Ancillary Ligand Effects in Niobocene Olefin Hydride Complexes and Hydrocarbon Oxidation by Palladium(II) Complexes

Thesis by

Lily Joy Ackerman

In Partial Fulfillment of the Requirements for the

Degree of Doctor of Philosophy

Division of Chemistry and Chemical Engineering

California Institute of Technology

Pasadena, California

2003

(Defended May 14, 2003)

For Victor, My Family, the SD crowd, and Kendra

Acknowledgements

There are many people I must thank who have helped me in some way during my graduate career both scientifically and emotionally. First, I must thank John Bercaw for his continuous support and encouragement throughout my career. John, you have given me unique opportunities to grow as a scientist and a person, and I have often thought of you and Diane as my "surrogate parents." Thank you for caring about me beyond the role of research advisor.

I have been very fortunate to interact with other individuals who I would also consider as research advisors. Jay Labinger has been extremely helpful whenever I have interacted with him. Thank you Jay for always taking the time to answer my questions and for helpful advice when I needed it. Malcolm and Jenny Green, my U.K. advisors, are just awesome. Thank you Malcolm and Jenny for allowing me to work in your labs at Oxford. Although I was only at the ICL for a short time, you both have treated me as if I was another one of your students. Your kind words have given me more confidence in myself especially when I needed it. Also thanks to Nick Rees at Oxford for teaching me the subtleties of NMR.

My Ph.D. committee is the best ever! Thank you to Bob Grubbs, Brian Stoltz, and Harry Gray for reading my proposals and thesis and for teaching me a lot. I admire the way all three of you have helped me learn and think about chemistry in my exams in a very constructive way. A special thanks to Harry, for inspiring me during three years of your 2nd term, Friday morning class, where I really learned something about inorganic chemistry. Also, thanks Harry, for being my friend and for listening to both my joys and woes.

What can I say about the Bercaw Group? Without you all, my years at Caltech would not have been filled with wild and crazy moments. Susan Schofer, you have been my best friend in the group almost since the beginning. I am going to really miss you and all of our long discussions outside of Noyes in various secret hiding places. Thanks for always taking the time to talk to me and for keeping me sane. I hope we continue to have great discussions in the future, maybe even in Europe! The current Bercaw group members have made the last few years unforgettable. It seems that each Christmas Party has gotten crazier

than the previous, culminating in gangsta rap karaoke, overturned water coolers, and a black eye in 2002. But 2001 was *not too shabby*, especially with Gerry getting wasted by the hoods in 209. Dave Weinberg has provided *good times* on many occasions with Big Fizz in tow. Dave's partner in crime, Theo Agapie, has been a great labmate and friend. Theo, I have great memories of dealing with cranes and dryboxes, putting out fires, and hanging out at the Pasadena DMV with you. The Famous Theo and Dave Candidacy Experience also made me feel like I wasn't alone when I was struggling to write my props and thesis. Thank you to Parisa Merhkodavandi and Heather Weincko for hanging out with me at Bercaw Bulls games. The Bercaw Bulls underwent a remarkable transformation in 2003 due to the basketball savvy of our coach, Jeff Byers. Jeff, your spirit and ability to have fun on the court inspire me. Thanks to Jonathan Owen for your enthusiasm for chemistry; it definitely helped keep me excited. Cliff Baar and Alan Heyduk both have shared their chemistry expertise with me. I truly appreciated Cliff's unique personality, and thanks Alan for always helping me with experiments and chemistry questions. I have two fun classmates, Endy Min and Sara Klamo. Endy, thank you for being kind and understanding person to talk to. A special thanks to Sara, for great chemistry discussions with me back in the nook, for being my TA buddy during Chem 112, for helping me understand Chem 153, and for hanging out behind the green box with me for hours!

The Bercaw Group members who have left during my stay have been greatly missed. There was a time when the south side of Noyes 209 was the place to be thanks to Alex Muci, Chris "Theory" Brandow, Seva Rostovtsev, and Joseph Sadighi. I have learned so much chemistry from each of you. Thanks Alex for supporting me and always being my friend. Thanks Theory for giving me a shoulder to lean on and for sharing your thoughts about life with me. Thanks Annita for helping me learn platinum chemistry; we also had a lot of fun in my little red car during your driving lessons. Graduate students Jeff Yoder, Steve Miller, Paul Chirik, Deanna Zubris and Postdocs Ola Wendt, John Scollard, and Chris Levy all helped me get started in lab in the very beginning. Thank you Paul and Deanna for sharing the Group 5 project with me and for helping me get started with what resulted in a substantial part of my thesis. A special thanks to Ola and Jeff for spending a lot of time explaining chemistry and especially NMR

to me. Also, thanks to Christoph Balzarek for being another great 209 labmate. Thank you to Antek Wong-Foy for always being willing to help anyone out, in lab or as a friend. Thanks Antek for helping me when I needed it most.

My friends in San Diego, Leslie Wilkins, Ryan Daniels, Jess Dalisay, Johnny Schneller, and Jenny and Dave Blood, have provided me with the most fun LA getaway party place one could ever hope for. Thank you guys for all of your support and for sticking by me throughout this California adventure. I couldn't have done it without all of you; you are my more than my friends, but also my family. I have always felt like I had a home at the apartment building on Narragansett where we have had so many good times with wigs, tattoos (go star tattoo gang!), Muad'Dib, hanging in OB, going to shows, or just getting wasted! Although I won't be as close by, our adventures together have just begun!

Thank you, Kendra Spivey, for continuing to be my best friend even though I have been across the country and even across the ocean. You have put up with late night phone calls when I have been freaking out. I especially appreciate all of the times I called you from England as I stood in the lonely, red phone booths. You have been my strength when I was the most desperate. I love ya, girl! My parents, Ron and Nga Ackerman, and my sister and family, Kim, John, and Auggie (Gus) Koepke have also been very supportive throughout my graduate career. Thank you all for putting up with my ups and downs. Also, this Ph.D. would not have been possible without the help and support of others at Caltech. Thanks to Pat Anderson and Dian Buchness for help and patience; to Larry Henling for all of the time you put into my crystal structures; to Paul Carroad, Chris Smith, and Steve Gould for keeping the department running; to Angelo DiBilio for your help with the EPR; to Scott Ross for NMR assistance; and of course to Rick Gerhart for your amazing glass blowing abilities. Also, thanks to Raissa Trend for being a good friend this past year.

Finally, I must thank the love of my life, Victor Rucker. Babe, we've come a long way, and I hope we continue to love and care for each other forever. Thank you for understanding me perhaps better than anyone else, and for sticking by me through all of the tough times. We are about to embark on one of the biggest adventures of our lives as we leave Caltech with our Ph.D.'s (finally!). I love you meeps, and I couldn't have made it without you.

Abstract

To examine the effects of cyclopentadienyl and olefin substitution on preferred stereochemistry, the preparation of a series of singly [$SiMe_2$]-bridged *ansa*-niobocene olefin hydride complexes is described. These complexes serve as stable transition state analogues for the much more kinetically labile group 4 metallocenium cationic intermediates in metallocene-catalyzed olefin polymerization. Characterization of the thermodynamically preferred isomers of niobocene olefin hydride complexes reveals that placement of a single alkyl substituent on the cyclopentadienyl ligand array may have a moderate effect on the stereochemistry of olefin coordination.

Using dynamic NMR methods the rates of hydrogen exchange following intramolecular ethylene insertion into the metal–hydride bond have been measured for singly and doubly bridged group 5 *ansa*-metallocene complexes. The singly bridged *ansa*-niobocenes exchange up to 3 orders of magnitude faster than unbridged complexes. However, the doubly bridged *ansa*-tantalocene complex exchanges at a rate comparable to that previously reported for the unlinked and much slower than a singly bridged complex. These "*ansa*-effects" were investigated by DFT calculations on model complexes. The computed exchange pathway showed the presence of an agostic ethyl intermediate. The calculated barriers for hydrogen exchange of model unbridged, singly bridged, and doubly bridged niobocenes correlate with the experimental results.

N,*N*'-Diaryl-α-diimine-ligated Pd(II) dimethyl complexes undergo protonolysis with HBF_4 (aq) in trifluoroethanol (TFE) to form the cationic complexes [(α-diimine)Pd(CH_3)(H_2O)][BF_4]. The cations activate benzene C–H

bonds at room temperature. Kinetic analyses reveal trends similar to those observed for the analogous Pt complexes: the C–H activation step is rate determining and is inhibited by H_2O, which is consistent with a mechanism in which benzene substitution proceeds by a solvent- (TFE-) assisted associative pathway. After benzene C–H activation under 1 atm O_2, the products of the reaction are biphenyl and a dimeric μ-hydroxide complex, $[(\alpha\text{-diimine})Pd(OH)]_2[BF_4]_2$. The Pd(0) formed in the reaction is reoxidized by O_2 after the oxidative C–C bond formation. Toluene and α,α,α-trifluorotoluene were investigated as substrates to examine the regioselectivity of arene coupling.

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