

# Electronic Structures of Perfunctionalized Dodecaborate Clusters

Thesis by  
L. Josef Schwan

In Partial Fulfillment of the Requirements for  
the degree of  
Doctor of Philosophy

The logo for the California Institute of Technology (Caltech), featuring the word "Caltech" in a bold, orange, sans-serif font.

CALIFORNIA INSTITUTE OF TECHNOLOGY  
Pasadena, California

2020  
(Defended March 5, 2020)

© 2020

Lars Josef Schwan  
ORCID: 0000-0002-1086-6698

*To my father*

## ACKNOWLEDGEMENTS

First and foremost, I want to thank Harry Gray for his encouragement and unwavering support. Under his mentorship I have enjoyed near limitless freedom to pursue my own path and to discover what it means to be a truly independent scientist. Harry is always accessible and happy to help, both in and out of the lab. He is glad to talk on a moment's notice, and I have never had to wait for more than a day or two to get his comments on drafts and new data. He truly makes his students and post-docs the top priority. I could not imagine a better advisor. I also want to thank Jay Winkler, who in many ways is the scientific engine of the lab. His uncanny ability to pick apart problems and make complex relationships seem simple has been invaluable throughout my studies. Nate Lewis deserves my gratitude for being my formal co-advisor, even as I scientifically drifted far away from the Lewis lab. Nate and his group have continued to welcome me, and I have appreciated partaking in many social events with the Lewis group.

I am likewise grateful to the members of my thesis committee. Doug Rees, my committee chair, has been incredibly supportive and willing to offer his advice on the big picture questions. He was a great collaborator during the initial two years of my graduate studies, when I attempted to develop methods for investigating the mechanism of nitrogenase enzymes using flash-quench techniques. Sarah Reisman has been a great help in answering complex organic chemistry questions and giving perspective on how our work on photoredox catalysts relates to the needs of the organic chemistry community. I also appreciate that she made sure to push the difficult questions during committee meetings. Bob Grubbs, who was the final addition to my committee, offered valuable help in identifying career opportunities and in making connections outside of the academic environment. The support of Doug, Sarah and Bob has been instrumental in getting me to where I am today and finding my path post-Caltech.

I could not have gotten through my graduate work without the help of my friends in the Gray lab. In particular, I want to thank Wes Kramer, Brian Sanders, Brendon McNicholas, Jillian Clinton, Brad Brennan and Javier Fajardo, who have been my greatest friends and supporters during my time at Caltech. Brad was my lab and office mate during my first year and a fantastic mentor throughout that period. He helped me get settled in the lab and pushed me to find direction in my work. Brendon's support during my second year was key in building momentum

in my research. I am also indebted to him for assisting last year, when I was struggling doing work in the lab due to health issues. I am thankful to Brian for mentoring me in the biochemistry lab while I was exploring nitrogenase enzymes, and for always being happy to assist in the laser lab. His calm presence provided refuge from the stressful reality of graduate school. Wes led the work on group 6 metal arylisocyanides, which was for a long time my main thesis project. Under his guidance I grew into a confident synthetic inorganic chemist and the independent scientist I am today. Javier was a great contributor and supporter during the later stages of my engagement in the metal arylisocyanide project and took over after I moved on to focus on the work presented in this thesis. It has been a pleasure to watch all the amazing research he has done over the past year. Jill has been a beacon of energy in the lab, and I am forever grateful for her support and for making our lab the fun and happy place it is today. I too owe thanks to all the other members of the Gray lab who have helped and supported me over the years (in no particular order): Sarah Del Ciello, Oliver Shafaat, Bryan Hunter, James Blakemore, Julian West, Katharina Brinkert, Patrycja Kielb, Dana Levine, Carl Blumenfeld, Emmanuelle Despagnet-Ayoub, Tony Vlcek, Jieun Shin, Astrid Mueller, Michelle DeBoever, and Michael Lichterman. I also want to thank two fantastic undergraduate researchers, Damien Berube and Joseph Schneider, who worked for me on the group 6 metal arylisocyanide project. Mentoring them was among enjoyable things I did at Caltech. Joseph helped develop synthetic schemes for naphthylisocyanides, while Damien worked on mixed carbonyl-arylisocyanide complexes. Their energy in the lab was a great inspiration.

During my time at Caltech I have sought out several collaborative projects. I am indebted to all my collaborators outside of the Gray lab. Most notably, I want to extend my gratitude to Alex Spokoyny at UCLA and his post-docs Jon Axtell and Julia Stauber. Alex, Jon and Julia have been key participants in developing this thesis. The Spokoyny lab developed the perfunctionalized dodecaborate clusters I explored and did all synthetic work. They have always been accessible and happy to provide compounds and assistance. Working with Alex and his group has been an amazing experience. I also owe gratitude to Christine Morrison from the Rees lab for all her encouragement and help while I was working on nitrogenase enzymes, and for Amylynn Chen, Andrey Vyatskikh and Julia Greer from the Greer lab who made reality out of my vision to use tungsten arylisocyanide complexes as two-photon lithography absorbers.

I am thankful to all the staff scientists and administrators who we depend on to keep Caltech running. Paul Oyala deserves special mention—his assistance with EPR experiments and interpretation has been a key part of my thesis research. He has also been a great friend over the past years. I additionally want to thank Mike Takase and Larry Henling who run the X-ray crystallography facility (special shout out to Larry for all the hours we have spent chatting in the Beckman Institute break room), Mona Shahgoli at the mass spec lab and Dave Vander Velde who supervises the NMR facility. They have all been incredibly helpful—always happy to assist with experiments and to discuss data. I am grateful to Rick Jackson, our group administrator, for taking care of us—his snack cabinet has saved me during many long nights in the lab. I also want to thank Siddharth Dasgupta, Alison Ross, Pat Andersson, Barbara Miralles, Kimberly Papadantonaki, Daniel Yoder, Laura Flower Kim, as well as everyone in the Graduate Office. They have all played important roles in helping me get through my studies without any administrative hiccups.

Beyond the scientific community around Caltech, I want to mention some of the people who helped me find my way to Caltech and provided personal support during my time here. First of all, I want to thank my mother for encouraging and supporting me, even when I spent my early twenties with no high school degree working in bars. She has visited me many times over the past few years and helped me remain connected to my roots. I want to thank my father, who regrettably passed away many years ago, for awakening my curiosity and inspiring me to question authority and ask challenging questions. My grandmother and my uncle Åke deserve special mention. Even though she is now 90, my grandmother twice made it out to visit California for Christmas and my thirtieth birthday. Åke has been a great supporter and has kept me updated on all that's ongoing back in Sweden.

Furthermore, I want to thank those who aided me during my undergraduate studies. Most importantly, I am forever grateful to Professors Leif Hammarström and Tomas Edvinsson at Uppsala University, who let me into their labs and gave me my first experiences with chemistry and chemical physics research. The graduate students and post-docs who guided me during my undergraduate research also deserve credit—Mohammad Mirmohades, Jesper Jacobsson and Starla Glover were both good friends and fantastic mentors. I am also grateful to my friends from the Chemical Engineering program: Erik Bamford, David Jonsson, Andreas Bengtsson,

Daniel Hedbom and Emil Olsson. We spent countless hours studying and solving problems together and without their support I would have never gotten to where I am today.

Finally, I am eternally grateful to my amazing girlfriend Courtney who has supported and pushed me through the final stages of my graduate studies. Having her by my side allowed me to approach my work with confidence and stay calm during stressful periods. The structure and motivation she has brought to my life has been invaluable—without her I would have undoubtedly needed an additional year (or two) to finish this thesis.

## ABSTRACT

This thesis summarizes my exploration of hypoelectronic aryloxy-perfunctionalized dodecaborate clusters ( $[\text{B}_{12}(\text{OR})_{12}]$ ). *Closo*-dodecaborate (*closo*- $[\text{B}_{12}\text{H}_{12}]^{2-}$ ) is only stable as a dianionic closed-shell species. However, some perfunctionalized dodecaborate clusters can be isolated in hypoelectronic oxidation states, such as *hypocloso*- $[\text{B}_{12}(\text{OR})_{12}]^{1-}$  and *hypercloso*- $\text{B}_{12}(\text{OR})_{12}$  (R = alkyl or aryl). Depopulation of the  $[\text{B}_{12}(\text{OR})_{12}]$  highest occupied molecular orbital (HOMO) give rise to strong visible absorption bands, which has opened up for their use as photoredox reagents. Furthermore, their inert nature and highly reversible redox behavior has inspired applications in charge-storage devices and as dopants in conducting polymers.

The work presented in Chapters 2–4 were part of a broad collaborative effort lead by Professor Alexander M. Spokoyny (University of California, Los Angeles). Chapter 2 discusses my early contributions, which aimed to spectroscopically investigate the photoredox properties of aryloxy-perfunctionalized *hypercloso*- $\text{B}_{12}(\text{OR})_{12}$  clusters. Obtaining reliable photophysical data proved exceedingly difficult, due to formation of *hypercloso*- $[\text{B}_{12}(\text{OR})_{12}]^{1+}$ , disproportionation and solvent-cluster interactions. Chapter 2 summarizes discoveries made while attempting to understand these issues, as well as the final luminescence data collected for *hypercloso*- $\text{B}_{12}(\text{OR})_{12}$  and *hypercloso*- $[\text{B}_{12}(\text{OR})_{12}]^{1+}$  clusters. Much of the discussion is speculative, but we felt it should be published here so that other researchers can learn from our struggles.

Given the issues we had with photophysical characterization of the aryloxy-perfunctionalized clusters discussed in Chapter 2, we turned our attention to the alkyloxy-perfunctionalized analogues, which we hoped would be more amenable to spectroscopic characterization. These clusters did not help our investigation of the photoredox behavior, however, while electrochemically characterizing  $[\text{B}_{12}(\text{OEt})_{12}]$  (Et =  $\text{C}_2\text{H}_5$ ) we discovered a third reversible oxidation wave, corresponding to the  $[\text{B}_{12}(\text{OEt})_{12}]^{1+/0}$  couple. Chapter 3 discusses this discovery and the characterization of super-oxidized  $[\text{B}_{12}(\text{OR})]^{1+}$  clusters.

Up until now, electronic structure descriptions of hypoelectronic dodecaborate clusters have been largely limited to computational work. Attempts to access the distribution of the frontier orbitals through electron paramagnetic resonance (EPR) spectroscopy had been hindered by the



lack of resolution in the continuous wave (CW) spectra of *hypocloso*-[B<sub>12</sub>]<sup>1-</sup> species. In chapter 4, we present Q-band pulsed EPR results that give a quantitative measure of the spin distribution of both *hypocloso*-[B<sub>12</sub>(OR)<sub>12</sub>]<sup>1-</sup> and super-oxidized [B<sub>12</sub>(OR)<sub>12</sub>]<sup>1+</sup> clusters. This is to our knowledge the first time pulsed EPR techniques have been applied to hypoelectronic dodecaborate clusters. Our results indicate that the frontier orbitals of *hypocloso*-[B<sub>12</sub>(OR)<sub>12</sub>] clusters are confined to the cluster core and delocalized evenly across the B<sub>12</sub> pseudo-icosahedron. The data for the super-oxidized [B<sub>12</sub>(OR)<sub>12</sub>]<sup>1+</sup> indicate a somewhat more localized spin distribution, which we suggest stems from increased elongation along the z-axis resulting in a concentration of spin density around the equatorial boron atoms. Furthermore, we provide UV-vis-NIR evidence indicating that visible and NIR electronic transitions in [B<sub>12</sub>(OR)<sub>12</sub>] occur between orbitals that are largely confined to the cluster core.

## PUBLISHED CONTENT AND CONTRIBUTIONS

Axtell, J. C.; Messina, M. S.; Liu, J.-Y.; Galaktionova, D.; Schwan, J.; Porter, T. M.; Savage, M. D.; Wixtrom, A. I.; Rheingold, A. L.; Kubiak, C. P.; Winkler J. R.; Gray H. B.; Kral P.; Alexandrova A. N.; Spokoyny A. M. Photooxidative Generation of Dodecaborate-Based Weakly Coordinating Anions. *Inorg. Chem.* **2019**, *58* (16), 10516–10526. DOI: 10.1021/acs.inorgchem.9b00935.

*L. J. S. performed photophysical characterization and experimental investigation of intermolecular interactions. Additionally, L. J. S. assisted with data interpretation and development of the photooxidative mechanism.*

Stauber, J. M.; Schwan, L. J.; Xhang, X.; Axtell, J. C.; Jung, D.; McNicholas, B. J.; Oyala, P. H.; Winkler, J. R.; Miller, T. F.; Gray H. B.; Spokoyny, A.M. Evidence for the Existence of Cationic Dodecaborate-based Clusters (*in preparation*).

*L. J. S. performed electrochemical, spectroelectrochemical, EPR and chemical oxidation studies, including the initial discovery of the cationic dodecaborate.*

Schwan, L. J.; Oyala P. H.; Axtell J. C.; McNicholas B. J.; Winkler, J. R.; Spokoyny A. M.; Gray H. B. Electronic Structures of Perfunctionalized Dodecaborates Clusters (*in preparation*).

*L. J. S. participated in conception of the project, experiment design, collection and analysis of data, and writing of the manuscript.*

Fajardo Jr. J.; Schwan, L. J.; Takase, M. K.; Winkler, J. R.; Gray, H. B. Third Generation W(CNAr)<sub>6</sub> Photosensitizers Featuring Fused-Ring and Alkynyl-Bridged Arylisocyanides (*in preparation*).

*L. J. S. participated in conception of the project, synthesis and spectroscopic characterization.*

## TABLE OF CONTENTS

Acknowledgements .....	iv
Abstract.....	viii
Published Content and Contributions .....	x
Table of Contents .....	xi
List of Figures.....	xiii
List of Tables.....	xvi
Introductory Remarks.....	xvii
Chapter I: Perfunctionalized Dodecaborate Clusters.....	1
1.1 Dodecaborate Clusters .....	2
1.2 Functionalization of <i>closo</i> -Dodecaborate .....	7
1.3 Hypoelectronic Dodecaborates .....	11
1.4 Applications of <i>hypercloso</i> -B <sub>12</sub> (OR) <sub>12</sub> .....	13
1.5 Concluding Remarks.....	18
Bibliography .....	19
Chapter II: Photochemistry of B <sub>12</sub> (OR) <sub>12</sub> .....	23
2.1 Background .....	24
2.2 Preliminary Photophysical Studies .....	27
2.3 Electrochemical Characterization and the [B <sub>12</sub> ] <sup>1-</sup> Monoanion .....	28
2.4 Interactions with Haloarenes.....	35
2.5 [F <sub>60</sub> ] <sup>1-</sup> Disproportionation .....	40
2.6 <i>hypocloso</i> -B <sub>12</sub> (OR) <sub>12</sub> <sup>0</sup> Emission .....	48
2.7 Conclusions .....	52
2.8 Experimental Details.....	55
Bibliography .....	62
Chapter III: The [B <sub>12</sub> (OR) <sub>12</sub> ] <sup>1+</sup> Cation .....	65
3.1 Introduction .....	66
3.2 Electrochemical Generation of [B <sub>12</sub> (OR) <sub>12</sub> ] <sup>1+</sup> .....	69
3.3 Chemical Generation of [B <sub>12</sub> (OR) <sub>12</sub> ] <sup>1+</sup> .....	77
3.4 Conclusions .....	83
3.5 Experimental Details.....	84
Bibliography .....	93
Chapter IV: Electronic Structures of Perfunctionalized Dodecaborate Clusters .....	97
4.1 Background .....	98
4.2 Pulsed EPR Investigation of <i>hypocloso</i> -[B <sub>12</sub> (OR) <sub>12</sub> ] <sup>1-</sup> .....	100
4.3 Pulsed EPR Investigation of Super-Oxidized [B <sub>12</sub> (OR) <sub>12</sub> ] <sup>1+</sup> .....	106
4.4 Electronic Transitions in [B <sub>12</sub> (OR) <sub>12</sub> ] Clusters.....	114
4.5 Conclusions .....	120
4.6 Experimental Details.....	121
Bibliography .....	126

Chapter V: Finishing Remarks.....	129
5.1 Current State of Affairs.....	130
5.2 Electronic Structure of Super-oxidized Clusters .....	131
5.3 Future Directions.....	133
Bibliography.....	135
Appendix A: Photooxidative Generation of Dodecaborate-Based Weakly Coordinating Anions .....	137
A.1 Introduction .....	138
A.2 Synthesis and Self-exchange Studies.....	140
A.3 Styrene Polymerization .....	142
A.4 Computational Analysis of Photoexcitation .....	144
A.5 Discussion of Photoinitiated Polymerization Studies.....	148
A.6 Conclusions .....	158
Bibliography.....	160

## LIST OF FIGURES

<i>Number</i>	<i>Page</i>
1.1 Crystal Structure of <i>closo</i> -[B <sub>12</sub> H <sub>12</sub> ] <sup>2-</sup> .....	4
1.2 Electronic Structure of <i>closo</i> -[B <sub>12</sub> H <sub>12</sub> ] <sup>2-</sup> .....	5
1.3 Synthesis of Ether and Ester Derivatives .....	10
1.4 Relationship between Hammett Constants and Redox Potentials.....	14
1.5 Photopolymerization of Isobutylene .....	15
1.6 A [B <sub>12</sub> (OR) <sub>12</sub> ] Redox Flow Battery .....	17
2.1. <sup>1</sup> H-NMR of Poly(isobutylene) .....	26
2.2. Cyclic Voltammograms of <b>F</b> <sub>60</sub> and <b>F</b> <sub>72</sub> .....	30
2.3. Scan Rate Dependence <b>F</b> <sub>60</sub> .....	31
2.4. Scan Rate Dependence <b>F</b> <sub>72</sub> .....	32
2.5. <b>F</b> <sub>60</sub> Spectroelectrochemistry in Benzonitrile.....	34
2.6. <b>F</b> <sub>60</sub> Spectroelectrochemistry in Dichloromethane.....	34
2.7. Beer's Law Study of <b>F</b> <sub>60</sub> <sup>0</sup> in Aromatic Solvents .....	36
2.8. Slow Addition of <b>F</b> <sub>60</sub> <sup>0</sup> to 1,2-dichlorobenzene .....	37
2.9. Addition of 1,2-Diiodotetrafluorobenzene to <b>F</b> <sub>60</sub> <sup>0</sup> .....	38
2.10. <b>F</b> <sub>60</sub> <sup>0</sup> Titrated with Hexafluorobenzene—Concentration Dependence....	39
2.11. <b>F</b> <sub>60</sub> <sup>0</sup> Titrated with Hexafluorobenzene—Time Dependence .....	39
2.12. <b>F</b> <sub>60</sub> Acid-Base Titration—Trifluoroacetic Acid .....	42
2.13. <b>F</b> <sub>60</sub> Acid-Base Titration—Triethylamine .....	42
2.14. <b>F</b> <sub>60</sub> in 2-MeTHF at Cryogenic Temperature .....	45
2.15. Variable Temperature UV-visible Study of <b>F</b> <sub>60</sub> in 2-MeTHF.....	45
2.16. Variable Temperature <sup>11</sup> B-NMR of <b>F</b> <sub>60</sub> in 2-MeTHF .....	46
2.17. Variable Temperature <sup>19</sup> F-NMR of <b>F</b> <sub>60</sub> in 2-MeTHF.....	47
2.18. Room-Temperature Emission of <b>F</b> <sub>60</sub> in 2-MeTHF .....	50
2.19. <b>F</b> <sub>60</sub> 77 K Emission in Toluene and 2-MeTHF Glass .....	51
2.20. <b>F</b> <sub>36</sub> <sup>0</sup> , <b>F</b> <sub>60</sub> <sup>0</sup> and <b>F</b> <sub>72</sub> <sup>0</sup> 77 K Emission in Perfluorinated Glass .....	51
3.1. Symmetry Lowering from I <sub>h</sub> to D <sub>3d</sub> .....	68

3.2.	Cyclic Voltammogram of $B_{12}(OEt)_{12}$ in Dichloromethane .....	70
3.3.	Scan Rate Dependence of the $[B_{12}(OEt)_{12}]^{1+/0}$ Couple .....	71
3.4.	Scan Rate Dependence of the $[B_{12}(OEt)_{12}]^{0/1-}$ Couple .....	72
3.5.	Scan Rate Dependence of the $[B_{12}(OEt)_{12}]^{1-/2-}$ Couple.....	73
3.6.	Oxidative Limit of $B_{12}(OEt)_{12}$ in Dichloromethane .....	76
3.7.	Cyclic Voltammogram of $B_{12}(OEt)_{12}$ in Acetonitrile.....	76
3.8.	Spectroelectrochemistry of $B_{12}(OEt)_{12}$ .....	78
3.9.	Titration of $B_{12}(OEt)_{12}^0$ in THF with Magic Blue.....	80
3.10.	Crystal Structure with 2-brominated Triphenylamines .....	80
3.11.	CW EPR Spectrum of $[B_{12}(OC_2H_4iPr)_{12}]^{1+}$ .....	82
3.12.	Open-Air Cyclic Voltammogram of $B_{12}(OEt)_{12}$ .....	86
3.13.	Randles-Sevcik Plot $[B_{12}(OEt)_{12}]^{1-/2-}$ .....	87
3.14.	Randles-Sevcik Plot $[B_{12}(OEt)_{12}]^{0/1-}$ .....	88
3.15.	Randles-Sevcik Plot $[B_{12}(OEt)_{12}]^{1+/0}$ .....	89
4.1.	Q-band ESE-EPR Spectra of $[1-3]^{1-}$ .....	101
4.2.	Davies ENDOR Spectra of $[1-3]^{1-}$ .....	103
4.3.	Mims ENDOR Spectra of $[1-3]^{1-}$ .....	104
4.4.	HYSCORE of $[3]^{1-}$ .....	105
4.5.	ESE-EPR Spectra of $[1-2]^{1+}$ .....	107
4.6.	Davies ENDOR Spectra of $[1-2]^{1+}$ .....	108
4.7.	Davies ENDOR Simulation of $[2]^{1+}$ .....	109
4.8.	HYSCORE of $[2]^{1+}$ .....	110
4.9.	HYSCORE of $[1]^{1+}$ .....	111
4.10.	Field Dependence of $[1]^{1+}$ Davies ENDOR.....	112
4.11.	UV-vis-NIR spectra of $1^0$ and $2^0$ .....	114
4.12.	UV-vis-NIR spectra of TBA[1] and TBA[2] .....	115
4.13.	UV-vis-NIR spectra of $4^0$ and $5^0$ .....	115
4.14.	Electrochemically Derived Visible Spectrum of $[4]^{1+}$ .....	118
4.15.	Field Dependent Davies ENDOR of $[1]^{1-}$ .....	124
4.16.	Field Dependent Davies ENDOR of $[2]^{1-}$ .....	124
4.17.	Field Dependent Davies ENDOR of $[3]^{1-}$ .....	125

A.1.	Properties of Combined Photooxidants and Pro-WCAs.....	139
A.2.	Synthesis and Properties .....	141
A.3.	Styrene Polymerization: Solvent Comparison .....	143
A.4.	TD-DFT Donor Orbitals.....	147
A.5.	TD-DFT Cluster-Monomer Interactions.....	147
A.6.	Styrene Polymerization: Conversion and $M_n$ as a Function of Time ....	149
A.7.	Styrene Polymerization: $M_n$ as a Function of Conversion.....	152
A.8.	Control Polymerizations .....	156
A.9.	Contact Ion Pairs .....	156

## LIST OF TABLES

<i>Number</i>	<i>Page</i>
1.1. <i>closo</i> -[B <sub>12</sub> (OR) <sub>12</sub> ] <sup>2-</sup> Clusters Reported by Hawthorne.....	10
1.2. <i>hypercloso</i> -B <sub>12</sub> (OR) <sub>12</sub> Clusters Obtained through Microwave Synthesis.....	12
2.1. Styrene Monomers .....	26
2.2. <b>F</b> <sub>60</sub> and <b>F</b> <sub>72</sub> Redox Potentials .....	29
3.1. Peak Parameters for [B <sub>12</sub> (OEt) <sub>12</sub> ].....	74
4.1. g-values and Hyperfine Tensors from Simulations.....	113
4.2. Excitation Energies and Extinction Coefficients .....	119



## INTRODUCTORY REMARKS

My time at Caltech has been defined by a number of collaborations spanning a range of topics. My first main project was developing flash-quench techniques for mechanistic investigation of nitrogenase enzymes together with colleagues from the Rees lab (Caltech) and Tezcan lab (UCSD). At the same time, I was involved in researching organic electrooxidation using metal catalysts, and semiconductor photochemistry together with members of the Lewis Lab. During my third year at Caltech, I became interested in doing more synthetic inorganic chemistry and transitioned into one of the Gray group's current focus areas—Group 6 Metal Arylisocyanide complexes. Within that project I developed new classes of alkyne-bridged arylisocyanide ligands, along with mixed ligand carbonyl-arylisocyanide complexes. Additionally, I initiated a partnership with the Greer lab (Caltech) to use metal arylisocyanide complexes as absorbers for two-photon nanofabrication.

The research presented in this thesis started during my second year but was until recently a side project of mine. It was part of a broad collaboration initiated by Professor Alex Spokoyny at UCLA, who develops perfunctionalized dodecaborate clusters and investigates their reactivity and applications. Chapter 2 covers much of my early work. At that time, we were fumbling in the dark trying to understand dodecaborate photoredox mechanisms and photophysics. I truly enjoyed all the little experiments I performed to test various hypothesis' and trying to patch together large sets of seemingly unrelated data. However, I never thought that work would lead to anything significant, much less an entire thesis.

Two key advances drove the dodecaborate work to the forefront of my research. The first discovery was made using the newly acquired Q-band pulsed EPR system at Caltech. We found that Electron Nuclear Double Resonance (ENDOR) techniques could be applied to obtain information on hyperfine interactions in open shell dodecaborate clusters, which allowed us to experimentally describe the dodecaborate frontier orbitals. The second development was my electrochemical observation of a new super-oxidized cationic state in the electrochemistry of alkoxy-perfunctionalized dodecaborate clusters. Both were major breakthroughs; the pulsed

EPR data provided experimental insights that had previously been inaccessible, and the discovery of cationic dodecaborates demonstrated that the clusters could reversibly reach oxidation states that were previously thought to be highly unstable.

About a year ago Harry suggested that the dodecaborate data I had was enough for a thesis and that I should “*just write it up*”. It was a difficult choice as I really enjoyed the metal arylisocyanide project, but I could not resist the draw of an earlier graduation date. Today, putting down the final words of this thesis, I am very happy about that decision. It has allowed me to finish my studies in good time and focus my energy toward future career goals. Additionally, I am excited about how the metal arylisocyanide project has evolved after I stepped away. Javier Fajardo has made amazing progress, both in continuing my work on alkyne-bridged isocyanides and in developing his own systems.

As I turn away from academia to pursue a career in consulting, I will surely miss Caltech and my time at the bench. It has been some of the most rewarding years of my life.

I hope you will enjoy reading this account of my Caltech experience!