

**SLATT UNDERGRADUATE RESEARCH FELLOWSHIP
FINAL REPORT**

SCHOLAR NAME:	Olivia Lanchoney
FACULTY ADVISOR:	Dr. Vlad Iluc
PROJECT PERIOD:	Winter Break 2020-2021
PROJECT TITLE:	Synthesis of a Three-Coordinate Nickel Alkylidene
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 a three-coordinate nickel alkylidene	Spectroscopic data of the proposed (dtbpe)Ni alkylidene suggests that the compound was successfully synthesized. However, crystallographic data was not able to be obtained, and therefore, the synthesis of the (dtbpe)Ni alkylidene cannot be confirmed.	90%
Characterize the compound through NMR spectroscopy and X-ray crystallography	Both the proposed alkylidene precursor, (dtbpe)Ni ⁰ with a side-bound <i>tert</i> -butyl diazomethane coordinated through the N=N double bond, and the target compound, (dtbpe)Ni alkylidene, were observed using ¹ H and ³¹ P NMR. However, due to low yields and solubility challenges, both compounds were unable to be isolated. Thus, crystals were not successfully grown for X-ray crystallography.	50%
Investigate compound through decomposition and reactivity	This goal was not achieved, as both products were not yet fully characterized.	0%

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	N/A
EXTERNAL AWARDS RECEIVED	N/A
JOURNAL ARTICLES IN PROCESS OR PUBLISHED	N/A
BOOKS AND CHAPTERS RELATED TO YOUR RESEARCH	N/A
PUBLIC PRESENTATIONS YOU MADE ABOUT YOUR RESEARCH	N/A
AWARDS OR RECOGNITIONS YOU RECEIVED FOR YOUR RESEARCH PROJECT	N/A
INTERNAL COLLABORATIONS FOSTERED	N/A
EXTERNAL COLLABORATIONS FOSTERED	N/A
WEBSITE(S) FEATURING RESEARCH PROJECT	N/A
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases,	N/A

software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)

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 most definitely met my expectations. I have worked in Iluc lab for three years now, and I have felt and continue to feel well-supported and challenged throughout my time there. Lab meetings pushed me out of my comfort zone and strengthened my public speaking skills as I discussed my research. While this was sometimes challenging for me, I felt very comfortable with the members of the lab, and they were all very approachable for help or questions. This created a great learning environment for me. Nothing else could have been done to improve my experience. The graduate students and Dr. Iluc are both extremely helpful and engaging, and I feel driven to work hard with them.

FINAL WRITTEN REPORT

(Please use the space below to describe your research project and objectives, any findings and results you can share, and graphs, charts, and other visuals to help us understand what you achieved as a result of this research experience.)

While I was unable to complete all of my goals, I made progress in the synthesis of (dtbpe)Ni alkylidene and its precursor. In order to make the precursor, (dtbpe)Ni⁰ with a side-bound *tert*-butyl diazomethane coordinated through the N=N double bond, (dtbpe)Ni⁰ was first synthesized by reducing (dtbpe)NiCl₂. After this, (dtbpe)Ni⁰ was stirred with *tert*-butyl diazomethane in pentane for thirty minutes. Both the ¹H and ³¹P NMR data of the product are consistent with the expected sidebound product (Figures 1 and 2).

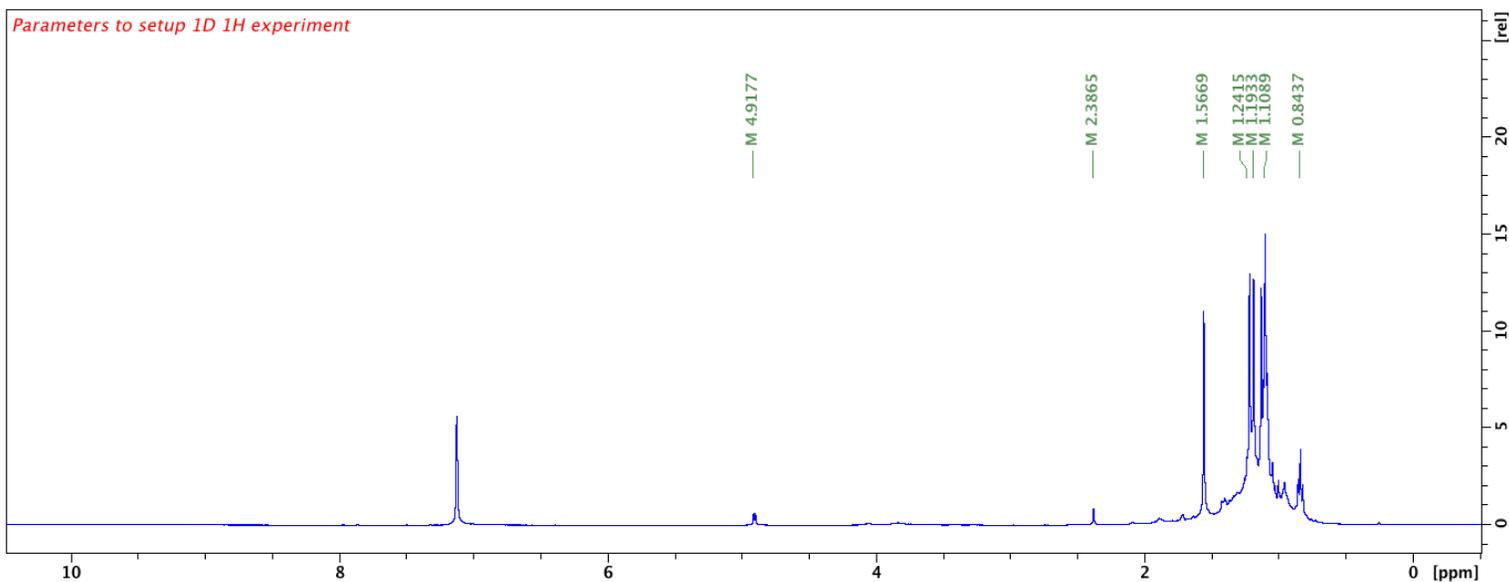


Figure 1. Crude ¹H NMR data for the synthesis of the (dtbpe)Ni alkylidene precursor, (dtbpe)Ni⁰ with a side-bound *tert*-butyl diazomethane.

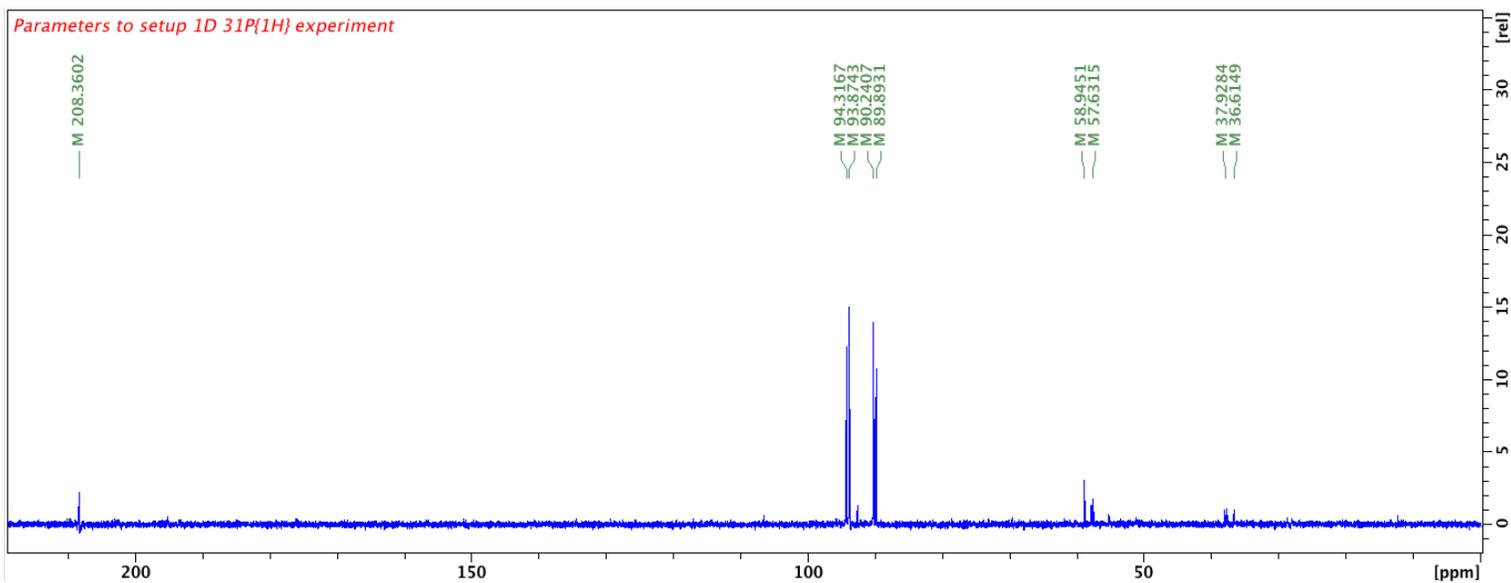


Figure 2. Crude ^{31}P NMR data for the synthesis of the (dtbpe)Ni alkylidene precursor, (dtbpe)Ni⁰ with a side-bound *tert*-butyl diazomethane. This spectrum was obtained in C₆D₆, and peaks δ 94.32, δ 93.87, δ 90.24, and δ 89.89 are consistent with the expected product.

This product was then exposed to UV light for 90 minutes. The ^1H and ^{31}P NMR data of the product suggest that the side-bound product converted to the (dtbpe)Ni alkylidene (Figures 3 and 4).

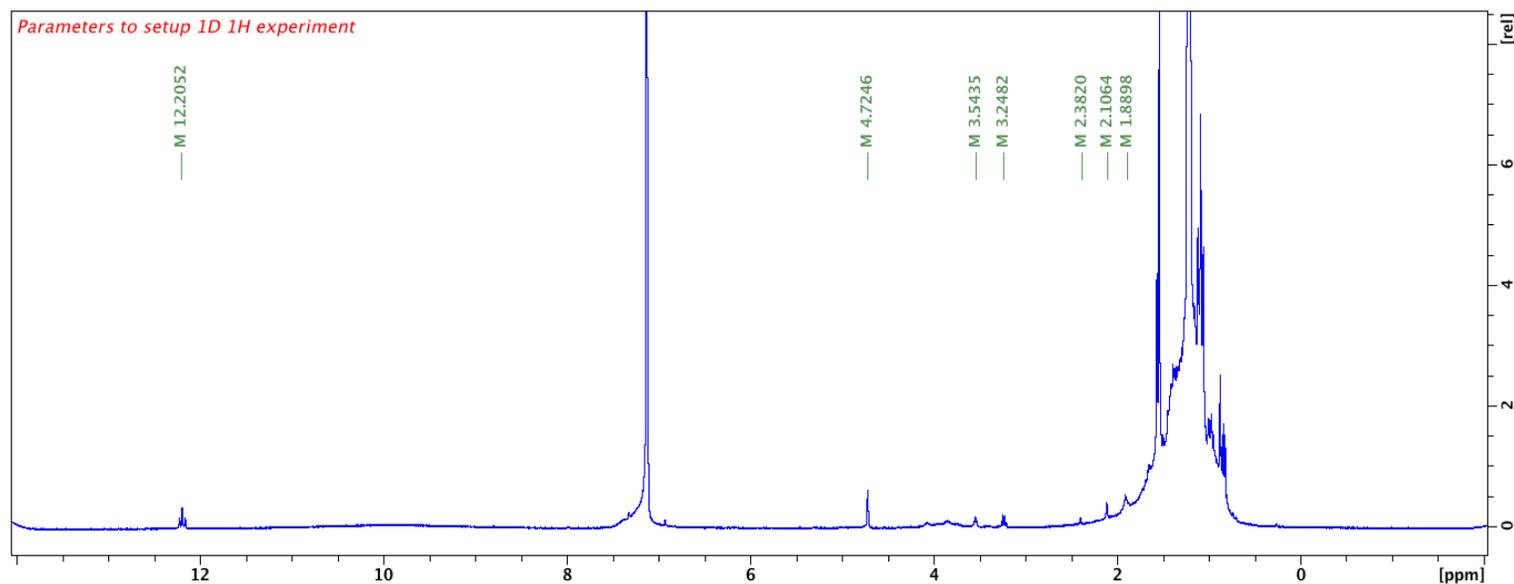


Figure 3. Crude ^1H NMR data for the synthesis of the (dtbpe)Ni alkylidene. This spectrum was obtained in C₆D₆. While this spectrum is very dilute, the triplet at δ 12.21 is consistent with the synthesis of the (dtbpe)Ni alkylidene.

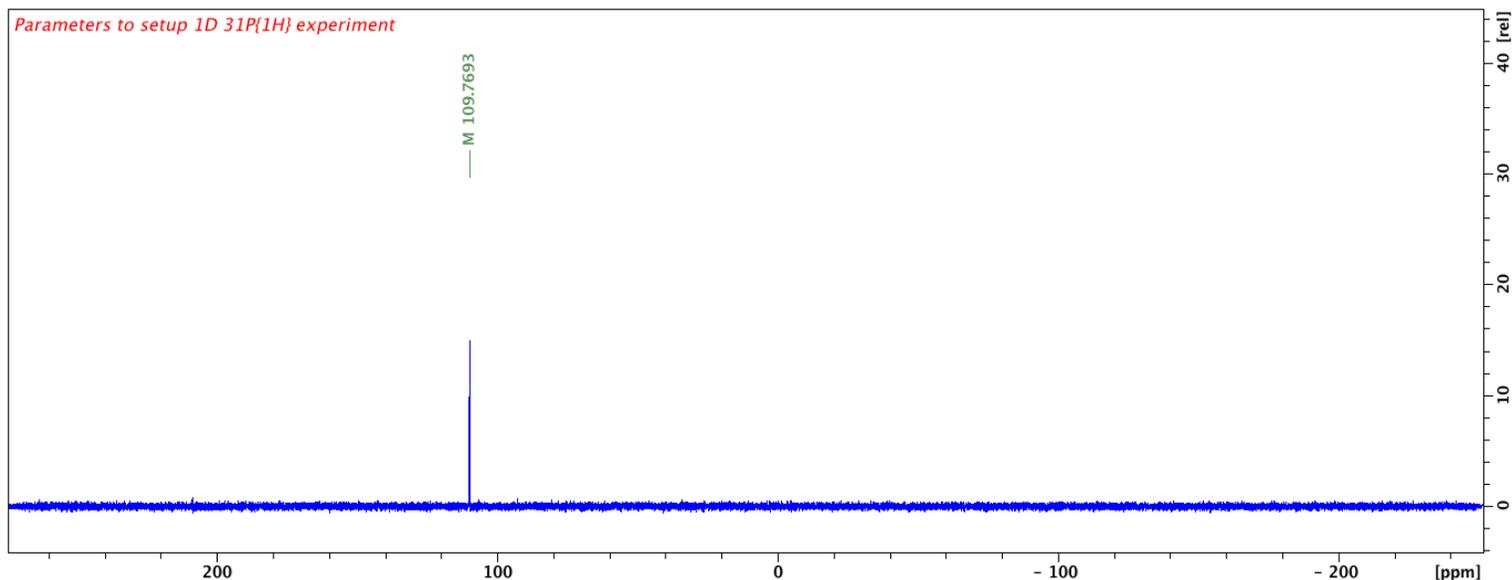


Figure 4. Crude ^{31}P NMR data for the synthesis of the (dtbpe)Ni alkylidene. This spectrum was obtained in C_6D_6 , and the peak at δ 109.77 is consistent with the expected product.

After this was achieved, the next step was to characterize both products by ^{13}C NMR and X-ray crystallography in order to confirm their syntheses. Due to solubility challenges with impurities and the targeted compounds, we were unable to isolate viable crystals of both compounds. Crystallization of both the alkylidene and the side-bound product was attempted with varying concentrations of diethyl ether and pentane, but both resulted in powder of the products. Furthermore, we struggled with a (dtbpe)Ni¹ chloride dimer impurity, which we believe was unable to be removed from the initial reduction of (dtbpe)NiCl₂ to (dtbpe)Ni⁰. To avoid this impurity, synthesis of (dtbpe)Ni⁰ was attempted with Ni(COD)₂ and the dtbpe ligand, but (dtbpe)Ni⁰ was not produced. Additionally, the reduction of (dtbpe)NiCl₂ was attempted with KC₈ and activated magnesium. These results were unsuccessful in eliminating the (dtbpe)Ni¹ chloride dimer impurity.

Thus, while NMR data suggest that the (dtbpe)Ni alkylidene precursor and the (dtbpe)Ni alkylidene itself were synthesized, future research is needed to purify and isolate these compounds in order to confirm their synthesis and fully characterize them.