 Synthesis of H_{4}NPPO-{(HCl)}_{2}

H_{2}O_{2} (510 μL, 4.5 mmol) was added to H_{4}NPP-{(HCl)}_{2} (2.8375 g, 3 mmol) in 25 mL CH_{2}Cl_{2} and stirred at room temperature for 1 h. 20 mL water was added and the layers were separated. The organic phase was washed with water (2 x 20 mL) and dried over Na_{2}SO_{4}. Volatiles were removed via rotary evaporation, affording a cream-colored solid residue, which was dissolved in 5 mL CH_{2}Cl_{2} and precipitated by addition of diethyl ether. The resulting white solid was isolated via filtration. Yield: 2.80 g, 95%.

^{1}H\{^{31}P\} NMR (400 MHz; CD_{2}Cl_{2}): δ 10.93 (s, 2H), 7.85 (d, J = 7.5 Hz, 8H), 7.79 (d, J = 7.1 Hz, 8H), 7.61 (t, J = 7.5 Hz, 4H), 7.47 (t, J = 7.4 Hz, 4H), 7.39 (q, J = 6.7 Hz, 16H), 6.81 (t, J = 8.1 Hz, 1H), 6.63 (s, 1H), 6.57 (dd, J = 8.1, 2.0 Hz, 2H), 4.99 (s, 4H). ^{13}C NMR (101 MHz; CD_{2}Cl_{2}): δ 139.63 (s), 134.62 (d, J = 3.0 Hz), 133.67 (d, J = 11.9 Hz), 132.52 (d, J = 3.7 Hz), 132.13
(d, J = 2.8 Hz), 131.47 (d, J = 3.7 Hz), 130.49 (d, J = 10.3 Hz), 129.96 (s), 129.34 (d, J = 13.8 Hz), 128.78 (d, J = 12.7 Hz), 119.45 (s), 118.47 (s), 115.12 (d, J = 8.2 Hz), 110.97 (t, J = 7.8 Hz), 28.76 (dd, J = 61.6, 56.4 Hz). \( ^{31}\text{P} \) NMR (162 MHz; CD\(_2\)Cl\(_2\)): δ 31.72 (s, 2P), 23.26 (d, J = 7.2 Hz, 2P). Crystals suitable for X-ray analysis were obtained from slow evaporation of acetonitrile solution of H\(_4\)NPPO-(HCl)\(_2\).

5.7.2.6 Synthesis of H\(_4\)NPPO

H\(_4\)NPPO-(HX)\(_2\) (1 mmol) was suspended in 10 mL toluene. NaN\(_2\) (71 mg, 2 mmol) was added. After stirring for 2 h, the solution was filtered and solvent was removed under reduced pressure to afford a yellow solid. Yield: 875 mg, 96%. \(^1\text{H} \) NMR (500 MHz, CD\(_2\)Cl\(_2\)) δ 7.54 (m, J = 3.4 Hz, 16H), 7.40 (m, J = 1.8 Hz, 4H), 7.29 (m, J = 3.7 Hz, 8H), 7.22 (m, J = 2.1 Hz, 4H), 7.11 (m, J = 3.7 Hz, 8H), 6.83 (m, J = 2.4 Hz, 1H), 6.19 (q, J = 3.3 Hz, 2H), 5.53 (s, 1H), 3.13 (t, J = 13.7 Hz, 4H). \(^{13}\text{C} \)\(^{\{1\text{H}\}}\) NMR (126 MHz, CD\(_2\)Cl\(_2\)) δ 151.22 (s), 134.41 (s), 133.59 (s), 132.47 (d, J = 10.0 Hz), 131.81 (s), 131.51 (s), 131.00 (d, J = 9.6 Hz), 130.72 (s), 129.76 (s, NCCH\(_2\)CHCH), 128.67 (q, J = 9.6 Hz), 116.13 (t, J = 15.2 Hz, NC\(_2\)HCN), 115.26 (d, J = 24.3 Hz, NC\(_2\)HC), 31.23 (dd, J = 36.1 Hz, PCH\(_2\)P). \(^{31}\text{P} \)\(^{\{1\text{H}\}}\) NMR (202 MHz, CD\(_2\)Cl\(_2\)) δ 13.72 (d, J = 15.2 Hz, 2P), -13.46 (d, J = 15.0 Hz, 2P). Crystals suitable for X-ray analysis were obtained by pentane diffusion into dichloromethane solution of H\(_4\)NPPO.
5.7.2.7 Synthesis of H₄NPPS-(HBr)₂

S₈ (32 mg, 0.125 mmol) was added to H₄NPP- (HBr)₂ (517 mg, 0.5 mmol) in 15 mL CH₂Cl₂. The solution was brought to reflux for 4 h. Volatiles were removed to afford a colorless solid. Yield: 545 mg, 99%. ¹H NMR (600 MHz, CD₂Cl₂): δ = 10.98 (br. s., 2 H), 7.96 (dd, J = 7.7, 13.9 Hz, 8 H), 7.85 (dd, J = 7.9, 13.5 Hz, 8 H), 7.58 (t, J = 7.5 Hz, 4 H), 7.45 - 7.30 (m, 20 H), 6.74 (t, J = 8.2 Hz, 1 H), 6.52 - 6.44 (m, 3 H), 5.35 - 5.23 (m, 4 H). ¹³C NMR (151 MHz, CD₂Cl₂) δ 139.62 (s), 135.17 (d, J = 3.1 Hz), 134.61 (d, J = 11.6 Hz), 132.19 (d, J = 2.9 Hz), 131.65 (d, J = 3.9 Hz), 131.36 (d, J = 11.4 Hz), 130.26 (s), 129.63 (d, J = 13.7 Hz), 129.09 (d, J = 13.1 Hz), 118.90 (s), 118.25 (s), 116.02 (d, J = 7.9 Hz), 112.00 (t, J = 6.9 Hz), 30.25 (dd, J = 47.6, 67.3 Hz). ³¹P NMR (243 MHz, CD₂Cl₂) δ 32.31 (d, J = 1.9 Hz, 2P), 31.81 (s, 2P).

5.7.2.8 Synthesis of H₄NPPS-(HCl)₂

S₈ (64 mg, 0.25 mmol) was added to H₄NPP- (HCl)₂ (946 mg, 1 mmol) in 50 mL CH₂Cl₂. The solution was brought to reflux for 4 h. Volatiles were removed to afford a white solid. Yield: 813 mg, 81%. ¹H NMR (600 MHz; CDCl₃): δ 10.96 (d, J = 6.7 Hz, 2H), 7.97 (dd, J = 14.0, 7.2 Hz, 8H), 7.86 (dd, J = 13.7, 7.3 Hz, 8H), 7.59 (td, J = 7.5, 1.7 Hz, 4H), 7.42-7.34 (m, 20H), 6.74 (t, J = 8.2 Hz, 1H), 6.53 (s, 1H), 6.48 (dd, J = 8.2, 1.8 Hz, 2H), 5.29 (dd, J = 17.2, 13.4 Hz, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 139.18 (s), 135.04 (d, J = 2.9 Hz), 134.44 (d, J = 11.6 Hz), 131.99 (d, J = 2.8 Hz), 131.83 (d, J = 3.8 Hz), 131.21 (d, J = 11.3 Hz), 130.19 (s), 129.56 (d, J = 13.7 Hz), 128.99 (d, J = 13.1 Hz), 118.67 (s), 117.88 (s), 116.09 (d, J = 7.6 Hz), 111.96 (t, J = 7.4 Hz), 30.14 (dd, J = 67.2, 47.8 Hz). ³¹P NMR (202
MHz; CDCl$_3$): δ 32.24 (s, 2P), 32.04 (s, 2P). Crystals suitable for X-ray analysis were obtained by diffusion of diethyl ether into dichloromethane solution of H$_4$NPPS-(HCl)$_2$.

5.7.2.9 Synthesis of H$_4$NPS

H$_4$NPPS-(HX)$_2$ (0.1 mmol) was suspended in 10 mL toluene and cooled to -78 °C. nBuLi (2.2 M, 0.09 mL, 0.2 mmol) was added slowly via syringe. The solution immediately turned yellow. The solution was allowed to warm to room temperature and stirred for 1 h. The solution was filtered and the solvent was removed under reduced pressure, yielding a yellow solid 89 mg, 95%. $^1$H NMR (500MHz, C$_6$D$_6$) δ = 7.97 - 7.88 (m, 8 H), 7.58 (dd, $J$ = 7.7, 11.4 Hz, 8 H), 6.96 - 6.82 (m, 27 H), 6.78 - 6.69 (m, 9 H), 6.01 (br. s., 1 H), 3.45 (t, $J$ = 13.6 Hz, 4 H). $^{31}$P NMR (202MHz, C$_6$D$_6$) δ = 26.61 (d, $J$ = 17.6 Hz, 2 P), -14.95 (d, $J$ = 17.6 Hz, 2 P). Crystals suitable for X-ray analysis were obtained by hexane diffusion into toluene solution of H$_4$NPPS.

5.7.3 Metalation Reactions

5.7.3.1 Synthesis of [H$_2$NPPO-Mg]$_2$

H$_4$NPPO (90.5 mg, 0.1 mmol) was dissolved in 5 mL THF. nBu$_2$Mg (1.0 M, 0.2 mL, 0.2 mmol) was added at room temperature. The solution was stirred for 1 h. A white, microcrystalline solid formed. The solution was heated to a vigorous boil and slowly cooled to room temperature. Colorless crystals of [H$_2$NPPO-Mg]$_2$ formed. The insolubility of the crystals precluded NMR analysis.
5.7.3.2 Synthesis of $[\text{H}_2\text{NPPO-Zn}]_2$

$\text{H}_4\text{NPPO}$ (90.5 mg, 0.1 mmol) was dissolved in 5 mL toluene. $\text{ZnEt}_2$ (1.0 M, 0.2 mL, 0.2 mmol) was added at room temperature. The solution was stirred for 1 h. A white, microcrystalline solid formed. Solvent was removed under reduced pressure. The solid residue was dissolved in 6 mL boiling THF and slowly cooled to room temperature. Colorless crystals of $[\text{H}_2\text{NPPO-Zn}]_2$ formed. The insolubility of the crystals precluded NMR analysis.

5.7.4 X-ray Crystallography

Single crystals were examined under Paratone-N oil. The datum crystals were affixed to a Mitegen mounting loop and transferred to a 120K nitrogen stream of a Bruker Kappa or Bruker APEX-II diffractometer, equipped with an Oxford Cryostream 700 series low-temperature apparatus. Cell parameters were refined using reflections harvested from data collection with $I \geq 10\sigma(I)$. All data were corrected for Lorentz and polarization effects, and runs were scaled using SADABS. Structure solution was by either direct or Patterson methods and refined by full-matrix least-squares analysis of $F^2$ against all reflections. Olex2 was used for structure visualization. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen atoms on carbons were placed at calculated geometries and allowed to ride on the position of the parent atom. Hydrogen thermal parameters were set to 1.2 (1.5 for methyl) times the equivalent isotropic $U$ of the parent atom. Where warranted, reflection intensities were corrected for solvent contribution through the SQUEEZE
routine in PLATON.\textsuperscript{[38,39]} Mercury was used for structure visualization and analysis, as well as the creation of figures.\textsuperscript{[40]}

5.7.5 Computational Details

The Gaussian 09 series of programs were used for the calculations.\textsuperscript{[41]} Molecules were allowed to freely optimize at the B3LYP/6-31G* level of theory. The crystal structure data from [H\textsubscript{2}NPPO-Mg\textsubscript{2}] and MgCl\textsubscript{2}(THF)\textsubscript{4}\textsuperscript{[42]} were used as a starting point for the calculations of the homo- and heteroleptic complexes, [H\textsubscript{2}NPPO*-Mg\textsubscript{2}] and [H\textsubscript{2}NPPO*-\{(MgCl(THF))\textsubscript{2}\}], and MgCl\textsubscript{2}(THF)\textsubscript{4}.

5.8 References


APPENDIX A:
CRYSTALLOGRAPHIC INFORMATION

TABLE A.1:
CRYSTALLOGRAPHIC DATA FOR [ZN(OPZ)2]ZnCl2, Zn(OPz)Br, AND Zn(OPz)Et

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<th>Compound</th>
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<th>Zn(OPz)Br</th>
<th>Zn(OPz)Et</th>
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<td>C_{19}H_{24}N_4OZn</td>
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<td>0.71073</td>
<td>0.71073</td>
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<td>Monoclinic</td>
<td>Triclinic</td>
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<td>P-1</td>
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<td>90</td>
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TABLE A.2:
CRystallographic data for Mg(OPz)$_2$, LiMgOAcMac-H$_2$O-MeCN, and
[LiZn$_2$OAc$_3$Mac]$_2$

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<th>Compound</th>
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<th>LiMgOAcMac-H$_2$O-MeCN</th>
<th>[LiZn$_2$OAc$_3$Mac]$_2$</th>
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<td>---------------</td>
<td>---------------</td>
<td>--------</td>
</tr>
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<td>a/Å</td>
<td>11.0814(11)</td>
<td>11.02654(7)</td>
<td>17.017(2)</td>
</tr>
<tr>
<td>b/Å</td>
<td>11.9154(13)</td>
<td>11.81970(7)</td>
<td>17.808(2)</td>
</tr>
<tr>
<td>c/Å</td>
<td>36.595(4)</td>
<td>37.1576(3)</td>
<td>20.688(3)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>4832.0(9)</td>
<td>4842.7(6)</td>
<td>6269.2(13)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>d_c calc/g cm⁻³</td>
<td>1.422</td>
<td>1.297</td>
<td>1.431</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>1.851</td>
<td>2.760</td>
<td>0.672</td>
</tr>
<tr>
<td>Size/mm³</td>
<td>0.144 × 0.108 × 0.1</td>
<td>0.127 × 0.094 × 0.081</td>
<td>0.347 × 0.201 × 0.136</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>73093</td>
<td>298125</td>
<td>165478</td>
</tr>
<tr>
<td>Ind. refln</td>
<td>12189 [R_int = 0.1354]</td>
<td>9310 [R_int = 0.0642]</td>
<td>7802 [R_int = 0.0522]</td>
</tr>
<tr>
<td>Max., min. transmission</td>
<td>0.8862, 0.7993</td>
<td>1.00000, 0.89883</td>
<td>0.7457, 0.6907</td>
</tr>
<tr>
<td>Parameters</td>
<td>581</td>
<td>583</td>
<td>370</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>0.990</td>
<td>1.160</td>
<td>1.054</td>
</tr>
<tr>
<td>R₁, wR² [I&gt;2σ(I)]</td>
<td>0.0589, 0.1073</td>
<td>0.0377, 0.1024</td>
<td>0.0427, 0.1079</td>
</tr>
<tr>
<td>R₁, wR² (all data)</td>
<td>0.1361, 0.1369</td>
<td>0.0382, 0.1026</td>
<td>0.0577, 0.1194</td>
</tr>
<tr>
<td>Largest peak, hole/e Å⁻³</td>
<td>0.507, -0.651</td>
<td>0.636, -0.418</td>
<td>0.978, -0.508</td>
</tr>
</tbody>
</table>
### Table A.4:

**CRYSTALLOGRAPHIC DATA FOR H₄NPPO-(HCl)₂, H₄NPPO, AND H₄NPPS-(HCl)₂.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>H₄NPPO-(HCl)₂</th>
<th>H₄NPPO</th>
<th>H₄NPPS-(HCl)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C₅₈H₅₅Cl₂N₃O₅P₄</td>
<td>C₅₆H₄₈N₂O₂P₄</td>
<td>C₅₉H₅₆Cl₈N₂P₄S₂</td>
</tr>
<tr>
<td><strong>FW</strong></td>
<td>1036.83</td>
<td>904.84</td>
<td>1264.65</td>
</tr>
<tr>
<td><strong>Wavelength/Å</strong></td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
<td>Triclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P 1 21/n 1</td>
<td>Pna2₁</td>
<td>P-1</td>
</tr>
<tr>
<td><strong>a/Å</strong></td>
<td>22.245(4)</td>
<td>24.936(3)</td>
<td>11.9412(6)</td>
</tr>
<tr>
<td><strong>b/Å</strong></td>
<td>11.037(2)</td>
<td>13.2055(14)</td>
<td>11.9799(6)</td>
</tr>
<tr>
<td><strong>c/Å</strong></td>
<td>23.122(4)</td>
<td>15.1364(16)</td>
<td>21.0872(11)</td>
</tr>
<tr>
<td><strong>α/°</strong></td>
<td>90</td>
<td>90</td>
<td>89.951(2)</td>
</tr>
<tr>
<td><strong>β/°</strong></td>
<td>112.353(3)</td>
<td>90</td>
<td>86.449(2)</td>
</tr>
<tr>
<td><strong>γ/°</strong></td>
<td>90</td>
<td>90</td>
<td>86.736(2)</td>
</tr>
<tr>
<td><strong>Volume/Å³</strong></td>
<td>5250.3(17)</td>
<td>4984.3(9)</td>
<td>3005.9(3)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>4</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td><strong>d_calc/g cm⁻³</strong></td>
<td>1.312</td>
<td>1.206</td>
<td>1.397</td>
</tr>
<tr>
<td><strong>µ/mm⁻¹</strong></td>
<td>0.294</td>
<td>0.194</td>
<td>0.591</td>
</tr>
<tr>
<td><strong>Size/mm³</strong></td>
<td>0.206 × 0.195 × 0.073</td>
<td>0.494 × 0.491 × 0.455</td>
<td>0.462 × 0.347 × 0.12</td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>140681</td>
<td>12593</td>
<td>54412</td>
</tr>
<tr>
<td><strong>Ind. refln</strong></td>
<td>12988 [R_int = 0.0857]</td>
<td>12593 [R_int = 0.0282]</td>
<td>15579 [R_int = 0.0219]</td>
</tr>
<tr>
<td><strong>Max., min. transmission</strong></td>
<td>0.9946, 0.9341</td>
<td>0.6394, 0.5934</td>
<td>0.7210, 0.6056</td>
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<tr>
<td><strong>Parameters</strong></td>
<td>635</td>
<td>548</td>
<td>712</td>
</tr>
<tr>
<td><strong>Goodness-of-fit on F²</strong></td>
<td>1.026</td>
<td>1.066</td>
<td>1.027</td>
</tr>
<tr>
<td><strong>R₁, wR² [I&gt;2σ(I)]</strong></td>
<td>0.0516, 0.1182</td>
<td>0.0354, 0.0909</td>
<td>0.0424, 0.1125</td>
</tr>
<tr>
<td><strong>R₁, wR² (all data)</strong></td>
<td>0.0842, 0.1361</td>
<td>0.0403, 0.0936</td>
<td>0.0533, 0.1197</td>
</tr>
<tr>
<td><strong>Largest peak, hole/e,Å⁻³</strong></td>
<td>0.995, -0.570</td>
<td>0.737, -0.280</td>
<td>1.491, -0.824</td>
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</table>
TABLE A.5:


<table>
<thead>
<tr>
<th>Compound</th>
<th>H₄NPPS</th>
<th>[H₂NPPO-MG]₂</th>
<th>[H₂NPPO-ZN]₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₆₃H₅₈N₂P₂S₂</td>
<td>C₇₂H₇₈MgN₂O₆P₄</td>
<td>C₇₂H₇₈N₂O₆P₂Zn</td>
</tr>
<tr>
<td>FW</td>
<td>1029.09</td>
<td>1215.55</td>
<td>1256.61</td>
</tr>
<tr>
<td>Wavelength/Å</td>
<td>0.71073</td>
<td>1.54178</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C 1 2/c 1</td>
<td>P-1</td>
<td>P-1</td>
</tr>
<tr>
<td>a/Å</td>
<td>40.034(7)</td>
<td>14.9686(7)</td>
<td>14.954(2)</td>
</tr>
<tr>
<td>b/Å</td>
<td>19.957(3)</td>
<td>15.6913(7)</td>
<td>15.598(2)</td>
</tr>
<tr>
<td>c/Å</td>
<td>15.203(2)</td>
<td>16.0628(7)</td>
<td>16.048(2)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
<td>110.798(2)</td>
<td>110.475(2)</td>
</tr>
<tr>
<td>β/°</td>
<td>94.341(5)</td>
<td>96.563(2)</td>
<td>96.789(3)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
<td>111.696(2)</td>
<td>111.817(2)</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>12112(3)</td>
<td>3143.4(3)</td>
<td>3120.3(8)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>d&lt;sub&gt;calc&lt;/sub&gt;/g cm&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>1.129</td>
<td>1.284</td>
<td>1.337</td>
</tr>
<tr>
<td>μ/mm&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>0.231</td>
<td>1.643</td>
<td>0.552</td>
</tr>
<tr>
<td>Size/mm&lt;sup&gt;3&lt;/sup&gt;</td>
<td>0.314 × 0.17 × 0.096</td>
<td>0.167 × 0.127 × 0.085</td>
<td>0.204 × 0.16 × 0.141</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>77255</td>
<td>68095</td>
<td>57075</td>
</tr>
<tr>
<td>Ind. refln</td>
<td>8695 [R&lt;sub&gt;int&lt;/sub&gt; = 0.1110]</td>
<td>11767 [R&lt;sub&gt;int&lt;/sub&gt; = 0.0377]</td>
<td>13821 [R&lt;sub&gt;int&lt;/sub&gt; = 0.0375]</td>
</tr>
<tr>
<td>Max., min. transmission</td>
<td>0.7455, 0.5115</td>
<td>0.6364, 0.5264</td>
<td>0.7455, 0.6922</td>
</tr>
<tr>
<td>Parameters</td>
<td>641</td>
<td>825</td>
<td>790</td>
</tr>
<tr>
<td>Goodness of fit on F&lt;sup&gt;2&lt;/sup&gt;</td>
<td>1.014</td>
<td>1.044</td>
<td>1.025</td>
</tr>
<tr>
<td>R₁, wR₂ [I&gt;2σ(I)]</td>
<td>0.0556, 0.1215</td>
<td>0.0329, 0.0866</td>
<td>0.0378, 0.0865</td>
</tr>
<tr>
<td>R₁, wR₂ (all data)</td>
<td>0.0942, 0.1411</td>
<td>0.0379, 0.0905</td>
<td>0.0529, 0.0930</td>
</tr>
<tr>
<td>Largest peak, hole/e&lt;sup&gt;-1&lt;/sup&gt;Å&lt;sup&gt;3&lt;/sup&gt;</td>
<td>0.306, -0.246</td>
<td>0.411, -0.287</td>
<td>0.981, -0.669</td>
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