Zinc–Phosphorus Clusters for Solution Synthesis of Zinc Phosphide Nanoparticles

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Abstract

Synthesis of zinc phosphide (Zn$_3$P$_2$) nanoparticles is an emerging topic of investigation as Zn$_3$P$_2$ is a candidate material for the next generation solar cells. Despite the early discovery of its favorable electronic properties that are well-suited for photovoltaic applications, a major focus of synthetic strategy has been vapor/chemical deposition methods. Solution methods with greater control over size, crystal structure and composition at a lower production cost, have been underdeveloped in comparison. In this context, this thesis describes the synthesis, characterization and reactivity of zinc phosphido clusters: [Zn$_2$(μ-PPh$_2$)$_2$(PPh$_2$)$_2$(NC$_5$H$_5$)$_2$], [Zn$_4$(μ-PPh$_2$)$_4$(OAc)$_4$(NC$_5$H$_5$)$_2$] and a phosphinidene cluster: [Zn$_6$(μ$_3$-PSiMe$_3$)$_4$(OAc)$_4$(NC$_5$H$_5$)$_5$] as potential single source precursors for solution synthesis of Zn$_3$P$_2$ nanoparticles. The clusters were prepared by reacting zinc acetate with silylphosphines and fully characterized via multinuclear NMR spectroscopy, single crystal XRD, melting point and combustion analysis. Use of the pyridine solvent was critical as pyridine ligands provided the necessary ligand stabilization for the isolation and crystallization of the clusters. When the zinc phosphido clusters were thermolyzed in pyridine, they yielded metallic zinc nanocrystals via a redox process. When the thermolysis was carried out with white phosphorus as an additive, soluble, zinc rich aggregates of zinc phosphides were produced. [Zn$_4$(μ-PPh$_2$)$_4$(OAc)$_4$(NC$_5$H$_5$)$_2$] showed reactivity with P(SiMe$_3$)$_3$, but a larger cluster framework could not be isolated. When thermolyzed in oleylamine, [Zn$_6$(μ$_3$-PSiMe$_3$)$_4$(OAc)$_4$(NC$_5$H$_5$)$_5$] produced highly crystalline, non-luminescent and soluble zinc phosphide nanoparticles, a first example of a direct cluster to nanoparticle conversion for Zn$_3$P$_2$.

Keywords
Summary for Lay Audience

Climate change continues to be an important issue of the generation with increasing cases of extreme weather and the rising sea level from melting glaciers. Of the many ways to mitigate anthropogenic contributions to this crisis is to shift our energy sources toward green and renewable energy such as solar in place of fossil fuels. Silicon based solar cells are the most widely used in the world due to the abundance of the element, but not for their efficiency. Indeed, there are other materials that could be more efficient at harvesting solar energy. Thus one strategy to improve our solar energy harvesting capability is to investigate these candidate materials to replace silicon. Zinc phosphide (Zn₃P₂) is one of such materials with properties that are better suited for applications in solar cells. However, it is not yet been commercialized with current efforts geared towards developing a method that is suitable for widespread use. This thesis contributes to this ongoing effort by investigating new routes towards synthesizing Zn₃P₂ nanoparticles.
Co-Authorship Statement

The work described in this thesis contains contributions from the author as well as co-workers Dr. John F. Corrigan and Dr. Yining Huang. The contributions of each are described below

Chapter 1 was written by the author and edited by Dr. Corrigan and Dr. Huang.

Chapter 2 describes the synthesis and the reactivity of a cluster compound prepared by the author. Dr. Corrigan is credited for crystallographic aspects of this chapter. The chapter was written by the author and edited by Dr. Corrigan and Dr. Huang.

Chapter 3 describes synthesis of cluster compounds by the author. Dr. Corrigan is credited for crystallographic aspects of this chapter. The chapter was written by the author and edited by Dr. Corrigan and Dr. Huang.

Chapter 4 was written by the author and edited by Dr. Corrigan and Dr. Huang.
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# Table of Contents

Abstract .................................................................................................................................. ii

Summary for Lay Audience ....................................................................................................... iii

Co-Authorship Statement ........................................................................................................ iv

Acknowledgements .................................................................................................................. v

Table of Contents .................................................................................................................... vii

List of Figures ........................................................................................................................ x

List of Schemes ....................................................................................................................... xiv

List of Appendices .................................................................................................................. xv

List of Abbreviations ................................................................................................................ xvi

Chapter 1 Introduction ............................................................................................................. 1

1.1 Semiconductor Nanoparticles (Quantum Dots) ............................................................... 1

1.1.1 Principles of Quantum Confinement and Size-Tunable Electronic Properties .... 1

1.1.2 Applications of Semiconductor Nanoparticles ......................................................... 4

1.1.3 Semiconductor Nanoparticles from Non-toxic and Earth-Abundant Elements .... 6

1.1.4 Preparative Methods .................................................................................................... 7

1.2 Atomically Precise Cluster Compounds ........................................................................... 10

1.2.1 Clusters as Model Systems, Intermediates and Precursors in Materials Chemistry .................................................................................................................. 10

1.2.2 Zinc Phosphido and Phosphinidene Clusters ......................................................... 13
Chapter 4 Conclusions and Outlook ................................................................. 66
4.1 Summary and Conclusions ........................................................................ 66
4.2 Outlook on Molecular Clusters for Developing Zinc Phosphide Nanoparticle Synthesis .................................................................................. 68
4.3 References ................................................................................................ 69
Appendices .................................................................................................... 70
Appendix 1 Permission to Reuse Copyright Material ........................................ 70
Appendix 2 Supporting Information for Chapter 2 ........................................... 76
Appendix 3 Supporting Information for Chapter 3 ........................................... 86
Curriculum Vitae ............................................................................................. 95
List of Figures

Figure 1.1 Changes in the energy level associated with an increase in the size of a semiconductor material. Discrete bands are closely spaced to form continuous bands with increasing size of the molecule to extended solids. Quantum dots are semiconductors at the nanometer regime where quantum confinement effect takes place. The size range of quantum dots is variable based on the material. ................................................................. 3

Figure 1.2 Quantum confinement effect in quantum dots. Spatial confinement leads to changes in the energy state of excitons leading to changes in emission. ................................. 4

Figure 1.3 Selected examples of applications of quantum dots: Live cell imaging with peptide labelled QDs, QD light-emitting diode, solar concentrators for increased performance for photovoltaic devices. Reproduced with permission from ref\textsuperscript{[30-32]}. Copyright 2017 © American Chemical Society. ........................................................................................................ 5

Figure 1.4 Minimum \$/W for 23 inorganic photovoltaic materials. The range of costs are between 0.327 \$/Watt for Ag\textsubscript{2}S and < 0.000002 \$/Watt for FeS\textsubscript{2}. Cost for Zn\textsubscript{3}P\textsubscript{2} (0.00069 \$/W) is indicated with a red arrow. Reproduced with permission from ref\textsuperscript{[35]}. Copyright © 2019 American Chemical Society. ........................................................................................................ 7

Figure 1.5 Nanoparticle synthesis by (a) hot-injection and (b) heat-up method. Adapted from ref\textsuperscript{[17]} with permission. Copyright © 2015 American Chemical Society. ......................... 8

Figure 1.6 A stainless steel autoclave vessel and a glass bottle with a Teflon\textsuperscript{TM} cap used in solvothermal synthesis. ........................................................................................................ 9

Figure 1.7 Proposed mechanism for the conversion of InP cluster to Cd\textsubscript{3}P\textsubscript{2}. Each transformation could be characterized using solution \textsuperscript{31}P NMR spectroscopy and powder XRD for direct comparisons. Adapted with from ref\textsuperscript{[97]} with permission. Copyright © 2017 American Chemical Society. ........................................................................................................ 11

Figure 1.8 Molecular structures of selected clusters: [(TMEDA)Zn(Sn\textsubscript{1}Bu\textsubscript{2})Se\textsubscript{3}], [Ni\textsubscript{12}(PMe)\textsubscript{10}(PET\textsubscript{3})\textsubscript{8}] and [In\textsubscript{37}P\textsubscript{20}(OBn)\textsubscript{51}] determined by single crystal XRD. Hydrogen
atoms were omitted for clarity. C = wireframe Zn = purple, Nitrogen = blue, Sn = grey, Se = green, Ni = emerald, P = yellow, O = red.\[86, 96, 102]\n
**Figure 1.9** Selected examples of zinc-phosphine, phosphido and phosphinidene clusters reported by Fenske and co-workers.\[103-105]\n
**Figure 2.1** $^{31}$P{$^1$H} NMR spectrum of Zn$_6$(μ$_3$-PSiMe$_3$)$_4$(OAc)$_4$(NC$_5$H$_5$)$_5$ in C$_6$D$_6$. \n
**Figure 2.2** Molecular structure of 1 in the crystal (ellipsoids drawn at the 40% probability level; hydrogen atoms not illustrated). Selected bond lengths (Å) and angles (°): Zn-N: 2.080(5)-2.100(9), Zn-O(μ-κ$^2$O-OAc): 2.042(4)-2.144(4), Zn-O (κ$^2$-OAc): 1.969(4), Zn-P: 2.311(2)-2.367(2), P-Si: 2.197(2)-2.211(3), Zn-P-Zn: 84.81(6)-116.71(7), P-Zn-P: 111.69(6)-116.42(6). \n
**Figure 2.3** $^1$H NMR spectra of 1 in pyridine-$d_5$ with increasing temperature. Spectra were taken approximately every 20 minutes. The chemical shifts at 2.41 and 0.09 (25 °C) are assigned to CH$_3$C(O) and PSiMe$_3$ groups in 1, respectively. The inset shows the increase in AcOSiMe$_3$ formed as reaction proceeds. Note that the CH$_3$C(O) shift from AcOSiMe$_3$ produced overlaps with that from the acetate units in 1......28

**Figure 2.4** SEM image of the micrometer sized aggregates of Zn$_3$P$_2$ nanoparticles synthesized by heating a pyridine solution of 1 in a steel autoclave at 130 °C for 24 hours. \n
**Figure 2.5** Overlaid powder XRD patterns of synthesized nanoparticles A, B and C (λ = 1.5406 Å). The black trace is the reference pattern for tetragonal α-Zn$_3$P$_2$ (Crystallography Open Database ID: 1010287). * is from the sample holder. \n
**Figure 2.6** TEM image of Zn$_3$P$_2$ nanoparticles A. \n
**Figure 2.7** TEM images of nanoparticles B grown at (left) 300 °C with 45 minutes of growth time and (right) C, 150 °C with 90 minutes of growth time. \n
**Figure 2.8** High resolution TEM image of Zn$_3$P$_2$ nanoparticles A. The highlighted lattice
fringe spacing of (2.8 Å) is consistent with the (220) planes of tetragonal α-Zn₃P₂.

**Figure 2.9** ATR-IR spectra and proposed assignments of 1 (red) and the Zn₃P₂ nanoparticles synthesized in oleylamine at 150 °C for 90 minutes (C, blue), 300 °C for 15 (A, black, top) and 45 minutes (B, black, bottom), respectively.

**Figure 3.1** Molecular structure of 1 in the crystal (ellipsoids drawn at 50% probability level; hydrogen atoms not illustrated for clarity). The molecule resides about a crystallographic inversion centre. Zinc and phosphorus atoms are shown as purple and orange spheres and carbon and nitrogen atoms are shown as grey and green wireframe. Selected bond lengths (Å): Zn-P(terminal): 2.3250(7), Zn-P(bridging): 2.4478(8), 2.4337(7). Selected bond angles (°): Zn-P-N: 89.95(2), 92.20(2).

**Figure 3.2** SEM image of the hexagonal and prismatic metallic zinc nanocrystals produced via thermolysis of 1.

**Figure 3.3** Powder XRD pattern of the grey solid (blue) produced from the thermolysis of 1, stacked with reference pattern for metallic zinc (Crystallography Open Database ID: 9008522).

**Figure 3.4** Powder XRD pattern of the thermolysis of 1 with P₄ (black) stacked with the reference pattern for α-Zn₃P₂ (Crystallography Open Database ID: 1010287). * are from the sample holder.

**Figure 3.5** SEM image of thermolysis product of 1 with P₄.

**Figure 3.6** ATR-IR spectrum of the dried thermolysis product of 1 with P₄.

**Figure 3.7** Molecular structure of 2 in the crystal (ellipsoids drawn at 50% probability level; hydrogen atoms not illustrated for clarity). Zinc and phosphorus atoms are shown as purple and orange spheres. Carbon, oxygen and nitrogen atoms are shown as grey, red and green wireframe. Selected bond lengths (Å): Zn-P: 2.353(1)-2.386(1), Zn-O(monodentate): 1.964(3)-1.966(3), Zn-O(bridging): 1.999(2)-2.073(2). Zinc to phosphorus bonds are intermediate in length (2.353(1)-2.386(1) Å) when compared to zinc bonded to bridging and
terminal phosphido ligands in 1................................................................. 55

Figure 3.8 Powder XRD pattern for the thermolysis product of 2 with P(SiMe₃)₃ overlaid with known phases of zinc phosphide. α-Zn₃P₂ (Crystallography Open Database ID: 1010287) (blue, top), Zn₃P₂-cubic (PDF-4+ 04-001-3699) (blue, bottom), ZnP₂-monoclinic (PDF-4+ 00-054-0208) (purple) and ZnP₄ (red) (PDF-4+ 00-038-1354)................................................................. 58

Figure 4.1 Molecular structures of new clusters presented in Chapter 2 and Chapter 3 of this thesis. ................................................................. 66
List of Schemes

**Scheme 1.1** Methanolysis of \{M(P(SiMe_3)_2)_2\}_2 (M = Cd and Zn) species. Methanolysis of the cadmium complex produces cadmium phosphido species *in situ*, which reacts further to form Cd_3P_2 nanoparticles. For the zinc analogue, cleavage of the zinc phosphorus bond is preferred due to oxophilicity of zinc. ................................................................. 14

**Scheme 1.2** One of Buriak’s binary synthesis with ZnMe_2 and P(SiMe_3)_3 in TOP (top). Cossairt’s ternary synthesis with Zn(OAc)_2, ZnEt_2 and P(SiMe_3)_3 in ODE (bottom). Proposed intermediates with corresponding ^31^P NMR shifts are shown. Hydrogen atoms were omitted for clarity. Zn = purple, O = red, C = grey. [43, 51, 107] .......................................................................................... 15

**Scheme 2.1** Synthesis of the cluster [Zn_6(μ_3-PSiMe_3)_4(OAc)_4(NC_5H_5)_5] 1 in pyridine (54% yield). ........................................................................................................................................ 25

**Scheme 3.1** Synthesis of 1 via two routes: 1) acid-base reaction 2) silyl deprotection The reaction progresses more slowly for the acid-base route with lower yield (80% versus 63%). ........................................................................................................................................ 48

**Scheme 3.2** Possible elimination mechanism for the diarylphosphido ligands from 1 ....... 49

**Scheme 3.3** Synthesis of 2 in pyridine (73% yield). ........................................................................................................................................ 54
List of Appendices

Appendix 1 Permission to Reuse Copyright Material ............................................................. 70

Appendix 2 Supporting Information for Chapter 2 ................................................................. 76

Appendix 3 Supporting Information for Chapter 3 ................................................................. 86
List of Abbreviations

HOMO Highest Occupied Molecular Orbital
LUMO Lowest Unoccupied Molecular Orbital
°C Degrees Celsius
Å Angstrom
Ar Aromatic Group
ATR Attenuated Total Reflection
Bn Benzyl Group
Bu Butyl Group
Cy Cyclohexyl Group
δ Chemical Shift
DCM Dichloromethane
EDX Energy Dispersive X-ray
Eg Band Gap Energy
Et Ethyl Group
eV Electron Volt
hr Hour
HR-TEM High-Resolution Transmission Electron Microscopy
ICP-MS Inductively Coupled Plasma Mass Spectroscopy
iPr Isopropyl Group
IR Infrared
Me Methyl Group
MeCN Acetonitrile
min Minute
ν Stretching
nm Nanometer
NMR Nuclear Magnetic Resonance
OAc Acetate Group
ODE 1-Octadecene
Ph Phenyl Group
py Pyridine
QDs Quantum Dots
rpm Rotations per Minute
RT Room Temperature
SEM Scanning Electron Microscopy
rBu tert-Butyl Group
TEM Transmission Electron Microscopy
THF Tetrahydrofuran
TMEDA Tetramethylethylenediamine
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>TMS</td>
<td>Trimethylsilyl Group</td>
</tr>
<tr>
<td>TOP</td>
<td>Trioctylphosphine</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<tr>
<td>V</td>
<td>Volts</td>
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<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
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Chapter 1
Introduction

1.1 Semiconductor Nanoparticles (Quantum Dots)

1.1.1 Principles of Quantum Confinement and Size-Tunable Electronic Properties

The band theory of solids defines semiconductors as materials with a full valence band and an empty conduction band separated by $E_g$, the band gap energy, with values of 1 to 4 eV (Figure 1.1, Bulk Semiconductor).\cite{1} Conceptually, as discrete molecules transition into extended solids, their molecular orbitals evolve from closely packed to ultimately produce the valence and the conduction bands. Hence the bands can be thought of as the bulk solids’ counterparts to molecular orbitals where the band gap energy corresponds to the HOMO-LUMO gap (Figure 1.1, Molecule). Similar to how the HOMO-LUMO gap can be fine-tuned in molecular systems by modifying the functional groups, the band gap energy of semiconductors can be engineered by changing composition. Just as different molecules have different HOMO-LUMO gaps, materials with different compositions have different band gap energies.

However, there is an intermediate state between molecular and bulk systems where the material’s electronic properties are not only governed by its composition, but by its size as well. Within a narrow size-regime, one can imagine breaking down the closely packed energy levels of the band structure by gradually removing the energy levels. This is achieved simply by removing the atoms or decreasing the size of the material which removes their contribution to the band structures. After a certain point, discrete energy levels exist near the Fermi level around both the conduction band and the valence band (Figure 1.1 Quantum Dot). The band gap energy may be modified in this regime where any addition or removal of atoms or simply put changing the size will have a direct effect on the energy levels that determine the band gap energy. This is termed the quantum confinement effect where size-tunability of the band gap is present which is not normally possible for bulk phase materials. This effect
is succinctly shown via the Brus equation, where the band gap is written as a function of \( r \), the radius/size of the material.\(^2\) When \( r \) approaches infinity as in the case of bulk materials, the terms that contain \( r \) in the denominator approach zero and their contribution to the band gap energy is negligible. However, when \( r \) is sufficiently small as in the case of nanomaterials, their contribution is significant to alter the band gap energy.

The band gap energy dictates the electronic properties of a material such as its optical absorption and emission. When an electron from the valence band is excited to the conduction via the absorption of light, it leaves behind a positively charged hole in the valence band forming an exciton. The electron-hole pair or an exciton may recombine resulting in the emission of a photon of light at an energy corresponding to the band gap energy, relax non-radiatively, or the charge carriers may be separated to generate an electric current. Given that the energy of the emitted photon is directly related to the band gap energy, this means the energy of the photon or the emission energy can be tuned by modifying the band gap energy. Whereas in bulk materials, electronic parameters are modified with doping, in nanomaterials this can be done by modifying particle size alone. Excitons have a physical radius associated with them, called the Bohr radius, the magnitude of which is material dependent. In bulk materials excitons behave as free particles, not confined by space. Changing the size of a material when its size is above a certain limit does not affect the excitons behavior as its Bohr radius is still several magnitudes smaller than the material. However, when the size of the material is reduced to a similar size of its excitons’ Bohr radius, the excitons are now confined by the material, leading to a change in their energy state affecting the emission energy (Figure 1.2).
Figure 1.1 Changes in the energy level associated with an increase in the size of a semiconductor material. Discrete bands are closely spaced to form continuous bands with increasing size of the molecule to extended solids. Quantum dots are semiconductors at the nanometer regime where quantum confinement effect takes place. The size range of quantum dots is variable based on the material.

\[ E_g(r) = E_g(r \rightarrow \infty) + \frac{\hbar^2 \pi^2}{2r^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.786e^2}{4\pi\varepsilon_0\varepsilon_r r} + O(r^{-3}) \]

**Equation 1.** Full Brus equation where \( E_g(r) \) is the band gap of the nanomaterial and \( E_g(r \rightarrow \infty) \) corresponds to the band gap of the bulk material. \( \hbar \) is the Planck constant, \( m_e^*, m_h^* \) are the effective mass of electron and hole, respectively. \( \varepsilon \) is the relative permittivity of the material, \( \varepsilon_0 \) is the vacuum relative permittivity, \( e \) is the elementary charge.\(^{[2]}\)
Figure 1.2 Quantum confinement effect in quantum dots. Spatial confinement leads to changes in the energy state of excitons leading to changes in emission.

1.1.2 Applications of Semiconductor Nanoparticles

Size-tunable electronic properties can be exploited in various ways, lending semiconductor nanoparticles or quantum dots (QDs) for versatile applications (Figure 1.3). As luminescent materials, they can be used in solid-state lighting. With tunable and narrow luminescence line widths, the nanoparticles can achieve suitable color purity for commercial applications in lighting and display technology. Commercial products with quantum dot displays are currently available, demonstrating the potential of this material as emitters. Another discipline that benefits from the luminescent nature of quantum dots is medicine where the quantum dots have shown utility in medical applications including live tissue imaging (Figure 1.3). In comparison to organic dyes, the quantum dots have unique advantages where quantum dots of different sizes and composition can be excited by a single light source to produce different emission colours with minimum overlap. Surface functionalization with biomolecules such as proteins, antibodies and peptides can be done
with well-established conjugation techniques allowing the quantum dots to bind to a variety of targets. They are also less susceptible to photobleaching and most importantly their emission can be tuned between 450 to 1500 nm, where the near-IR region is particularly useful for imaging tissues.\textsuperscript{[14]} QDs are also under intense investigation for their potential in photovoltaic applications.\textsuperscript{[15-20]} Although silicon-based solar cells remain the most widely used around the globe, they are not without downsides.\textsuperscript{[21]} Silicon’s indirect band gap structure and a band gap energy of 1.1 eV makes it unsuitable to efficiently harvest solar energy. In addition, its low absorption coefficient necessitates fabrication of thick layers, increasing material costs and also reducing performance from participation of phonons. Hence several lead chalcogenides and cadmium chalcogenides have been extensively studied due to their excellent performance from their direct band gap structure and suitable band gap energy to match the solar energy distribution for efficient light harvesting.\textsuperscript{[5, 22-29]}

**Figure 1.3** Selected examples of applications of quantum dots: Live cell imaging with peptide labelled QDs, QD light-emitting diode, solar concentrators for increased performance for photovoltaic devices. Reproduced with permission from ref\textsuperscript{[30-32]}. Copyright 2017 © American Chemical Society.
1.1.3 Semiconductor Nanoparticles from Non-toxic and Earth-Abundant Elements

Despite their rich potential, several limitations are present for commercial use of the most well developed QDs. Historically many of the pioneering studies and developments were made with cadmium-based quantum dots, as one of the earliest quantum dots discovered. Given their inherent toxicity, cadmium based system faces a significant barrier to commercialization over environmental concerns, as exemplified the ban of cadmium in electric and electronic devices sold in Europe by the European Commission by October 2019. Hence there is a clear need to develop materials that are based not only on Earth-abundant and inexpensive elements to reduce manufacturing costs, but materials based on non-toxic elements to minimize their hazardous effects on the environment.[14, 18, 33-34] A recent cost-benefit analysis on 23 semiconducting materials to determine possible alternatives to crystalline silicon.[35] This analysis considered factors such as natural abundance and raw material cost and found nine materials which can meet or exceed the worldwide demand in addition to decreased cost (Figure 1.4). Notable examples from this set of materials include multinary copper chalcogenides and iron sulfide.[33, 36-38] Among the materials selected as a potential candidate was zinc phosphide (Zn₃P₂). Several binary phases are known such as α-Zn₃P₂ (tetragonal), β-Zn₃P₂ (cubic), α-ZnP₂ (tetragonal), β-ZnP₂ (cubic), ZnP₂ (monoclinic), and ZnP₄ (monoclinic).[39] In particular, α-Zn₃P₂ has been incorporated into Li batteries as an anode material.[40-41] The potential for Zn₃P₂ in photovoltaic applications has been hinted at since the early work from the 1980s where a thin-film of Zn₃P₂ in a Schottky-junction solar cell achieved a power conversion efficiency of 6%.[42] However, while solution syntheses of nanoparticles of many earth-abundant and inexpensive inorganic materials with photovoltaic applications have been established, analogous syntheses for Zn₃P₂ nanoparticles are comparatively less well-developed.[43] Indeed the majority of the reported methods for the synthesis of Zn₃P₂ nanostructures is based on deposition methods with fewer solution methods, despite the fact that solution methods are more economical and enable more control of the material properties during synthesis.[43-51] Among the small number of earlier works are inadequate characterization such as the lack of powder X-ray diffraction or electron microscopy studies.[52-53] A set of robust solution based syntheses and characterization has
only been reported recently.\textsuperscript{[43, 51, 54]} Mechanistic studies and surface chemistry investigations of colloidal Zn$_3$P$_2$ are scarce.\textsuperscript{[55-56]}

![Figure 1.4](image.png)

**Figure 1.4** Minimum $\$/$W for 23 inorganic photovoltaic materials. The range of costs are between 0.327 $\$/Watt for Ag$_2$S and < 0.000002 $\$/Watt for FeS$_2$. Cost for Zn$_3$P$_2$ (0.00069 $\$/W) is indicated with a red arrow. Reproduced with permission from ref\textsuperscript{[35]}. Copyright © 2019 American Chemical Society.

1.1.4 Preparative Methods

There are several ways to prepare nanoparticles that have been developed over the past few decades, but the most prominent and well-studied is the hot-injection method, first reported by Bawendi and co-workers.\textsuperscript{[57-58]} It involves the rapid injection of precursor reagents into a heated high-boiling surfactant solvent and fast decomposition of the precursors to form nanoparticle ‘monomers’ which grow over the course of the reaction to
form the nanoparticles (Figure 1.5a).\textsuperscript{[59]} One of the most important advantages of this method is the precise temporal separation of nucleation and growth events. Immediately after injection, the precursors are decomposed to form the monomers and when the concentration of the monomer exceeds the critical point/concentration, they will nucleate and act as ‘seeds’ which will grow into larger particles. It is important that the nucleation and the growth phase are temporally separated without overlap. The mixing of the events will lead to higher particle size dispersity when the reaction is quenched because not all the nuclei will have had the same growth period.\textsuperscript{[60]} In addition, by the process of Ostwald ripening, small particles will be consumed to grow larger particles, further increasing the dispersity. A similar method to the hot-injection method is the heat-up method, where a solution of the precursors is steadily heated to initiate nucleation and subsequent particle growth (Figure 1.5b).\textsuperscript{[17, 61-63]} Combined, these two methods have been used to prepare a large number of nanomaterials based on both transition metal and main group elements.

\textbf{Figure 1.5} Nanoparticle synthesis by (a) hot-injection and (b) heat-up method. Adapted from ref\textsuperscript{[17]} with permission. Copyright © 2015 American Chemical Society.
Another method that is comparatively less explored is the solvothermal method.\cite{64-68} This method involves a reaction carried out in a closed system, typically in a stainless steel autoclave where the vessel is heated beyond the boiling point of the solvent used (Figure 1.6). This results in an autogenous pressure generated from the solvent vapor and thus the reaction is carried out at an elevated temperature and pressure. Contrary to solution methods at ambient conditions, the combination of elevated pressure and temperature allows for the use of otherwise insoluble compounds resulting in unusual reactivity, providing a unique route to condensed materials such as nanoparticles, gels, thin films, and chiral structures.\cite{69-71}

Figure 1.6 A stainless steel autoclave vessel and a glass bottle with a Teflon™ cap used in solvothermal synthesis.
1.2 Atomically Precise Cluster Compounds

1.2.1 Clusters as Model Systems, Intermediates and Precursors in Materials Chemistry

Atomically precise clusters of metals, main-groups and their multinary compounds are of interest to a wide range of chemists.\textsuperscript{[72-91]} As a collection of atoms with precise number and structure with sizes that are between small molecules and bulk solids, clusters have been viewed as a bridge to connect the two vastly different size regimes.\textsuperscript{[92-93]} In the context of materials chemistry, clusters occupy a very special position for a number of reasons. They are not exposed to surface defects and polydispersity induced effects that affect the photophysical properties. This allows clusters to be studied as an ideal model systems to elucidate structure-activity relationships and surface chemistry among others without the influence of surface induced energy traps.\textsuperscript{[55, 73, 94]} Solubilizing/capping ligands play an important role in the shape, size and size-distribution of nanoparticles, and their effect can be studied with exchange reactions at the nanocluster surface. The ligand exchange can be precisely characterized with NMR and IR spectroscopies and even single crystal XRD.\textsuperscript{[55, 95]} Cluster intermediates identified in nanoparticle synthesis can also be as a robust platform for studying reaction chemistry that is responsible for nanoparticle growth offering mechanistic details which are very important, but difficult to study.\textsuperscript{[73]} For example, Cossairt and co-workers isolated a stable In\textsubscript{37}P\textsubscript{20} intermediate en route to InP nanoparticles from a low temperature (100 °C) reaction of In(OAc)\textsubscript{2} and P(SiMe\textsubscript{3})\textsubscript{3}, which at higher temperatures produces InP nanoparticles.\textsuperscript{[96]} The cluster was used to study the elementary steps of nanoparticle growth by monitoring the transformation of the cluster to larger Cd\textsubscript{3}P\textsubscript{2} (Figure 1.7).\textsuperscript{[97]}
Figure 1.7 Proposed mechanism for the conversion of InP cluster to Cd$_3$P$_2$. Each transformation could be characterized using solution $^{31}$P NMR spectroscopy and powder XRD for direct comparisons. Adapted with from ref$^{[97]}$ with permission. Copyright © 2017 American Chemical Society.

A more direct application of clusters in materials chemistry is demonstrated by their use as molecular precursors for nanostructured assemblies.$^{[73]}$ Early examples of this strategy can be found from the 1990s, where small complexes/clusters of cadmium, gallium and indium were used to directly yield the bulk or nanomaterials with corresponding elemental composition.$^{[98-101]}$ At present there are many materials that have been synthesized using clusters as precursors including quaternary systems such as copper zinc tin selenide (Figure 1.8).
Figure 1.8 Molecular structures of selected clusters: [(TMEDA)Zn(SnrBu2)Se3], [Ni12(PMe)10(PEt3)8] and [In37P20(OBn)51] determined by single crystal XRD. Hydrogen atoms were omitted for clarity. C = wireframe Zn = purple, Nitrogen = blue, Sn = grey, Se = green, Ni = emerald, P = yellow, O = red. [86, 96, 102]
1.2.2 Zinc Phosphido and Phosphinidene Clusters

Although there is a large number of metal-phosphido and phosphinidene complexes known and well-characterized for their reactivity including applications in catalysis, there are far fewer zinc analogues containing these ligand classes. Fenske and co-workers reported zinc-phosphine, phosphido and phosphinidene clusters, but they were not investigated further beyond their initial discovery and structural characterization (Figure 1.9).[104] Buhro and co-workers reported several Group 12 and 14 silylphosphido complexes, \{M(P(SiMe$_3$)$_2$)$_2$\}$_2$ (M = Zn, Cd, Hg, Sn and Pb) and even showed that for cadmium, the dinuclear species can be reacted with methanol to produce Cd$_3$P$_2$ nanoparticles (Scheme 1.1).[106] Dinuclear zinc species was reacted the same way, but the formation of zinc methoxide was observed instead of Zn$_3$P$_2$ nanoparticles, where the methanolysis of Zn-P bonds were preferred over P-Si bonds. Although Zn$_3$P$_2$ nanoparticles could not be accessed, the work illustrated that simple molecular species can be used as single source precursors for preparing colloidal metal phosphide nanoparticles.

Figure 1.9 Selected examples of zinc-phosphine, phosphido and phosphinidene clusters reported by Fenske and co-workers.[103-105]
Methanolysis of \{M(P(SiMe\textsubscript{3})\textsubscript{2})\textsubscript{2}\} \textsubscript{2} (M = Cd and Zn) species. Methanolysis of the cadmium complex produces cadmium phosphido species \textit{in situ}, which reacts further to form Cd\textsubscript{3}P\textsubscript{2} nanoparticles. For the zinc analogue, cleavage of the zinc phosphorus bond is preferred due to oxophilicity of zinc.

Colloidal synthesis of zinc phosphide nanoparticles developed sporadically from the 1980s, but a robust method with well-characterized particles remained elusive until recently when the groups of Buriak and Cossairt independently reported their binary and ternary methods.\textsuperscript{[43, 51]} Buriak reported two sets of reactions: the first uses ZnMe\textsubscript{2} with trioctylphosphine in 1-octadecene and the second uses ZnMe\textsubscript{2} with P(SiMe\textsubscript{3})\textsubscript{3} in trioctylphosphine to produce 3~7 and 15 nm Zn\textsubscript{3}P\textsubscript{2} nanoparticles, respectively (Scheme 1.2). In the reaction of ZnMe\textsubscript{2} with P(SiMe\textsubscript{3})\textsubscript{3} they proposed the initial formation of a dinuclear intermediate [Me\textsubscript{2}Zn(μ-P(SiMe\textsubscript{3})\textsubscript{2})\textsubscript{2}], with a bridging phosphido moiety. This was based on spectroscopic observations (\textsuperscript{1}H and \textsuperscript{31}P NMR) and a literature precedent by Steigerwald and co-workers, where the formation of [Me\textsubscript{2}In(μ-P(SiMe\textsubscript{3})\textsubscript{2})\textsubscript{2}] from the reaction of Me\textsubscript{3}In and P(SiMe\textsubscript{3})\textsubscript{3} was reported.\textsuperscript{[98]} Cossairt and co-workers’ ternary system involved the reaction of Zn(OAc)\textsubscript{2}, ZnMe\textsubscript{2} and P(SiMe\textsubscript{3})\textsubscript{3} in 1-octadecene (Scheme 1.2). Their strategy involved a two-step process where Zn(OAc)\textsubscript{2} first reacts with ZnMe\textsubscript{2}, forming a pentanuclear zinc cluster [Zn\textsubscript{5}(OAc)\textsubscript{6}(Et)\textsubscript{4}], previously reported by Williams and co-workers, \textit{in situ}.\textsuperscript{[107]} The cluster then reacts with P(SiMe\textsubscript{3})\textsubscript{3} to form 2.6±0.5 nm Zn\textsubscript{3}P\textsubscript{2} nanoparticles. The motivation for their strategy was to pre-form a cluster containing Zn-P bonds, which then reacts to form the nanoparticles. Similar to Buriak’s work they also identified a molecular intermediate [(Et\textsubscript{2}Zn)(ZnOAc)\textsubscript{2}(μ\textsubscript{3}-PSiMe\textsubscript{3})], which they proposed contained the Zn-P bond they were targeting based on spectroscopic observations in the form of a phosphinidene moiety. Despite the strong spectroscopic evidence and the potential importance of these intermediates in the synthesis of Zn\textsubscript{3}P\textsubscript{2} nanoparticles, these molecular intermediates were not able to be isolated or characterized further.
Scheme 1.2 One of Buriak’s binary synthesis with ZnMe₂ and P(SiMe₃)₃ in TOP (top). Cossairt’s ternary synthesis with Zn(OAc)₂, ZnEt₂ and P(SiMe₃)₃ in ODE (bottom). Proposed intermediates with corresponding ³¹P NMR shifts are shown. Hydrogen atoms were omitted for clarity. Zn = purple, O = red, C = grey. [43, 51, 107]
1.3 Scope of Thesis

This thesis explores the molecular chemistry of zinc phosphido and phosphinidene clusters from their syntheses and their ability to serve as precursors to zinc phosphide nanoparticles. Chapter 2 focuses on the synthesis and characterization of a new hexanuclear zinc phosphinidene cluster and investigating its thermolysis pathway to yield colloidal zinc phosphide nanoparticles. Chapter 3 describes the synthesis of zinc phosphido clusters and their reactivity with common phosphorus sources used in metal phosphide nanoparticle synthesis. Chapter 4 summarizes the results of the previous chapters and discusses future objectives for the project.
1.4 References


Chapter 2

Facile synthesis of a hexanuclear zinc-acetato trimethylsilylphosphi nidene cluster: a single-source precursor to Zn$_3$P$_2$ nanoparticles

(A version of this work is published in the journal Chemical Communications.)


2.1 Introduction

Atomically-precise binary clusters comprised of metals and main group elements are a topic of significant interest not only for their structural features in fundamental research, but also as tools to study materials via these model systems together with a demonstrated utility as precursors and key intermediates to larger nanoscale assemblies.$^{[1-4]}$ The cluster chemistry of cadmium chalcogenides in particular has been developed extensively and found direct applications in binary and ternary semiconductor research, where cadmium chalcogenide clusters are used to prepare corresponding nanomaterials.$^{[2, 3]}$ Using these well-established syntheses allows study of ligand effects on the photophysical properties of the corresponding nanoparticles.$^{[5]}$ Significant insights have been gained from developing these systems but there is also a clear need to expand to other materials due to increasing environmental concerns over cadmium’s toxicity.$^{[6]}$ In this regard, first row d-block metal chalcogenides and phosphides have emerged as inexpensive and less toxic alternatives to Cd-Group 16 nanomaterials while retaining desirable properties of the former, such as the direct bandgap structure.$^{[6-7]}$ Notable progress in preparing such alternative nanomaterials has been made in the past decade but the complementary cluster chemistry of such systems is still underdeveloped.$^{[1]}$

Zinc phosphide (Zn$_3$P$_2$) is a binary semiconductor with non-toxic, Earth abundant and inexpensive constituent elements. With its direct bandgap structure, bandgap energy of
1.5 eV and a large absorption coefficient ($> 10^4$ cm$^{-1}$), it is a promising material well suited for optoelectronic applications.$^{[8-10]}$ Despite the favourable properties known since the 1980s, the development of solution based methods to access nanomaterials based on Zn$_3$P$_2$ was not firmly established until recently.$^{[8, 11-16]}$ The groups of Buriak and Cossairt independently reported two- and three-component synthesis of Zn$_3$P$_2$ nanocrystals, respectively, where evidence of first formed species was provided.$^{[8, 15]}$

Although the reported sizes and thus properties of the synthesized nanocrystals were different, both works proposed the initial formation of intermediate molecular (cluster) species prior to nanoparticle nucleation, based on spectroscopic observations. Even though there are examples of small complexes and larger covalent clusters of zinc and phosphorus reported, they have not been identified as key intermediates in any of the reported syntheses.$^{[17-24]}$ Indeed, the complementary cluster chemistry of such Zn-P systems is still lagging in the context of applications in materials synthesis. We speculated that low temperature reactions involving P(SiMe$_3$)$_3$ and solubilized Zn(OAc)$_2$ would result in the formation of cluster frameworks that might serve as useful precursors to higher order nanoparticle assemblies as Cossairt has described the spectroscopic characterization of a trinuclear cluster [([Et$_2$Zn](ZnO$_2$CMe)$_2$(μ$_3$-PSiMe$_3$)) and its reaction with P(SiMe$_3$)$_3$ to yield well defined, luminescent Zn$_3$P$_2$ nanoparticles.$^{[15]}$ Herein we report the room temperature synthesis and full characterization of the hexanuclear cluster [Zn$_6$(μ$_3$-PSiMe$_3$)$_4$(OAc)$_4$(NC$_5$H$_5$)$_5$] 1. We demonstrate that 1 serves as an easily handled, single-source precursor to nanoscopic Zn$_3$P$_2$ under lyothermal conditions in oleylamine. Detailed characterization of the nanoparticles is provided via UV-visible absorption, IR and NMR spectroscopies, powder XRD, ICP-MS, together with SEM, TEM and HR-TEM analyses.
2.2 Results and Discussion

Zinc precursors such as alkylzinc reagents, zinc halides and zinc \( \text{bis[bis(trimethylsilyl)amides]} \) have resulted in examples of molecular \( \text{Zn-P(SiR}_3)_2 \) (\( R = \text{Me, Ph} \)) and \( \text{Zn-P(SiMe}_3) \) based on the starting silylphosphine.\(^\text{[17-19, 21, 24-25]} \) Recently, Cossairt and coworkers have developed a ternary system for the synthesis of zinc phosphide nanoparticles using \( \text{Zn(OAc)}_2, \text{ZnEt}_2 \) and \( \text{P(SiMe}_3)_3 \).\(^\text{[15]} \) They showed in their synthesis that the particles are produced directly from the decomposition of the tetrahedrally-coordinated phosphorus precursor that is formed by the reaction of an \textit{in situ} generated pentanuclear zinc cluster with \( \text{P(SiMe}_3)_3 \).\(^\text{[26]} \) However, the intermediate [\((\text{Et}_2\text{Zn})(\text{ZnO}_2\text{CR})_2(\mu_3\text{-PSiMe}_3)\)] (\( R = \text{Me, (CH}_2)_2\text{Me} \)) could not be isolated due to its instability, even when longer chain zinc carboxylates used in this preparation were replaced with OAc.\(^\text{[15]} \) We observed that when pyridine solutions of \( \text{Zn(OAc)}_2 \) are reacted with 0.67 equivalent of \( \text{P(SiMe}_3)_3 \) at room temperature, a colour change from colourless to pale yellow was observed immediately, which intensified over the course of 1 hour (Scheme 2.1).

![Scheme 2.1 Synthesis of the cluster [Zn₆(μ₃-PSiMe₃)₆(OAc)₄(NC₅H₅)₅] 1 in pyridine (54% yield).](image)

\(^{31}\text{P}\{^1\text{H}\} \) NMR spectra of reaction solution samples indicate the consumption of \( \text{P(SiMe}_3)_3 \) (\( \delta = -252 \)) and the clean conversion to a single phosphorus containing species (\( \delta = -313 \)) (Figure 2.1). This value is in a similar range to the chemical shift reported (\( \delta = -276 \)) for [\((\text{Et}_2\text{Zn})(\text{ZnO}_2\text{CMe})_2(\mu_3\text{-PSiMe}_3)]\).\(^\text{[15]} \) The use of pyridine as a solvent/stabilizing donor
ligand was motivated in part by previous work with imine-stabilized zinc chalcogenolate complexes from Zn(OAc)$_2$ and E(SiMe$_3$)$_2$ (E = S, Se, Te).\cite{27} The introduction of additional equivalent of P(SiMe$_3$)$_3$ in these reactions does not lead to signals beyond that for 1 and excess phosphine being observed in these $^{31}$P{$^1$H} NMR spectra. Central to this reaction is the need for the donor solvent.

Layering reaction solutions with heptane leads to the precipitation of 1 in the form of pale yellow crystals (yield: 54%). The structure of 1 was determined by single crystal XRD: the cluster features an adamantane-type core, with the four $\mu_3$-PSiMe$_3$ occupying the vertices and six Zn(II) lying along the cluster edges (Figure 2.2). These ligands arise from the activation of two P-Si bonds from the starting phosphine and the generation of AcOSiMe$_3$. Each of the tetrahedral zinc completes its coordination environments via the three $\mu$-$\kappa^2$O-OAc together with either one ligated NC$_5$H$_5$ (Zn1-2; Zn4-6) or the fourth $\kappa^1$O-OAc (Zn3). The overall Zn$_6$P$_4$ arrangement in 1 is an example of the well-known adamantane cluster framework as reported in the anionic clusters [Zn$_4$(SPh)$_{10}$]$^{2-}$ (Dance), [Zn$_6$I$_6$(PSiMe$_3$)$_4$]$^{2-}$ (Fenske) and other Group 12 clusters.\cite{25,28,29} The phosphinidene ligands in 1 each bridge

**Figure 2.1** $^{31}$P{$^1$H} NMR spectrum of Zn$_6$(μ$_3$-PSiMe$_3$)$_4$(OAc)$_4$(NC$_5$H$_5$)$_5$ in C$_6$D$_6$.  

The phosphinidene ligands in 1 each bridge
three Zn(II) rather symmetrically (2.3108(15)-2.3668(18) Å). In addition to this cluster being a rare example of a Zn-PSiMe₃ complex, its novelty is rooted in its inherent Zn₆:(PSiMe₃)₄:(OAc)₄ stoichiometry as thermal activation of the remaining P-Si bonds via inter- or intracluster AcOSiMe₃ formation could lead to Zn₃P₂. Importantly, crystals of 1 can be prepared in multigram quantities and show no signs of decomposition upon exposure to air for several hours. Given the stability of 1, its utility as a precursor to Zn₃P₂ was probed.

**Figure 2.2** Molecular structure of 1 in the crystal (ellipsoids drawn at the 40% probability level; hydrogen atoms not illustrated). Selected bond lengths (Å) and angles (°): Zn-N: 2.080(5)-2.100(9), Zn-O(μ-κ²O-OAc): 2.042(4)-2.144(4), Zn-O (κ²-OAc): 1.969(4), Zn-P: 2.311(2)-2.367(2), P-Si: 2.197(2)-2.211(3), Zn-P-Zn: 84.81(6)-116.71(7), P-Zn-P: 111.69(6)-116.42(6).
Figure 2.3 $^1$H NMR spectra of 1 in pyridine-$d_5$ with increasing temperature. Spectra were taken approximately every 20 minutes. The chemical shifts at 2.41 and 0.09 at 25 °C are assigned to $\text{CH}_3\text{C}(\text{O})$ and $\text{PSiMe}_3$ groups in 1, respectively. The inset shows the increase in $\text{AcOSiMe}_3$ formed as reaction proceeds. Note that the $\text{CH}_3\text{C}(\text{O})$ shift from $\text{AcOSiMe}_3$ produced overlaps with that from the acetate units in 1.

Thermal activation of 1 was monitored by variable-temperature NMR spectroscopic experiments in deuterated pyridine and observing the production of $\text{AcOSiMe}_3$ (Figure 2.3). Despite the presence of different acetate groups in the solid state, only one chemical shift assigned to this group is observed in the $^1$H NMR spectrum of 1 at room temperature ($\delta = 2.41$). Notably, when heating solutions of 1 at temperatures as low as 45 °C, signals assigned to $\text{AcOSiMe}_3$ are observed in the $^1$H NMR spectrum. The reaction is also accompanied by a
colour change from pale yellow to orange to deep red as it progresses. No other molecular species/intermediates were observed based on $^1$H and $^{31}$P{$_^1$H} NMR spectra. Consumption of 1 (21 x 10$^{-3}$ M solution) is still incomplete after 148 hours at this temperature. At a temperature of 95 °C, spectra still show signals from 1 after 20 minutes of heating. However, when pyridine solutions of 1 are reacted at higher temperatures (130 °C; 24 hours) in a sealed autoclave, a deep red solution is obtained with no molecular phosphorus species observable via $^{31}$P{$_^1$H} NMR spectroscopy. Precipitation of red solids leads to micrometer sized aggregates of Zn$_3$P$_2$ nanoparticles (Figure 2.4).

$\textbf{Figure 2.4}$ SEM image of the micrometer sized aggregates of Zn$_3$P$_2$ nanoparticles synthesized by heating a pyridine solution of 1 in a steel autoclave at 130 °C for 24 hours.

Freely soluble Zn$_3$P$_2$ nanoparticles can be synthesized by thermolysis of 1 in oleylamine. At 300 °C, injection of solutions of 1 rapidly change colour from yellow to dark red. Nanoparticles can be isolated from these reaction solutions via their precipitation with the addition of methanol. Analysis of the resultant solids by powder X-ray diffraction confirms a diffraction pattern for Zn$_3$P$_2$ (Figure 2.5). An estimation of particle size from a
Scherrer analysis using the diffraction peak at 45° 2θ indicated but a small difference based on growth time post injection (A 15 min, ~7.7 nm; B 45 min, ~8.0 nm). Dynamic light scattering (DLS) measurements also confirmed a small increase in particle size with increased reaction time. The sizes of these particles are similar to those prepared from the injection of ZnEt$_2$ and P(SiMe$_3$)$_3$ in 1-octadecene/hexadecylamine at similar temperatures over 90 minutes.$^{[13]}$ Thermolysis of 1 in oleylamine at a lower temperature (150 °C; C) leads to consumption of the cluster and nanoparticle formation but materials that are qualitatively less stable under ambient atmospheric conditions.

![Overlaid powder XRD patterns of synthesized nanoparticles A, B and C (λ = 1.5406 Å). The black trace is the reference pattern for tetragonal α-Zn$_3$P$_2$ (Crystallography Open Database ID: 1010287). * is from the sample holder.](image)

**Figure 2.5** Overlaid powder XRD patterns of synthesized nanoparticles A, B and C ($\lambda = 1.5406$ Å). The black trace is the reference pattern for tetragonal α-Zn$_3$P$_2$ (Crystallography Open Database ID: 1010287). * is from the sample holder.
Nanoparticles A had an average diameter of 7.9 ± 1.4 nm, as determined by transmission electron microscopy (counting 100 individual particles as displayed in Figure 2.6). While DLS measurements of filtered samples of B indicated an increase in particle size with prolonged heating time at this temperature, TEM images of precipitated materials showed them to be present as larger aggregates (Figure 2.7). This is in agreement with experimental observations: cooling of oleylamine solutions of B leads to the formation of precipitates. TEM analysis of isolated particles C indicate that they, too, were largely present as aggregates of smaller species (Figure 2.7). HR-TEM micrographs of nanoparticles A illustrate the crystalline nature and lattice fringe spacing of 2.8 Å can be identified, consistent with the (220) planes of tetragonal α-Zn₃P₂ (Figure 2.8).
**Figure 2.7** TEM images of nanoparticles B grown at (left) 300 °C with 45 minutes of growth time and (right) C, 150 °C with 90 minutes of growth time.

**Figure 2.8** High resolution TEM image of Zn$_3$P$_2$ nanoparticles A. The highlighted lattice fringe spacing of (2.8 Å) is consistent with the (220) planes of tetragonal α-Zn$_3$P$_2$. 

32
IR spectroscopic analysis of particles A (15 min; 300 °C) showed, in addition to characteristic peaks assignable to the coordinated amine ligands (notably at 3005 and 1464 cm\(^{-1}\)), evidence for the presence of residual OAc, PSiMe\(_3\) and PH, based on previous observations and assignments (Figure 2.9).\(^{[13, 29]}\) \(^1\)H NMR spectra do not indicate significant amounts of such species. For comparison, the IR spectrum of the cluster I also displays bands that can be assigned to \(\mu_3\)-PSiMe\(_3\) with absorbances at 1236 (\(\rho\) SiMe\(_3\)) and 830 (\(\nu\) Si-C) cm\(^{-1}\) (Figure 2.9).\(^{[13, 30]}\) Notably, no signs of P-H in the IR spectrum via decomposition of I is evident after handling solid samples in air.
Figure 2.9 ATR-IR spectra and proposed assignments of 1 (red) and the Zn$_3$P$_2$ nanoparticles synthesized in oleylamine at 150 °C for 90 minutes (C, blue), 300 °C for 15 (A, black, top) and 45 minutes (B, black, bottom), respectively.
2.3 Experimental

2.3.1 General Considerations and Characterization Methods

All syntheses described were conducted under an atmosphere of high-purity dry dinitrogen using standard double-manifold Schlenk line techniques unless otherwise noted. Zinc acetate (99.99%) was purchased from Sigma and stored in a dinitrogen atmosphere glove box. *Tris*(trimethylsilyl)phosphine (CAUTION: spontaneously flammable in air; toxic; causes burns!) was prepared following a literature procedure. All solvents used were placed over molecular sieves and stored under dinitrogen gas: Oleylamine (70%) was purchased from Sigma, dried over CaH₂ and vacuum distilled. Anhydrous methanol was purchased from Fischer. Pentane and heptane were collected using an MBraun MB-SP Series solvent purification system. Deuterated solvents (benzene and pyridine) were purchased from Sigma. NMR spectra were recorded on Bruker 400 and Inova 600 spectrometers. \(^1H\), and \(^13C\{^1H\} \) chemical shifts are externally referenced to SiMe₄. \(^31P\{^1H\} \) chemical shifts are externally referenced to H₃PO₄ (75%). NMR experiments were carried out in NMR tubes with a J-Young valve.

X-ray measurements were made on a Bruker Kappa Axis Apex2 diffractometer equipped with graphite monochromated Mo Kα (\( \lambda = 0.71073 \) Å) radiation at a temperature of 110 K. The samples were mounted on a Mitegen polyimide micromount with a small amount of Paratone N oil. The unit cell dimensions were determined from a symmetry constrained fit of 9833 reflections with 5.38° < 2θ < 54.32°. The data collection strategy was a number of 2θ and φ scans which collected data up to 51.49° (2θ). The frame integration was performed using SAINT.\(^{32}\) The resulting raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS.\(^{33}\) The structure was solved by using a dual space methodology using the SHELXT program.\(^{34}\) All non-hydrogen atoms were obtained from the initial solution. The hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent atom. The structural model was fit
to the data using full matrix least-squares based on $F^2$. The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structure was refined using the SHELXL program from the SHELXTL suite of crystallographic software.\[35\] The difference Fourier map indicated residual solvent peaks for pyridine and (likely) pentane which could not be refined satisfactorily. As such, they were treated as a diffuse contribution to the overall scattering by SQUEEZE/PLATON.\[36\] Additional information and other relevant literature references can be found in the reference section of this website (http://xray.chem.uwo.ca). Atoms Zn3, Zn4, Zn5 as well as two of the $\mu$-$\kappa^2$-OAc and two of the coordinated C$_5$H$_5$N ligands were satisfactorily refined with a two site disorder (occupancy 82:18). C and N atoms associated with the minor component were refined isotropically. The hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent atom. The structural model was fit to the data using full matrix least-squares based on F2. The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. CCDC 1934903 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Powder XRD patterns were collected on Inel CPS powder diffractometer equipped with a Cu radiation source ($\lambda = 1.5406 \text{ Å}$). SEM imaging and energy-dispersive X-ray (EDX) spectroscopy analysis were performed using a LEO (Zeiss) 1540XB FIB/SEM system at Western Nanofabrication Facility, London, Canada. Prior to imaging, a thin film of amorphous osmium metal was deposited on the samples using a Filgen osmium plasma coater OPC80T to prevent charging and reduce damage from the electron beam during imaging. TEM and HR-TEM imaging were performed at the Canadian Centre for Electron Microscopy at McMaster University, Hamilton, Canada with Titan (ThermoFisher-Fei) CEOS image corrected microscope operated at 300 kV. Dynamic light scattering spectra were collected on Zetasizer Nano S from Malvern. Prior to measurement, nanoparticle solutions were filtered through ProMax™ Syringe Filter 13 mm 0.22 μm. UV-Vis spectra were recorded on Cary 5000 UV-Vis-NIR spectrophotometer. ATR-IR spectra were recorded on Spectrum Two FT-IR spectrometer. ESI-TOF mass spectra were acquired with Bruker microOTOF 11 with positive ion mode at the Western Chemistry Mass Spectrometry Facility,
London, Canada. Elemental analysis was performed with Perkin Elmer 2400 Series II at St. Mary’s University, Halifax, Canada. Samples were dried under dynamic vacuum (< 10 mTorr) for at least 48 hours prior to shipment in a vacuum-sealed ampoule. Samples from separate batches were used to ensure accuracy of the analyses. ICP-MS was performed with Agilent 7700 Series at the Biotron at the University of Western Ontario, London, Canada. High purity nitric acid was used to digest the nanoparticles and the solution was diluted with Milli-Q water.

2.3.2 Synthesis

Synthesis of Zn$_6$(μ$_3$-PSiMe$_3$)$_4$(OAc)$_4$(NC$_5$H$_5$)$_5$ (1): A 500 mL Schlenk flask was charged with Zn(OAc)$_2$ (3.0 g, 16 mmol) and a magnetic stir bar. The solid was dissolved in 50 mL of pyridine. The mixture was stirred rapidly for 20 minutes or until the solid dissolved completely. To this solution, P(SiMe$_3$)$_3$ (3.1 mL, 11 mmol) was added and stirred for 1 hour at room temperature. A yellow color developed as the reaction progressed. The stir bar was removed and the solution was layered with heptane, which gave rapidly desolvating crystals of 1 after 72 hours. Isolated crystals were washed with pentane and dried under dynamic vacuum (2.0 g, 54% yield); m.p. 158-160 °C (decomposition). $^1$H NMR (NC$_5$D$_5$, 400.13 MHz) δ 8.74 (9H, s, CH$_{Ar}$), 7.58 (5H, m, CH$_{Ar}$), 7.22 (9H, m, CH$_{Ar}$), 2.43 (12H, s, CH$_{Me}$), 0.08 (36H, s, CH$_{Me}$); $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 100.61 MHz) δ 178.4 (s, C$_{CO}$), 150.2 (s, C$_{Ar}$), 137.7 (s, C$_{Ar}$), 124.3 (s, C$_{Ar}$), 25.5 (s, C$_{Me}$), 5.1 (s, C$_{Me}$). $^{31}$P{$^1$H} NMR (C$_6$D$_6$, 161.98 MHz) δ -313 (s). Anal. Calcd for C$_{45}$H$_{73}$N$_5$O$_8$P$_4$Si$_4$Zn$_6$: C, 37.52; H, 5.11; N, 4.86. Found: C, 35.84; H, 4.94; N, 4.78. *Observed values correspond to 1 with a loss of 0.5 pyridine molecule: Anal. Calcd for C$_{42.5}$H$_{70.5}$N$_{4.5}$O$_8$P$_4$Si$_4$Zn$_6$: C, 36.43; H, 5.07; N, 4.5 and are consistent with $^1$H NMR data.

NMR Spectroscopy Experiments: Ramped temperature increase: A solution of 1 (21 x 10$^{-3}$ M) in pyridine-$d_5$ was added to a J-Young NMR tube. Starting from 25 °C, the NMR tube was held at a constant temperature for 10 minutes before acquiring $^1$H and $^{31}$P{$^1$H} NMR
spectra and subsequently raising the temperature by 10 °C (2 °C/min). This was repeated at regular intervals until a final temperature of 95 °C. Constant temperature: A solution of I (21 x 10^{-3} M) in pyridine-\textit{d}_5 was added to a J-Young NMR tube and placed in an oil bath that was preheated to 45 °C. The reaction progress was monitored by removing the NMR tube from the oil bath, cooling to room temperature and acquiring the \textsuperscript{1}H and \textsuperscript{31}P\{\textsuperscript{1}H\} NMR spectra.

**Synthesis of Zn\textsubscript{3}P\textsubscript{2} Nanoparticles by Hot-Injection Method:** A 100 mL Schlenk flask equipped with a condenser was charged with oleylamine (16 mL) and heated to 300 °C under dinitrogen atmosphere. In a separate vessel, I (400 mg, 0.28 mmol) was dissolved in oleylamine (4 mL) and sonicated to obtain a homogeneous solution. Once the oleylamine reached 300 °C, the solution of I was rapidly injected to hot oleylamine. The reaction was allowed to proceed for the desired time before removing from the heating mantle and immediately cooled with compressed air to room temperature. The rest of the procedure was performed under ambient atmosphere. Anhydrous methanol (50 mL) was added to the solution to precipitate the nanoparticles, which were isolated by centrifuging the mixture at 4000 rpm for 20 minutes and discarding the supernatant. Additional washing cycles with resuspension and flocculation was found to be detrimental to the solubility of the particles. After the first flocculation, solid nanoparticles were washed several times with methanol and dried under dynamic vacuum for 12 hours prior to analysis. (Typical mass yield: 100 ~ 105 mg).

**Synthesis of Zn\textsubscript{3}P\textsubscript{2} Nanoparticles by Ramped Heating:** A 100 mL Schlenk flask was charged with oleylamine (16 mL) and heated to 100 °C under dinitrogen atmosphere. In a separate vessel, I (400 mg, 0.28 mmol) was dissolved in oleylamine (4 mL) and sonicated to obtain a homogeneous solution. Once the oleylamine reached the desired temperature, the solution of I was rapidly injected to hot oleylamine. The temperature of the flask was raised to 150 °C at a controlled rate (2 °C/min) and held at that temperature for the desired time before removing from the oil bath and cooling with compressed air to room temperature. The
rest of the procedure was performed under ambient atmosphere. Anhydrous methanol (50 mL) was added to the solution to precipitate the nanoparticles, which were isolated by centrifuging the mixture at 4000 rpm for 20 minutes. Additional washing cycles with resuspension and flocculation was found to be detrimental to the solubility of the particles. After the first flocculation, solid nanoparticles were washed several times with methanol and dried under dynamic vacuum for 12 hours prior to analysis. (Typical mass yield: 100 ~ 105 mg).
2.4 Conclusions

The room temperature reaction of Zn(OAc)$_2$ and P(SiMe$_3$)$_3$ leads to the selective formation of the hexanuclear zinc-acetato-phosphinidene cluster Zn$_6$(μ$_3$-P$\text{SiMe}_3$)$_4$(OAc)$_4$(NC$_5$H$_5$)$_5$, which can be prepared on a multigram scale and, despite the presence of P-SiMe$_3$, shows good stability against oxidation and hydrolysis in the solid state under air. $^{31}$P{$^1$H} NMR spectra of similar reactions in pyridine of the long chain carboxylate Zn(oleate)$_2$ with P(SiMe$_3$)$_3$ also show evidence for phosphinidene complexes being formed although several signals/species are observed. Future experiments will focus on further developing these systems by expanding to a wider variety of reaction conditions and solvents for further nanoparticle size control.
2.5 References


Chapter 3

Synthesis and reaction chemistry of zinc-diarylphosphido clusters with phosphorus precursors

(A version of this work is submitted for publication.)

3.1 Introduction

The metal phosphido (M–PR₂) complex is a chemically versatile functionality that finds use in catalysis and metal-mediated phosphorus bond transfer reactions.[1-3] Phosphido ligands can typically be coordinated to metals by reacting a metal halide with lithiated phosphides, metal alkyls with secondary phosphines and metal acetates with silylphosphines. The synthetic chemistry of these phosphido complexes is well-developed with many well-characterized species of early, late transition, and lanthanide metals as well as main group elements.[4-12] While these complexes largely remained within the domain of molecular synthetic chemists as reagents to study fundamental reactivity and catalytic applications, such metal and non-metal phosphorus species are also highly relevant in materials chemistry. For example several homoleptic complexes of silylphosphido ligands are known where the ligands are both bridging and terminally coordinated, as in the case of {M[P(SiMe₃)₂]₂}₂ (M = Zn, Cd, Hg, Sn, Pb, Mn).[6] Methanolation of the cadmium species leads to the formation of Cd₃P₂ nanoparticles, showing that judicious choice of reaction conditions allows for direct conversion of molecular metal phosphido species to their corresponding metal phosphide nanoparticles.[6] There are notable examples of the synthesis of gallium and indium phosphides and arsenides from thermolysis of their alkyl/silylphosphido molecular complexes.[10, 13]

Metal phosphide and chalcogenide solids containing first-row transition metals are materials of great interest for their potential as inexpensive semiconductors for photovoltaic applications.[14] Some of these materials are synthetically well-developed with robust solution syntheses.[15-21] Many of them are multi-component reactions where molecular
precursors are reacted in one pot at high temperatures to form the nanomaterials. However, comparatively simpler systems are known where a single reagent that contain more than one precursor element can be used as a source for multiple elements.\textsuperscript{[22]} In addition to clusters being utilized as model systems for studying growth mechanism and surface chemistry of nanoparticles, they are used as molecular precursors for nanoparticle synthesis for a number of materials.\textsuperscript{[22]} This includes not only binary systems, but more complex, ternary and quaternary systems.\textsuperscript{[23]} For example, the synthesis of cadmium chalcogenides, europium sulfide, lanthanum sulfide, gallium selenide and telluride, copper indium chalcogenides and copper zinc tin chalcogenides are examples of materials prepared from molecular clusters.\textsuperscript{[24-30]} Using molecular precursors for materials synthesis dates back to the 1990s, encompassing phosphides of both the main-group elements such as gallium, germanium, indium and d-block metals such as cadmium.\textsuperscript{[10, 13, 31]} With current efforts of materials chemists directed towards developing solution syntheses of nanomaterials based on non-toxic and Earth-abundant elements, there is great potential for further developing the corresponding cluster based approach to these syntheses to study their growth mechanism and surface chemistry.\textsuperscript{[22]}

Many zinc chalcogenolates and, to a lesser extent, phosphido and phosphinidene clusters have been reported since the early 1990s.\textsuperscript{[5-7, 11-12, 32-34]} Despite the emerging importance of zinc phosphide (\(\text{Zn}_3\text{P}_2\)) as a direct band gap semiconductor with a suitable band gap energy for photovoltaic applications, there is little attention paid for the potential use of the phosphido and phosphinidene clusters to serve as molecular precursors. The importance of developing cluster chemistry for this material is further substantiated by the evidence of cluster intermediates from two distinct syntheses of \(\text{Zn}_3\text{P}_2\) nanoparticles. The zinc phosphido and phosphinidene complex/clusters \([\text{MeZn}(\mu-\text{P(SiMe}_3)_2)]_2\) and \([(\text{Et}_2\text{Zn})(\text{ZnOAc})_2(\mu-\text{PSiMe}_3)]\) have been proposed by Buriak and Cossairt groups as intermediates towards zinc phosphide nanoparticles, supported by spectroscopic observations.\textsuperscript{[35-36]} We have recently communicated the reaction of \(\text{Zn}(\text{OAc})_2\) with \(\text{P(SiMe}_3)_3\) in pyridine at room temperature allowed for the isolation of a hexanuclear zinc phosphinidene cluster. When thermolyzed, the hexanuclear cluster yielded zinc phosphide nanoparticles.\textsuperscript{[37]}

Herein, we report the synthesis and reactivity of two zinc phosphido clusters \([\text{Zn}_2(\mu-\text{P(})...
PPh₂(PPh₂)₂(NC₅H₅)₂ (1) and [Zn₄(µ-PPh₂)₄(OAc)₄(NC₅H₅)]₂ (2). The clusters are easily accessed on a multigram scale with high yields from the room temperature reaction of Zn(OAc)₂ with Me₃SiPPh₂ in pyridine. When thermolyzed, 1 yielded zinc nanocrystals via a redox elimination of Ph₄P₂. When thermolysis of 1 was carried out with the addition of P₄ as a phosphorus source, micrometer-sized aggregates of zinc phosphide were produced. 2 showed similar reactivity to 1, when 2 was thermolyzed with P₄. Room temperature reaction of 2 with 0.75 equivalent of P(SiMe₃)₃ yielded an intractable mixture of phosphido and phosphinidene species based on the ³¹P{¹H} NMR spectrum. Thermolysis of 2 with P(SiMe₃)₃ produced aggregates of zinc phosphide activation of P-Si bonds with acetate ligands from 2.
3.2 Results and Discussion

The reactivity of metal acetates with silylchalcogens and silylphosphines has been used extensively to yield small complexes and clusters of zinc.\cite{30, 38-39} Syntheses of ligand stabilized mononuclear zinc complexes with [ESiMe$_3$] (E = S, Se, Te) are straightforward with zinc acetate and the corresponding E(SiMe$_3$)$_2$ with tetramethylethylenediamine or lutidine as stabilizing ligands.\cite{38} When the analogous reaction was carried out with Me$_3$SiPPh$_2$ (Zn(OAc)$_2$:Me$_3$SiPPh$_2$ = 1:2), the reaction consistently produced a highly insoluble white powder regardless of the solvents used (DCM, THF, MeCN, CHCl$_3$). The formation of a coordination polymer of zinc and diphenylphosphide is likely to be the cause of the apparent insolubility in common laboratory solvents over a wide range of polarity. Such coordination polymers are known for silver and copper alkane thiolates with phosphine ligands.\cite{40}

![Figure 3.1](image)

**Figure 3.1** Molecular structure of 1 in the crystal (ellipsoids drawn at 50% probability level; hydrogen atoms not illustrated for clarity). The molecule resides about a crystallographic inversion centre. Zinc and phosphorus atoms are shown as purple and orange spheres and carbon and nitrogen atoms are shown as grey and green wireframe. Selected bond lengths (Å): Zn-P(terminal): 2.3250(7), Zn-P(bridging): 2.4478(8), 2.4337(7). Selected bond angles (°): Zn-P-N: 89.95(2), 92.20(2).
Although the white powder was insoluble in nearly every solvent tested, it was highly soluble in pyridine and lutidine, which most likely break the coordination polymer and stabilize molecular units. Indeed, when the reaction was carried out in pyridine, addition of Me₃SiPPh₂ to a solution of Zn(OAc)₂ immediately yielded a clear yellow solution with no precipitate observed. The $^{31}$P{¹H} NMR spectrum of the reaction showed clean consumption of the starting phosphine ($\delta$ -56 ppm) to a single species with a broad peak at -45 ppm (48 Hz at FWHM) (Scheme 3.1). When the reaction was repeated with replacing zinc and phosphorus reagents with Zn[N(SiMe₃)₂]₂ and Ph₂PH, it also yielded the same spectroscopic observations, although the reaction progressed more slowly compared to when Zn(OAc)₂ and Me₃SiPPh₂ were used based on the $^{31}$P{¹H} NMR spectra. Layering the reactions with heptane yielded crystals of [Zn₂(μ-PPh₂)(PPh₂)₂(NC₅H₅)₂] (1) after several hours (Figure 3.1). 1 features the phosphido ligands in both bridging and terminal coordination modes, which, likely explains the broad signal observed in the $^{31}$P{¹H} NMR spectra. The individual signals for two phosphido ligands could not be resolved even at low temperatures, suggesting the ligands may be in rapid exchange in solution. The two bridging phosphido ligands with zinc atoms form a symmetric 4-membered ring that is reminiscent of many reported main-group/metal dinuclear complexes with bridging phosphido ligands.⁶⁻¹⁰

1) 2 Zn[N(SiMe₃)₂]₂ + 4 HPPH₂ → - 4 HN(SiMe₃)₂ → pyridine
2) 2 Zn(OAc)₂ + 4 Me₃SiPPh₂ → - 4 AcOSiMe₃ → RT

**Scheme 3.1** Synthesis of 1 via two routes: 1) acid-base reaction 2) silyl deprotection The reaction progresses more slowly for the acid-base route with lower yield (80% versus 63%).

The implication of dinuclear zinc species with bridging phosphido ligands in the synthesis of zinc phosphide nanoparticles, prompted the investigation of 1 as a single source precursor to Zn₃P₂. In the case of [MeZn(μ-P(SiMe₃)₂)]₂, the organic fragments are eliminated as Me₄Si upon thermolysis.³⁵ For 1, the loss of organic fragments could occur
A) P-C Bond Cleavage

\[
\begin{array}{c}
\Delta \\
[Zn_2(\mu\text{-PPPh}_2)\text{(PhPh}_2)\text{(NC}_5\text{H}_5)_2] & \rightarrow & "ZnP\text{-PPPh}_2" + 2 \text{PPPh}_3 \\
& \rightarrow & \text{Zn}_3\text{P}_2 \text{ NPs}
\end{array}
\]

B) Reduction of Zn(II) by [Ph}_2\text{P}^*

\[
\begin{array}{c}
\Delta \\
[Zn_2(\mu\text{-PPPh}_2)\text{(PhPh}_2)\text{(NC}_5\text{H}_5)_2] & \rightarrow & \text{Zn}(0) + 2 \text{Ph}_4\text{P}_2
\end{array}
\]

Scheme 3.2 Possible elimination mechanism for the diarylphosphido ligands from 1.

via P-C bond cleavage and the elimination of PPh\textsubscript{3}, while some diphenylphosphide ligands can act an X-type surface ligand for the synthesized nanoparticles (Scheme 3.2A). When a solution of 1 in pyridine was thermolyzed under solvothermal conditions (130 °C/24 hours), a grey suspension was produced. When the suspension was left undisturbed, these grey precipitates could be separated from a green supernatant solution. The \textsuperscript{31}P{\textsuperscript{1}H} NMR spectrum of the supernatant showed a single sharp peak at -15 ppm indicative of Ph\textsubscript{4}P\textsubscript{2}.\textsuperscript{41}

The precipitate was analyzed by SEM, which showed hexagonal crystals ~1 µm in diameter along with prisms with the length of a few micrometers (Figure 3.2). Elemental composition of the structures were analyzed by EDX, which revealed a majority of zinc (~30, atomic %) for both structures with very little amount of phosphorus (< 1, atomic %) (Carbon grids were used for this analysis, thus it was excluded from evaluating elemental composition). The hexagonal crystal habit and the color of the solid, qualitatively matched that of zinc metal.\textsuperscript{42}

The powder XRD pattern of the precipitate gave conclusive evidence for metallic zinc (Figure 3.3). The formation of metallic zinc must proceed via a redox process where two diphenylphosphide ligands eliminate to reduce one equivalent of Zn(II) (Scheme 3.2B).
Figure 3.2 SEM image of the hexagonal and prismatic metallic zinc nanocrystals produced via thermolysis of 1.

Figure 3.3 Powder XRD pattern of the grey solid (blue) produced from the thermolysis of 1, stacked with reference pattern for metallic zinc (Crystallography Open Database ID: 9008522).
The preparation of metal phosphide nanoparticles where the M(0) species is the relevant precursor is known for In, Pb and Zn.\[^{[43]}\] This preparation involves the initial reduction of a metal halide with sodium napthalenide, then a subsequent reaction with a solution of P\(_4\). After heating the mixture, the nanoparticles are isolated by flocculation with \(i\)PrOH. The \textit{in situ} generation of Zn(0) species during thermolysis of 1 in pyridine, prompted the thermolysis of 1 with P\(_4\) as a phosphorus additive. [PPh\(_2\)]\(^{-}\) is more likely to reduce P(0) from P\(_4\) to P(-III) instead of reducing Zn(II) based on the reduction potentials (-0.063 V versus -0.7618 V).\[^{[44]}\] Room temperature reaction of 1 with P\(_4\) generated Ph\(_4\)P\(_2\) as determined by \(^{31}\)P\{\(^{1}\)H\} NMR spectroscopy. When the thermolysis of 1 was carried out with 0.67 equivalent of P\(_4\), a red solution was obtained after 24 hours at 130 °C without any observable zinc metal. The molecular species present in solution was Ph\(_4\)P\(_2\) based on \(^{31}\)P\{\(^{1}\)H\} NMR spectroscopy as expected. Typically metal phosphide nanoparticles are flocculated with alcohols (MeOH or \(i\)PrOH), however addition of MeOH to the thermolysis product of 1 and P\(_4\) did not result in precipitates for the solution, but a yellow translucent solution was obtained. No solid could be separated even after extended centrifuging at 4000 rpm.

In sharp contrast, the addition of a hydrocarbon solvent (pentane, hexane and heptane) to reaction solutions produced red solids which were large enough to be isolated by filtration. The solid was determined to be air sensitive after discoloration to white and ultimately yellow after prolonged exposure to normal atmosphere. Under the thermolysis conditions used for this study, pyridine is the only ligand that is available for the nanoparticles, although not unprecedented it is an uncommon surfactant compared to the more widely used oleylamine.\[^{[45-46]}\] This likely results in inadequate protection at the nanoparticle surface compared to long chain alkyl amines, resulting in the nanoparticle’s increased sensitivity to air.
Figure 3.4 Powder XRD pattern of the thermolysis of 1 with P₄ (black) stacked with the reference pattern for α-Zn₃P₂ (Crystallography Open Database ID: 1010287). * are from the sample holder.

The red solid was analyzed by powder XRD and showed a broad reflection between 20° to 30°. Although similar broad reflections were previously observed for ~3 nm Zn₃P₂ nanoparticles, the absence of a strong reflection at 45° 2θ that is diagnostic for α-Zn₃P₂ was not observed (Figure 3.4).[36] The powder pattern also did not match with any of the known phases for zinc phosphides (Zn₃P₂ (cubic), ZnP₂ and ZnP₄). SEM analysis of drop-cast solution of the red solid showed micrometer-sized aggregates of smaller nanostructures (Figure 3.5). Analysis of elemental composition with EDX showed a zinc to phosphorus ratio of 3:4, suggesting a phosphorus rich composition when compared to 3:2 that would be observed for Zn₃P₂. ICP-MS conclusively confirmed a phosphorus rich system with zinc to phosphorus ratio of 3.10:5.70. Zn₃P₂ nanoparticles with a phosphorus rich-shell have been characterized from high temperature (~ 350 °C) synthesis with ZnMe₂ and trioctylphosphine, where excess P(0) byproduct is formed during the reduction of P(±3) from trioctylphosphine
Those nanoparticles also showed air-sensitivity similar to the red solid in this study. It is possible that during the thermolysis of 1 with P₄, an amorphous shell of P(0) forms before sufficient growth into more crystalline, larger particles is achieved. ATR-IR spectrum of the red solid displayed bands (1580, 1476, 1431 and 1066 cm⁻¹) that can be assigned to pyridine, but bands assignable to aromatic groups were not observed indicating diphenylphosphide ligands were not present (Figure 3.6).

In contrast to the preparation of 1, the reaction of Zn(OAc)₂ with Me₃SiPPh₂ in a 1:1 ratio yields [Zn₄(μ-PPh₂)₄(OAc)₄(NC₅H₅)₂] (2), with a characteristic ³¹P{¹H} NMR peak at -52 ppm (305 Hz at FWHM) (Scheme 3.3). Layering the solution with heptane yielded crystals of 2 allowing for molecular structure determination via single crystal XRD (Figure 3.7). Unlike for the synthesis of 1 where all the acetates are eliminated as AcOSiMe₃, substoichiometric use of the silylphosphine leaves residual acetates allowing for their incorporation into the cluster framework. The zinc metal and phosphido ligands form an octanuclear core in a distorted boat-boat conformation with two μ₂-κ²- and two terminally bound OAc.

**Figure 3.5** SEM image of thermolysis product of 1 with P₄.
Figure 3.6 ATR-IR spectrum of the dried thermolysis product of 1 with P₄.

Scheme 3.3 Synthesis of 2 in pyridine (73% yield).
Figure 3.7 Molecular structure of 2 in the crystal (ellipsoids drawn at 50% probability level; hydrogen atoms not illustrated for clarity). Zinc and phosphorus atoms are shown as purple and orange spheres. Carbon, oxygen and nitrogen atoms are shown as grey, red and green wireframe. Selected bond lengths (Å): Zn-P: 2.353(1)-2.386(1), Zn-O(monodentate): 1.964(3)-1.966(3), Zn-O(bridging): 1.999(2)-2.073(2). Zinc to phosphorus bonds are intermediate in length (2.353(1)-2.386(1) Å) when compared to zinc bonded to bridging and terminal phosphido ligands in 1.

With a similar Zn-PPh₂ make-up, 2 should display similar reactivity with 1 upon towards P₄. Indeed, when 2 was reacted with P₄ in pyridine at room temperature, Ph₄P₂ was again observed in the ³¹P{¹H} NMR spectrum. Reaction of 2 with P₄ under thermolysis conditions (130 °C/24 hours) was done to probe whether residual acetates can behave as X-type ligands and favorably aid the growth of crystalline nanoparticles. After thermolysis, a red solid was isolated via filtration and analyzed by powder XRD, which showed a broad reflection, similar to that observed for thermolysis product of 1 with P₄. Solubilizing agglomerated Zn₃P₂ nanoparticles with X-type ligands has been demonstrated in a previous
However the solubilizing mechanism isn’t a simple coordination, but a two-step process that relies first on the reaction of the acidic proton from the ligand (oleic acid, *n*-decylphosphonic acid and 1-octadecanethiol) with the reactive surface moieties such as Zn-Me and Zn-P(SiMe₃)₂ to release CH₄ or silanes. This is followed by the coordination of the conjugate base to the open surface site. Residual acetates from Zn₄ is unlikely to solubilize the particles this way, especially when a large excess of them are not present to outcompete the pyridine ligands.

In contrast to the similar redox chemistry of 1 and 2, acetates from the cluster framework of 2 are potential sites of further functionalization with silylphosphines. Hence 2 was stirred with 0.75 equivalent P(SiMe₃)₃ at room temperature for 12 hours. While 2 and P(SiMe₃)₃ were entirely consumed, the $^{31}\text{P}$ NMR spectra showed a mixture of phosphido and phosphinidene species determined based on relative chemical shifts.$^{[5,49-50]}$ No single species could be isolated from this mixture. The reaction of 2 with P(SiMe₃)₃ was carried out under thermolysis conditions which yielded a clear dark red solution, that is qualitatively similar to the thermolysis product of 1 with P₄. The $^{31}\text{P}$ NMR spectra of the solution showed Ph₄P₂ with the hydrolysis product Ph₂PH and residual 2 (0.2:1:0.3 from integration). No precipitate was produced when MeOH was added, but hydrocarbon solvents were able to induce the precipitation of red solids. Powder XRD pattern of the solid showed a similar broad reflection from 20 to 30° that did not match with known phases of Zn₃P₂ and others (Figure 3.8). Although a different source of phosphorus was used the thermolysis likely proceeded similarly where P(-III) was generated from cleavage of P-Si bonds with OAc, but the redox elimination to generate zinc nanocrystals was also occurring simultaneously removing Zn(II) needed for nanoparticle growth.
Figure 3.8 Powder XRD pattern for the thermolysis product of 2 with P(SiMe$_3)_3$ overlaid with known phases of zinc phosphide. α-Zn$_3$P$_2$ (Crystallography Open Database ID: 1010287) (blue, top), Zn$_3$P$_2$-cubic (PDF-4+ 04-001-3699) (blue, bottom), ZnP$_2$-monoclinic (PDF-4+ 00-054-0208) (purple) and ZnP$_4$ (red) (PDF-4+ 00-038-1354).
3.3 Experimental

3.3.1 General Considerations and Characterization Methods

All syntheses described were conducted under an atmosphere of high-purity dry dinitrogen using standard double-manifold Schlenk line techniques unless otherwise noted. Zinc acetate (99.99%) was purchased from Sigma and stored in a dinitrogen atmosphere glove box. Diphenylphosphine (98%) was purchased from Sigma and stored under a dinitrogen atmosphere. Trimethylsilyldiphenylphosphine and zinc \( \text{bis[bis(trimethylsilyl)amide] } \) were prepared following literature procedures.\textsuperscript{[51,52]} All solvents used were placed over molecular sieves and stored under dinitrogen gas. Pentane and heptane were collected using an MBraun MB-SP Series solvent purification system. Anhydrous pyridine was purchased from Caledon Laboratories. Deuterated pyridine was purchased from Sigma and degassed by three freeze-pump-thaw cycles. 1,3,5-trimethoxybenzene (≥99%) was purchased from Sigma. NMR spectra were recorded on Bruker 400 and Inova 600 spectrometers. \(^1\)H, and \(^{13}\)C\{\(^1\)H\} chemical shifts are externally referenced to \( \text{SiMe}_4 \). \(^{31}\)P\{\(^1\)H\} chemical shifts are externally referenced to \( \text{H}_3\text{PO}_4 \) (75%).

Single crystal X-ray measurements for 1 and 2 were made on a Bruker Kappa Axis Apex2 diffractometer equipped with graphite monochromated Mo Ka (\( \lambda = 0.71073 \) Å) radiation at a temperature of 110 K. For 1, the unit cell dimensions were determined from a symmetry constrained fit of 9904 reflections with 5.02° < 2q < 64.34°. The data collection strategy was a number of \( w \) and \( j \) scans which collected data up to 65.134° (2q). For 2, the unit cell dimensions were determined from a symmetry constrained fit of 9904 reflections with 5.44° < 2q < 52.06°. The data collection strategy was a number of \( w \) and \( j \) scans which collected data up to 52.46° (2q). The frame integration was performed using SAINT.\textsuperscript{[53]} The resulting raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS.\textsuperscript{[54]} The structure was solved by using a dual space methodology using the SHELXT program.\textsuperscript{[55]} All non-hydrogen atoms were obtained from the initial solution. The hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent atom. The structural model was fit to the data using full matrix
least-squares based on $F^2$. The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structure was refined using the SHELXL program from the SHELXTL suite of crystallographic software.\cite{56} Graphic plots were produced using the NRCVAX program suite.\cite{57} Additional information and other relevant literature references can be found in the reference section of this website (http://xray.chem.uwo.ca).

Powder XRD patterns were collected on Inel CPS powder diffractometer equipped with a Cu radiation source ($\lambda = 1.5406$ Å). SEM imaging and energy-dispersive X-ray (EDX) spectroscopy analysis were performed using a LEO (Zeiss) 1540XB FIB/SEM system at Western Nanofabrication Facility, London, Canada. Prior to imaging, a thin film of amorphous osmium metal was deposited on the samples using a Filgen osmium plasma coater OPC80T to prevent charging and reduce damage from the electron beam during imaging. ATR-IR spectra were recorded on Spectrum Two FT-IR spectrometer. ICP-MS was performed with Agilent 7700 Series at the Biotron at the University of Western Ontario, London, Canada. High purity nitric acid was used to digest the nanoparticles and the solution was diluted with Milli-Q water. Elemental analysis was performed in duplicates with Fisons-EA-1108 CHNS-O Element Analyzer at the Laboratoire d'analyse élémentaire at the Université de Montréal, Montreal, Canada and vario ISOTOPE cube at the Biotron at The University of Western Ontario, London, Canada. Samples were dried under dynamic vacuum ($< 10$ mTorr) for at least 12 hours prior to analysis. Samples were shipped in a vacuum sealed ampoule.

### 3.3.2 Synthesis

**Synthesis of [Zn$_2$(PPh$_3$)$_4$(NC$_5$H$_5$)$_2$] (1): Method A:** A 100 mL round-bottom Schlenk flask was charged with Zn(OAc)$_2$ (1.0 g, 5.5 mmol) and a magnetic stir bar. The solid was dissolved in 25 mL of pyridine. The mixture was stirred rapidly for 10 minutes or until the solid dissolved completely. To this solution, Me$_3$SiPPh$_2$ (2.8 g, 11 mmol) was added and stirred for 3 hours at room temperature. A bright yellow color instantly developed when the phosphine was added. The stir bar was removed and the solution was layered with heptane,
which gave crystals of 1 after several days. Isolated crystals were washed with pentane and dried under dynamic vacuum (2.3 g, 80% yield). Method B: A 100 mL round-bottom Schlenk flask was charged with Zn[N(SiMe$_3$)$_2$]$_2$ (1.0 g, 2.6 mmol), a magnetic stir bar and 25 mL of pyridine. To this solution, Ph$_2$PH (0.96 g, 5.2 mmol) was added and stirred for 6 hours at room temperature. A yellow color slowly develops as the reaction progressed. The stir bar was removed and the solution was layered with heptane, which gave crystals of 1 after several days. Isolated crystals were washed with pentane and dried under dynamic vacuum (0.83 g, 63% yield). m.p. 117-119 °C (decomposition). $^1$H NMR (NC$_5$D$_5$, 400.13 MHz) δ 8.75 (4H, m, CH$_{Ar}$), 7.70 (16H, d, CH$_{Ar}$), 7.59 (2H, m, CH$_{Ar}$), 7.22 (4H, m, CH$_{Ar}$), 7.13 (24H, m, CH$_{Ar}$). $^{13}$C{$^1$H} NMR (NC$_5$D$_5$, 100.61 MHz) δ 150.8 (t, C$_{Ar}$), 145.2 (s, C$_{Ar}$), 136.5 (t, C$_{Ar}$), 134.4 (d, C$_{Ar}$), 128.8 (s, C$_{Ar}$), 125.3 (s, C$_{Ar}$), 124.5 (t, C$_{Ar}$). $^{31}$P{$^1$H} NMR (NC$_5$D$_5$, 161.98 MHz) δ -46 (s). Anal. Calcd for C$_{58}$H$_{50}$N$_2$P$_4$Zn$_2$: C, 67.65; H, 4.89; N, 2.72. Found: C, 67.60; H, 5.01; N, 2.95.

**Synthesis of [Zn$_4$(PPh$_2$)$_4$(OAc)$_4$(NC$_5$H$_5$)$_2$] (2):** A 500 mL round-bottom Schlenk flask was charged with Zn(OAc)$_2$ (5.0 g, 27 mmol) and a magnetic stir bar. The solid was dissolved in 75 mL of pyridine. The mixture was stirred rapidly for 10 minutes or until the solid dissolved completely. To this solution, Me$_3$SiPPh$_2$ (7.0 g, 6.8 mmol) was added and stirred for 1 hour at room temperature. A yellow color developed when the phosphine was added. The stir bar was removed and the solution was layered with heptane, which gave crystals of 2 after several days. Isolated crystals were washed with pentane and dried under dynamic vacuum (7.0 g, 73% yield). m.p. 145-146 °C (decomposition). $^1$H NMR (NC$_5$D$_5$, 400.13 MHz) δ 8.74 (4H, m, CH$_{Ar}$), 7.78 (16H, s, CH$_{Ar}$), 7.59 (2H, m, CH$_{Ar}$), 7.22 (4H, m, CH$_{Ar}$), 7.12 (24H, m, CH$_{Ar}$), 2.25 (12H, s, CH$_{Me}$). $^{13}$C{$^1$H} NMR (NC$_5$D$_5$, 100.61 MHz) δ 178.8 (s, C$_{CO}$), 150.8 (t, C$_{Ar}$), 136.5 (t, C$_{Ar}$), 135.0 (s, C$_{Ar}$), 128.9 (s, C$_{Ar}$), 126.6 (s, C$_{Ar}$), 124.5 (s, C$_{Ar}$), 24.1 (s, C$_{Me}$). $^{31}$P{$^1$H} NMR (NC$_5$D$_5$, 161.98 MHz) δ -52 (s). Anal. Calcd for C$_{66}$H$_{62}$N$_2$O$_8$P$_4$Zn$_4$: C, 56.76; H, 4.47; N, 2.01. Found: C, 56.70; H, 4.515; N, 2.28.
3.4 Conclusions

We have described a facile, multigram synthesis of two zinc diarylphosphido clusters both from the reaction of Zn(OAc)$_2$ and Me$_3$SiPPh$_2$. Dinuclear phosphido species has been implicated as an intermediate for the synthesis of zinc phosphide nanoparticles. Thermolysis of [Zn$_2$(μ-PPh)$_2$(PPh)$_2$(NC$_5$H$_5$)$_2$] lead to the production of metallic zinc nanoparticles, which have been used as a zinc source with white phosphorus as the phosphorus source. However, under the conditions tested, the dinuclear complex in this study yielded a phosphorus rich zinc phosphide. Although the tetranuclear cluster [Zn$_4$(μ-PPh)$_4$(OAc)$_4$(NC$_5$H$_5$)$_2$] showed some reactivity with P(SiMe)$_3$, larger cluster frameworks could not be isolated. Reacting the two species under solvothermal conditions again yielded as phosphorus rich zinc phosphide mixture. The same redox process involving diphenylphosphide ligands likely depleted available Zn(II) species in solution, preventing the growth of Zn$_3$P$_2$ nanoparticles. Future work will involve further developing zinc phosphorus cluster frameworks to improve our understanding of Zn$_3$P$_2$ nanoparticle synthesis.
3.5 References


Chapter 4
Conclusions and Outlook

4.1 Summary and Conclusions

The work in this thesis describes the multigram and facile syntheses of stable cluster compounds of zinc and phosphorus and their potential as single source precursors for the solution synthesis of zinc phosphide nanoparticles. The reactivity of metal acetate salts with silyl protected chalcogenides and phosphines has been well investigated to prepare numerous metal chalcogen/phosphorus complexes from low nuclearity systems to large polynuclear assemblies. This reactivity was developed to prepare several clusters with covalently bound zinc-phosphorus moieties in the form of zinc phosphido and zinc phosphinidene complexes.

Figure 4.1 Molecular structures of new clusters presented in Chapter 2 and Chapter 3 of this thesis.
The zinc phosphido clusters were synthesized by reacting Zn(OAc)$_2$ with varying amounts of Me$_3$SiPPh$_2$. Reaction of Zn(OAc)$_2$ with 2.0 equivalents of Me$_3$SiPPh$_2$ produced [Zn$_2$(μ-PPh$_2$)$_2$(PPh$_2$)$_2$(NC$_5$H$_5$)$_2$], a dinuclear species with both the bridging and terminal phosphido ligands. When this dinuclear cluster was reacted under solvothermal conditions in pyridine, metallic zinc nanocrystals were produced with the redox elimination of phosphido ligands to yield Ph$_4$P$_2$ as a byproduct. When this cluster was reacted with P$_4$ under solvothermal conditions, a phosphorus rich mixture of zinc phosphide was obtained. When 0.25 equivalent of Me$_3$SiPPh$_2$ was reacted with Zn(OAc)$_2$, a tetranuclear cluster [Zn$_4$(μ-PPh$_2$)$_4$(OAc)$_4$(NC$_5$H$_5$)$_2$] was produced where residual acetates are incorporated to the cluster framework as bridging and terminally bound ligands. This cluster showed reactivity towards P(SiMe$_3$)$_3$ via P-Si bond activation, but an intractable mixture of phosphido and phosphinidene species were produced. Thermolysis product of the cluster with P(SiMe$_3$)$_3$ was similar to the thermolysis product of the dinuclear cluster with P$_4$ where a phosphorus rich mixture of zinc phosphide was produced again. In both cases, the reduction of Zn(II) to metallic Zn(0) nanocrystals likely hindered Zn$_3$P$_2$ nanoparticle synthesis by removing Zn(II) species from solution with a shell of excess P(0) further preventing particle growth.

The phosphinidene cluster [Zn$_6$(μ$_3$-PSiMe$_3$)$_6$(OAc)$_4$(NC$_5$H$_5$)$_5$] was synthesized from the reaction of Zn(OAc)$_2$ with P(SiMe$_3$)$_3$ in pyridine at room temperature. Its molecular structure is congruent to M$_4$E$_{10}$ or M$_6$E$_4$ frameworks that are known for Group-12 chalcogen and phosphorus clusters. The cluster showed remarkable stability when exposed to air despite its reactive phosphorus silicon bonds. The zinc phosphinidene cluster prepared was a suitable single source precursor via the elimination of Me$_3$SiOAc upon thermolysis in oleylamine where the inorganic core was a source of zinc and phosphorus. Thermolysis of the cluster could be done at a relatively low temperature at 150 °C to produce the nanoparticles, but the particles produced via hot-injection at 300 °C were qualitatively more stable towards oxidation. Although not luminescent, the nanoparticles were highly crystalline as evidenced by its powder pattern with nearly perfect zinc to phosphorus ratio of 3 to 2 determined by ICP-MS.
4.2 Outlook on Molecular Clusters for Developing Zinc Phosphide Nanoparticle Synthesis

The zinc phosphido and zinc phosphinidene clusters discussed in this thesis demonstrated how clusters with Zn-P functionalities are easily synthesized with the key contribution from pyridine as the coordinating solvent. The ability of pyridine to stabilize the clusters metal-phosphide and metal-phosphinidene motifs should be investigated whether it can also stabilize the analogous clusters for different elements such as Cd, Hg and In.

Recently N-heterocyclic carbenes and cyclic alkyl amino carbenes have been used in materials chemistry to prepare small clusters of coinage metals to metal monolayers.\textsuperscript{[1-3]} With their versatile steric and electronic properties, these ligands may allow access to larger zinc phosphorus clusters, which would allow systematic investigations of surface chemistry and growth mechanism of Zn\textsubscript{3}P\textsubscript{2} nanoparticles similar to what was done with In\textsubscript{37}P\textsubscript{20} cluster.\textsuperscript{[4-6]} The tetranuclear cluster and the hexanuclear clusters in particular still have the untapped potential with its reactive acetates and P-Si bonds respectively. The reaction of the tetranuclear cluster was only briefly studied in this thesis and merits further investigation with additional silyl protected reagents such as \textit{bis}(trimethylsilyl)chalcogenides to generate to potentially generate mixed zinc phosphorus chalcogen cluster. The coordinating motifs that are possible for chalcogens may lead to interesting structural frameworks. Similarly the hexanuclear cluster could be reacted with various metal acetates to generate heterometallic clusters. Without growing larger cluster frameworks, it may be possible to study the growth mechanism for Zn\textsubscript{3}P\textsubscript{2} with the current Zn\textsubscript{6} framework by performing the cation mediated transformation of Zn\textsubscript{3}P\textsubscript{2} into Cd\textsubscript{3}P\textsubscript{2} magic sized clusters with cadmium carboxylate salts.\textsuperscript{[5]}

68
4.3 References


Appendices

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Appendix 2 Supporting Information for Chapter 2
**Figure A2.1** $^1$H NMR spectrum of 1 in C$_6$D$_6$ (top), NC$_5$D$_5$ (middle) and with 1,3,5-trimethoxybenzene in NC$_5$D$_5$ (bottom).

**Figure A2.2** $^{13}$C{$^1$H} NMR spectrum of 1 in C$_6$D$_6$.
Figure A2.3 $^1$H NMR spectrum of 1 in pyridine-$d_5$ after heating at 45 °C for 7 days; integration shows ca. 67% consumption of 1.

Figure A2.4 Molecular structure of 1 in the crystal (40% probability). Zinc, phosphorus, silicon, nitrogen, oxygen and carbon atoms are shown as purple, orange, yellow, green, red and grey spheres respectively. Hydrogen atoms were omitted for clarity.
Figure A2.5 Growth in particle size analyzed by dynamic light-scattering with aliquots taken at 15 (black), 45 (red) and 90 (blue) minutes during synthesis of Zn$_3$P$_2$ nanoparticles at 300 °C in oleylamine.

Figure A2.6 UV-Vis absorption spectrum of Zn$_3$P$_2$ nanoparticles in hexane. Nanoparticles were synthesized with hot-injection method (oleylamine/300 °C) with 15 minutes (A; red) and 45 minutes (B; black) of growth time. These solutions of Zn$_3$P$_2$ nanoparticles did not display any measurable luminescence.
Figure A2.7 Size distribution of particles A grown at 300 °C with 15 minutes of growth time. 100 particles were measured.
Figure A2.8 $^1$H NMR spectra of nanoparticles A, B and C in C$_6$D$_6$. 
Table A2.1 Zinc to phosphorus ratio of the nanoparticles as determined by ICP-MS.

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<th>Zinc (mg/g)</th>
<th>Phosphorus (mmol/g)</th>
<th>Zinc (mmol/g)</th>
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Figure A2.9 $^{31}$P\{H\} NMR spectrum of the reaction of Zn(oleate)$_2$ with 0.67 equivalent of P(SiMe$_3$)$_3$ (in NC$_5$H$_5$; reaction stirred for 1 hour at room temperature).
Figure A2.10 ESI-TOF mass spectrum of 1 dissolved in pyridine (positive ion mode).
Figure A2.11 Isotopic distributions for the major peaks in the ESI mass spectrum of 1 (see Figure A2.10). i, ii and iii are grouped with experimental data (top) and calculated pattern (bottom). Ion i is assigned to \([\text{Zn}_6(\mu_3-\text{PSiMe}_3)_4(\text{OAc})_3(\text{NC}_5\text{H}_5)]^+\) (1 with one OAc and four NC$_5$H$_5$ dissociated); the major ion ii corresponds to \([\text{Zn}_6(\mu_3-\text{PSiMe}_3)_4(\text{OAc})_3]^+\) (1 with one OAc and all five NC$_5$H$_5$ dissociated); iii matches a partially hydrolyzed fragment of 1, \([\text{Zn}_5(\text{PSiMe}_3)_3(\text{OAc})_2(\text{P(H)OAc})]^+\).
### Table A2.2 Crystallographic data for Zn₆(μ₃-PSiMe₃)₄(OAc)₃(NC₅H₅)₅.

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R₁ = Σ |Fo| - |Fc| / Σ Fo
wR₂ = [ Σ (w(Fo² - Fc²)²) / Σ(wFo²) ]¹⁄₂
GOF = [ Σ (w(Fo² - Fc²)²) / (No. of reflns. - No. of params.) ]¹⁄₂
Appendix 3 Supporting Information for Chapter 3
Figure A3.1 $^1$H, $^{13}$C{$^1$H}, $^{31}$P{$^1$H} and $^{31}$P NMR spectra for 1 in NC$_3$D$_5$. Internal standard is marked with grey. Peak at -40 in $^{31}$P{$^1$H} NMR spectrum corresponds to Ph$_2$PH.
**Figure A3.2** Molecular structure of 1 in the crystal (40% probability). Zinc, phosphorus, nitrogen, and carbon atoms are shown as purple, orange, yellow, light blue and grey spheres respectively. Hydrogen atoms were omitted for clarity.

**Figure A3.3** SEM image of the nanometer sized globular structures forming the micrometer sized aggregates.
Figure A3.4 $^1$H NMR spectrum for 2 in NC$_5$D$_5$. Internal standard is marked with grey.

Figure A3.5 $^{13}$C{$^1$H} NMR spectrum for 2 in NC$_5$D$_5$. Internal standard is marked with grey.
**Figure A3.6** $^{31}\text{P}\{^1\text{H}\}$ and $^{31}\text{P}$ NMR spectra for 2 in NC$_5$D$_5$. Peak at -40 in $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum corresponds to Ph$_2$PH.
Figure A3.7 Molecular structure of 2 in the crystal (40% probability). Zinc, phosphorus, nitrogen, oxygen and carbon atoms are shown as purple, orange, yellow, light blue, red and grey spheres respectively. Hydrogen atoms were omitted for clarity.

Figure A3.8 Powder XRD pattern for the thermolysis product of 2 with P₄ (II).
Figure A3.9 $^{31}$P{¹H} NMR spectrum of the reaction of 2 with 0.75 equivalent of P(SiMe$_3$)$_3$ in pyridine at room temperature (top). $^{31}$P NMR spectrum of the reaction mixture of 2 with 0.75 equivalent of P(SiMe$_3$)$_3$ after thermolysis (bottom).
Table A3.1 Zinc to phosphorus ratio of the thermolysis products as determined by ICP-MS.

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### Table A3.2 Crystallographic data for \([\text{Zn}_2(\mu-\text{PPh}_2)_2(\text{PPh}_2)_2(\text{NC}_5\text{H}_5)_2]\) and \([\text{Zn}_4(\mu-\text{PPh}_2)_4(\text{OAc})_4(\text{NC}_5\text{H}_5)_2]\).

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<td>2604.8(14)</td>
<td>10132.7(7)</td>
<td>6458(5)</td>
</tr>
<tr>
<td>(Z)</td>
<td>2</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>(\mu) (cm(^{-1}))</td>
<td>1.086</td>
<td>1.113</td>
<td>1.621</td>
</tr>
<tr>
<td>(\rho) calc. (g/cm(^3))</td>
<td>1.363</td>
<td>1.350</td>
<td>1.436</td>
</tr>
<tr>
<td>2(\theta) max (°)</td>
<td>65.342</td>
<td>65.134</td>
<td>52.46</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>70663</td>
<td>137673</td>
<td>95873</td>
</tr>
<tr>
<td>Ind. Reflections</td>
<td>19030</td>
<td>36111</td>
<td>12956</td>
</tr>
<tr>
<td>Rmerge</td>
<td>0.0217</td>
<td>0.0394</td>
<td>0.0784</td>
</tr>
<tr>
<td>R1, wR2 ([I &gt; 2\sigma(I)])</td>
<td>0.0845</td>
<td>0.0770</td>
<td>0.0872</td>
</tr>
<tr>
<td>R1, wR2 (all data)</td>
<td>0.0897</td>
<td>0.0848</td>
<td>0.0954</td>
</tr>
<tr>
<td>GOF</td>
<td>1.025</td>
<td>1.011</td>
<td>1.054</td>
</tr>
<tr>
<td>Max, min residual electron density (e/Å(^2))</td>
<td>0.003</td>
<td>0.001</td>
<td>0.002</td>
</tr>
</tbody>
</table>

\[ R1 = \frac{\Sigma(\text{Fo} - \text{Fc})}{\Sigma \text{Fo}} \]
\[ wR2 = \left[ \frac{\Sigma(w(\text{Fo}^2 - \text{Fc}^2)^2)}{\Sigma(w \text{Fo}^4)} \right]^{1/2} \]
\[ \text{GOF} = \left[ \frac{\Sigma(w(\text{Fo}^2 - \text{Fc}^2)^2)}{(\text{No. of reflns.} - \text{No. of params.})^{1/2}} \right] \]
Curriculum Vitae

Kyungseop Jay Lee

**Education**

University of Western Ontario  
Sept. 2017 - Present  
Master of Science in Chemistry  
Co-supervisors: John F. Corrigan and Yining Huang

University of Toronto, St. George  
Honours Bachelor of Science in Chemistry  
Supervisor: G. Andrew Woolley

**Awards/Honours**

Dean’s List at University of Toronto (2012)  
St. Michael's College In-Course Scholarship (2013)  
University of Toronto Excellence Awards (2015)

**Research Experience**

University of Toronto Summer Abroad Program  
April 2014 - July 2014  
*Computational study on thermodynamics of isomers with formula C₃H₄O₂*  
- Theoretical analysis on formation of various isomers. Comparison of transition states and thermodynamics.

Supervisor: Imre G. Csizmadia, University of Szeged, Hungary

St. Michael’s College Independent Project Course  
Sept 2014 - April 2015  
*Thermodynamics of plaque formation for Alzheimer’s disease*  
- Theoretical analysis in thermodynamics of beta-turn dipeptide structures.

Supervisor: Imre G. Csizmadia, University of Toronto, St. George
University of Toronto Excellence Awards  
Feb 2015 - Aug 2015  
*Development of an iron catalyst for asymmetric hydrogenation of polar bonds*  
- Synthesis of amine N-heterocyclic carbene bidentate ligand and subsequent preparation of metal complexes for applications in transfer hydrogenation catalysis.  
*Computational study on acidity of transition metal hydrides*  
- DFT studies on pKa of metal hydrides for implications in metal hydride intermediates in hydrogenation catalysis

Supervisor: Robert H. Morris, University of Toronto, St. George

**CHM499: Undergraduate Thesis**  
**Sept 2015 - April 2016**  
*Selecting partner proteins for cyclic photoactive yellow protein with phage display*  
- Preparation of protein samples from cloned plasmids and UV-Vis studies with photoactive proteins for reversible protein-protein interaction

Supervisor: G. Andrew Woolley, University of Toronto, St. George

**Work Experience**

**Teaching Assistant at University of Toronto**  
**Sept 2014 - April 2015**  
*Supervised undergraduate research students in computational chemistry projects. Assistance in using Gaussian09 software and Gaussview*

**Teaching Assistant at University of Western Ontario**  
**Sept 2017 - April 2019**  
*Supervised first and second year undergraduate students in general and organic chemistry courses (Chem 1302 and Chem 2213). Responsible for operation of lab practical sessions and related marking.*

**Publications**


Presentations
4th Visegrad Symposium on Structural Systems Biology (2014)
- Poster presentation

Undergraduate summer poster presentation at University of Toronto (2015)
- Poster presentation

44th annual Southern Ontario Undergraduate Student Chemistry Conference (2016)
- Poster presentation

Undergraduate Thesis Poster Session at University of Toronto (2016)
- Poster presentation

102nd Canadian Chemistry Conference and Exhibition (2019)
- Oral presentation

Graduate Courses
Chemistry 9521 Catalysis 86
Chemistry 9541 Crystallography I 86
Chemistry 9571 Vibrational Spectroscopy of Solid State Materials 80
Chemistry 9581 Basics of Solid-state NMR Spectroscopy 86