

**THE DEVELOPMENT OF WATER-SOLUBLE  
OLEFIN METATHESIS CATALYSTS  
CONTAINING AN *N*-HETEROCYCLIC  
CARBENE LIGAND**

Thesis by

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*To Mom, Dad, Uncle Matt, and Aunt Jill.*

*You have really made a difference in my life.*

*“Of all tyrannies a tyranny sincerely exercised for the good of its victims may be the most oppressive. It may be better to live under robber barons than under omnipotent moral busybodies. The robber baron’s cruelty may sometimes sleep, his cupidity may at some point be satiated; but those who torment us for our own good will torment us without end, for they do so with the approval of their own conscience.”*

–C.S. Lewis

*“Liberty is the very last idea that seems to occur to anybody, in considering any political or social proposal. It is only necessary for anybody for any reason to allege any evidence of any evil in any human practice, for people instantly to suggest that the practice should be suppressed by the police.”*

*“The free man owns himself. He can damage himself with either eating or drinking; he can ruin himself with gambling. If he does he is certainly a damn fool, and he might possibly be a damned soul; but if he may not, he is not a free man any more than a dog.”*

–G. K. Chesterton

*“The preservation of freedom is the protective reason for limiting and decentralizing governmental power. But there is also a constructive reason. The great advances of civilization, whether in architecture or painting, in science or in literature, in industry or agriculture, have never come from centralized government.”*

–Milton Friedman

*“The American Republic will endure, until politicians realize they can bribe the people with their own money.”*

–Alexis d’Tocqueville

*“I do not agree with what you have to say, but I’ll defend to the death your right to say it.”*

–Voltaire

## ACKNOWLEDGEMENTS

Finally! We come to a section where the first person can be used with reckless abandon. Anyway, nobody is an island, and many people have contributed to my six years as a graduate student at Caltech. First, Professor Grubbs has been tremendously supportive through the years. I am grateful for both his patience and sound advice. One particularly poignant memory is when we conversed about my future beyond graduate school. Bob sensed my burgeoning desire to leave the field of chemistry, was very supportive and discussed with me possible careers that I might better enjoy, a topic that I was struggling with at the time. When I finally found that job, the one that “just felt right,” Bob nicely assisted my application by both writing a recommendation letter and giving pointers on my job talk. While I am grateful for everything, for this in particular, Bob, I say thank you.

I have also been blessed with an excellent committee. Professors Tirrell and Goddard have been with me since candidacy, and both handled my often-rambling mannerisms with aplomb. I am grateful for the time and effort both of you have spent on my behalf, and your letters of recommendation are very much appreciated. Professors Jonas Peters and John Bercaw also served on my committee. I am thankful to Jonas for making time to participate in my proposal defense in the middle of his move to MIT. Of course this move to MIT required that I find a replacement committee member. I am indebted to John for his willingness to serve in this capacity.

As a rule, the Grubbs Group is always packed with talented chemists who are also fun to be around. In the interest of space I will not name everyone, but please know that I very much enjoyed the time that I spent with this fine group of people. However, I would like to highlight the contributions of a few of these individuals to my life.

First, I would like to acknowledge those graduate students and postdocs that had the greatest impact on my chemistry. I began my time in the group wanting to perform polymer synthesis. As a polymer chemist, Oren Scherman was the first to welcome me to the group and taught this micro-pipet-using bioorganic chemist how to perform chemistry that is sensitive to both air and moisture. It was Justin Gallivan who recruited me into aqueous metathesis. He was largely responsible for much of the research elaborated in chapter 2, and for this I am grateful. Brian Connell, Greg Beutner, Chris Douglas, Sebastian Smidt and J. P. Morgan were a valuable resource for answers to questions regarding general chemistry and lab technique. Brian Connell was a veritable well of chemical knowledge, which I drew from continuously. To this day, I am surprised that he never cringed at my sometimes-constant barrage of questions.

Professor Louis Kuo spent his sabbatical with the group in the summer of 2006. He came brimming with ideas for aqueous metathesis and the willingness to bring them to fruition. During his time at Caltech, he examined the ability of “my” catalysts to perform cross metathesis on ruthenium dyes and became the first to join two different cross-partners by aqueous cross metathesis. He also was an excellent resource for basic information regarding protein research. I am grateful for his ideas, efforts, and assistance.

Far and away the most important collaboration of my graduate career was with Soon Hong. Soon and I became a team while examining the effect of water on the stability of metathesis catalysts containing an *N*-heterocyclic carbene ligand. During this time, Soon became more interested in aqueous metathesis and decided to add his expertise to the development of water-soluble catalysts. His presence gave the aqueous-metathesis project a shot in the arm by producing the first catalyst capable of mediating the ring-closing

metathesis of  $\alpha,\omega$ -dienes in water. Soon is a good chemist and an even better person whose contributions to my graduate career I greatly appreciate.

Graduate school was more than just research, and many members of the Grubbs Group particularly enriched my everyday life. I was the second student to join the group of a class of four: Andrew Hejl, Jacob Berlin, Tim Funk, and I. While I never joined “Funk ‘n Hejl” for their weekly game of golf, our viewings of the Fox TV show, *24*, became an enjoyable staple of my winter evenings. Jacob organized the Grubbs Group basketball team for most of my time here and did not yell at me too much as I “ran” up and down the court bricking layups and allowing our opponents to score.

John “Beef” Matson took over coaching basketball once Jacob left, and ensured that I got a good workout at least once a week. I swear I that I lost at least 10 pounds while playing under Coach Beef. John also was one of the organizers for the quarterly Grubbs Group Tribute to Inebriation, also called a pub crawl. While my memory of those events is suspect, I always enjoyed them. Finally, anyone who knows my dietary preferences understands that John’s nickname is sufficient for me to hold him in high esteem.

I have had some fun bay mates over the years: Tim Funk, Kevin Kuhn, Paul Clark, and, most recently, Matthew Whited. Tim was a great man to work beside, and our shared love of Christmas music made the holiday season that much more enjoyable.

Kevin Kuhn joined me in Church 217 when Tim left to become a member of the merry band of “130C.” Kevin loves movies and awoke my dormant enjoyment of that entertainment medium. We constantly discussed films, and, Kevin, if you are reading this, I still insist that *Lost in Translation* was incredibly overrated. Also thanks to Kevin, I find myself saying “that makes sense” far more often.

My last partner in crime in Church 217 was Paul Clark. It seemed that every time I turned around Paul was running a 100 g column. For Paul these large columns became so routine that he supplemented his chromatographic experience by doing crunches, as large columns were, evidently, not painful enough in themselves. Even so, Paul always had a smile on his face and never hesitated to offer a helping hand when he saw the need. He was a great guy to work beside.

My last bay mate was Matt Whited. Along with the rest of my bay mates, Matt was a very friendly and fun guy to be around. Also, he was willing to participate in long discussions on virtually any topic. Finally, a small demonstration of this man's character: when making change after our lunch at Matsuri's, Matt Whited gave me the *good* ten-dollar bill.

Two of my best friends in the group were Dan Sanders and Ron Walker. Like me, Dan comes from the fine state of Minnesota. More than that, we actually spent much of our lives within a few miles of each other, though we did not meet until our time here in the group. Being from Minnesota, Dan shared my state of complete football enlightenment, as he is also a Vikings fan. I am especially thankful to Dan for his willingness to meet with the "men in the dark suits" as a character reference for my national security clearance.

Ron Walker was a SURF in the group during the summer of 2002 before joining the group as a graduate student in 2003. Ron has an identical twin brother, which I discovered the hard way. (I came into lab one morning to find Ron sitting at his desk working. I next walked into the computer room to again see "Ron," this time at a computer. Classic double take ensued.) Ron and I shared a few hobbies, which we often discussed. Also, I attended Ron's wedding and left loaded for bear with Ron stories from his bachelor



party. Last, Ron had two excellent practical skill sets, cars and barbecue. Ron was always a great resource when my minivan had issues, and, trust me, **NEVER** miss an opportunity to partake of Ron's barbecue ribs. No sacrifice is too great. Ron is a good man and a good friend, and he also volunteered to meet the suits as a character reference for my security clearance. Ron, thank you.

My group of friends at Caltech extended beyond the Grubbs Group. In no particular order these are Uttam Tambar, Gretchen Keller, Jason "Texas Teacup" Keith, Dave Weinberg, Jonathon Owen, Ted Corcovilos, Steve Baldwin, Greg Drummand, Alex "Foos" Papendrew, Theo Agapie, Jeff Byers, Brian Leigh, Christine Thomas, and Yenn Nguyen. There are others, but I spent the most time with these individuals at different points in my graduate career. I would like to give a particular shout-out to my poker buddies: Dave, Gretchen, Steve, and Ted. Dave in particular is acknowledged for arranging these events. Also, Jason Keith gave me the nickname "Beaker" (after the Muppet scientist), which stuck. I know that there were/are people who do not know my actual name. I am thankful to all of these individuals for making my time at Caltech that much more enjoyable.

This brings me to my family. I have been blessed to have an aunt and uncle who live in Southern California. Matt and Jill are both fantastic people, and they have a terrific family of four sons. Their oldest, Shane, was one of the first people I saw upon moving to California. When I first saw Shane, he was still just dating Jen. I then shared a beer with Shane at their engagement party, attended their wedding, watched them buy their first house, and was at the hospital for the birth of their first-born son, my aunt and uncle's first grandchild, Lucas. Taylor Jordan is also a great guy, though a referee should always be present when he and I compete at a game of Catch Phrase. With a "legendary" fashion

sense and a laid-back attitude, Grant was always nice to hang with. As he lives in Alexandria, I have not seen as much of Justin. Even so, he is a good guy with whom to share a cigar on a lazy evening, and I look forward to spending more time with him when I move to Virginia.

Uncle Matt is a bit like The Godfather of the California Jordans. If you ever need anything, he is always the guy to call, and his generosity, particularly with his family, will not be found wanting. He gave me the minivan that I have driven these past four years and has treated me to more steaks than I can count. He also introduced me to the joy of spending time with friends and family while drinking fine wine and smoking a good cigar. He is very supportive, and his advice is always sound. Lastly, his many puns and his pantomimes during games of charades are always amusing and are the source of fond memories.

Aunt Jill is a fun person to know. She effortlessly mixes the desire to party with responsible behavior. Being an excellent cook, her ribs are a culinary masterpiece. She also spoils me mercilessly with Dutch Babies (pastry) on the mornings of most of my visits. She always made me feel welcome and happily provided me with a home away from home.

That all said, Uncle Matt, Aunt Jill, Shane, Justin, Taylor, and Grant, the “Fifth Beatle” says thank you. You make me feel like a member of your family. I greatly enjoy my time with all of you, and I will remember my many days with you with fondness.

Uncle Dick and Aunt Michelle also contributed to my time on the West Coast. I often spent Thanksgiving with them in Nevada. You would be hard pressed to find a nicer guy than Dick, and Michelle was a lot of fun. They both were very supportive, and their daughter, Chandler, has also been a friend.

The greatest blessing in my life has always been my mother and father. It is impossible to exaggerate the amount of loving support these two people have given me over the years. I can only hope to emulate their example should I ever have a child of my own.

My father, Jim, is a man of very high character. He is always ready and willing to help when he sees a need and is a source of a great deal of encouragement. He also gives sound advice, which I have come to respect more as I get older. He always puts the needs of his family first and is unstinting in his aid. In other words, my father is a man of quality and has demonstrated by example how to live a good life.

My mom, Dee, is the most giving and selfless person that I know, and my life is pleasantly riddled with her many selfless actions. She always cares about what I think and how I feel and is very generous with her love. She is willing and even eager to provide a listening ear. My mom also embodies the definition of hard work. However, even after a long day of intense effort, she can find it in herself to smile and offer her assistance when the need presents itself.

Mom, Dad, I do not think that I will ever be able to fully express the depths of my gratitude. Whatever success I have experienced can be directly traced back to the foundation of support and love that you have provided. Thank you.

Finally, I would like to thank God. Things have turned out very well for me in this life, and I often see the hand of a higher power at work. My experience through these last six years took me down paths that I never expected to traverse, and I would be negligent to ignore the influence of divinity over this time in my life.

## ABSTRACT

This research describes the development of new olefin metathesis catalysts that are stable and active in water. Earlier water-soluble metathesis catalysts rely on phosphine ligands functionalized with ionic groups. In contrast to these bis(phosphine) complexes, the catalysts reported in this research harness the increased stability and activity provided by *N*-heterocyclic carbene (NHC) ligands. As a result, these catalysts display an activity and stability that are unprecedented in aqueous olefin metathesis.

Initial efforts to produce the desired water-soluble metathesis catalysts employed poly(ethylene glycol) (PEG) to generate a complex that was soluble in water (Chapter 2). This catalyst was capable of the ring-opening metathesis polymerization (ROMP) of a challenging *endo*-norbornene monomer, which an earlier bis(phosphine) complex catalyzed poorly. While demonstrating the potential of NHC ligands to improve the activity of water-soluble metathesis catalysts, this catalyst was not sufficiently stable to mediate metathesis transformations involving acyclic olefins in water.

A careful examination of the described PEG catalyst inspired a few strategies to produce olefin metathesis catalysts with improved activities in water (Chapter 3). This strategic vision was honed by studies examining the effect of water on the decomposition of catalysts that contain an NHC ligand (Chapter 4). These studies indicated that phosphine ligands play an active role in the aqueous decomposition of ruthenium methylidene complexes, which are vital complexes for metathesis reactions involving terminal olefins. With these results in hand, incorporating NHC ligands into phosphine-free ruthenium complexes was pursued as a promising approach to producing active metathesis catalysts that are stable in water.

Catalysts supported by both isopropoxybenzylidene and NHC ligands were modified to include ammonium salts (Chapter 5). The water-soluble catalysts produced were stable in water and competently initiated aqueous ROMP. More importantly, these catalysts readily catalyzed the ring-closing metathesis of  $\alpha,\omega$ -dienes in water. The described catalysts were also able to homodimerize allyl alcohol and homoallyl alcohol in water, which are among the few known examples of cross metathesis in neat water.

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