

SLATT UNDERGRADUATE RESEARCH FELLOWSHIP FINAL REPORT

SCHOLAR NAME:	Stephanie Mueller
FACULTY ADVISOR:	Vlad Iluc
PROJECT PERIOD:	Winter 2020-2021
PROJECT TITLE:	Zinc (II) Carbene Synthesis and Reactivity
CONNECTION TO ONE OR MORE ENERGY-RELATED RESEARCH AREAS (CHECK ALL THAT APPLY):	<input checked="" type="checkbox"/> Energy Conversion and Efficiency <input type="checkbox"/> Sustainable and Secure Nuclear <input type="checkbox"/> Smart Storage and Distribution <input type="checkbox"/> Transformation Solar <input type="checkbox"/> Sustainable Bio/Fossil Fuels <input type="checkbox"/> Transformative Wind

MAJOR GOALS AND ACCOMPLISHMENTS

Summarize your research goals and provide a brief statement of your accomplishments (no more than 1-2 sentences). Indicate whether you were able to accomplish your goals by estimating the percentage completed for each one. Use the next page for your written report.

RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETED
Synthesize [(PCHP)ZnCl]	The desired molecule was isolated by reacting ZnCl ₂ with (PCHP)Li. NMR spectra and a crystal structure of the compound were obtained in order to characterize it.	100
Synthesize Zn (II) carbene	Several precursor molecules were synthesized and characterized.	N/A
Obtain crystal structures of novel products	Crystal structures of 5/5 novel molecules were obtained.	100
Obtain clean ¹H-NMR, ¹³C-NMR, and ³¹P-NMR of novel products	Clean ³¹ P-NMRs of 5/5 novel molecules were obtained. Clean ¹ H-NMRs and ¹³ C-NMRs of the 5 novel molecules are in the process of being obtained by purifying the samples via filtration and recrystallization.	33

RESEARCH OUTPUT

Please provide any output that may have resulted from your research project. You may leave any and all categories blank or check with your faculty advisor if you are unsure how to respond.

CATEGORY	INFORMATION
EXTERNAL PROPOSALS SUBMITTED	(Sponsor, Project Title, PIs, Submission Date, Proposal Amount)
EXTERNAL AWARDS RECEIVED	(Sponsor, Project Title, PIs, Award Date, Award Amount)
JOURNAL ARTICLES IN PROCESS OR PUBLISHED	(Journal Name, Title, Authors, Submission Date, Publication Date, Volume #, Page #s)
BOOKS AND CHAPTERS RELATED TO YOUR RESEARCH	(Book Title, Chapter Title, Authors, Submission Date, Publication Date, Volume #, Page #s)
PUBLIC PRESENTATIONS YOU MADE ABOUT YOUR RESEARCH	(Event, Presentation Title, Presentation Date, Location)
AWARDS OR RECOGNITIONS YOU RECEIVED FOR YOUR RESEARCH PROJECT	(Purpose, Title, Date Received)
INTERNAL COLLABORATIONS FOSTERED	(Name, Organization, Purpose of Affiliation, and Frequency of Interactions)
EXTERNAL COLLABORATIONS FOSTERED	(Name, Organization, Purpose of Affiliation, and Frequency of Interactions)
WEBSITE(S) FEATURING RESEARCH PROJECT	(URL)
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	(Please describe each item in detail)

RESEARCH EXPERIENCE

Please let us know what you thought of your research experience: Did this experience meet your expectations? Were lab personnel helpful and responsive to your needs? What else could have been done to improve your experience or achieve additional results?

This experience more than met my expectations. Before the Winter session, I had not made much progress on my project, as I was unable to dedicate more than 6 hours a week to it. I greatly expanded on my project after spending 40 hours a week in the lab during the Winter session.

The lab personnel were composed of graduate students and a principal investigator. They all helped me by answering my questions and providing suggestions. However, my project was entirely my own. I cannot think of anything that could have been done to improve my experience.

Overall, I have learned that I really enjoy chemical research. I know that I definitely want to pursue a career in research. I am now hoping to apply to MD/PhD programs.

FINAL WRITTEN REPORT

Before the Winter session began, ZnCl_2 was reacted with bis[2-(*di-iso*-propylphosphino)phenyl]methane (PCH_2P) to obtain $[(\text{PCH}_2\text{P})\text{ZnCl}_2]$. This was characterized by $^1\text{H-NMR}$ and $^{31}\text{P-NMR}$.

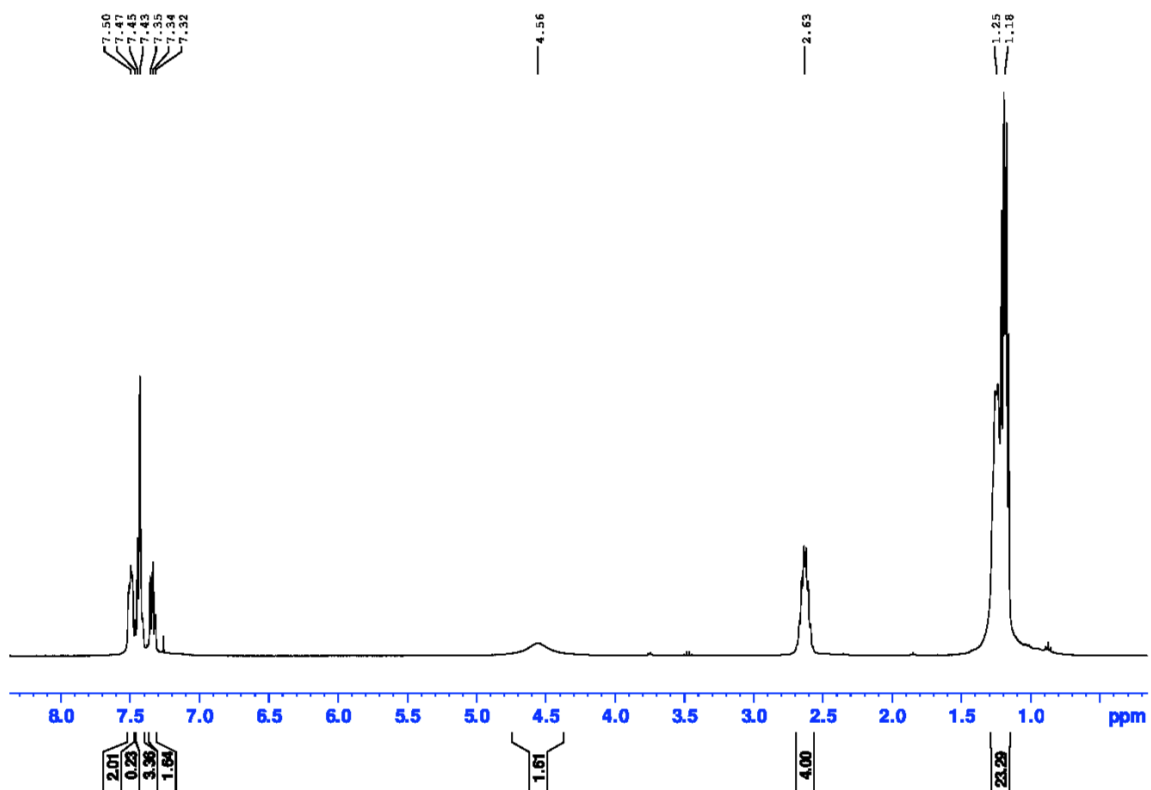


Figure 1a: $^1\text{H-NMR}$ of $[(\text{PCH}_2\text{P})\text{ZnCl}_2]$

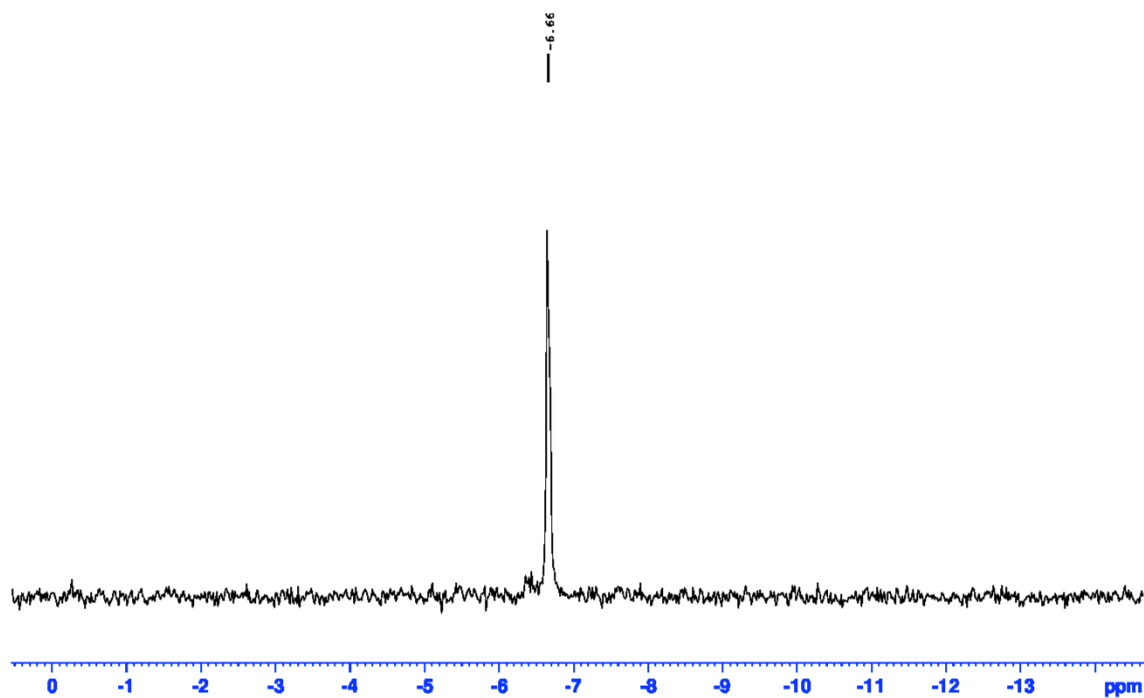


Figure 1b: $^{31}\text{P-NMR}$ of $[(\text{PCH}_2\text{P})\text{ZnCl}_2]$

During the Winter session, a crystal structure of $[(\text{PCH}_2\text{P})\text{ZnCl}_2]$ was obtained by X-ray diffraction analysis (XRD) of a single crystal.

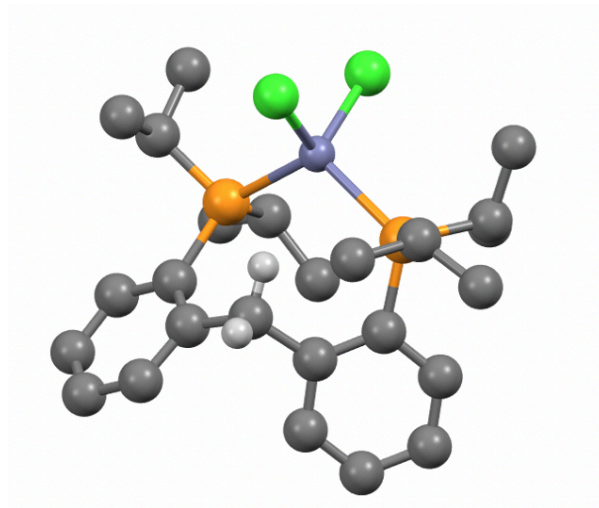


Figure 2: Crystal structure of $[(PCH_2P)ZnCl_2]$

Dehydrohalogenation of $[(PCH_2P)ZnCl_2]$ was attempted in the presence of a strong base and heat in order to synthesize $[(PCHP)ZnCl]$. This was unsuccessful, instead leading to the decomposition of $[(PCH_2P)ZnCl_2]$.

In order to synthesize $[(PCHP)ZnCl]$, PCH_2P was deprotonated with nBuLi to obtain $(PCHP)Li$. Then, $(PCHP)Li$ was reacted with $ZnCl_2$ to make $[(PCHP)ZnCl]$, which was isolated and characterized by NMR and XRD.

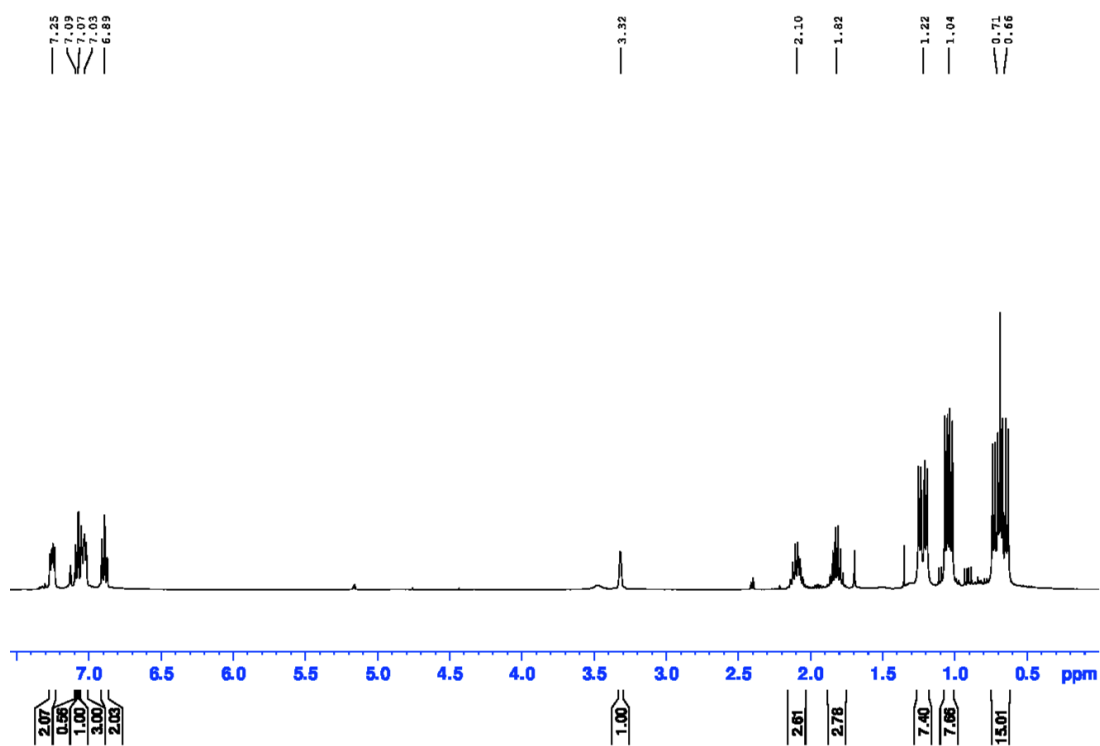


Figure 3a: 1H -NMR of $[(PCHP)ZnCl]$

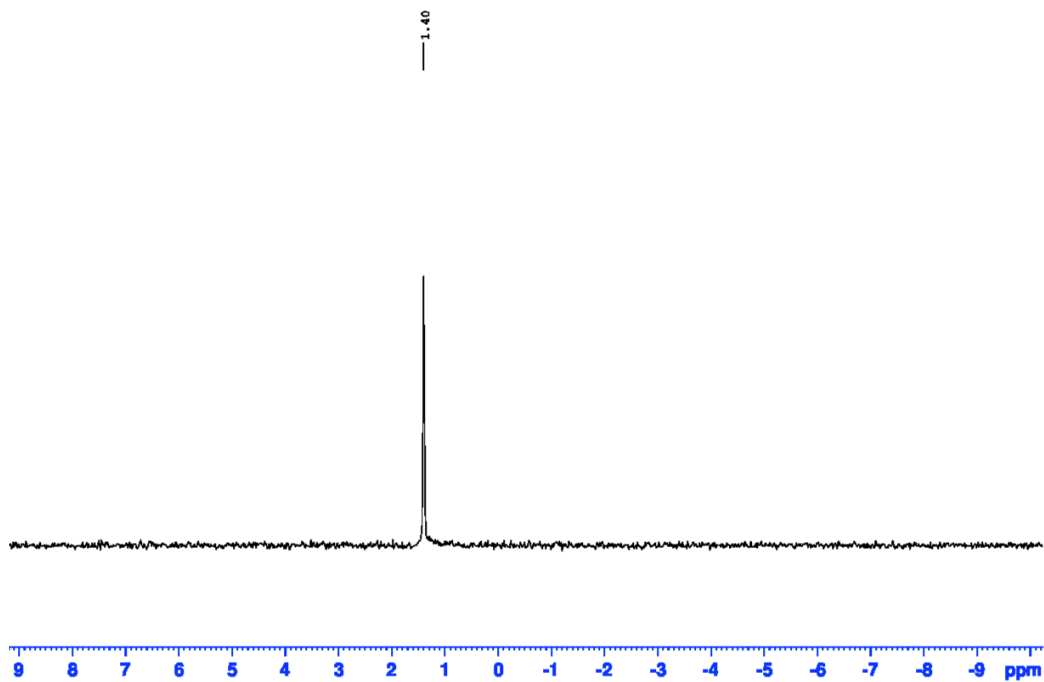


Figure 3b: ^{31}P -NMR of $[(\text{PCHP})\text{ZnCl}]$

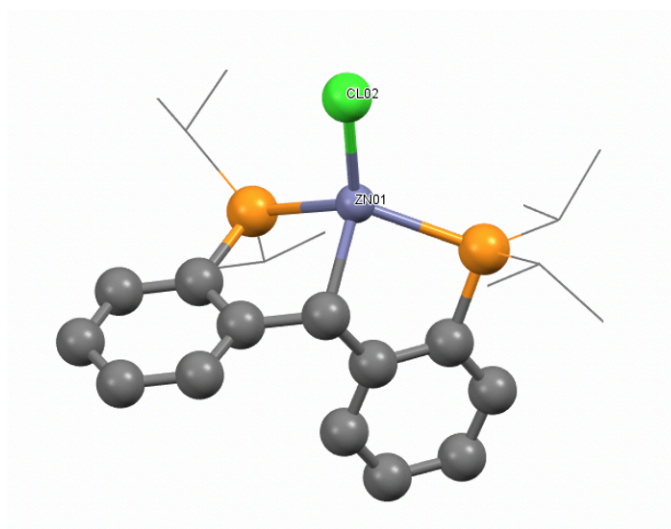


Figure 3c: Crystal structure of $[(\text{PCHP})\text{ZnCl}]$

The next step was to synthesize a Zn (II) carbene by the deprotonation of $[(\text{PCHP})\text{ZnCl}]$. The first attempt was to react $[(\text{PCHP})\text{ZnCl}]$ with potassium bis(trimethylsilyl)amide ($\text{KN}(\text{TMS})_2$) and trimethyl phosphene. This did not lead to the desired product, even after extensive heating. Instead, the isolated product was $[(\text{PCHP})\text{ZnN}(\text{TMS})_2]$, which was isolated and characterized by NMR and XRD.

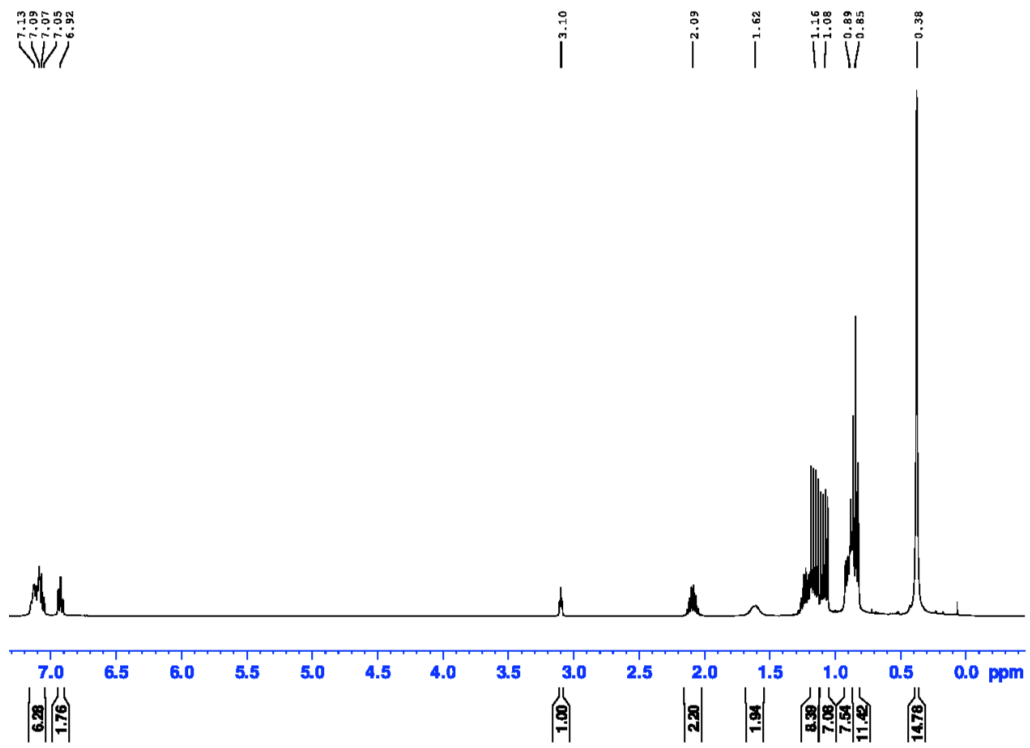


Figure 4a: $^1\text{H-NMR}$ of $[(\text{PCHP})\text{ZnN}(\text{TMS})_2]$

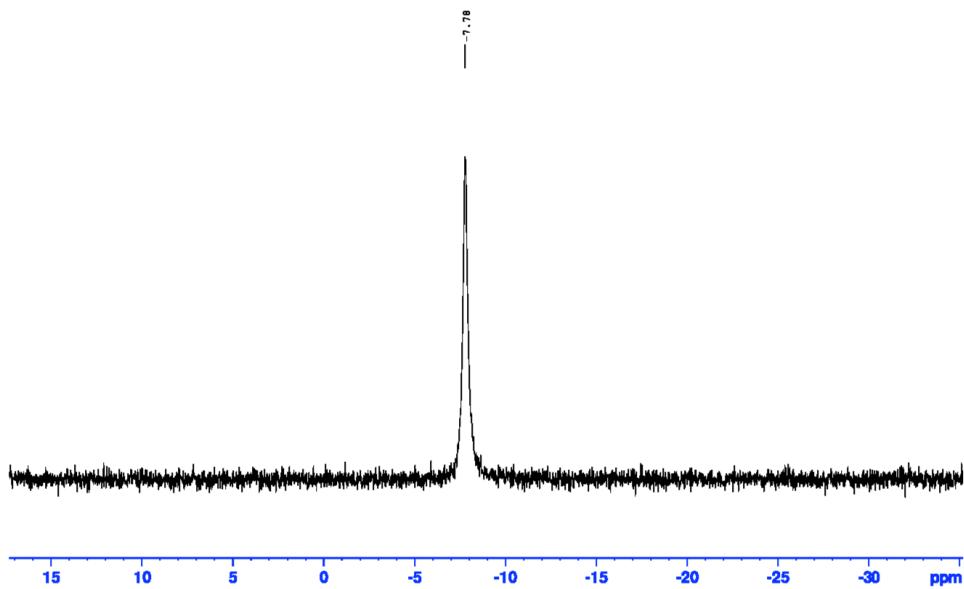


Figure 4b: $^{31}\text{P-NMR}$ of $[(\text{PCHP})\text{ZnN}(\text{TMS})_2]$

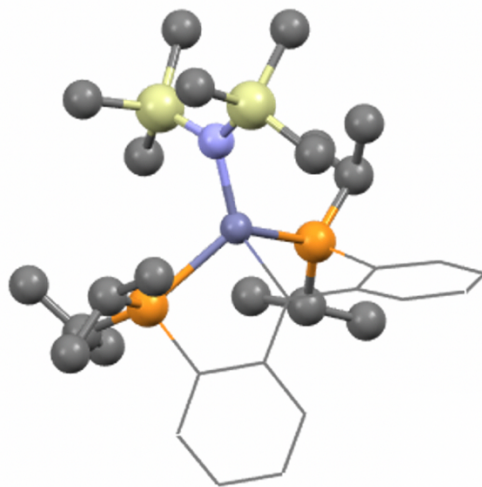


Figure 4c: Crystal structure of $[(\text{PCHP})\text{ZnN}(\text{TMS})_2]$

From there, deprotonation of $[(\text{PCHP})\text{ZnN}(\text{TMS})_2]$ was attempted by heating the complex in the presence of $^t\text{BuCN}$. This led to the decomposition of $[(\text{PCHP})\text{ZnN}(\text{TMS})_2]$.

Then methylation of $[(\text{PCHP})\text{ZnCl}]$ with methyllithium was attempted in order to obtain $[(\text{PCHP})\text{ZnCH}_3]$. This was isolated and characterized this via NMR and XRD.

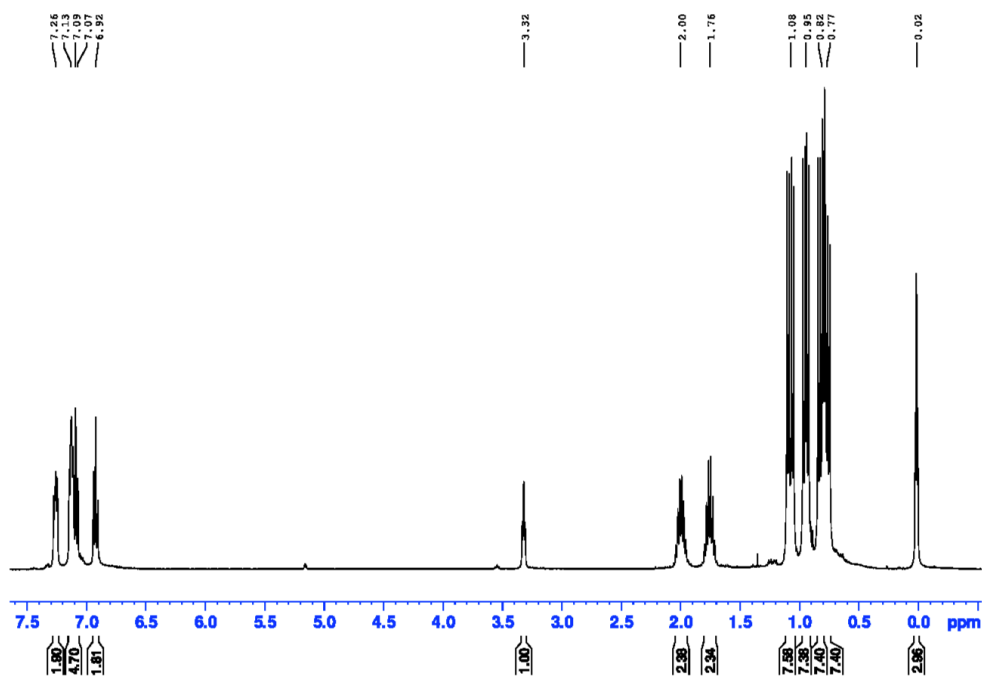


Figure 5a: ^1H -NMR of $[(\text{PCHP})\text{ZnCH}_3]$

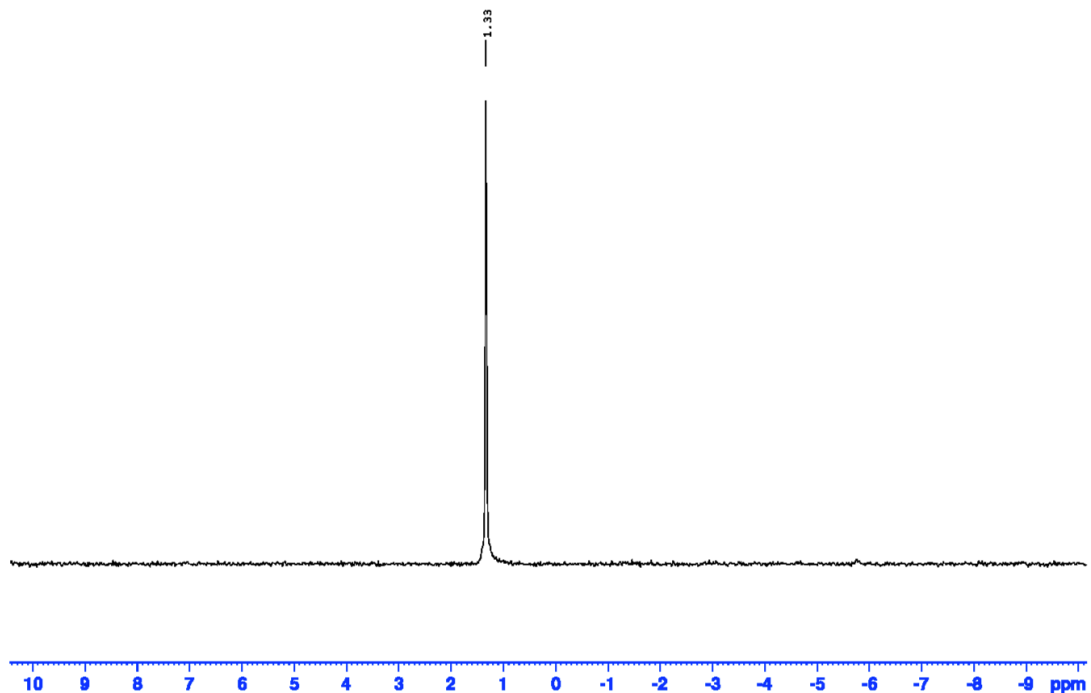


Figure 5b: ^{31}P -NMR of $[(\text{PCHP})\text{ZnCH}_3]$

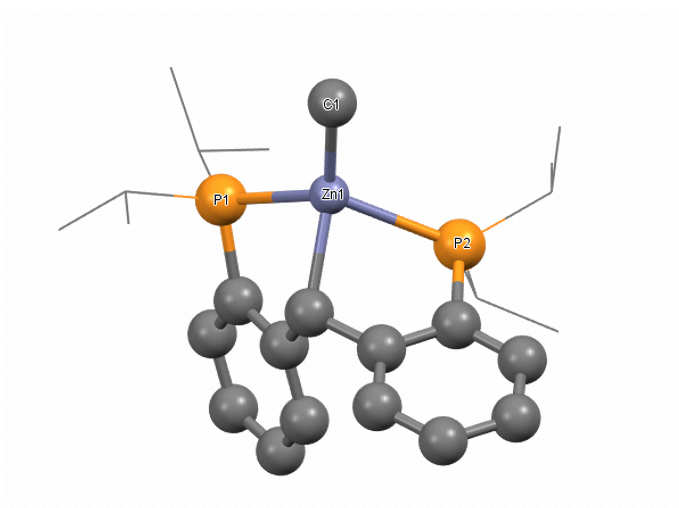


Figure 5c: Crystal structure of $[(\text{PCHP})\text{ZnCH}_3]$

Deprotonation of $[(\text{PCHP})\text{ZnCH}_3]$ was attempted by heating it in the presence of ${}^t\text{BuCN}$. This led to the decomposition of $[(\text{PCHP})\text{ZnCH}_3]$.

Due to steric hinderance, ${}^t\text{Bu}^-$ is a stronger base than CH_3^- . In another attempt to synthesize a Zn (II) carbene, $[(\text{PCHP})\text{ZnCl}]$ was reacted with ${}^t\text{BuLi}$. The product $[(\text{PCHP})\text{Zn}{}^t\text{Bu}]$ was isolated and characterized by NMR and XRD.

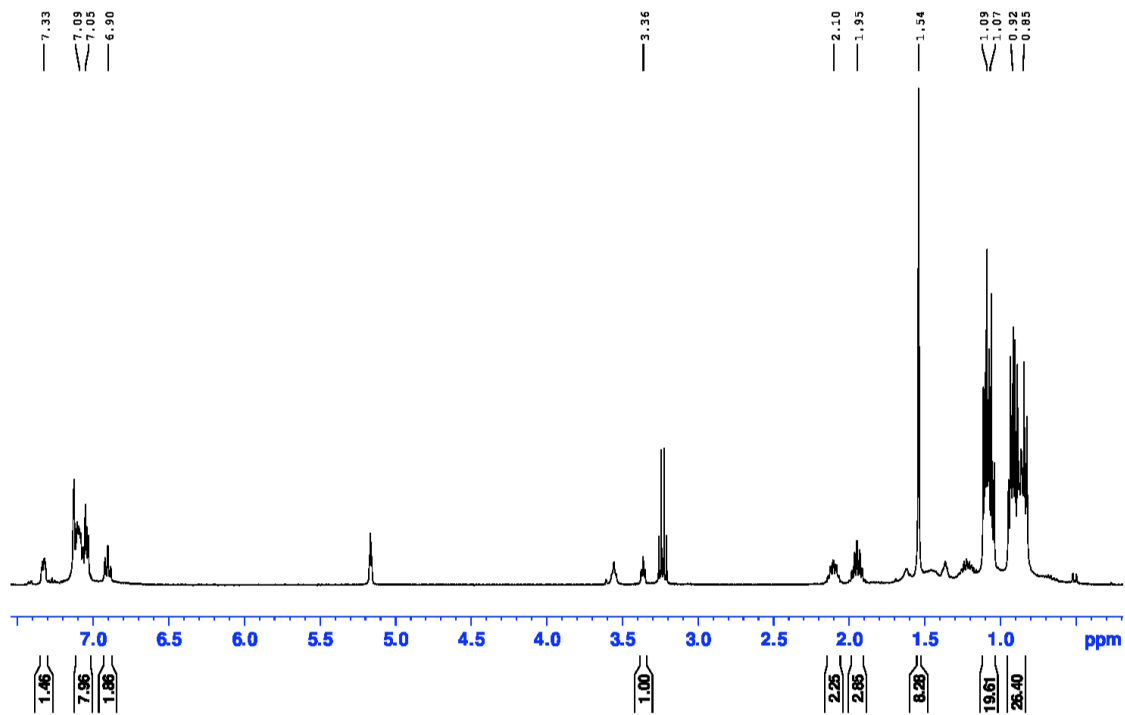


Figure 6a: Crude $^1\text{H-NMR}$ of $[(\text{PCHP})\text{Zn}^t\text{Bu}]$

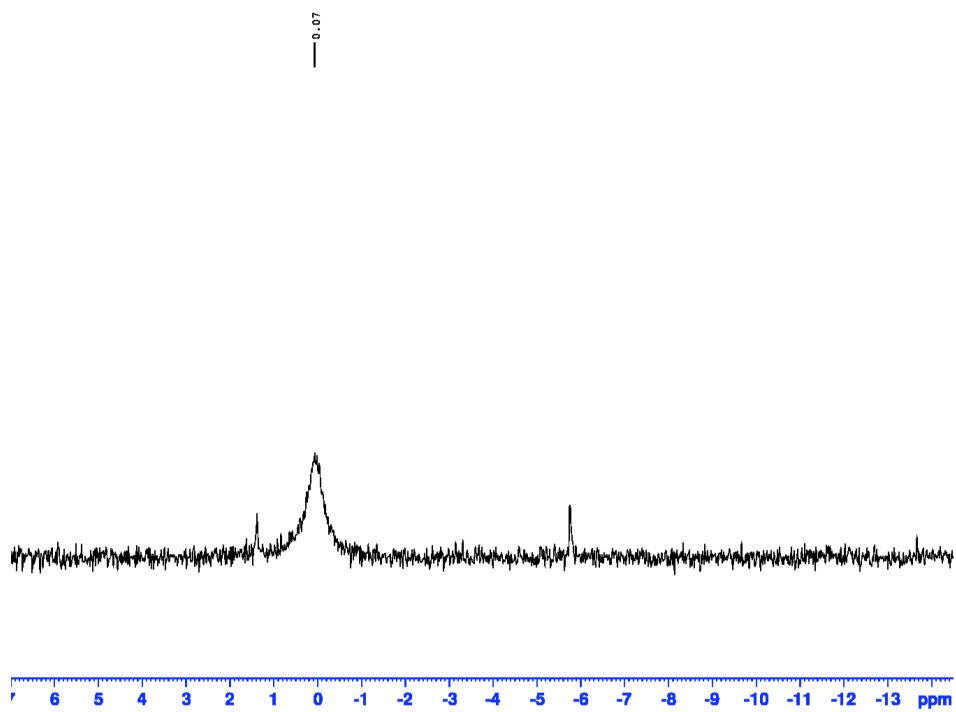


Figure 6b: Crude $^{31}\text{P-NMR}$ of $[(\text{PCHP})\text{Zn}^t\text{Bu}]$

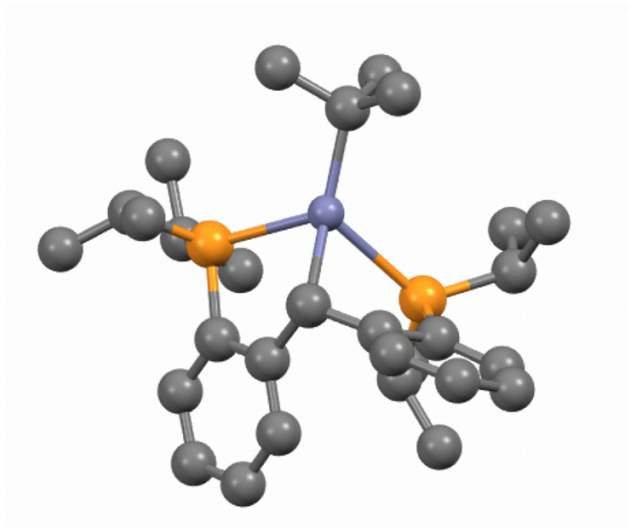


Figure 6c: Crystal structure of [(PCHP)Zn^tBu]

Deprotonation of [(PCHP)Zn^tBu] was attempted by heating it in the presence of ^tBuCN. This led to the decomposition of [(PCHP)Zn^tBu].

It is possible that the synthesis of a Zn (II) carbene by deprotonation of [(PCHP)ZnX] (X = Cl, N(TMS)₂, CH₃, ^tBu) has been unsuccessful due to 4-coordinate Zn(II)'s preferred tetrahedral geometry. This geometry makes it impossible for the backbone carbon of the desired [(PCP)ZnY] (Y = a neutral ligand) to be in the same plane as the phenyl rings, breaking any possible resonance that would stabilize the carbene. In order to overcome this restricting geometry, a 5-coordinate [(PCHP)ZnY₂] complex will be synthesized, which could have a square pyramidal geometry. This geometry could put the backbone carbon in the proper plane to allow deprotonation.

The next step in this project is to synthesize a five-coordinate [(PCHP)ZnY₂] complex by reacting [(PCHP)ZnX] (X = Cl, CH₃, ^tBu, or N(TMS)₂) with a strong bidentate ligand, such as 1,10-phenanthroline and 2,2'-bipyridine. It is expected that the leaving group will deprotonate the backbone proton once the bidentate ligand binds to Zn (II). If this does not occur, the reaction will be heated to induce deprotonation.