Ruthenium-Based Olefin Metathesis Catalysts: Synthesis, Mechanism, and Activity

Thesis by

Eric Lee Kuiokalani Dias

In Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

1998

(Submitted September 22, 1997)

To my family

Acknowledgments

First and foremost, I would like to thank Professor Bob Grubbs for allowing me to work in his group. After working for an assistant professor at MIT, with whom I interacted on a daily basis, I was a bit wary of joining a group with an advisor that seems to define the phrase "hands-off." However, I now view the latitude Bob allows his students as a freedom which I learned to cherish. By allowing me to pursue the paths that interested me, no matter how inconsequential, Bob has taught me how to be an independent researcher. This did not happen overnight, as I remember spending a fair amount of time feeling somewhat lost in the beginning, but I now know that I became a better scientist as a result. In addition, Bob has taught me a lot about subjects outside of chemistry, including some rock climbing moves and the infamous technique of "leaning on trees" during the annual group camping trip. Overall, I feel that I could not have found a graduate school experience like this anywhere else in the world, and it is something for which I am extremely grateful.

I would also like to take this time to thank the other members of my committee—Professors Jack Richards, Jackie Barton, and John Bercaw—for helping me to get this far. I am also grateful to Professor Dennis Dougherty for agreeing to be on my committee on such extremely short notice.

Other members of the staff to whom I am deeply indebted are Dian Buchness and Rich Gerhardt. It was always a pleasure chatting with Dian to take my mind off of things, and she helped me get my head together too many times to count. Rick is a glassblower of exceptional talent, not to mention a nice guy, and he went out of his way to get my vacuum line back to me ASAP several times when it needed to be repaired.

Next on my list of people to thank is Dr. SonBinh Nguyen, who helped me get started and taught me inert atmosphere techniques. During the aforementioned times when I was a bit lost, the Binner often helped to steer me in the right direction, or at least in some

kind of direction, which was better than wandering around in circles. His outlook on life, as revealed in some interesting late night philosophical discussions, often helped me to put things in perspective and persevere at times when I was particularly down on chemistry. His enduring enthusiasm for science has always been a quality worthy of admiration, if only because I wish I could love chemistry as much as he obviously does.

Doctors Zhe Wu, Alto Benedicto, and Jerome Claverie also provided many helpful discussions. Zhe, Alto, and Jerome were always there when I wanted to talk about kinetics and life, not necessarily in that order. Zhe and Alto shared some of their initial findings about the ruthenium triphenylphosphine catalysts with me, which initially inspired me to start looking at the mechanism for metathesis. Jerome was always there to tell me if some wacky mechanism I'd proposed was kinetically feasible, or as often was the case, kinetically impossible. Because they were all senior students, they often had a different outlook about life in general—one which I didn't understand then, but understand all too well now. Looking back, I'm impressed by the patience they all had for me, and thank them for keeping me company late at night when I needed to talk to someone.

Doctors T. Randy Lee, Osamu Fujimura, and Cassandra Fraser provided the postdoctoral support in the group. I would especially like to thank Randy, who really helped to keep me sane over the past four years. It was a lot of fun with him around late at night—the 1 a.m. trips down to Monterey Park for Chinese food were a very memorable part of my first few years here, as were the times when he would invite us (often Vijaya and myself) over to his place to watch really bad movies on TV at 3 or 4 a.m. I can distinctly remember when Osamu first arrived here, and he didn't speak much English. However, through chemistry, and later hiking, he became a good friend to have around. His advice about synthetic chemistry was always helpful, and his knowledge of California hiking is unmatched (although Andres Kim comes in a close second). Through him, I also got to re-experience some things about America that I often took for granted, and the hiking trips he helped organize were often a much needed break from the lab—it really is hard to

worry about chemistry when you're sucking air and sweating your butt off on the side of a mountain. Cassandra was always around for a good squash game—I can't say I've met many people more competitive about sports than her—and her calm demeanor was often a breath of fresh air when things were tense. Shoot, I almost forgot about Dr. Greg Fu, who was often coming in to the lab when I was leaving. His success has been an inspiration to me, and his guarded sense of humor has often caught me by surprise.

Doctors Scott Miller and Geoff Coates were also very helpful, albeit in a somewhat different way. Between the two of them, I learned quite a lot about the academic world that waits out there, if I choose to follow in their footsteps. It's always interesting to talk with people from other groups, who had entirely different graduate school experiences, and these two were definitely no exception. Between their knowledge of chemistry and their numerous stories about their different graduate school experiences, I don't think I ever had a boring conversation with them.

Okay, on to the current generation of Grubbies. Bill Zuercher has been a good friend for the last few years. His sense of humor and goofy laugh are truly infectious, so much so that I now make dumb jokes for him in his absence (I can't do the laugh, however). He's always been a lot of fun to hang around with, playing guitar, watching the Simpsons, going to the movies or the beach, and a bunch of other things I can't think of at the moment. Thanks to Mike Wagaman, along with Marcus Weck, I got to enjoy a few operas and concerts in the last year. Bobby Maughon used to be a tried and true member of the late night lab crew. There were many trips to Denny's during that time (often with Jason as well), so that we even became friends with the waiter (Han, who should also be acknowledged for bending the rules a bit with our orders). Bobby has also been helpful in providing enough material (*i.e.* trashy books) for me to read in my spare time. Ned Bowden was also a member of that bunch. He was always a lot of fun in and out of the lab, and he and Brenda often kept me informed about some of the more unusual aspects of undergraduate life at Caltech.

Dave Lynn gets infinitely many thanks for going above and beyond the call of duty in proofreading most of this thesis. Thanks to Dave, Bill, Helen Blackwell, Tom Kirkland, Marcus Weck (and Sylvia, of course) and more recently Todd Ross Younkin, I have had an incredibly enjoyable time here the last few years. I consider myself extremely lucky to have had such a great group of people to work with, and I am really going to miss them when I leave (except maybe Bill). I really can't express in words how lucky I consider myself to have them as friends, so I hope they will accept my apologies for making this paragraph so short (maybe some beer would help, too).

Finally, I want to thank my girlfriend, Norma Tom, who for reasons I don't fully understand still puts up with me. She has made my last few years here even more special, more than she can possibly know. She has stood behind me the entire time, and is always very patient and tolerant when I'm being an idiot. She, along with everybody else, has helped me through some of the tougher times, and has been responsible for many of the happier times as well.

There are plenty of other people that I need to thank. Delwin Elder, for his enthusiasm for softball and being a generally happy guy. Tom Willhelm, for keeping the computers running. Everybody in 214 Church, if not mentioned already, for generally providing a pleasant working environment. Darryl Denning also deserves thanks—his guitar classes have helped me immensely during the time I've been here, and helped me to achieve a level of playing that I didn't think would be possible. And of course, my family and friends outside of Caltech, who supported me the entire time, and kept me in touch with the world outside of graduate school.

Abstract

Several ruthenium-based olefin metathesis catalysts of the formula $(PR_3)_2X_2Ru{=}CHCHCPh_2$ have been synthesized, and relative catalyst activities were determined by monitoring the ring-closing metathesis of the acyclic diene diethyl diallylmalonate. The following order of increasing activity was determined: X = I < Br < Cl, and $PR_3 = PPh_3 << P^iPr_2Ph < PCy_2Ph < P^iPr_3 < PCy_3$. Additional studies were conducted with the catalyst $(PCy_3)_2Cl_2Ru{=}CH_2$ to probe the mechanism of olefin metathesis by this class of catalysts. The data support a scheme in which there are two competing pathways: the dominant one in which a phosphine dissociates from the ruthenium center, and a minor one in which both phosphines remain bound. Higher catalyst activites could be achieved by the addition of CuCl to the reaction.

The carbenes $(PCy_3)_2Cl_2Ru{=}CHR$ (R = $CHCPh_2$, Ph) react with the bridged-chloride dimers $[(p\text{-cymene})RuCl_2]_2$, $[(p\text{-cymene})OsCl_2]_2$, and $[(^tBu_2Cp)RhCl_2]_2$ to quantitatively form bimetallic, bridged-chloride ruthenium carbenes and and one equivalent of each corresponding piano-stool complex. In the ring-opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene, catalyst activity was found to increase in the order M = Ru < Os < Rh for the ancillary metal centers, with all of the bimetallic catalysts having higher activities. The kinetics of ROMP were studied, and the data support an associative mechanism of olefin metathesis.

Reaction of excess pyridine with $(PCy_3)_2(Cl)_2Ru{=}CHPh$ produces the stable, bis(pyridine) adduct $(PCy_3)(pyr)_2(Cl)_2Ru(CHPh)$. In solution, an equilibrium is established with the mono(pyridine) adduct $(PCy_3)(pyr)(Cl)_2Ru(CHPh)$. Reaction of thallium salts of β-diketonates with $(PCy_3)_2Cl_2Ru{=}CHR$ (R = $CHCPh_2$, Ph) produces the complexes $(PCy_3)(L)_2Ru(CHR)$ (L = acac, $^tBu_2$acac; R = $CHCPh_2$, Ph). While the pyridine complexes are stable and completely initiate RCM, the propagating methylidene is very unstable, decomposing as fast as, or faster than, it is formed. The β-diketonate complexes initiate ROMP in the presence of HCl and RCM in the presence of CuCl.

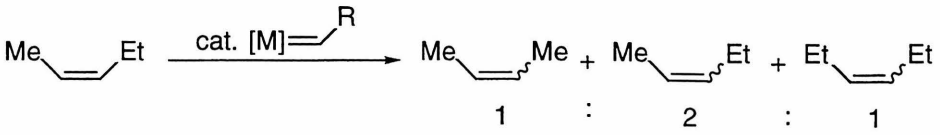
Table of Contents

List of Tables, Schemes, and Figures

Chapter 2

Introduction

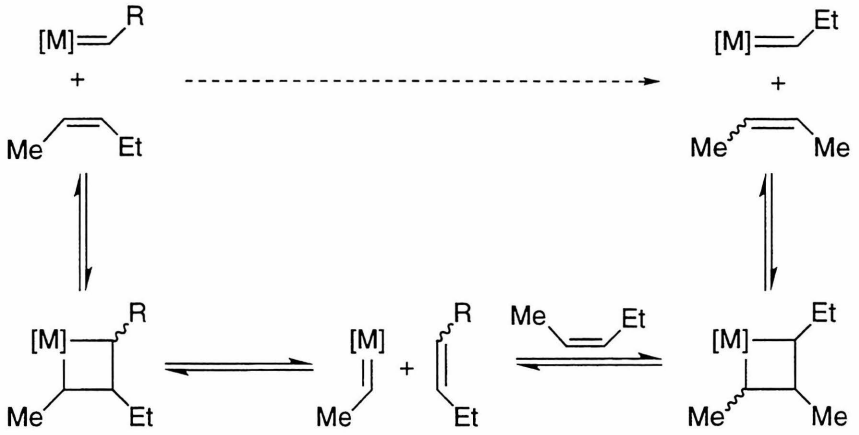
The olefin metathesis reaction is a transition-metal carbene catalyzed transformation in which the vicinal substituents on two olefins are effectively interchanged.[1] For example, a well-studied reaction is the metathesis of *cis*-2-pentene to ultimately form an equilibrium mixture of *cis* and *trans* 2-butenes, 2-pentenes, and 3-hexenes (eq. 1). The mechanism



(1)

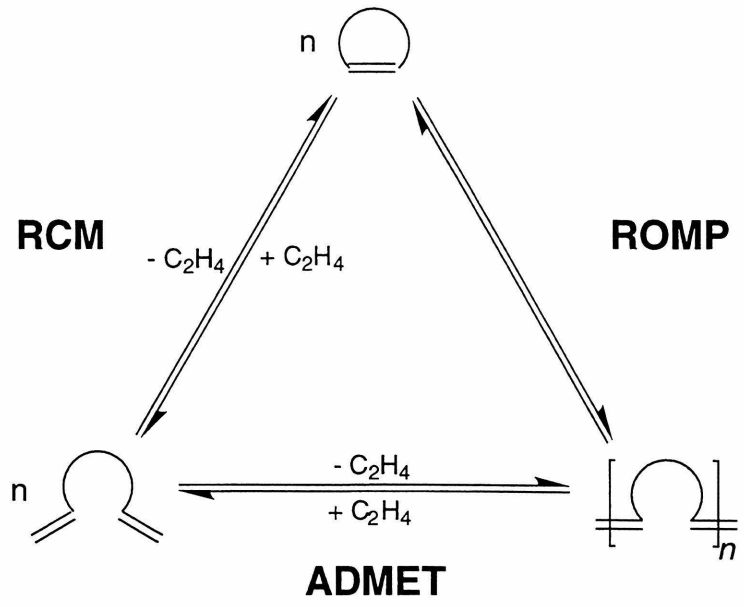
for this reaction, initially proposed by Chauvin,[2] involves the formation and subsequent cleavage of a metallacyclobutane intermediate (Scheme 1). Cleavage can occur either non-productively to yield the starting olefin and metal carbene, or productively to generate a new olefin and a new metal carbene. Repetition of this process produces all of the olefins shown in eq. (1).

Scheme 1



In addition to this type of basic cross-metathesis reaction, three other classes of transformations which can be performed *via* olefin metathesis are shown in Scheme 2. Ring-openeing metathesis polymerization (ROMP) is the oldest of these three reactions.[13] Typically, a strained cycloalkene can be polymerized to yield the corresponding polyolefin. Highly strained substrates, such as norbornene, are easily polymerized using a variety of

Scheme 2



single and multicomponent systems. Because polymerizations are entropically disfavored, it is the enthalpic contribution provided by the release of ring strain in the monomer that supplies the ultimate driving force for this reaction. Accordingly, olefins with less ring strain are more difficult to polymerize—only the more active catalysts polymerize cyclooctenes and cyclopentenes, and cyclohexenes can only be oligomerized at very low temperatures (thus decreasing the entropic contribution). ROMP has been successfully used to synthesize a variety of telechelic,[4] electroluminescent,[5] and liquid-crystalline[6] polymers in a controlled manner, often with narrow molecular weight distributions.

On the other hand, the ring-closing metathesis (RCM) of α,ω-dienes to produce cycloolefins (Scheme 2) is a relatively new reaction.[1,7] In addition to simple RCM to form five, six, seven, and eight membered rings, macrocyclic and solid-supported compounds have also been successfully cyclized.[1,7] Increasingly, RCM is being utilized as a key step in the synthesis of natural products and natural product analogs.[1,7,8] The thermodynamic profile of RCM is exactly opposite to ROMP—the formation of cyclic olefins is

enthalpically disfavored, while the production of ethylene provides an entropic driving force for the reaction.

Acyclic diene metathesis polymerization (ADMET) (Scheme 2) is the least common of these three reactions.[1,9] The thermodynamics of ADMET are similar to RCM, although the enthalpic change is approximately zero. In general, ADMET reactions can produce a variety of cyclic and macrocyclic olefins, in addition to the desired polymers, resulting in a complex mixture of products.[1] Because of this, ROMP is generally favored over ADMET for the synthesis of polyolefins.

In addition to these elementary transformations, seemingly endless combinations and variations of these reactions have been investigated. For instance, alkynes can be polymerzied to form poly(acetylenes) with more active catalysts.[1] Incorporation of unsaturation into α,ω-dienes in the form of either alkynes or cycloalkenes has been used to synthesize a wide variety of bicyclic compounds.[1,10] The latter transformation, being a combination of ring-opening and ring-closing metathesis, has been used to synthesize polymers containing cyclopentene units from commercially available 1,2-poly(butadiene).[11] The ring-opening cross-metathesis of cycloalkenes in the presence of terminal olefins has also been used to synthesize several small, organic and silicon-containing molecules.[12]

Despite the large variety of olefin metathesis-based transformations that have been studied, a relatively small number of single component, transition-metal catalysts have been developed (Figure 1).[1] In general, bimolecular decomposition of non-heteroatom substituted metal carbenes to form the carbene coupling products (*e.g.* olefins) is very facile, accounting for this observation. As a result, very sterically bulky ligands have commonly been employed to protect the metal alkylidenes. In addition, bulky substituents on the carbene moiety itself are also required. However, in the case of the titanium carbenes, the metallacyclobutane is lower in energy than the carbene, providing a convenient method of stabilization.[1]

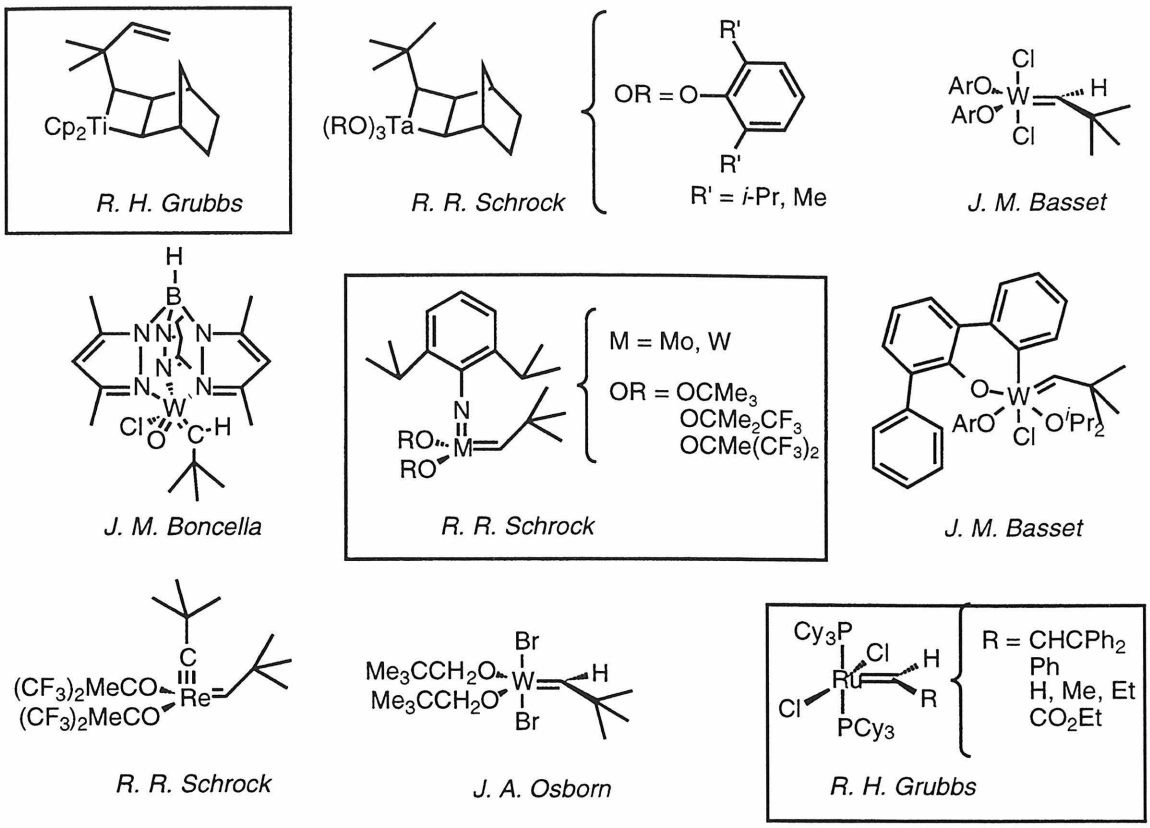


Figure 1: Single-component transition metal catalysts for olefin metathesis.

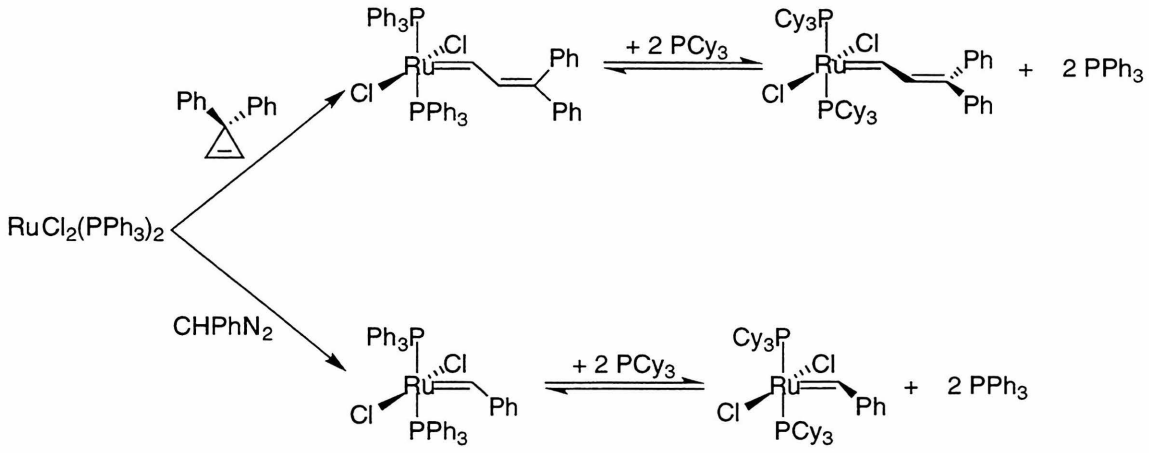
The titanacyclobutane complexes (Fig. 1) were the first example of an isolated metallacyclobutane intermediate in olefin metathesis, providing direct evidence for the Chauvin mechanism. Cleavage of the titanacylobutane occurs to form a titanium carbene, which subsequently reacts with other olefins to form new titanacyclobutanes. Reaction with *gem*-disubstituted olefins produces stable, β,β-disubstituted titanacyclobutanes—titanacycles that are unsubstituted at the β-position decompose to form allyl complexes *via* what appears to be β-hydride elimination, followed by reductive elimination of propene.[1,13] It was demonstrated that the titanacyclobutane could polymerize norbornene in a living fashion.[1,14] However, the reactivity of titanium carbenes in olefination reactions with carbonyls including esters (*cf.* Tebbe reagent), ketones, and aldehydes severely limits the substrates that can be employed.[1]

The molybdenum and tungsten catalysts developed by Schrock *et al.* (Fig. 1) have been commonly used for olefin metathesis.[1,15] The commercial availability of the molybdenum catalyst makes it especially convenient for routine use, as the syntheses of both it and the tungsten catalyst are somewhat involved. Both catalysts exhibit remarkably high activities, and can even be used to polymerize alkynes or cyclooctatetraenes to make poly(acetylenes). It has been demonstrated that substrates which provide bulky alkylidene substituents when ring-opened, such as norbornene and barrelene-based monomers, can be polymerized in a living manner. The living polymerization of cyclobutene by the tungsten catalyst could also be accomplished in the presence of trimethylphosphine, which acts as a reversibly binding ligand.[16] In addition, it has been found that these catalysts are particularly useful in RCM to produce tri- and tetrasubstituted olefins, although their use in the RCM of *ene-yne-ene* substrates is limited. However, in conjunction with their high activities, these catalysts show limited stability, decomposing slowly at room temperature under inert atmosphere (even in the solid state in the case of molybdenum), such that rigorous exclusion of oxygen and water is necessary when these catalysts are used. Their stabilities toward functional groups are also limited—the molybdenum catalyst will

olefinate aldehydes, and the tungsten catalyst both ketones and aldehydes. Thus, although highly active, these catalysts have several practical limitations.

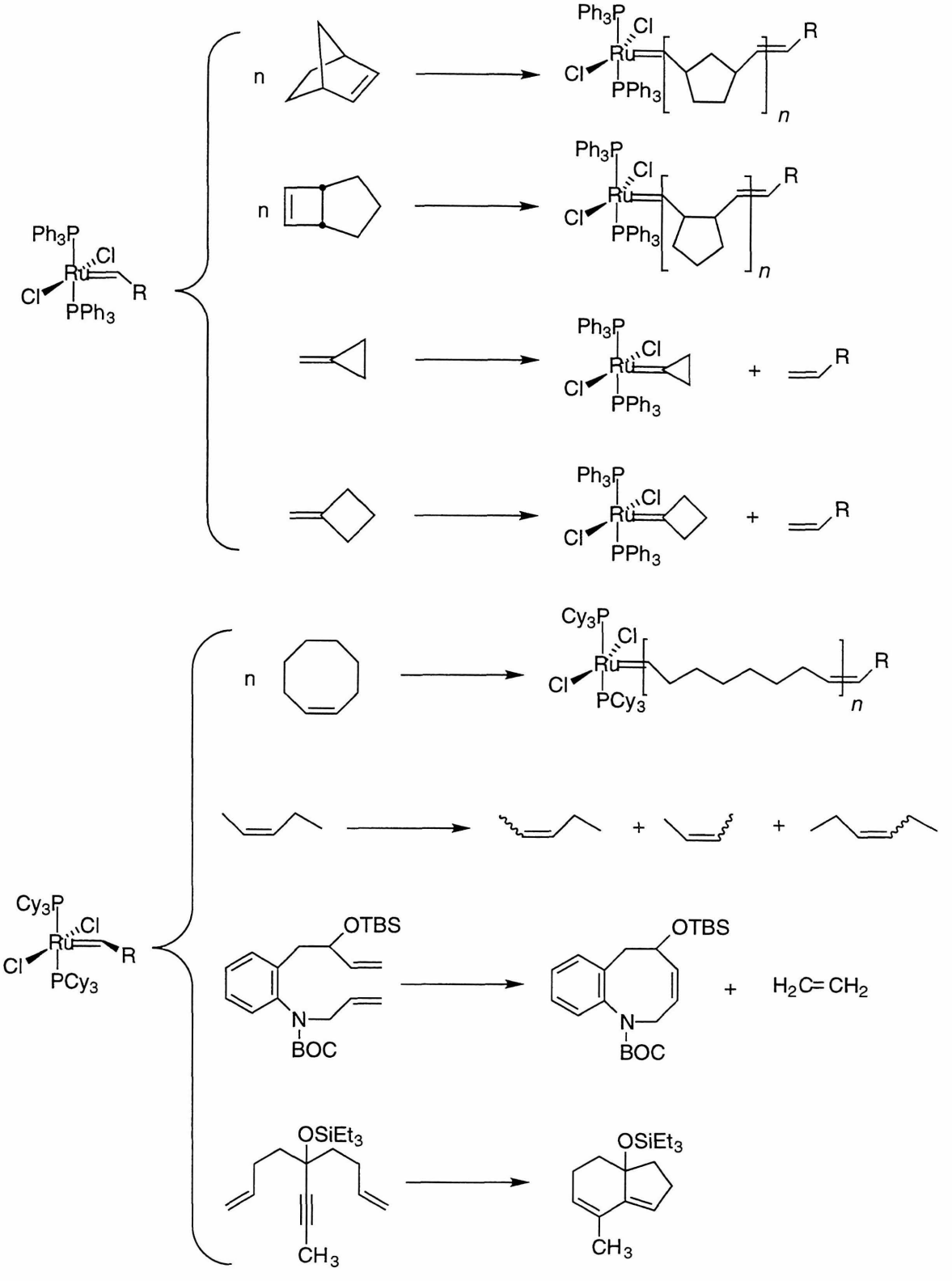
Recently, several routes for the synthesis of ruthenium(II) carbenes (Fig. 1) have been developed.[1,17] The two most common routes to ruthenium carbenes are the reaction of $RuCl_2(PPh_3)_3$ with either 3,3-diphenylcyclopropene or phenyldiazomethane to form $(PPh_3)_2Cl_2Ru{=}CHR$ (R = $CHCPH_2$, Ph), followed by phosphine exchange with tricyclohexylphosphine (Scheme 3).[1,17] Generally, these compounds are stable to air in the solid state, and react with oxygen slowly in solution to produce the corresponding aldehydes. Their stabilities toward several different functional groups—including aldehydes, alcohols, amides, and carboxylic acids—while retaining metathesis activity has been demonstrated,[18] and their stabilities toward water eliminates the need for drying solvents and reagents.

Scheme 3



The catalysts containing triphenylphosphine ligands react only with highly-strained cyclic and exocyclic olefins (Scheme 4).[17d,19] When catalysts containing tricyclohexylphosphines are employed, however, the reactivity of these catalysts is expanded to include unstrained olefins as well[17c] (Scheme 4)—a trend opposite to that observed for the tungsten and molybdenum catalysts, in which more electron withdrawing ligands generally correlate with higher catalyst activities. It was believed that the more

Scheme 4


Ph3P
Cl
Ru
Cl
R
PPh3
n
n
Ph3P
Cl
Ru
Cl
R
PPh3
n
Ph3P
Cl
Ru
Cl
PPh3
+
R
Ph3P
Cl
Ru
Cl
PPh3
+
R
Cy3P
Cl
Ru
Cl
R
PCy3
n
Cy3P
Cl
Ru
Cl
PCy3
R
n
+
+
OTBS
N
BOC
OTBS
N
BOC
+
H2C= CH2
OSiEt3
CH3
OSiEt3
CH3

electron-donating tricyclohexylphosphines primarily stabilized the ruthenacyclobutane intermediate, presumed to be higher in energy than the carbene due to the formal oxidation state of ruthenium(IV). However, triphenylphosphine catalysts containing different anionic ligands (*e.g.* Br, I, OAc, TFA) appeared to show the opposite trend.[20]

The activities of these ruthenium catalysts are at least two orders of magnitude lower than those of the molybdenum and tungsten catalysts, as determined from the metathesis of *cis*-2-pentene.[17c] In addition, these catalysts generally cannot be used for the synthesis of tri- and tetrasubstituted olefins, and do not react with cyclooctatetraene. Unlike the molybdenum and tungsten catalysts, however, the ruthenium catalysts can be used in the living polymerizations of cycloolefins that do not produce bulky propagating alkylidenes.[18a] This surprising stability towards bimolecular decomposition is even exhibited by the ruthenium methylidene catalyst $(PCy_3)Cl_2Ru{=}CH_2$, which has now been isolated in good synthetic yields using several methods. Despite these findings concerning the reactivity and stability of these ruthenium catalysts, however, little was known about the general relationship between the ligand sphere and the stability and activity of ruthenium carbenes.

The first chapter of this thesis explores the relationship between the ligand sphere and catalyst activity for this particular class of ruthenium carbenes. By varying the ligand sphere in a systematic way, trends in activity as a function of the steric and electronic environment could be identified. Further investigations were carried out to provide some insight into the mechanism by which these catalysts operate, such that the observed trends in activity could be explained in terms of well-established principles. As a result, an elegant relationship between the nature and geometry of the intermediates and the stability and activity of the catalysts is described.

Using this mechanistic insight, the synthesis of more active ruthenium catalysts was undertaken, as described in the second chapter. Incorporation of a second, ancillary metal center provides stable complexes with only one phosphine coordinated to ruthenium. The

reaction that forms these complexes has been extended to several transition metal dimers with bridging chloride ligands. By varying the ancillary metal center, catalysts with a wide range of activities can be synthesized, all of which are more active than the parent catalysts. Further studies indicate that the mechanism for these catalysts differs from the parent sytems. Additionally, the binary nature of these complexes allows for the ROMP of cycloolefins followed by *in situ* hydrogenation of the resulting polymers.

The last chapter explores the synthesis, stability, and reactivity of ruthenium carbene complexes containing β-diketonate and pyridine ligands. When pyridine ligands are employed, both 16- and 18-electron complexes containing either one or two pyridines can be isolated. Although these complexes are somewhat stable, they decompose rapidly in the presence of olefins. Eighteen electron complexes containing β-diketonate ligands can also be synthesized; however, CuCl or HCl must be added to achieve metathesis activity. The mechanism for activation is explored, as well as potential applications of this methodology.

Finally, several concluding remarks are made to summarize the more important findings in this thesis, and to elucidate more subtle details that are not discussed in the individual chapters. The importance of stereochemistry, sterics, and electronics upon the stability and activity of ruthenium carbenes is outlined, and the implications of these results for future catalyst design are discussed.

References and Notes

[1]Ivin, K. J.; Mol, J. C. *Olefin Metathesis*; 2nd ed.; Academic Press: London, 1997.

[2]Herisson, J-L.; Chauvin, Y. *Makromol. Chem.* **1971**, *141*, 161.

[3]For a recent review, see Ivin, K. J. *Makromol. Chem., Macromol. Symp.* **1991**, *42-43*, 1-14.

[4]Hillmyer, M. A.; Nguyen, S. T.; Grubbs, R. H. *Macromolecules* **1997**, *30*, 718-721.

[5]For recent examples, see (a) Wagaman, M. W.; Grubbs, R. H. *Syn. Met.* **1997**, *84*, 327-328. (b) Boyd, T. J.; Geerts, Y.; Lee, J. K.; Fogg, D. E.; Lavoie, G. G. et al. *Macromolecules* **1997**, *30*, 3553-3559. (c) Tasch, S.; Grapner, W.; Leising, G.; Pu, L.; Wagaman, M. W. et al. *Adv. Mat.* **1996**, *8*, 125. (c) Pu, L.; Wagaman, M. W.; Grubbs, R. H. *Macromolecules* **1996**, *29*, 1138-1143. (d) Schattenmann, F. J.; Schrock, R. R. *Macromolecules* **1996**, *29*, 8990-8991. (e) Baigent, D. R.; Friend, R. H.; Lee, J. K.; Schrock, R. R. *Syn. Met.* **1995**, *71*, 2171-2172. (f) Lee, J. K.; Schrock, R. R.; Baigent, D. R.; Friend, R. H. *Macromolecules* **1995**, *28*, 1966-1971.

[6]For recent examples, see (a) Maughon, B. R.; Weck, M.; Mohr, B.; Grubbs, R. H. *Macromolecules* **1997**, *30*, 257-265. (b) Arehart, S. V.; Pugh, C. *J. Am. Chem. Soc.* **1997**, *119*, 3027-3037. (c) Pugh, C.; Liu, H.; Arehart, S. V.; Narayanan, R. *Macromol. Symp.* **1995**, *98*, 293-310. (d) Ungerank, M.; Winkler, B.; Eder, E.; Stelzer, F. *Macromol. Chem. Phys.* **1995**, *196,* 3623. (e) Pugh, C. *Macromol. Symp.* **1994**, *77,* 325.

[7]For recent reviews, see (a) Hashimi, A. S. K. *J. Prakt. Chem.* **1997**, *339*, 195-199. (b) Schmalz, H.-G. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1833-1836. (c) Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446-552.

[8]For recent examples, see (a) Furstner, A.; Langemann, K. *Synthesis* **1997**, *July*, 792-803. (b) Nicolaou, K. C.; Winssinger, N.; Pastor, J.; Ninkovic, S.; Serabia, F. *et al. Nature*, **1997**, *387*, 268-272. (c) Nicolaou, K. C.; He, Y.; Vourloumis, D.; Vallberg, H.; Yang, Z. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2399-2401. (d) Meng, D. F.; Su,

D. S.; Balog, A.; Bertinato, P.; Sorenson, E. J.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1997**, *119*, 2733-2734.

[9]For recent examples, see (a) Wolfe, P. S.; Gomez, F. J.; Wagener, K. B. *Macromolecules* **1997**, *30*, 714-717. (b) Konzelman, J.; Wagener, K. B. *Macromolecules* **1996**, *29*, 7657-7660. (c) Chauvin, Y.; Saussine, L. *Macomolecules* **1996**, *29*, 1163-1166.

[10](a) Kim, S.-H.; Zuercher, W. J.; Bowden, N. B.; Grubbs, R. H. *J. Or.g. Chem.* **1996**, *61*, 1073-1081. (b) Kim, S.-H.; Bowden, N.; Grubbs, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 10801-10802. (c) Zuercher, W. J.; Hashimoto, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 6634-6640.

[11]Coates, G. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 229-230.

[12](a) Schneider, M. F.; Lucas, N.; Velder, J.; Blechert, S. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 257-259. (b) Schneider, M. F.; Blechert, S. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 410.

[13]Tebbe, F. N.; Parshall, G. W.; Reddy, G. *J. Am. Chem. Soc.* **1978**, *100*, 3611.

[14]Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733.

[15]For a review of Group VI transition metal alkylidenes, see Feldman, J.; Schrock, R. R. *Progress in Inorg. Chem.* **1991**, *39*, 1.

[16]Wu, Z.; Wheeler, D. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 146-151.

[17](a) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100-110. (b) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2039-2041. (c) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858-9859. (d) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3974-3975.

[18](a) [18](a) Maughon, B. R.; Grubbs, R. H. *Macromolecules* **1997**, *30*, 3459-3469. (b) Hillmyer, M. A.; Laredo, W. R.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 6311-6316.

[19](a) Wu, Z.; Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 5503-5511.

[20]Nguyen, S. T. Ph. D. Thesis, 1995.

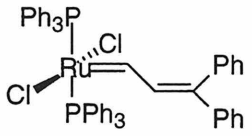
Chapter 1:
Well-Defined Ruthenium Olefin Metathesis Catalysts: Mechanism and Activity

Abstract

Several ruthenium-based olefin metathesis catalysts of the formula $(PR_3)_2X_2Ru{=}CHCHCPh_2$ have been synthesized, and relative catalyst activities were determined by monitoring the ring-closing metathesis of the acyclic diene diethyl diallylmalonate. The following order of increasing activity was determined: X = I < Br < Cl, and $PR_3 = PPh_3 << P^iPr_2Ph < PCy_2Ph < P^iPr_3 < PCy_3$. Additional studies were conducted with the catalyst $(PCy_3)_2Cl_2Ru{=}CH_2$ to probe the mechanism of olefin metathesis by this class of catalysts. The data support a scheme in which there are two competing pathways: the dominant one in which a phosphine dissociates from the ruthenium center, and a minor one in which both phosphines remain bound. Higher catalyst activites could be achieved by the addition of CuCl to the reaction.

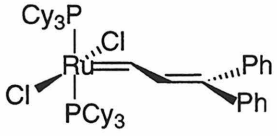
Introduction

The synthesis and isolation of the ruthenium vinylcarbene **1** opened the door to the development of well-defined, late transition metal, low-oxidation state complexes that catalyze olefin metathesis.[1] In addition to the activity of **1** in the metathesis of strained cyclic[1,2] and exocyclic[3] olefins, the remarkable functional group tolerance and stability toward several conditions such as air, water, and acids,[1] has made this class of catalyst particularly attractive for practical applications.



1

By exchanging the triphenylphosphines in **1** for tricyclohexylphosphines, it was found that the catalyst **2a** could also be easily synthesized and isolated.[4] However, **2a** proved to be a much more active catalyst than **1**, reacting with relatively low-strain cyclic olefins[4,5] as well as straight-chain alkenes,[4] while retaining the stability of **1** towards air and protic media.[4] The ring-closing metathesis of functionalized α,ω-dienes to produce five, six, seven,[6,7] and eight membered rings,[7,8] as well as macrocycles and covalently stabilized β-turns,[7] and likewise *ene-yne-ene* systems to make fused or tethered bicyclic molecules,[9] are examples of the particular reactivity and synthetic utility of these catalysts.[10]



2a

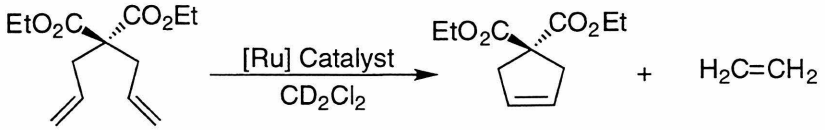
Until now, a systematic investigation of the factors governing catalyst activity and the mechanism by which these catalysts perform olefin metathesis has not been reported.

The present study was undertaken to address both of these topics in the following ways. By varying the ligand sphere around the ruthenium catalyst, we wished to determine how the electronic and steric properties of the ligands affect catalyst activity. Likewise, by examining the kinetics of olefin metathesis, we hoped to gain some insight as to the mechanistic pathway(s) by which these catalysts operate. Once the relationship between the mechanism, ligands, and catalyst activity was understood, we sought to apply this knowledge and tune catalyst activity in a desired fashion.

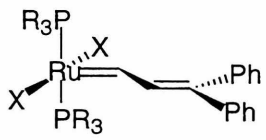
Results and Discussion

To determine the relative activities of the ruthenium catalysts, the ring-closing metathesis of commercially available diethyl diallylmalonate was studied, as shown in Scheme I. Diethyl diallylmalonate was chosen as the substrate for two reasons: (1) it has been observed that ring-closing metathesis to the corresponding cyclopentene diester is quantitative and relatively facile,[11] and (2) the rates of ring-closing are slow enough to be followed by ^{1}H NMR but fast enough to be experimentally feasible. We chose ring-closing olefin metathesis rather than ring-opening polymerization or *cis*-2-pentene metathesis because there is only one propagating species, as opposed to the other systems in which more than one propagating species is observed.[4,12] Methylene chloride was found to be a suitable solvent for these studies: ring-closing is approximately three times faster than in benzene, and minimal catalyst decomposition occurs in this solvent.

Scheme I



Catalysts **2abc**, **3abc**, **4abc**, and **5abc** were synthesized to explore the changes in catalyst activity as the phosphine and halogen ligands are systematically varied. P^{i}Pr$_3$ has a



2a: $PR_3=PCy_3$, X=Cl
2b: $PR_3=PCy_3$, X=Br
2c: $PR_3=PCy_3$, X=I

3a: $PR_3=PCy_2Ph$, X=Cl
3b: $PR_3=PCy_2Ph$, X=Br
3c: $PR_3=PCy_2Ph$, X=I

4a: $PR_3=P^iPr_3$, X=Cl
4b: $PR_3=P^iPr_3$, X=Br
4c: $PR_3=P^iPr_3$, X=I

5a: $PR_3=P^iPr_2Ph$, X=Cl
5b: $PR_3=P^iPr_2Ph$, X=Br
5c: $PR_3=P^iPr_2Ph$, X=I

slightly smaller cone angle than PCy_3, but similar electronic properties. On the other hand, P^iPr_2Ph and PCy_2Ph should have cone angles similar to or perhaps slightly smaller than P^iPr_3 and PCy_3 respectively, with substantially different electronic properties than the trialkylphosphines.[13] In this way, the effects of changing the steric or electronic properties of the phosphine can be studied independently. The halogens, on the other hand, pose a more complex problem. While Cl, Br, and I all have different electronic properties, the size of the halogens also varies substantially down the series. Because of this, the effects of the halogens cannot readily be separated into predominantly steric or predominantly electronic in nature. The catalyst activities, measured under a standard set of conditions which provided reasonable rates for study, are summarized in Table 1.

Ligand Effects Upon Catalyst Activity. As previously demonstrated by the remarkable difference in reactivities between catalysts **1** and **2a**, it was found that varying the nature of the phosphine ligands resulted in substantial changes in catalyst activity. Catalysts **2abc** with PCy_3 ligands were found to be more active than the respective catalysts **4abc** with P^iPr_3 ligands. Likewise, catalysts **3abc** with PCy_2Ph ligands are more active than the respective catalysts **5abc** with P^iPr_2Ph ligands. These results suggest that phosphines with larger cone angles generate catalysts with greater activities.

A more dramatic electronic effect is observed. Catalysts **2abc** with PCy_3 ligands are much more active than the respective catalysts **3abc** with PCy_2Ph ligands. Similarly, catalysts **4abc** with P^iPr_3 ligands are much more active than the respective catalysts **5abc** with P^iPr_2Ph ligands. Thus, merely changing one cyclohexyl or ispropyl group to a phenyl group--and thereby making the phosphine less electron donating--results in a

Table 1: Relative Activities of the Catalysts $(PR_3)_2X_2Ru{=}CH{-}CH{=}CPh_2$ in the Ring-Closing Metathesis of Diethyl diallylmalonate[a]

Catalyst	PR_3	X	Activity (turnovers/hr)[b]
2a	PCy_3	Cl	19.0
2b		Br	15.4
2c		I	1.4
3a	PCy_2Ph	Cl	8.0
3b		Br	4.5
3c		I	----[c]
4a	P^iPr_3	Cl	17.5
4b		Br	13.9
4c		I	1.1
5a	P^iPr_2Ph	Cl	5.5
5b		Br	2.3
5c		I	----[c]

[a]Conditions: $[\text{diethyl diallylmalonate}]_0 = 0.2$ M; [catalyst] = .010 M; temperature = 20°C. [b]Turnover numbers were obtained by fitting data of [product] vs. time to a double-exponential expression (see Figure 1) and using the product concentration from the one-hour time point of the curve fit. [c]Catalyst showed no activity in the metathesis reaction over several hours.

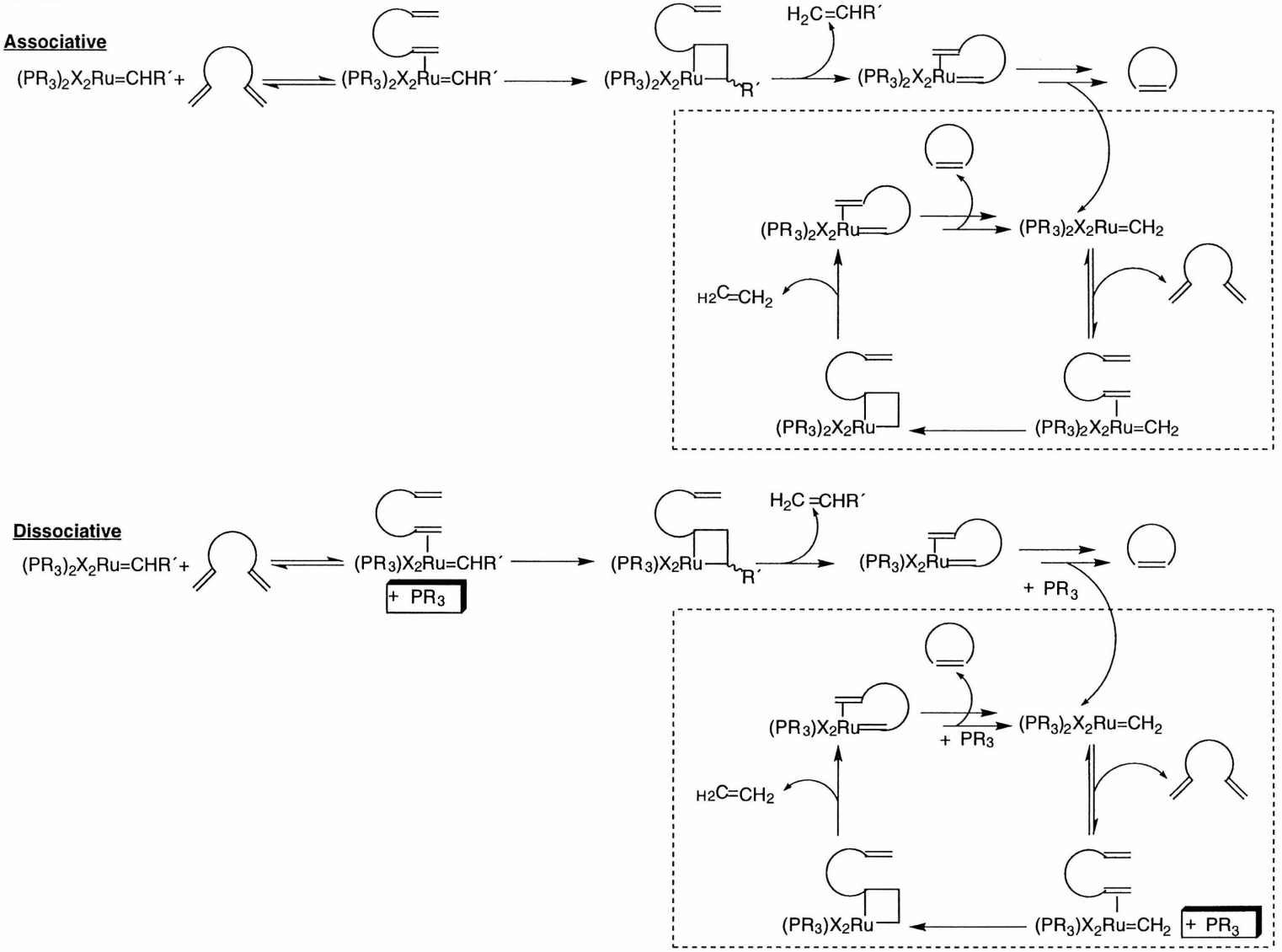
marked decrease in catalyst activity. This trend is even further illustrated by the fact that **1**, which has PPh_3 ligands, is totally inactive for the metathesis of diethyl diallylmalonate, and will only react with suitably strained olefins.

An interesting trend is observed when the halogens are varied. Comparing catalyst **2a**, **2b**, and **2c**, it is easily seen that going down the series from Cl to Br to I corresponds to a decrease in catalyst activity. It should be noted that in going from Cl to Br, catalyst activity is depressed only slightly, while changing to I has a precipitous effect. Similar effects are observed for catalysts **3**, **4**, and **5**, with catalysts **3c** and **5c** being sufficiently slow that ring-closing is negligible at 20°C. These observations are puzzling, as they suggest that the more electron withdrawing and smaller halogens generate more active catalysts--trends that are exactly *opposite* to those observed when varying the phosphines.[14]

While consistent trends are observed throughout this series of catalysts, it appears that the steric and electronic effects of the phosphines upon catalyst activity are opposite to those observed for the halogens. *Phosphines which are larger and more electron-donating, and likewise halogens which are smaller and more electron-withdrawing, lead to more active catalysts.*

Mechanism of Olefin Metathesis. Initially, two general mechanisms for olefin metathesis by these catalysts were proposed (Scheme 2). The top pathway, termed "associative" (NOT in the classical ligand-exchange sense), assumes that the olefin simply coordinates to the catalyst to form the intermediate 18-electron olefin complex, followed by the actual metathesis steps to form the product. The bottom pathway, termed "dissociative," assumes that upon binding of the olefin, a phosphine is displaced from the metal center to form a 16-electron olefin complex, which undergoes metathesis to form the cyclized product, regenerating the catalyst upon recoordination of the phosphine. (It should be noted that the "associative" mechanism at first appeared more attractive, because all of the intermediates have either 16 or 18 electrons. In the "dissociative" pathway, all of

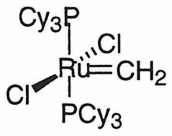
Scheme 2


Associative
(PR3)2X2Ru=CHR´+
(PR3)2X2Ru=CHR´
(PR3)2X2Ru
R´
H2C=CHR´
(PR3)2X2Ru=CH2
H2C=CH2
Dissociative
(PR3)2X2Ru=CHR´+
(PR3)X2Ru=CHR´
+ PR3
(PR3)X2Ru
R´
H2C=CHR´
(PR3)X2Ru=CH2
+ PR3
H2C=CH2

the intermediates also have either 16 or 18 electrons, with the exception of the 14 electron metallacyclobutane). In order to distinguish between these two mechanisms, the kinetics of the reaction were examined by monitoring product formation (or substrate disappearance) over time.

Inspection of the plots of product versus time for the ring-closing reaction with catalysts **3-5** indicated that the kinetics did not exhibit first-order behavior with respect to diene. In fact, the curves fit remarkably well to a double-exponential expression, as shown in Figure 1.

We considered the possiblity that the unexpected kinetic behavior might be due to differences between the initiating carbene ($Ru=CH-CH=CPh_2$) and the propagating carbene ($Ru=CH_2$). The synthesis and isolation of the ruthenium methylidene catalyst **6**,[15] which was used in all of the following kinetic experiments, allowed us to resolve this issue. We observed similar results with catalyst **6**: the kinetics still did not exhibit first-order behavior with respect to the diene, and instead fit very well to a double-exponential



6

expression. These observations led us to conclude that the differences between the initiating and propagating carbenes were not responsible for the unexpected kinetic behavior.

Because the dissociative pathway in Scheme II relies on a phosphine dissociating upon olefin binding, we added excess phosphine to the reaction, reasoning that addition of phosphine would disfavor the equilibrium for olefin binding. Likewise, if the associative pathway were active, adding excess phosphine would have little or no effect upon the reaction kinetics. Two important results were obtained from these experiments. First, addition of 0.25-1.0 equiv (0.005M-0.020M) of phosphine (with respect to 0.020 M

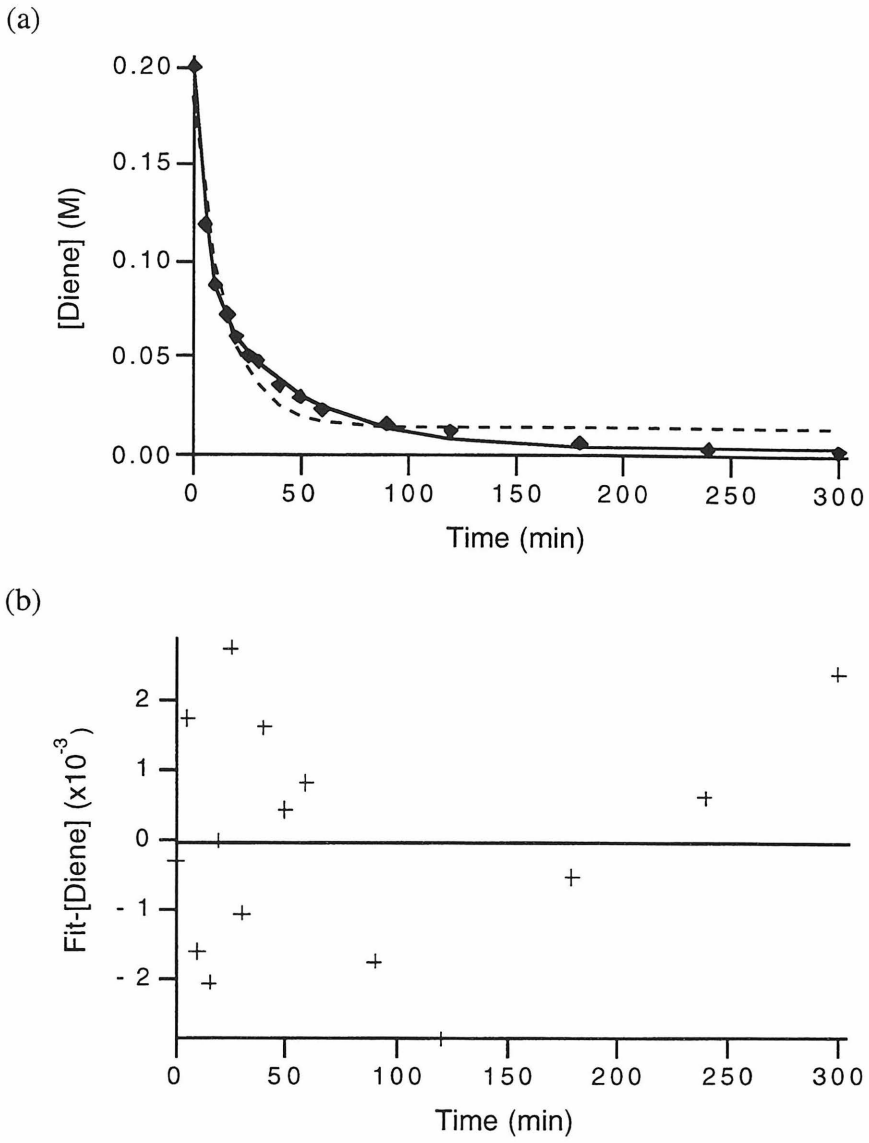


Figure 1. (a) Representative plot of diene concentration vs. time from catalyst **4a**. The reaction was carried out with $[diene]_0 = 0.2$ M and [catalyst (**4a**)] = 0.01 M in CD_2Cl_2 at 20°C. The filled diamonds are the data points, and the solid line is the double-exponential fit: $[diene](t) = K_0 + K_1exp(-K_2t) + K_3exp(-K_4t)$. The dashed line is the best first-order fit $[diene](t) = K_0 + K_1exp(-K_2t)$. The constants K_n are generic constants that are calculated by the curve-fitting procedure. (b) The residuals (crosses) from the double-exponential fit in (a), found by taking the difference between the data and the curve fit at each point.

catalyst) depresses the rate dramatically, with the reaction proceeding up to twenty times slower upon the addition of 1.0 equiv (0.020 M) of phosphine. Second, as shown in Figure 2, the kinetics become *pseudo-first order* with respect to diene upon addition of phosphine. This fortuitous result allows us to obtain a pseudo-first order rate constant k_{obs}, which can be used to determine the relationship between k_{obs} and phosphine concentration. The plot of k_{obs} vs. reciprocal phosphine concentration in Figure 3 shows a linear correlation, and the positive intercept indicates that there is an additional phosphine independent term in the rate expression.

To determine the complete rate expression for the ring-closing reaction, experiments were conducted to determine the rate dependence upon catalyst concentration. Because of the complex kinetics in the absence of excess phosphine, we could not measure an observed rate constant k_{obs} for the ring-closing reaction under these conditions. The fact that these curves fit to a double-exponential expression was utilized to find the rate at each point in time simply by taking the derivative of the double-exponential curve fit. The plots of rate of diene disappearance vs. diene concentration for different catalyst concentrations are shown in Figure 4. The data are obviously not first-order--at least not initially. (It appears, however, that the reaction eventually reaches a steady-state, which occurs after more than half of the substrate has been consumed.) By comparing these calculated rates at identical diene concentrations, as summarized in Table 2, we find an *approximate* square-root dependence on catalyst concentration.

Finally, to determine the *actual* catalyst order in the rate expression, the reactions in which the catalyst concentration was varied were repeated in the presence of a constant concentration of excess phosphine. By adding the excess phosphine, the pseudo-first order rate constants could be obtained. A plot of k_{obs} vs. catalyst concentration is shown in Figure 5.

A good linear correlation is observed, and it can be concluded that the reaction is first-order with respect to catalyst concentration. The final rate expression is shown in

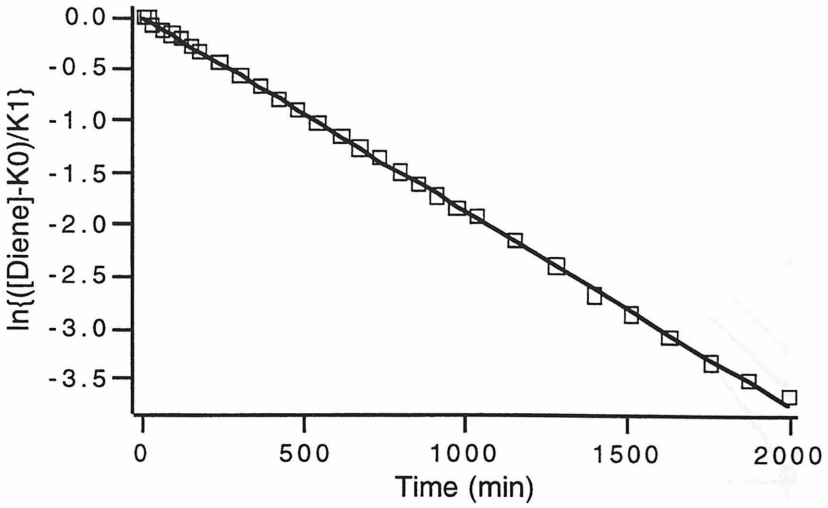


Figure 2. Log plot of diene concentration vs. time for the ring-closing metathesis of diethyl diallylmalonate in the presence of 0.02 M PCy_3, where $[Ru]_0$ (**6**) = 0.02 M and [diene] = 0.2 M. The reactions were carried out in CD_2Cl_2 at 30°C. K_0 and K_1 are the constants from the first-order fit $[diene](t) = K_0 + K_1 exp(-K_2 t)$, and K_2 is the slope of the line, where the constants K_n are generic constants calculated by the curve-fitting procedure. The boxes are the data points and the line is the linear fit. Intercept = (6.45± 7.64) x 10^{-3}; slope = (-1.88± 0.01) x 10^{-3}; linear correlation coefficient = 1.00.

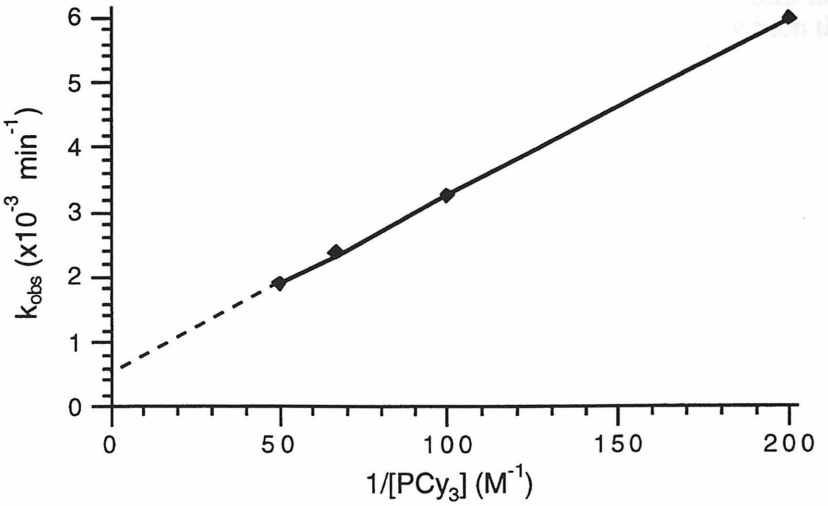


Figure 3. Plot of k_{obs} vs. reciprocal phosphine concentration for the ring-closing metathesis of diethyl diallylmalonate at varying phosphine concentrations, with [diene] = 0.2 M and $[Ru]_0$ (**6**) = 0.02 M. The reactions were carried out in CD_2Cl_2 at 30°C. The filled diamonds are the data points, the solid line is the linear fit $k_{obs} = K_0 + K_1(1/[PCy_3])$ where the constants K_n are generic constants calculated by the curve-fitting procedure, and the dashed line is the extrapolation of the linear fit to the intercept. Intercept = (5.27± 0.13) x 10^{-4}; slope = (2.73± 0.01) x 10^{-5}; linear correlation coefficient = 1.00.

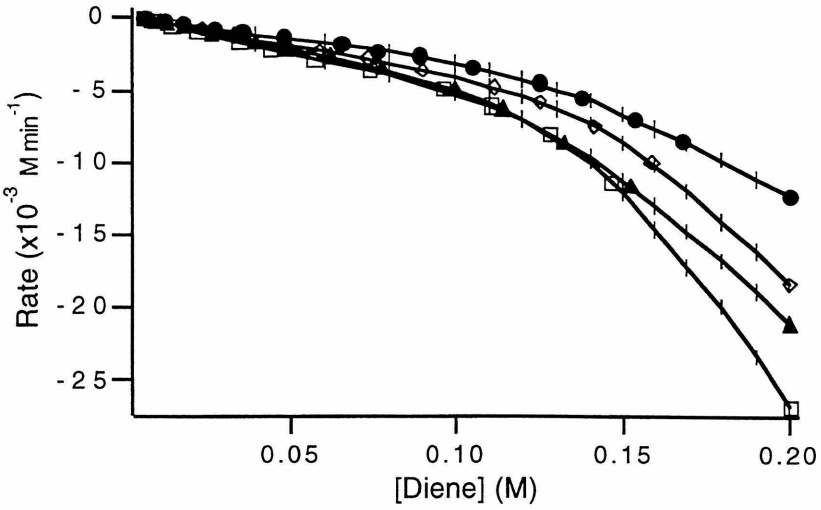


Figure 4. Plot of reaction rate vs. diene concentration for the ring-closing metathesis of diethyl diallylmalonate at varying concentrations of catalyst (**6**), with $[diene]_0 = 0.2$ M. The reactions were carried out at 25°C in CD_2Cl_2. The data points and concentrations of catalyst **6** are: filled circles, .005M; open diamonds, .010M; filled triangles, .015M; open squares, .020M. The data points were obtained by first fitting the plots of [diene](t) vs. time to the double-exponential expression: $[diene](t) = K_0 + K_1 exp(-K_2 t) + K_3 exp(-K_4 t)$, where the constants K_n are generic constants calculated by the curve-fitting procedure. Using the derivative of this equation and the calculated values for the constants K_n, the rate can be calculated as a function of time. The diene concentration is already expressed as a function of time in the double-exponential relationship above, so the rate can be expressed more usefully as a function of diene concentration, represented by the solid lines in the above figure. The vertical hash marks are the diene concentrations at which the rates were compared, for which the data is summarized in Table 2.

Table 2: Ratios of Rates for Ring-Closing Metathesis with Varying Catalyst Concentrations

	Ratio of Catalyst Concentrations		
	(0.010 M)/(0.005 M)	(0.015 M)/(0.005 M)	(0.020 M)/(0.005 M)
Average[a]	1.33	1.61	1.81
1σ[b]	0.0741	0.111	0.185
2σ[b]	0.148	0.222	0.370
3σ[b]	0.222	0.333	0.555

[a]The rates of olefin metathesis for different catalyst concentrations were determined at the diene concentrations designated by vertical hash marks in Figure 4. The rates of metathesis for the different catalyst concentrations were then compared at several *identical* diene concentrations (so that the rate dependence on diene concentration cancels out), and the ratios calculated at these diene concentrations were averaged accordingly. Thus, the ratios shown above show the effect of doubling, tripling, and quadrupling (from left to right) the catalyst concentration upon the rate of metathesis. By doubling the catalyst concentration, the rate of metathesis increases by a factor of 1.33; by tripling the catalyst concentration, the rate increases by a factor of 1.61, and by quadrupling the catalyst concentration, the rate increases by a factor of 1.81. This appears to demonstrate an *approximate* square-root dependence upon catalyst concentration, where the rate would increase by a factor of 1.41, 1.73, and 2.00 respectively.

[b]σ = standard deviation calculated from the data.

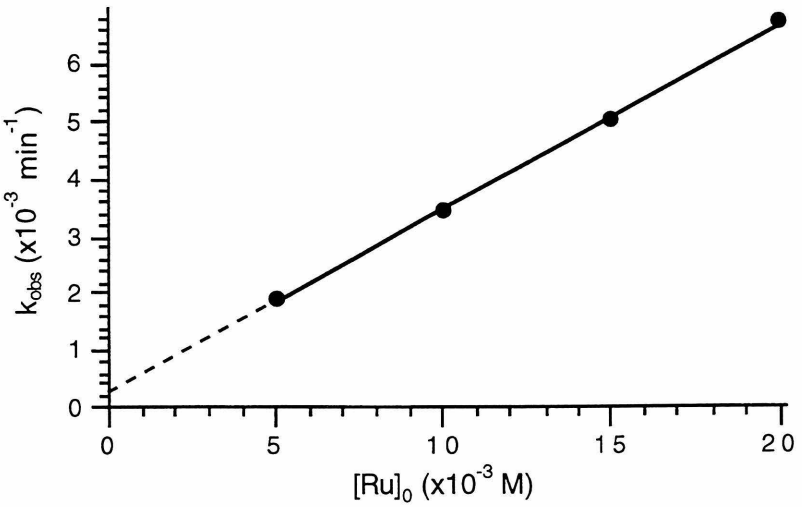


Figure 5. Plot of k_{obs} vs. catalyst concentration for the ring-closing metathesis of diethyl diallylmalonate at varying catalyst concentrations in the presence of 0.005M PCy_3, with $[diene]_0 = 0.2$ M. The reactions were carried out in CD_2Cl_2 at 30°C. The filled circles are the data points, the solid line is the linear fit $k_{obs} = K_0 + K_1([Ru]_0)$ where the constants K_n are generic constants calculated by the curve-fitting procedure, and the dashed line is the extrapolation of the linear fit to the intercept. Intercept = (2.42± 0.72) x 10^{-4}; slope = 0.323± 0.005; linear correlation coefficient = 1.00.

Equation 1, where k_{obs} is the expression within parentheses, and $[Ru]_0$ is the concentration of catalyst (i.e., the total concentration of ruthenium in the system).

$$-\frac{d[\text{diene}]}{dt} = \left(\frac{A}{[PCy_3]} + B\right)[Ru]_0[\text{diene}] \quad (1)$$

In order to explain this result, we have proposed a mechanism in Scheme 3 in which both the "associative" and "dissociative" pathways from Scheme 2 are operating. Because no intermediates are observed during the course of reaction, the rate of disappearance of diene is equal to the rate of product formation. We assumed that in both cases, metallacycle formation is the rate determining step[16,17]--in the "dissociative" pathway, the metallacyclobutane is a 14-electron complex,[18] and in the "associative" pathway, the metallacyclobutane is a 16-electron complex with a sterically demanding environment--the metallacyclobutane being the highest energy intermediate. The rate of disappearence of diene based on Scheme 3 is shown in Equation 2:

$$-\frac{d[\text{diene}]}{dt} = k_3[I_2] + k_4[I_1] \quad (2)$$

By solving the equilibria for the concentrations of $[I_1]$ and $[I_2]$, one easily obtains:

$$[I_1] = K_1[\mathbf{6}][\text{diene}] \quad \text{and} \quad [I_2] = K_2\frac{[I_1]}{[PCy_3]} = K_1K_2\frac{[\mathbf{6}][\text{diene}]}{[PCy_3]} \quad (3)$$

Substituting Equation 3 into Equation 2 yields the final rate expression:

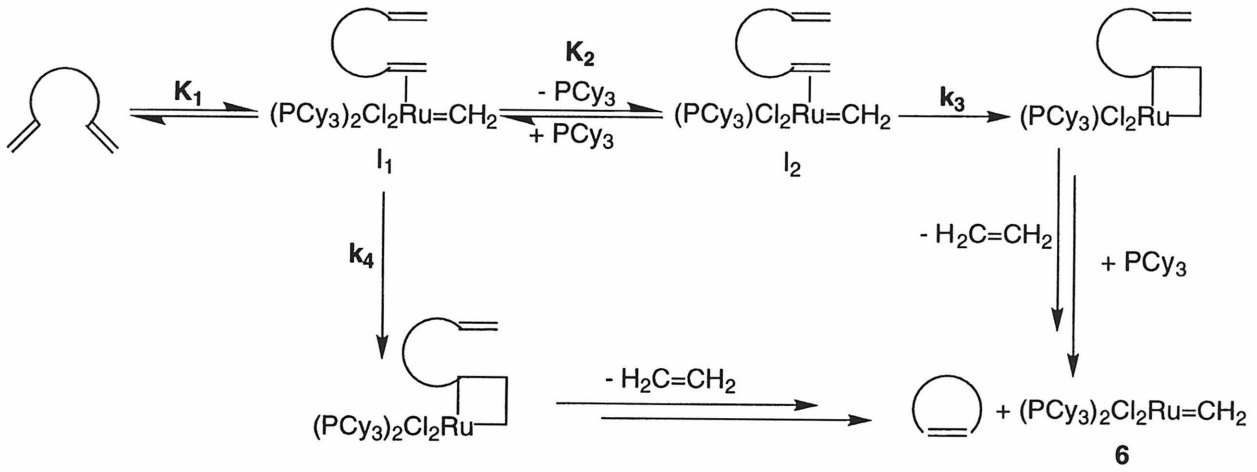
$$-\frac{d[\text{diene}]}{dt} = \left(k_3\frac{K_1K_2}{[PCy_3]} + k_4K_1\right)[\mathbf{6}][diene] \quad (4)$$

By comparing Equation 4 with the empirical rate expression in Equation 1, where [**6**] = $[Ru]_0$, we find that the constants A and B are:

$$A = k_3K_1K_2 \quad \text{and} \quad B = k_4K_1 \quad (5)$$

Referring back to Equation 1, we can attribute the first part of k_{obs} to the

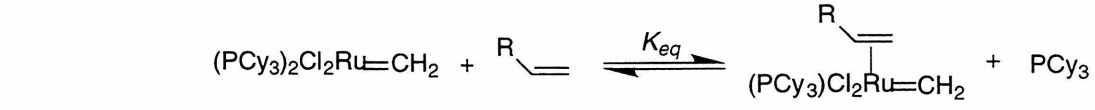
Scheme 3


K1
(PCy3)2Cl2Ru=CH2
I1
K2
- PCy3
+ PCy3
(PCy3)Cl2Ru=CH2
I2
k3
(PCy3)Cl2Ru
k4
- H2C=CH2
+ PCy3
(PCy3)2Cl2Ru
- H2C=CH2
+ (PCy3)2Cl2Ru=CH2
6

"dissociative" pathway--the rate is inversely proportional to the concentration of unbound phosphine, and directly proportional to the concentrations of both catalyst and diene. The second part of k_{obs} can be attributed to the "associative" pathway--the rate is directly proportional to the concentrations of both catalyst and diene, and independent of the concentration of unbound phosphine. From the data in Figure 3, however, we concluded that B, the observed rate constant for the "associative" pathway, is relatively small compared to the quotient $A/[PCy_3]$, such that in the absence of excess phosphine, the "dissociative" part of the expression clearly dominates (>90-95%).

We can rationalize the kinetic behavior as follows. Because the starting catalyst (with both phosphines) is the only species observed by NMR during the reaction, and likewise no unbound phosphine is observed, we can assume that the amount of unbound phosphine does not exceed 5% of the catalyst concentration. In considering the equilibrium for diene coordination and phosphine dissociation, the concentration of unbound phosphine at every point in time should be proportional to the square root of the catalyst concentration, as shown in Scheme 4. The approximate square-root dependence of the rate on catalyst concentration, observed previously in the absence of added phosphine (Table 2), is consistent with this analysis.

Scheme 4



$$x = [PCy_3] = \sqrt{K_{eq}[Ru]_0[Diene]_t}$$

The addition of a mere 0.25-1.0 equiv (0.005-0.020 M) of phosphine (with respect to 0.020 M catalyst) is sufficient to swamp the concentration of unbound phosphine orginating from the catalyst. Because the phosphine concentration is constant, the kinetics

become pseudo-first order with respect to diene, as demonstrated by Equation 1. Finally, when the catalyst concentration is varied in the presence of added phosphine (and thus keeping a constant phosphine concentration), the linear correlation between k_{obs} and catalyst concentration can be extracted.

Stereochemistry of Intermediates. Before we can consider an explanation for the ligand effects in Table 2, we must first determine the stereochemistry of the postulated intermediates I_1 and I_2 in our proposed mechanism (Scheme 3). Scheme 5 describes what we at first considered to be the two most plausible stereochemical pathways for the "dissociative" pathway in Scheme 3--the "dissociative" pathway, being responsible for 95% of catalyst turnover, will also be responsible for the differences in catalyst activity.

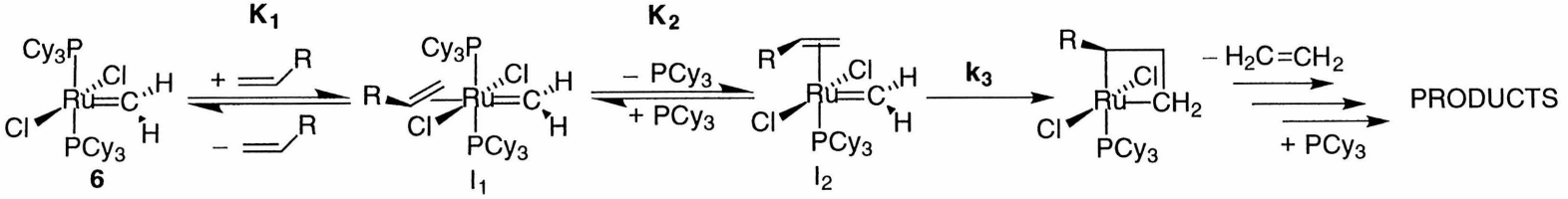
From the crystal structures of the vinylcarbene[4] and benzylidene[15] ruthenium catalysts $(PCy_3)_2Cl_2Ru{=}CHR$, we know that they both have a raised square pyramidal geometry with the carbene occupying the apical position. The carbene moiety lies in the Cl-Ru-Cl plane, as opposed to the crystal structure of catalyst **1**[1] in which the carbene moiety lies in the P-Ru-P plane. This is reflected by the coupling constant $^3J_{HP}$ between H_α on the carbene and the phosphorous nuclei in the ^{1}H NMR spectra--$^3J_{HP}$ is approximately zero in the spectrum of the vinylcarbene and benzylidene catalysts $(PCy_3)_2Cl_2Ru{=}CHR$,[4,15] and 11-12 Hz in the spectrum of **1**.[1] From this we conclude that $^3J_{HP}$ closely follows the Karplus relationship for the P-Ru-C_α-H_α dihedral angle.[4]

Because $^3J_{HP}$ is approximately zero in the methylidene catalyst **6**, we have concluded that the carbene moiety lies in the Cl-Ru-Cl plane.[19] Furthermore, because it is necessary that the carbene moiety and olefin approach each other in a face-to-face manner to effect metallacycle formation, the carbene orientation must be considered in our analysis. According to these arguments, an olefin coordinated in one of the positions currently occupied by PCy_3 will be in the required face-to-face orientation with the ruthenium-carbene double bond.

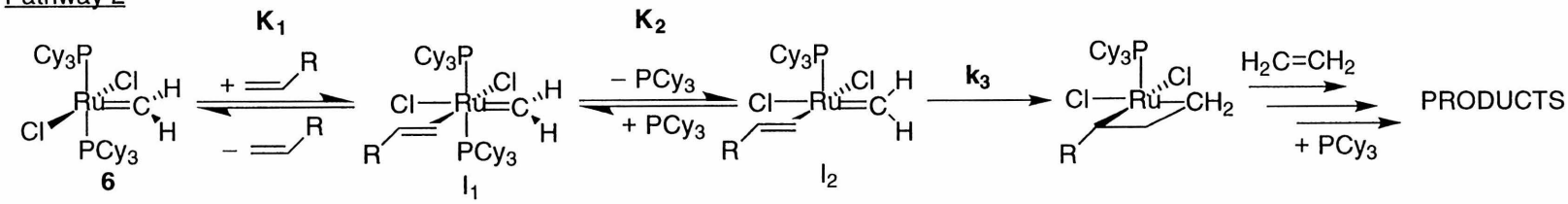
In Scheme 5, pathway 1 depicts olefin coordination *trans* to the carbene to make an

Scheme 5

Pathway 1



Pathway 2

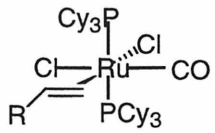


18 electron intermediate I_1, followed by phosphine dissociation with olefin migration to form a 16-electron intermediate I_2 in which the olefin is *cis* to the carbene. Assuming that the carbene retains its orientation, this 16-electron intermediate has the required geometry for metallacyclobutane formation and subsequent metathesis.

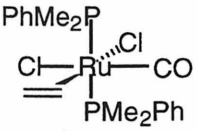
Pathway 2 depicts I_1 with the olefin coordinating *cis* to the carbene and chloride migrating to the position *trans* to the carbene. It should be noted that, with the olefin coordinated as shown in I_1 , the carbene must *rotate* ninety degrees before metallacycle formation can occur. Subsequent phosphine dissociation, along with carbene rotation, forms the 16-electron intermediate I_2 which has the required geometry for metallacycle formation.

In a comparison of these two mechanisms, pathway 1 appeared to be more plausible. The olefin coordinates in what appears to be the open coordination site, and phosphine dissociates with olefin migration to a position from which metallacycle formation can occur. However, after examining the proposed intermediates in greater detail, we have concluded that pathway 2 is more likely based on the following analysis.

Although we have not been able to directly observe olefin complexes of the catalysts **2-6**, olefin complexes of the compound $(PCy_3)_2Cl_2Ru(CO)$ have been reported in the literature. Carbon monoxide is an excellent model for the carbene moiety--substantial pi-bonding is expected for CO bound to an electron rich Ru(II) metal center, such that a CO ligand will occupy the same ruthenium orbitals as the carbene moiety (in either orientation). Olefin complexes of strong pi-acids such as acrylonitrile and 1,2-dicyanoethylene bound to $(PCy_3)_2Cl_2Ru(CO)$ have been characterized by IR and ^{31}P NMR spectroscopy, and in all cases the olefin is coordinated as shown below in **7a** and **7b**.[20] In addition, a crystal structure of the ethylene complex **8**[21] depicts an identical ligand geometry, in which the olefin is bound *cis* to the CO ligand. Based on these structures, we believe that the olefin complex I_1 is correctly depicted in pathway 2 (Scheme 5).

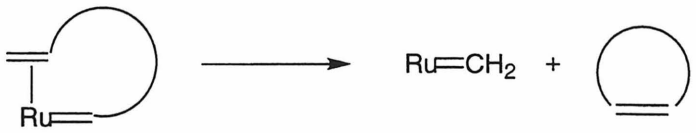


7a: olefin = acrylonitrile
7b: 1,2-dicyanoethylene



8

Further evidence that the olefin must coordinate *cis* to the carbene moiety is provided by the second step in the ring-closing metathesis reaction (Equation 6):



(6)

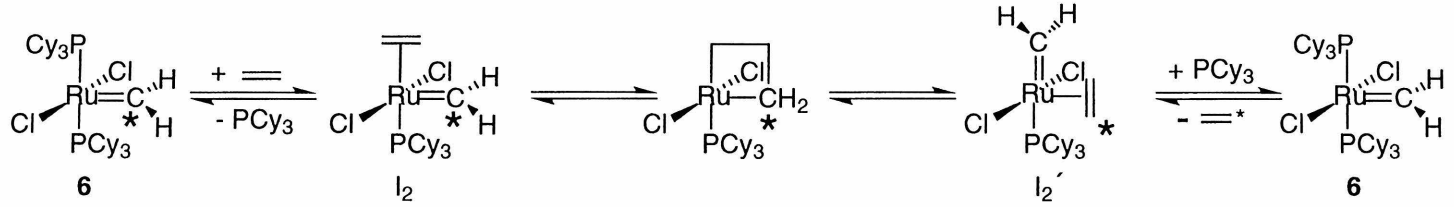
For small to moderate sized rings, the pendant olefin can only coordinate *cis* to the carbene to which it is tethered--a *trans* coordinated olefin of this type would almost certainly have a prohibitive amount of strain energy. Excepting the unlikely event in which the olefin coordinates in different places depending on whether or not it is tethered to the carbene, these geometric constraints indicate that pathway 2 (Scheme 5) accurately depicts the olefin complex I_1.

For symmetric catalysts such as **1-6**, consideration of the principle of microscopic reversibility[22] has interesting consequences for the possible mechanisms of olefin metathesis. For the ruthenium catalysts, it is easiest to consider a degenerate metathesis reaction, as shown in Scheme 6.

According to pathway 1, the square pyramidal intermediate I_2, in which the carbene occupies the apical position and the olefin a basal position, directly precedes metallacyclobutane formation. Productive cleavage of the metallacyclobutane places the carbene in a basal position and the departing olefin in the apical position, intermediate I_2'. In order to regenerate the starting catalyst **6**, some type of ligand rearrangement must occur along with phosphine recoordination and displacement of the product olefin. Because this is a degenerate reaction, the principle of microscopic reversibility requires that the reverse

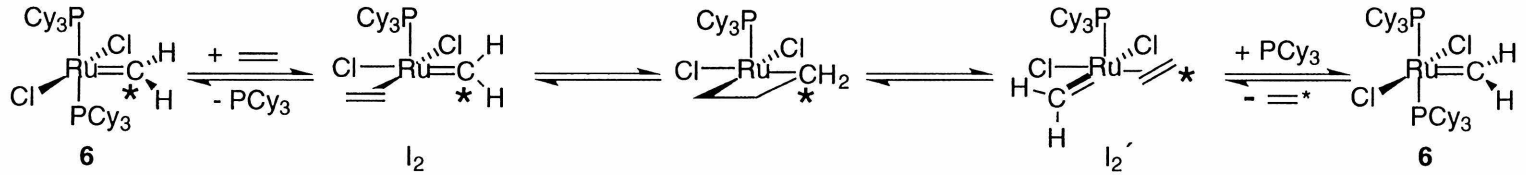
Scheme 6

Pathway 1



6 I_2 I_2' 6

Pathway 2



6 I_2 I_2' 6

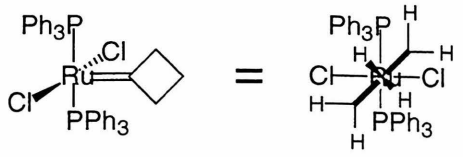
reaction occur at the same rate as the forward reaction. In regarding pathway 1, therefore, two pathways must actually be occuring simultaneously to effect "productive" metathesis--the direct result of having an asymmetric energy profile for a degenerate reaction. The extension of this to non-degenerate olefin metathesis results in there being two competing "dissociative" pathways which may or may not be kinetically distinguishable from each other.

In pathway 2, on the other hand, formation of the metallacyclobutane from I_2 and subsequent cleavage produces the intermediate I_2', which is actually the enantiomer of I_2. Recoordination of the phosphine and displacement of the product olefin directly regenerates the starting catalyst **6** without the need for any additional ligand rearrangements. Furthermore, because the energy profile is symmetric, no additional pathways are implicated by this mechanism.

When the associative pathway that is implied by the reaction kinetics is also taken into account, pathway 2 becomes even more attractive. In Scheme 3, we have proposed that the olefin complex with two phosphines is a common intermedate in both the associative and dissociative pathways. In pathway 1, however, there is no plausible intermediate that can satisfy both pathways. Either the ligands must rearrange to a species in which the bulky tricyclohexylphosphines are *cis* to each other, or an altogether separate pathway must exist in which the olefin coordinates as shown in pathway 2--which in the end provides another reason why pathway 2 is more likely.

By accepting pathway 2 as the more probable mechanism, we are left to rationalize the required ninety-degree carbene rotation that must preceed metallacycle formation . This may not be as energetically unfavorable as it may first appear.[19] In catalyst **1**, the conformation of the carbene is already rotated ninety-degrees (as compared to **2**-**6**). In compound **9** the carbene is oriented at a 45 degree angle such that it bisects the Cl-Ru-Cl and P-Ru-P planes as determined by x-ray crystallography,[3] indicating that linear combinations of the two available pi-bonding orbitals on the metal center exist such that the

Ru=C pi bond is not broken during the rotation process.



9

Additionally, we have found by ^1H NMR spectroscopy that during ligand exchange reactions in which PCy_3 (or another exchangeable phosphine) is added to **1**, the carbene in the mixed phosphine intermediate is oriented as in **1**. It is only upon reaction of the second equivalent of PCy_3 that the carbene rotates. We therefore find it very feasible that, upon dissociation of PCy_3 from the intermediate I_1 in pathway 2, the carbene rotates ninety-degrees as the steric and/or electronic environment is changed.

From the above analysis, the preponderance of evidence supports pathway 2 as the more likely mechanism by which the ruthenium catalysts **2-6** operate. We have depicted what we propose to be the complete, detailed mechanism in Scheme 7. Based on this, the relationship between the ligand sphere and catalyst activity can be rationalized.

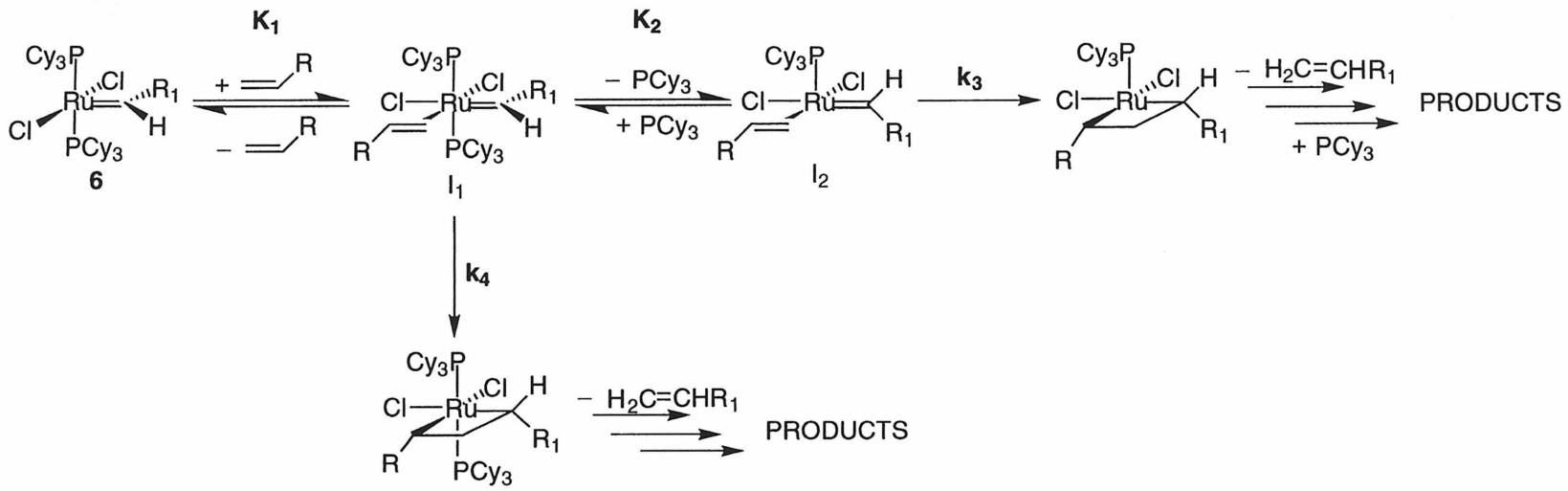
Explanation of Ligand Effects Upon Catalyst Activity.

To explain the ligand effects upon catalyst activity, we will refer to the "dissociative" (top) pathway shown in Scheme 7, and Equation 7, which is the part of equation 4 which corresponds to the "dissociative" pathway. Because the "dissociative" pathway accounts for approximately 95% of the catalyst turnover, we will ignore the "associative" pathway in our discussion of relative catalyst activities.

$$-\frac{d[\text{diene}]}{dt} = \left(k_3 \frac{K_1 K_2}{[PCy_3]} \right) [\mathbf{6}][diene] \qquad (7)$$

In deriving equations 4 and 7, we have assumed that formation of the 14-electron metallacyclobutane intermediate is the rate determining step. All the steps following

Scheme 7


K1
K2
Cy3P
Cl
R1
Ru
H
PCy3
6
+
R
–
I1
– PCy3
+ PCy3
I2
k3
– H2C=CHR1
+ PCy3
PRODUCTS
k4

metallacycle formation should be faster, including intramolecular reaction with the second olefin of the diene to make the cyclic product and regenerate the catalyst. (Independent investigations have confirmed that alkyl-substituted carbenes are more reactive than the unsubstituted methylidene.)[15] From (7), it is easily seen that the rate, and therefore catalyst activity, is directly proportional to three constants: K_1, the equilibrium constant for olefin binding; K_2, the equilibrium constant for phosphine dissociation; and k_3, the rate constant for metallacylobutane formation from the monophosphine olefin complex I_2.

Effect of Halogens. The catalyst activities decrease as the halogens are changed from Cl to Br to I (Table I). Because the olefin binds *trans* to one of the halogens, their *trans* influencing abilities will have a substantial effect upon the relative ruthenium-olefin bond strengths. The *trans* influence of the halogens increases down the series from Cl to Br to I,[23] so the olefin should be bound *tighest* for Cl and *weakest* for I. Therefore, K_1 will decrease down the series from Cl to I, and we expect a corresponding decrease in the rate. Since *cis* effects are generally weak, phosphine dissociation should not be affected by the change in halogens, and K_2 should remain relatively unchanged. We believe that k_3 also remains relatively unaffected, so an overall decrease in rate, and therefore catalyst activity, will result when changing from Cl to Br to I.

The size of the halogens should also affect the equilibrium for olefin binding. Because the olefin binds *cis* to one of the halogens, we expect that larger halogens such as iodide would disfavor olefin binding due to steric crowding in the halogen-olefin-carbene plane, resulting in a decrease in K_1 . By the same reasoning as above, we again predict that catalyst activity will decrease down the series from Cl to I.

Effect of Phosphines. The catalyst activities increase as both the cone angle and the electron donating ability of the phosphines increase. Although these effects are exactly contrary to those observed for the halogens, the proposed mechanism provides a reasonable explanation.

As the cone angle of the phosphine increases, it should be obvious that phosphine

dissociation from the sterically crowded 18-electron olefin complex I_1 should be favored, corresponding to an increase in K_2. Although this steric crowding is expected to destabilize I_1, and therefore decrease K_1, the relief of steric crowding should stabilize the monophosphine olefin complex I_2 even further--i.e. bulkier phosphines will favor the overall equilibrium for olefin binding and phosphine dissociation, represented by the product K_1K_2. The product K_1K_2, and hence the rate, is therefore expected to increase as the phosphine cone angle increases.

As the electron donating ability of the phosphines increases, the relative *trans*-influence also increases.[24] Because of this, we expect more electron donating phosphines to favor dissociation--by stabilizing the vacant coordination site *trans* to them in the 16-electron monophosphine olefin complex I_2, and especially in the 14-electron metallacyclobutane intermediate. This is analagous to the *trans* effect observed in dissociative ligand substitutions at octahedral metal centers--the rate of substitution increases as the *trans* influence of the appropriate ligand increases, due to weakening of the bond in the ground state and/or stabilization of the five-coordinate intermediate.[24,25] In addition, more electron donating phosphines may facilitate the two electron oxidation of the metal center to form the metallacyclobutane. This will increase both K_2 and k_3, so we expect the rate to increase substantially as the electron donating ability of the phosphines is increased. The magnitude of these two effects is manifested in the astonishing difference in activity between catalysts **1** and **2a**.

Rate Enhancement by CuCl. The final and perhaps most important aspect of understanding the mechanism of olefin metathesis by these catalysts is the ability to rationally tune catalyst activity in a desired fashion. For example, the rate of metathesis by the ruthenium catalysts is slow compared to the well-known molybdenum and tungsten alkylidenes,[26] and it would be desirable to tailor the system in such a way as to increase catalyst activity.

With these goals in mind, we wish to report a substantial increase in the rate of

olefin metathesis by ruthenium catalysts upon the addition of CuCl. We reasoned that if a "dissociative" pathway accounts for 95% of metathesis in our systems, the equilibrium for phosphine dissociation could be driven by the addition of CuCl, which is known to react with phosphines to make a marginally soluble, ill-defined complex.[27] We found that the addition of 10 equivalents of CuCl to a ring-closing reaction effects a rate-enhancement in the case of catalysts **2-5**. In some cases, however, the catalyst dies before the reaction goes to >95% completion. The most dramatic effect was observed when CuCl was added to a reaction employing the catalyst $(PCy_3)_2I_2Ru$=CH-CH=CPh_2 (**2c**), shown in Figure 6. In the absence of copper chloride, this catalyst was relatively slow (Table 1). Upon addition of CuCl, however, the activity of this catalyst rivals that of the most active catalyst **2a**, $(PCy_3)_2Cl_2Ru$=CH-CH=CPh_2--an increase by a factor of 20. Furthermore, the addition of CuCl to previously inactive catalysts such as **5c** initiates product formation.[28]

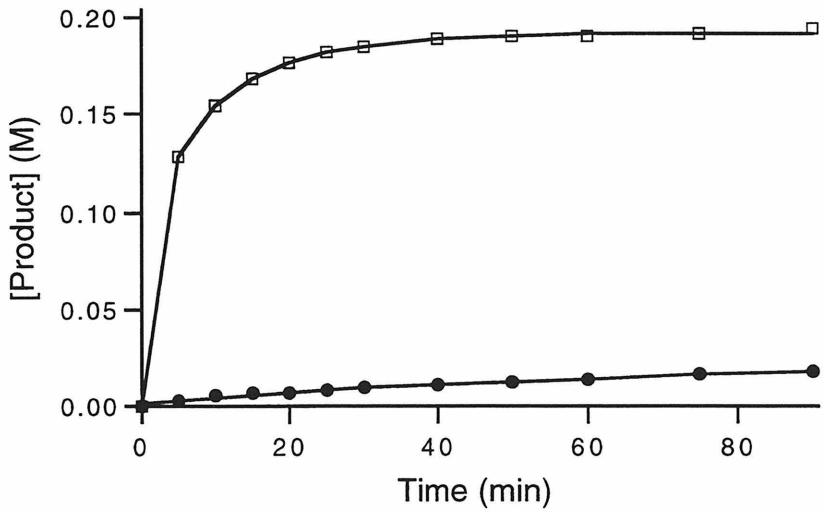


Figure 6. Plot of diene concentration vs. time for catalyst **2c** without (filled circles) and with (open squares) 10 equivalents of CuCl added to the reaction. The reactions were carried out with $[diene]_0$ = 0.2 M and [catalyst (**2c**)] = 0.01 M in CD_2Cl_2 at 20°C.

A control experiment employing $CuCl_2$ as the phosphine scavenger was performed, since it is possible that the increase in catalyst activity is due to a redox process involving

trace amounts of Cu(II). Because $CuCl_2$ reacts with phosphines in a manner similar to CuCl, we expected either a further increase in catalyst activity if a redox process were operating, or a similar increase in catalyst activity if the copper were scavenging the phosphine. We obtained the same results using $CuCl_2$, lending support to the belief that it is the phosphine being taken up by copper, and not a redox process involving Cu(II), that is responsible for the observed rate-enhancement.

The nature of the species generated by adding CuCl to a ruthenium catalyst is unknown. It is possible that a highly reactive, 14-electron monophosphine compound is simply generated, but some recent results suggest that the $CuCl{\bullet}PR_3$ adduct may actually chelate the ruthenium center via bridging chloride ligands. Such bimetallic catalysts with bridging chlorides have been isolated, and are under current investigation.

Conclusions

In exploring the reactivity of many analogous ruthenium catalysts **2-5**, some surprising features were uncovered. It was found that the ligand effects upon catalyst activity were exactly opposite for the phosphines and the halogens. *Larger and more electron donating phosphines* produced more active catalysts, while *smaller and more electron withdrawing halogens* likewise produced more active catalysts. These apparently contradictory effects could not be easily explained on the basis of pure steric and/or electronic arguments, prompting further investigation into the mechanism of olefin metathesis by these catalysts.

Mechanistic studies allowed us to formulate an empirical rate equation for the ring-closing of diethyl diallylmalonate by catalyst **6**. The major pathway was found to involve phosphine dissociation from the metal center, such that a minor associative pathway in which both phosphines remain bound can be considered to operate only at higher phosphine concentrations--i.e. when excess phosphine is added to the reaction mixture. We were surprised by the relative importance of the "dissociative" pathway, as it suggests

that there is a 14-electron metallacyclobutane intermediate--an electron defficient intermediate for a late transition metal such as ruthenium.

We have concluded that the mechanism in Scheme VII is in agreement with all of the kinetic evidence, as well as additional evidence found in the literature. The olefin binding site is presumed to be *cis* to the carbene, based upon analagous compounds characterized in the literature employing carbon monoxide in place of the carbene moiety, in addition to the geometric constraints required by the ring-closing metathesis reaction. Furthermore, metallacycle formation and breakdown is thought to occur in a symmetric fashion. If it were to occur in an asymmetric fashion, the mechanism would involve two competing "dissociative" pathways, as well as complex ligand rearrangements about the metal center. One very interesting implication of this mechanism is that in order for metathesis to occur, the carbene must rotate ninety degrees sometime during or after the olefin coordination or phosphine dissociation steps. Using this mechanism as a guide, a self-consistent picture emerges in which the ligand effects can be explained in terms of well-established principles, and a full understanding of the precise nature of metathesis in these systems is gained.

Regarding the "dissociative" pathway, the ligand effects could be rationalized in terms of well-studied systems. Bulkier phosphines favor phosphine dissociation by relief of steric crowding around the ruthenium center. Likewise, the greater *trans* influence of more electron donating phosphines favors phosphine dissociation by stabilizing the 16-electron monophosphine olefin complex, and more importantly the electron defficient 14-electron metallacyclobutane. Halogens, on the other hand, find their primary effects in their relative *trans* influencing abilities. Because the olefin binds *trans* to one of the halogen ligands, more electron withdrawing halogens with a smaller *trans* influence will stablilize the ruthenium-olefin complex. Because the olefin binds *cis* to the other halogen ligand, larger halogens should destabilize the olefin complex due to unfavorable steric crowding.

Finally, reactions were carried out in the presence of CuCl, which is known to

complex phosphines. By adding CuCl to the reaction mixture, we hoped to increase the amount of mono-phosphine species present in the system, and thereby increase the rate of metathesis. Dramatic increases in catalyst activity resulted. The rates of metathesis by slower catalysts in the presence of CuCl rival that of the fastest catalysts studied, and previously inactive catalysts could now perform the ring-closing reaction. It may be the case that a bimetallic copper-ruthenium species is being formed in these reactions, analagous to other bimetallic catalysts which are currently under investigation.

Experimental

All manipulations were performed using standard Schlenk techniques. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). Solid organometallic compounds were transferred and stored in a nitrogen-filled Vacuum Atmospheres drybox. All ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in CD_2Cl_2 on a JEOL JNM-GX400 (399.80 MHz ^{1}H). All NMR tubes and septa used were dried under vacuum and stored in a drybox.

All solvents were vacuum transferred from sodium-benzophenone ketyl, except for chlorinated solvents (includiing CD_2Cl_2) which were vacuum transferred from CaH_2. All solvents were degassed by several freeze-pump-thaw cycles.

Diethyl diallylmalonate obtained from Aldrich was purified by repeated passage through activated alumina, until all discoloration was gone. The liquid was placed in a Kontes flask with a teflon stopcock and degassed by several freeze-pump-thaw cycles. The pure, degassed reagent was stored inside the drybox.

Lithium bromide and sodium iodide were dehydrated by placing the solid inside of a large Schlenk flask and heating at 150-160^{o}C under vacuum overnight. ^{1}H NMR spectra of the salts were obtained in d^{8}-THF to verify that all excess water had been removed. However, it should be mentioned that water does not harm the reactions or cause catalyst decomposition under reaction conditions.

$(PPh_3)_2Cl_2Ru(CHCHCPh_2)$ was synthesized from $Ru(PPh_3)_4Cl_2$ according to published procedures.[1] The bromine and iodine containing catalysts (**2b-5b**, **2c-5c**) were synthesized from their chlorine containing analogs (**2a-5a**) by Finklestein type chemistry, described below. All catalysts synthesized below can be used without further purification. If necessary, they can be recrystallized from CH_2Cl_2/pentane at low temperature.

Mass spectral analysis was performed at the Southern California Mass Spectrometry Facility at the University of California at Riverside. Elemental Analyses were performed by Quantitative Technologies Inc.

Synthesis of $(PCy_3)_2Cl_2Ru(CHCHCPh_2)$ (**2a**). Inside the drybox, 2.35 g (2.64 mmol) of $(PPh_3)_2Cl_2Ru(CHCHCPh_2)$ (**1**) were weighed into a 150 ml Schlenk flask equipped with stirbar and dissolved in 70 ml of CH_2Cl_2. 2.50 g (5.35 mmol) of tricyclohexylphosphine were added to the green solution. The flask was capped with a rubber septum, removed from the drybox, placed under argon on the Schlenk line, and stirred overnight at room temperature, during which time the solution changed from green to deep red. The solvent was removed *in vacuo*, and the product was washed liberally with pentane to remove excess phosphines. A small amount of benzene may also be added to help break up the solid. The solid is isolated by cannula filtration, and the washing procedure is repeated. After three or four washes, the remaining red solid is dried in vacuo.

It can easily be determined if there is any remaining starting material **1** by ^1H or ^{31}P NMR spectroscopy. If there is any starting material remaining, the above procedure can be repeated (using as much PCy_3 as deemed necessary) until it is all converted to product. 2.08 g (85% yield) of the desired product $(PCy_3)_2Cl_2Ru(CHCHCPh_2)$ were collected and stored inside the drybox. ^1H NMR: δ 19.07 (d, 1 H, Ru=C*H*, $^3J_{HH}$ = 11 Hz), 8.68 (d, 1 H, C*H*=CPh_2, $^3J_{HH}$ = 11 Hz). ^{31}P NMR: δ 37.59 (s). ^{13}C NMR: δ 289.3 (d of t, Ru=*C*, $^1J_{CH}$ = 150 Hz).

Synthesis of $(PCy_2Ph)_2Cl_2Ru(CHCHCPh_2)$ (3a). The procedure for the

synthesis of catalyst **2a** outlined above was followed, with the exception that a larger excess of dicyclohexylphenylphosphine was used (at least 2.5 eq) and the procedure had to be repeated three times to get complete conversion, due to the poorer equilibrium for phosphine exchange with PPh_3. The product was obtained as a reddish-brown solid. The yields in these cases were typically lower (ca. 60-75%). ^{1}H NMR: δ 19.16 (d, 1 H, Ru=C*H*, $^3J_{HH}$ = 11 Hz), 8.84 (d, 1 H, C*H*=CPh_2, $^3J_{HH}$ = 11 Hz). ^{31}P NMR: δ 45.48 (s). ^{13}C NMR: δ 290.9 (d of t, Ru=*C*, $^1J_{CH}$ = 149 Hz). FAB-HRMS: *m/z* calcd for $C_{51}H_{66}Cl_2P_2Ru$ (M^+) 912.3060. Found 912.3023.

Synthesis of $(P^iPr_3)_2Cl_2Ru(CHCHCPh_2)$ (4a). The procedure for the synthesis of catalyst **2a** was followed using triisopropylphosphine, and the product was obtained as a red solid. ^{1}H NMR: δ 19.19 (d, 1 H, Ru=C*H*, $^3J_{HH}$ = 11 Hz), 8.79 (d, 1 H, C*H*=CPh_2, $^3J_{HH}$ = 11 Hz). ^{31}P NMR: δ 46.71 (s). ^{13}C NMR: δ 290.7 (d of t, Ru=*C*, $^1J_{CH}$ = 152 Hz). FAB-HRMS: *m/z* calcd for $C_{33}H_{54}Cl_2P_2Ru$ (M^+) 684.2121. Found 684.2126.

Synthesis of $(P^iPr_2Ph)_2Cl_2Ru(CHCHCPh_2)$ (5a). The procedure for the synthesis of **3a** was followed using diisopropylphenylphosphine, and the product was obtained as a reddish-brown solid. ^{1}H NMR: δ 19.12 (d, 1 H, Ru=C*H*, $^3J_{HH}$ = 11 Hz), 8.95 (d, 1 H, C*H*=CPh_2, $^3J_{HH}$ = 11 Hz). ^{31}P NMR: δ 55.96 (s). ^{13}C NMR: δ 290.5 (d of t, Ru=*C*, $^1J_{CH}$ = 153 Hz). FAB-HRMS: *m/z* calcd for $C_{39}H_{50}Cl_2P_2Ru$ (M^+) 752.1808. Found 752.1840.

Synthesis of $(PCy_3)_2Br_2Ru(CHCHCPh_2)$ (2b). Inside the dry box, 200 mg of LiBr were weighed into a small Schlenk flask equipped with a stirbar and dissolved in 1-2 ml of THF. 100 mg of $(PCy_3)_2Cl_2Ru(CHCHCPh_2)$ (**2a**) were then added, followed by 3-4 ml of CH_2Cl_2 . The flask was capped with a rubber septum, removed from the dry box, and stirred for 3-4 hours on the Schlenk line under argon at room temperature. The solvents were removed *in vacuo*, and the product was extracted with 3 x 3 ml portions of benzene. The supernatant was collected by cannula filtration into a small

Schlenk flask, and the benzene was removed by a freeze-drying procedure in which the flask was placed in a bath of liquid nitrogen to freeze the solution, evacuated, and placed in an ice-water bath. The frozen benzene was sublimed at 0°C, usually overnight, and the reddish-brown solid was collected and stored inside the drybox. Freeze-drying the product in this manner reduces static such that the solid is easily collected. Yields are typically between 90-100%. ^{1}H NMR: δ 18.88 (d, 1 H, Ru=C*H*, $^3J_{HH}$ = 11 Hz), 8.79 (d, 1 H, C*H*=CPh$_2$, $^3J_{HH}$ = 11 Hz). ^{31}P NMR: δ 37.82 (s). ^{13}C NMR: δ 291.7 (d of t, Ru=*C*, $^1J_{CH}$ = 152 Hz). Anal. Calcd for $C_{51}H_{78}Br_2P_2Ru$: C, 60.41; H, 7.75. Found: C, 60.66; H, 7.70.

Synthesis of (PCy$_2$Ph)$_2$Br$_2$Ru(CHCHCPh$_2$) (3b). The procedure for the synthesis of catalyst **2b** was followed using 100 mg of (PCy$_2$Ph)$_2$Cl$_2$Ru(CHCHCPh$_2$) (**3a**), and the product was obtained as a reddish-brown solid. ^{1}H NMR: δ 18.93 (d, 1 H, Ru=C*H*, $^3J_{HH}$ = 11 Hz), 8.91 (d, 1 H, C*H*=CPh$_2$, $^3J_{HH}$ = 11 Hz). ^{31}P NMR: δ 44.81 (s). ^{13}C NMR: δ 293.2 (d of t, Ru=*C*, $^1J_{CH}$ = 149 Hz). FAB-HRMS: *m/z* calcd for $C_{51}H_{66}Br_2P_2Ru$ (M$^+$) 1002.2030. Found 1002.2088.

Synthesis of (P^{i}Pr$_3$)$_2$Br$_2$Ru(CHCHCPh$_2$) (4b). The procedure for the synthesis of catalyst **2b** was followed using 100 mg of (P^{i}Pr$_3$)$_2$Cl$_2$Ru(CHCHCPh$_2$) (**4a**), and the product was obtained as a reddish-brown solid. ^{1}H NMR: δ 19.03 (d, 1 H, Ru=C*H*, $^3J_{HH}$ = 11 Hz), 8.88 (d, 1 H, C*H*=CPh$_2$, $^3J_{HH}$ = 11 Hz). ^{31}P NMR: δ 46.21 (s). ^{13}C NMR: δ 293.3 (d of t, Ru=*C*, $^1J_{CH}$ = 152 Hz). FAB-HRMS: *m/z* calcd for $C_{33}H_{54}Br_2P_2Ru$ (M$^+$) 774.1091. Found 774.1078.

Synthesis of (P^{i}Pr$_2$Ph)$_2$Br$_2$Ru(CHCHCPh$_2$) (5b). The procedure for the synthesis of catalyst **2b** was followed using 100 mg of (P^{i}Pr$_2$Ph)$_2$Cl$_2$Ru(CHCHCPh$_2$ (**5a**), and the product was obtained as a reddish-brown solid. ^{1}H NMR: δ 18.94 (d, 1 H, Ru=C*H*, $^3J_{HH}$ = 11 Hz), 9.01 (d, 1 H, C*H*=CPh$_2$, $^3J_{HH}$ = 11 Hz). ^{31}P NMR: δ 54.59 (s). ^{13}C NMR: δ 293.1 (d of t, Ru=*C*, $^1J_{CH}$ = 147 Hz).

Synthesis of (PCy$_3$)$_2$I$_2$Ru(CHCHCPh$_2$) (2c). Inside the dry box, 200 mg

of NaI were weighed into a small Schlenk flask equipped with a stirbar and suspended in 1-2 ml of THF. 100 mg of $(PCy_3)_2Cl_2Ru(CHCHCPh_2)$ (**2a**) were then added, followed by 3-4 ml of CH_2Cl_2 . The flask was capped with a rubber septum, removed from the dry box, and stirred for 4-5 hours on the Schlenk line under argon at room temperature. The solvents were removed *in vacuo*, and the product was extracted with 3 x 3 ml portions of benzene. The supernatant was collected by cannula filtration into a small Schlenk flask, and the benzene was removed by the freeze-drying procedure described above for **2b**. The greenish-brown solid was collected and stored inside the drybox. Yields are typically between 90-100%. (Note: It has been found that if this reaction is stirred for too long, some catalyst decomposition can occur as evidenced by the appearance of the carbene coupling product Ph_2C=CH-CH=CH-CH=CPh_2 in the ^{1}H NMR spectrum. This can be removed by washing the product with pentane, although care should be taken as the catalyst is partially soluble in pentane.) ^{1}H NMR: δ 18.54 (d, 1 H, Ru=C*H*, $^3J_{HH}$ = 11 Hz), 8.81 (d, 1 H, C*H*=CPh_2, $^3J_{HH}$ = 11 Hz). ^{31}P NMR: δ 38.51 (s). ^{13}C NMR: δ 297.9 (d of t, Ru=*C*, $^1J_{CH}$ = 150 Hz).

Synthesis of $(PCy_2Ph)_2I_2Ru(CHCHCPh_2)$ (3c). The procedure for the synthesis of catalyst **2c** was followed using 100 mg of $(PCy_2Ph)_2Cl_2Ru(CHCHCPh_2)$ (**3a**), and the product was obtained as a greenish-brown solid. ^{1}H NMR: δ 18.52 (d, 1 H, Ru=C*H*, $^3J_{HH}$ = 11 Hz), 8.87 (d, 1 H, C*H*=CPh_2, $^3J_{HH}$ = 11 Hz). ^{31}P NMR: δ 42.78 (s). ^{13}C NMR: δ 299.6 (d of t, Ru=*C*, $^1J_{CH}$ = 149 Hz). FAB-HRMS: *m/z* calcd for $C_{51}H_{66}I_2P_2Ru$ (M^+) 1096.1773. Found 1096.1817.

Synthesis of $(P^iPr_3)_2I_2Ru(CHCHCPh_2)$ (4c). The procedure for the synthesis of catalyst **2c** was followed using 100 mg of $(P^iPr_3)_2Cl_2Ru(CHCHCPh_2)$ (**4a**), and the product was obtained as a greenish-brown solid. ^{1}H NMR: δ 18.62 (d, 1 H, Ru=C*H*, $^3J_{HH}$ = 11 Hz), 8.84 (d, 1 H, C*H*=CPh_2, $^3J_{HH}$ = 11 Hz). ^{31}P NMR: δ 45.74 (s). ^{13}C NMR: δ 299.8 (d of t, Ru=*C*, $^1J_{CH}$ = 152 Hz).

Synthesis of $(P^iPr_2Ph)_2I_2Ru(CHCHCPh_2)$ (5c). The procedure for the

synthesis of catalyst **2c** was followed using 100 mg of $(P^iPr_2Ph)_2Cl_2Ru(CHCHCPh_2$ (**5a**), and the product was obtained as a greenish-brown solid. ^1H NMR: δ 18.52 (d, 1 H, Ru=C*H*, $^3J_{HH}$ = 11 Hz), 8.92 (d, 1 H, C*H*=CPh$_2$, $^3J_{HH}$ = 11 Hz). ^{31}P NMR: δ 50.62 (s). ^{13}C NMR: δ 300.1 (d of t, Ru=*C*, $^1J_{CH}$ = 153 Hz).

Ring-closing metathesis of diethyl diallylmalonate. Reactions for kinetic studies were performed inside the dry box in screw-cap NMR tubes available from Wilmad, sealed with teflon lined screw caps. Product formation and diene disappearance were monitored by integrating the allylic methylene peaks, using mesitylene as an internal standard.

(1) Relative catalyst activity experiments. A 5X stock solution of the diene was made by diluting 1.21 ml diethyldiallylmalonate (5 mmol) with 3.79 ml of CD_2Cl_2, with 3.86 µl of mesitylene (5.55 µmol) added as an internal standard, and stored at -40°C inside the drybox freezer. All reactions were performed inside the drybox by weighing .005 mmol of catalyst into the screw-cap NMR tube and dissolving the solid in 400 µl CD_2Cl_2 added by gastight syringe. 100 µl of the 5X diene stock solution were added by gastight syringe and the tube was capped, shaken, removed from the drybox, and wrapped with Parafilm. The resulting concentration of catalyst is 0.010 M (1 eq) and diene is 0.20 M (20 eq).

(2) Phosphine dependence experiments. 145.2 µl of diethyl diallylmalonate was placed in a vial with teflon lined cap, and 37.2 µl of mesitylene were added. A 5X catalyst stock solution was made immediately prior to use by dissolving 37.3 mg (.05 mmol) of **6** in .5 ml CD_2Cl_2. A phosphine stock solution was made immediately prior to use by dissolving 14.0 mg of tricyclohexylphosphine (.05 mmol) in .5 ml CD_2Cl_2. The four reactions were set up simultaneously by adding 30.4 µl of diene/mesitylene solution to either 25, 50, 75, or 100 µl of phosphine solution, and CD_2Cl_2 was added to bring the total volume to 400 µl. 100 µl of catalyst stock solution were finally added. The NMR tubes were capped, removed from the dry box, wrapped well with Parafilm, and

placed in an oil bath preheated to 30°C. The final concentrations are: diene, 0.20 M (10 eq); catalyst, 0.020 M (1 eq); and phosphine, 0.005 M, 0.010 M, 0.015 M, or 0.020 M.

(3) Catalyst dependence experiments (no phosphine). The diene/mesitylene and catalyst **6** stock solutions were made exactly as above in (2) immediately prior to use. The catalyst stock solution was stored in the dry box freezer in a vial with teflon-lined screw cap, and the diene/mesitylene solution was stored in a vial with a teflon backed septum screw cap and removed from the dry box. The reactions were performed sequentially as follows. Inside the dry box, 25, 50, 75, or 100 μl of catalyst stock solution were added to the NMR tube, and CD_2Cl_2 was added to bring the volume to 400 μl. The NMR tube was sealed with a teflon backed septum screw cap, removed from the dry box, and wrapped well with Parafilm. The diene/mesitylene solution was added via gastight syringe immediately before the sample was dropped in the NMR probe, with the temperature preset to 25°C. The final concentrations are: diene, 0.20 M ; and catalyst, 0.005 M, 0.010 M, 0.015 M, or 0.020 M.

(4). Catalyst dependence experiments (excess phosphine). The diene/mesitylene, catalyst **6**, and tricyclohexylphosphine stock solutions were made exactly as above in (2) immediately prior to use. The reactions were set up simultaneously by adding 25 μl of phosphine solution to 25, 50, 75, and 100 μl of catalyst solution. CD_2Cl_2 was added to bring the volume to 470 μl, and 30.4 μl of diene/mesitylene solution were finally added. The NMR tubes were capped, removed from the dry box, wrapped well with Parafilm, and placed in an oil bath preheated to 30°C. The final concentrations are: diene, 0.20 M; phosphine, 0.005 M; and catalyst, 0.005 M, 0.010 M, 0.015 M, or 0.020 M.

Acknowledgments. Support has been provided by the National Science Foundation, Rohm and Haas, and the National Institute of Health.

Appendix

The explanation for the observed trend in catalyst activities presented in this chapter is based on the assumption that the halogens play little, if any, role in either stabilizing or destabilizing the Ru(IV) metallacyclobutane. Although there is little evidence to either support or refute this assertion, there is one study worth noting in which redox potentials are reported for an analagous series of ruthenium chlorides and bromides.[29]

In particular, the authors' data shows that for the IV/III redox couple, the chloride compounds are *easier* to reduce than their bromide analogs; however, the chloride compounds are actually *harder* to reduce for the III/II redox couple. One interpretation of these results is that the chlorides are more electron donating for the lower oxidation states, and more electron withdrawing for the higher oxidation states—possibly another facet of the "hard" and "soft" interpretation of chemical bonding, with Ru(II) behaving as a "soft" metal center and Ru(IV) as a "hard" metal center. Regardless of the interpretation, the net effect is that for oxidation of Ru(II) to Ru(IV), the chloride compounds are only slightly harder to oxidize than their bromide analogs, since the opposing effects of the II/III and III/IV redox couples substantially dampen the expected differences caused by variation of the halides.

References and Notes

[1]Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3974-3975.

[2]Wu, Z.; Benedicto, A. D.; Grubbs, R. H. *Macromolecules* **1993**, *26*, 4975-4977.

[3]Wu, Z.; Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 5503-5511.

[4]Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858-9859.

[5]Hillmyer, M. A.; Laredo, W. R.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 6311-6316.

[6](a) Holder, S.; Blechert, S. *Synlett.* **1996** (June), 505-506. (b) Crimmins, M. T.; King, B. W. *J. Org. Chem.* **1996**, *61*, 4192-4193. (c) Garro-Helion, F.; Guibe, F. *Chem. Commun.* **1996**, 641-642. (d) Fu, G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9856-9857.

[7](a) Furstner, A.; Langemann, K. *J. Org. Chem.* **1996**, *61*, 3942-3943. (b) Miller, S. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 5855-5856. (c) Borer, B.; Deerenberg, S.; Bieraugel, H.; Pandit, U. K. *Tetrahedron Letters*, **1994**, *35*, 3191-3194.

[8]Miller, S. J.; Kim, S.-H.; Chen, Z.-R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 2108-2109.

[9]Kim, S.-H.; Bowden, N.; Grubbs, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 10801-10802.

[10]For a recent review of olefin metathesis catalysts in organic synthesis, see Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446-452.

[11]Bowden, N.; Grubbs, R. H. Unpublished results.

[12]By propagating species, we refer to the resting state of the catalyst as determined by NMR spectroscopy, which is the species $(PR_3)_2X_2Ru{=}CH_2$ in this ring-closing metathesis reaction.

[13]For background reading on the steric and electronic properties of phosphines, see (a) Brown, T. L.; Lee, K. J. *Coord. Chem. Rev.* **1993**, *128*, 89-116. (b) Wilson, M. R.;

Woska, D. C.; Prock, A.; Giering, W. P. *Organometallics*, **1993**, *12*, 1742-1752. (c) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313-348.

[14]The same trend is observed for the polymerization of norbornene by the compounds $(PPh_3)_2X_2Ru=CH-CH=CPh_2$ (X=Cl, Br, I). To further explore the relative electron withdrawing abilities of the X ligands, we synthesized the two compounds $(PPh_3)_2(Cl)(X)Ru=CH-CH=CPh_2$ ($X=CH_3CO_2$, CF_3CO_2). We found that the trifluoroacetate containing catalyst polymerized norbornene at least ten times faster than the acetate containing catalyst, and therefore conclude that more electron withdrawing X groups produce more active catalysts.

[15]Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100-110.

[16] It may be argued that breakdown of the metallacycle is the rate determining step, in which case our differential equations are only slightly altered, and still in agreement with our empirically derived rate expression. However, we believe that metallacycle formation is rate determining, as it corresponds to a formal two electron oxidation of the ruthenium center.

[17]We also believe that the second metathesis step, the intramolecular reaction to form the cyclized product, is faster than the first, intermolecular metathesis, due to the decreased activation entropy. This is evidenced by the fact that we never observe the intermediate which preceeds the cyclization step even when excess phosphine is added, as opposed to the cyclization of 1,7-octadiene to cyclohexene, during which this intermediate is observed by ^1H NMR in the presence of excess phosphine.

[18]The possiblity that the diene chelates the metal center to form a 16-electron complex cannot be ruled out, although entropically this seems unlikely without any predisposition of the diene towards chelation as in the case of butadiene, norbornadiene, or 1,5-cyclooctadiene.

[19]Chemical exchange decoupling of the phosphines has been ruled out, since the

ruthenium-bound phosphine peak is not averaged with the unbound phosphine peak in the ^{31}P NMR spectrum when excess PCy_3 is added. In fact, the ^{1}H and ^{31}P NMR resonances for **6** remain unchanged from 20°C to 80°C in C_6D_6 (catalyst decomposition is significant at this temperature) in both the presence and absence of excess PCy_3, indicating relatively high barriers to both phosphine exchange and carbene rotation.

[20]Moers, F. G.; Langhout, J. P. *J. Inorg. Nucl. Chem.* **1977**, *39*, 591-593.

[21]Brown, L. D.; Barnard, C. F. J.; Daniels, J. A.; Mawby, R. J.; Ibers, J. A. *Inorg. Chem.* **1978**, *17*, 2932-2935.

[22]For a brief discussion of the principle of microscopic reversibility, see for example Laidler, K. J. *Chemical Kinetics*, 2nd ed.; McGraw-Hill: New York, 1965; pp 110-112.

[23]For a brief discussion of the ligand *trans*-influences and the kinetic *trans*-effect, see for example Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science: Mill Valley, 1987; pp 241-244, and references therein.

[24]Garlatti, R. D.; Tauzher, G. *Inorg. Chim. Acta* **1988**, *142*, 263-267.

[25](a) Seibles, L.; Deutsch, E. *Inorg. Chem.* **1977**, *16*, 2273-2278. (b) Trogler, W. C.; Stewart, R. C.; Marzilli, L. G. *J. Am. Chem. Soc.* **1974**, *96*, 3697-3699. (c) Tauzher, G.; Dreos, R.; Costa, G.; Green, M. *J. Chem. Soc., Chem. Commun.* **1973**, 413-414. (d) Crumbliss, A. L.; Wilmarth, W. K. *J. Am. Chem. Soc.* **1970**, *92*, 2593-2594.

[26]For a discussion of molybdenum and tungsten catalyst activities, see *Progress in Inorganic Chemistry,* Lippard, S. J., Ed.; Wiley: New York, 1991; Vol. 39, and references therein.

[27]*Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: New York, 1987; Vol. 5.

[28]It is likely that there is some degree of halogen exchange when catalysts containing Br or I are used. However, complexation of free phosphine is undoubtedly the predominant

effect, since Cl containing compounds such as **2c** are activated by addition of CuCl to the extent that the ring-closing reaction is too fast to study under the standard reaction conditions.

[29]Duff, C. M.; Heath, G. A. *J. Chem. Soc. Dalton Trans.* **1991**, 2401-2411.

Chapter 2:
Synthesis and Investigation of Homo- and Heterobimetallic Ruthenium Olefin Metathesis Catalysts Exhibiting Increased Activities

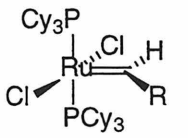
Abstract

The previously reported ruthenium carbenes $(PCy_3)_2Cl_2Ru{=}CHR$ (R = $CHCPh_2$ **1a**, Ph **1b**) react with the bridged-chloride dimers [(*p*-cymene)$RuCl_2]_2$, [(*p*-cymene)$OsCl_2]_2$, and [(^{t}Bu$_2$Cp)$RhCl_2]_2$ to quantitatively form the bimetallic, bridged-chloride ruthenium carbenes **2a,b**, **4a,b**, and **6a,b** and one equivalent of each corresponding piano-stool complex. In the ring-opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene, catalyst activity was found to increase in the order M = Ru < Os < Rh for the ancillary metal centers, with all of the bimetallic catalysts having higher activities than **1a,b**. The kinetics of ROMP of the derivatized norbornene **9** were studied using catalyst **2a**, and the data support an associative mechanism of olefin metathesis, contrary to the mechanism of olefin metathesis proposed for the parent catalysts **1a,b**.

Introduction

The olefin metathesis reaction has found a wide variety of applications in both organic and polymer synthesis. Beginning with the simple ring-closing metathesis (RCM) of α,ω-dienes to cycloalkenes,[1] additional unsaturation in the form of alkynes[2] or cycloalkenes[3] can be incorporated in a substrate to make several different molecular geometries accessible. The ring-opening metathesis polymerization (ROMP) of cycloalkenes has also found several applications in the synthesis of internally and terminally functionalized polymers,[4] electroluminescent and conducting polymers,[5] and sidechain liquid-crystalline polymers.[6] In conjunction with research in these areas, our group is also developing transition metal alkylidene catalysts which are suitable for these applications.[7]

The ruthenium diphenylvinyl alkylidene (**1a**) was the first example of a well-defined, single component ruthenium catalyst that is active for the metathesis of low-strain cyclic and acyclic olefins.[7c] The slow rate of initiation (relative to propagation) of **1a**, however, prompted the development of the ruthenium benzylidene **1b**.[7a,b] A comparison of these compounds showed that **1b** initiates metathesis significantly faster than **1a**, to the point where the rate of initiation is comparable to or faster than the rate of propagation. In addition, it was found that **1b** reacts with terminal olefins to produce new alkylidenes, such as **1c** and **1d**, that are easily isolated.[7a,b] However, because both **1a** and **1b** produce the same propagating species upon initiation, these types of modifications are limited in their ability to significantly alter catalyst activity.



1a: R = $CHCPh_2$
1b: R = Ph
1c: R = H
1d: R = Me

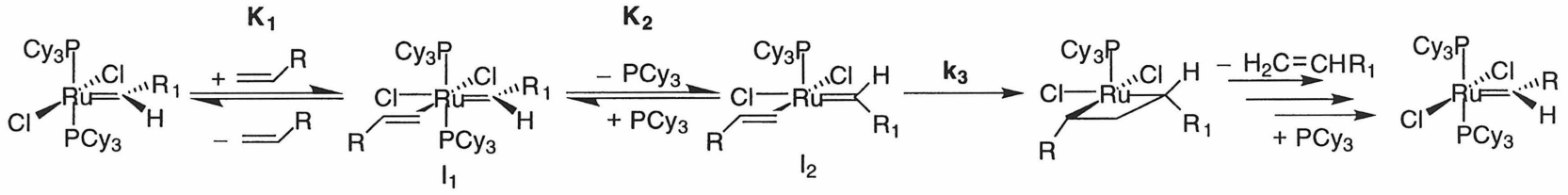
Several ruthenium vinyl alkylidenes containing different phosphines and halogens have been syntheszied, and it was found that the original catalysts **1a** and **1b** containing chlorides and tricyclohexylphosphines are the most active in the ring-closing metathesis of diethyl diallylmalonate.[8] Mechanistic studies indicate that, during metathesis, a phosphine reversibly dissociates from the ruthenium center. In accordance with this, it was found that addition of a phosphine scavenger such as CuCl activates these catalysts. Although faster turnover rates can be achieved in this manner, the catalyst lifetimes under these conditions are relatively short.[8]

This contribution introduces a new class of well-defined, single-component ruthenium catalysts which are in some cases up to 80 times more active than the class of catalysts represented by **1a** and **1b**. These compounds are synthesized by a surprisingly general reaction that allows for several different derivatives to be prepared. In addition, the stability of these compounds is addressed, and a mechanism for olefin metathesis by these catalysts is presented.

Results and Discussion

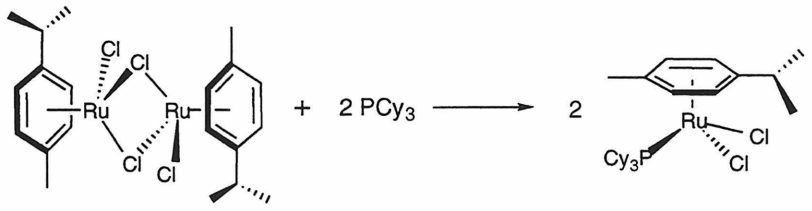
Synthesis of Bimetallic Ruthenium Alkylidenes. Previously, we proposed a mechanism for olefin metathesis by catalysts **1a** and **1b**.[8] The major pathway involves a pre-equilibrium for olefin binding and phosphine dissociation, followed by formation of a 14-electron metallacyclobutane, which is believed to be the rate determing step. Subsequent breakdown of the metallacyclobutane and displacement of the product olefin by phosphine finish the catalytic cycle (Scheme 1). We have found that the equilibrium for olefin binding and phosphine dissociation is very poor, to the extent that even in the presence of a large excess of olefin, no free phosphine can be detected. (An exception to this is that during the ROMP of cyclobutenes functionalized with coordinating functional groups, free phosphine is often observed due to coordination from the pendant polymer.[4a]) Additionally, this pre-equilibrium makes the *effective* catalyst order

Scheme 1



approximately 1/2, such that the rate of olefin metathesis depends upon the square-root of the catalyst concentration. In the interests of designing a more active catalyst, we therefore reasoned that a compound containing only one phosphine and a hemilabile chelating ligand would make the rate equation first-order in catalyst concentration and provide a group that dissociates easily.

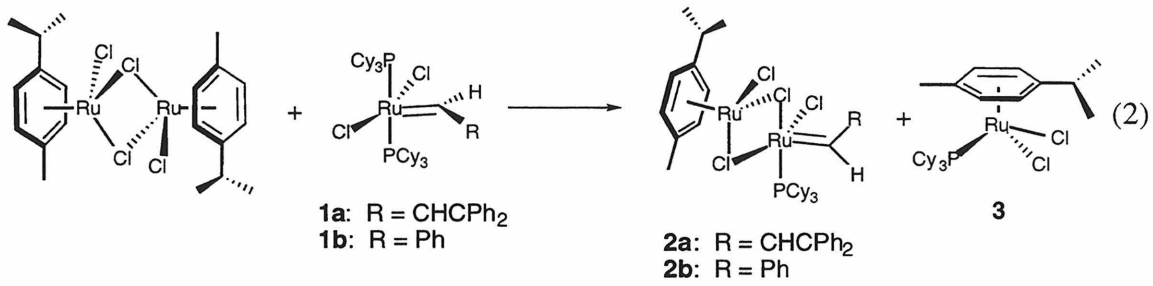
We have also reported the use of CuCl as a phosphine scavenger to increase catalyst activity.[8] Addition of CuCl to solutions of several catalysts containing different phosphines and halogens in the presence of an olefin substrate was found to increase the respective activities in all cases. Although CuCl is well-known to coordinate phosphines, the resulting $CuCl{\bullet}PR_3$ complex is ill-defined, and is believed to have an oligomeric structure in solution.[9] Furthermore, it is difficult to add one equivalent of CuCl due to the heterogeneous nature of the reaction. To further study this effect, we looked for compounds that would react quickly and cleanly with phosphines in a stoichiometric fashion. For example, the reaction of phosphines with transition metal dimers containing bridging chloride ligands has been well established.[10] The reaction of tricyclohexylphosphine with $[Ru(p\text{-cymene})Cl_2]_2$ is shown in Equation (1).



(1)

Upon addition of one equivalent of $[Ru(p\text{-cymene})Cl_2]_2$ to a solution of either **1a** or **1b** in benzene at room temperature, the transformation shown below in eq. 2 proceeds cleanly and quantitatively, as determined by ^1H and ^{31}P NMR spectroscopy. While the $[Ru(p\text{-cymene})Cl_2]_2$ dimer reacts with one equivalent of phosphine to generate the three-legged piano stool compound (**3**) as expected, the remaining fragment chelates the

ruthenium alkylidene *via* the bridging chloride ligands and thus serves to stabilize it towards decomposition.



(2)

These two products can be easily separated by washing the crude solids with benzene or a mixture of acetone and approximately 5-10% benzene. The alkylidene is isolated as either a yellow-orange (**2a**) or yellow-green (**2b**) analytically pure solid in 60-65% yield, and can be recrystallized from either dichloromethane/pentane or toluene/pentane if necessary. These bimetallic complexes are soluble in chlorinated solvents (dichloromethane, chloroform, chlorobenzene, *o*-dichlorobenzene) and sparingly soluble in aromatic solvents (benzene, toluene).

The bimetallic alkylidene products have been characterized by ^{1}H and ^{31}P NMR spectroscopy (Figure 1). The ^{31}P NMR spectrum of **2b** shows a single sharp peak at 48.68 ppm, and the ^{1}H NMR spectrum has several interesting features. The alkylidene H_{α} proton is coupled to the ^{31}P nucleus, indicating that the alkylidene moiety is coplanar with the Ru-P bond, contrary to what is observed for **1a** and **1b**. The four aromatic protons on the *p*-cymene ligand are inequivalent, resolved as four separate doublets. Likewise, the two methyl groups on the *p*-cymene ligand are inequivalent as well, resolved as two separate doublets. The *p*-cymene ligand is thus bound in an asymmetric environment, such that **2b** is chiral.

Reaction of $[Ru(benzene)Cl_2]_2$ with **1a** or **1b** produces the expected bimetallic alkylidenes only transiently as detected by ^{1}H NMR spectroscopy, followed by decomposition to produce the corresponding alkylidene coupling products—1,1,6,6-

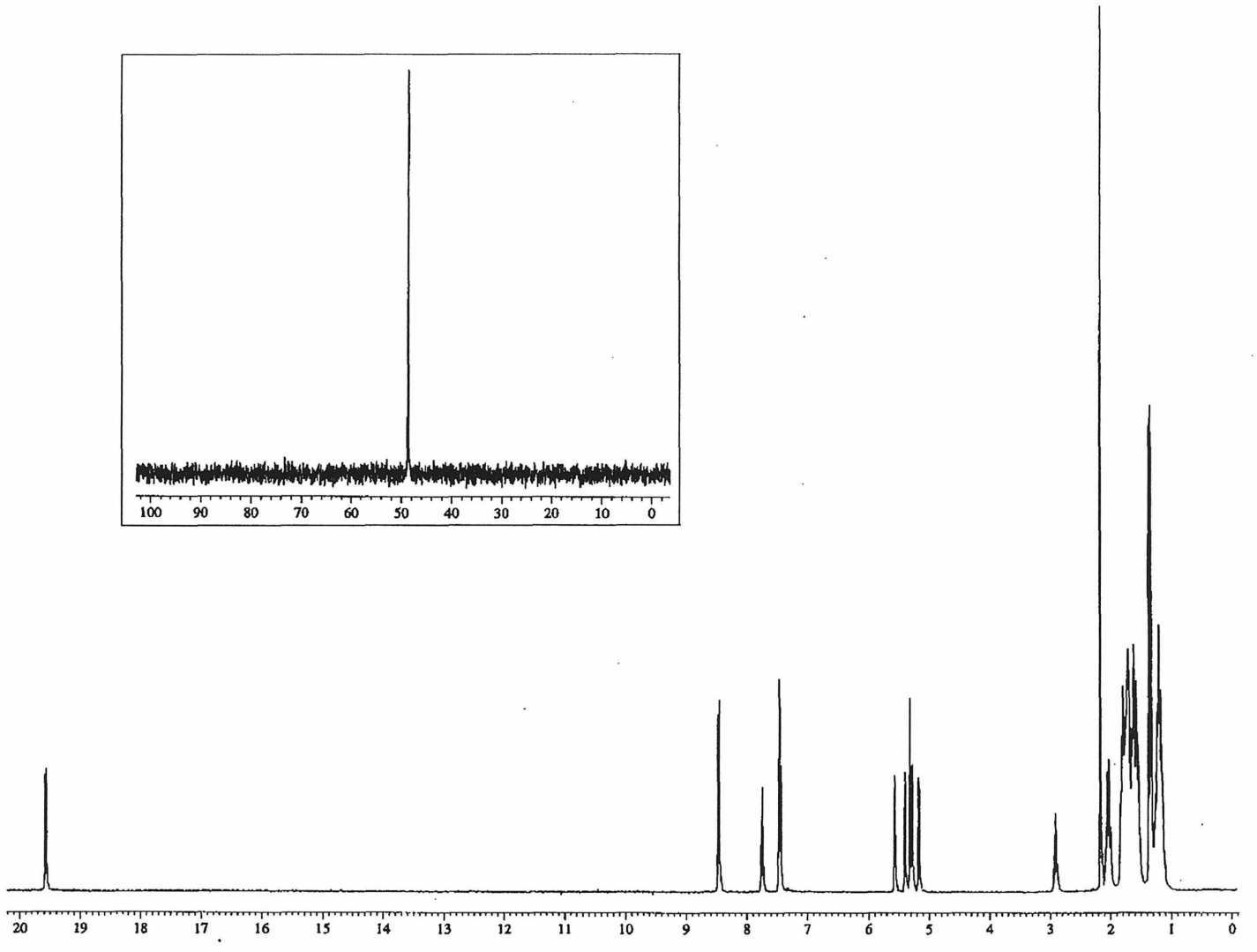
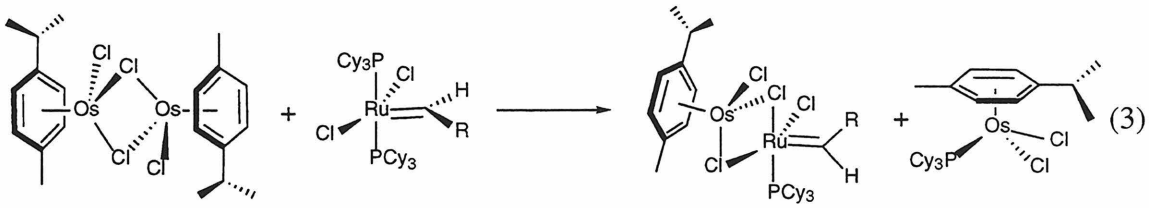


Figure 1: ^{1}H and ^{31}P (inset) NMR spectra of **2b** in CD_2Cl_2.

tetraphenyl-1,3,5-hexatriene for **1a** and stilbene for **1b**. Likewise, bimolecular decomposition products are also observed upon reaction of the ruthenium methylidene (**1c**) or ethylidene (**1d**) with [Ru(*p*-cymene)Cl_2]$_2$. In the particular case of the ruthenium methylidene (**1c**), a ruthenium-ethylene complex is observed in the ^{1}H NMR spectrum. Therefore, although the reaction in eq. 2 proceeds for many ruthenium dimers and alkylidenes, the stability of the resulting products appears to depend dramatically upon the steric bulk of the ligand sphere. These results prompted us to explore the generality of this reaction and determine if this methodology can be extended to complexes of other transition metals.

[Os(*p*-cymene)Cl_2]$_2$ reacts with **1a** and **1b** in an analagous fashion (eq. 3). The reaction proceeds cleanly and quantitatively to form the heterobimetallic osmium-ruthenium alkylidenes **4a** amd **4b**. The products of this reaction are more difficult to separate than the products of the



1a: R = CHCPh$_2$
1b: R = Ph

4a: R = CHCPh$_2$
4b: R = Ph

(3)

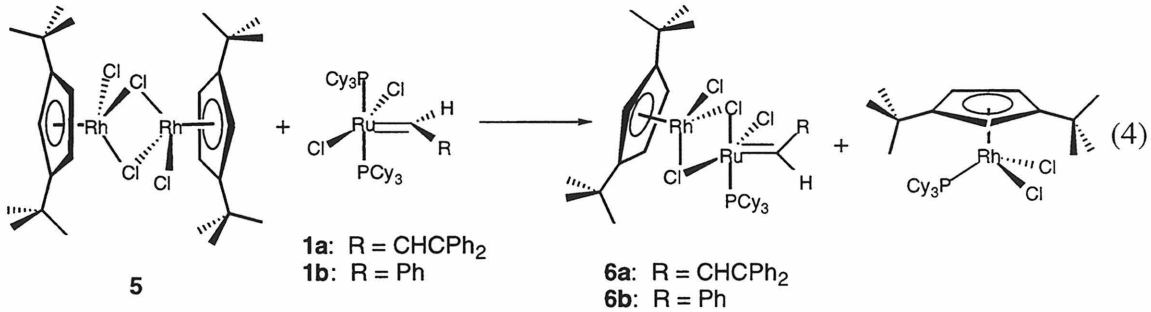
reaction with [Ru(*p*-cymene)Cl_2]$_2$, due to the increased solubility of **4a** and **4b** in organic solvents. However, **4a** and **4b** can be isolated from the crude solids in moderate yield by preferential recrystallization from a mixture of toluene/pentane. The crystals can be washed with a benzene/pentane mixture to give a 40% isolated yield of analytically pure products. The vinylalkylidene **4a** is isolated as a yellow solid, and the benzylidene **4b** is isolated as a green solid. Their corresponding ^{1}H and ^{31}P NMR sprectra are similar to those for **2a** and **2b**, with only slight differences in chemical shifts.

The isoelectronic compounds [Co(Cp*)Cl_2]$_2$, [Rh(Cp*)Cl_2]$_2$ and [Ir(Cp*)Cl_2]$_2$ all

react with **1a** and **1b** in a similar fashion; however, the heterobimetallic alkylidenes are not stable. The reactions of $[Co(Cp^*)Cl_2]_2$ and $[Rh(Cp^*)Cl_2]_2$ with **1b** are slower than the reactions in eqs. (1) and (2)—the alkylidene products initially build up to a steady-state concentration, followed by decomposition to produce the carbene coupling products described above. When the iridium dimer is used, the bimetallic alkylidene is formed very rapidly, but decomposes with a half-life of approximately thirty minutes. These observations prompted the use of bulkier cyclopentadienyl ligands to stabilize the alkylidenes towards decomposition.

Lithium *tert*-butyl cyclopentadienide (Li(^{t}BuCp)) reacts with $RhCl_3 \cdot xH_2O$ in refluxing methanol to afford the dimer $[Rh(^t BuCp)Cl_2]_2$. $[Rh(^t BuCp)Cl_2]_2$ reacts rapidly with **1a** or **1b** to form the corresponding rhodium-ruthenium alkylidenes quantitatively, but these products decompose with a half-life of approximately 4 hrs at room temperature. Thus, while the bulkier, less electron-rich ^{t}BuCp ligand increases the rate of the dimer-forming reaction, it affords only limited product stability towards bimolecular decomposition.

Di-*tert*-butyl cyclopentadiene ($^t Bu_2CpH$) reacts with $RhCl_3 \cdot xH_2O$ to afford the dimer $[Rh(^t Bu_2Cp)Cl_2]_2$, (**5**) which can be recrystallized from ethanol to yield an analytically pure red solid. Reaction of $[Rh(^t Bu_2Cp)Cl_2]_2$ with **1a** and **1b** proceeds cleanly and quantitatively to form the corresponding rhodium-ruthenium alkylidenes **6a** and **6b** (eq. 4). The products of this



(4)

reaction are easily separated by washing the crude solids with acetone, to yield **6a** and **6b**

as analytically pure yellow and red solids respectively . The ^1H NMR spectrum indicates that the two *tert*-butyl groups on the cyclopentadiene ligand are equivalent, as are the two adjacent cyclopentadienyl protons. Otherwise, the ^1H and ^{31}P NMR spectra are similar to those for the other bimetallic alkylidenes. **6a** and **6b** decompose slowly in solution at room temperature, having a half-life of approximately one day

The following conclusions can be drawn from these results. First, the generality of the reaction to form bimetallic species extends to bridging chloride dimers of osmium, cobalt, rhodium, and iridium, as well as ruthenium. Second, there is a rigorous steric requirement imposed upon both the carbene moiety and the ligands bound to the ancillary metal center to prevent bimolecular decomposition of the bimetallic alkylidenes. Stability of the homobimetallic ruthenium alkylidenes increases as H < Me < Ph ≈ $CHCPh_2$ for the carbene substituents, and (benzene) < (*p*-cymene) for the arene ligands. The heterobimetallic rhodium-ruthenium alkylidenes show a similar trend: in order of increasing stability, Cp* < ^{t}BuCp < ^{t}Bu$_2$Cp. The rate of reaction increases in the order Cp* < ^{t}BuCp ≈ ^{t}Bu$_2$Cp, which can be attributed either to the increased steric bulk or the decreased electron-donating ability of the *tert*-butyl substituted ligands.

General Stability of Bimetallic Ruthenium Alkylidenes. The bimetallic compounds **2a,b**, **4a,b**, and **6a,b** are stable to air in the solid state. The ruthenium and osmium dimers **2a,b** and **4a,b** are also stable for days in a solution of dichloromethane under inert atmosphere. In a solution of chloroform under air, it was found that **2a** decomposed to produce 3,3-diphenyl propenal—the result of oxidation of the carbene fragment. (The ruthenium containing products are unknown.) The bimetallic alkylidenes are also stable to water, as demonstrated by the addition of D_2O to solutions of the compounds in a mixture of 1:1 CD_2Cl_2/d_8-THF. Upon heating in CD_2Cl_2 or a mixture of CD_2Cl_2/C_6D_6 the alkylidenes decompose to produce the piano-stool compounds (cf. **3**) and the alkylidene coupling products.

Activities of Bimetallic Ruthenium Alkylidenes. The metathesis activities of

the bimetallic catalysts were compared to those of the parent catalysts **1a** and **1b** for the ROMP of 1,5-cyclooctadiene (COD). COD was chosen as the substrate because the rates of polymerization were slow enough to be studied by ^{1}H NMR spectroscopy—it was found that the previously studied RCM of diethyl diallylmalonate was too fast to follow by NMR when the bimetallic catalysts were used.

The kinetics of the ROMP of COD by the **1a** and **1b** are complex, similar to what was previously observed for the RCM of diethyl diallylmalonate.[8] When the bimetallic catalysts are used, however, the kinetics are pseudo-first order with respect to COD (Figure 2). In order to compare the relative activities of the bimetallic catalysts to the parent catalysts, the kinetics of **1a** and **1b** were approximated by first-order curve fits such that (artificial) pseudo-first order rate constants could be extracted, which in fact *overestimate* the rates of metathesis by these catalysts. The relative rate constants k_{rel} obtained in this manner are summarized in Table 1.

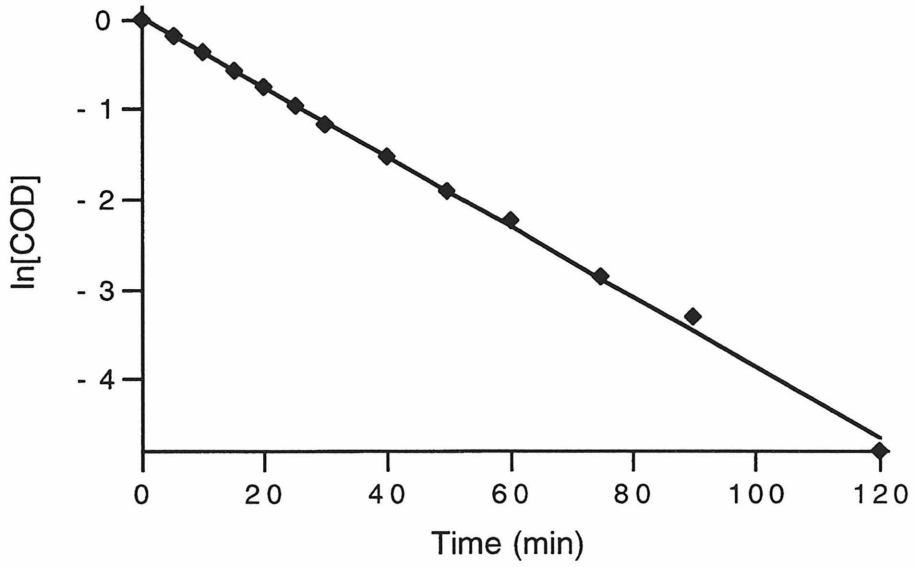
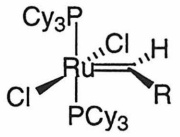
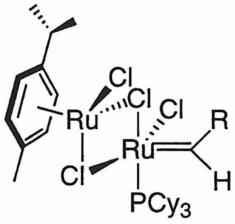
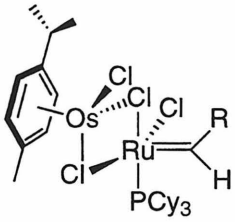
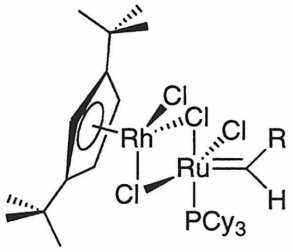


Figure 2: Log plot of [COD] vs time for catalyst **2b** in CD_2Cl_2 at 16°C where $[COD]_0$ = 0.730 M and [**2b**] = 3.25 mM. The filled diamonds are the data points and the solid line is the best linear fit. Slope = -0.0388±0.0006, intercept = 0.0218±0.0323, linear correlation coefficient = 0.999.

Table 1: Activities of Bimetallic Ruthenium Catalysts in the ROMP of 1,5-Cyclooctadiene

Structure	Compound	k_{rel}[a]
	**1a**: R = $CHCPh_2$	1
	1b: R = Ph	14
	**2a**: R = $CHCPh_2$	22
	2b: R = Ph	34
	**4a**: R = $CHCPh_2$	37
	4b: R = Ph	41
	**6a**: R = $CHCPh_2$	72
	6b: R = Ph	86

[a]Conditions: [catalyst] = 3.25 mM, [COD] = 0.73 M in CD_2Cl_2, temperature = 16.0°C.

From Table 1, it is apparent that the activities of the bimetallic catalysts are substantially greater than those of the parent catalysts. The ruthenium catalysts **2a,b** exhibit rates approximately 20 times that of catalyst **1a**. When the analagous osmium catalysts **4a,b** are used, the reaction rate increases further—approximately 40 times that of **1a**. The rhodium-containing catalysts **6a,b**, however, show the most dramatic increase in catalyst activity by far, exhibiting relative rates that are *approximately 80 times* that of **1a**!

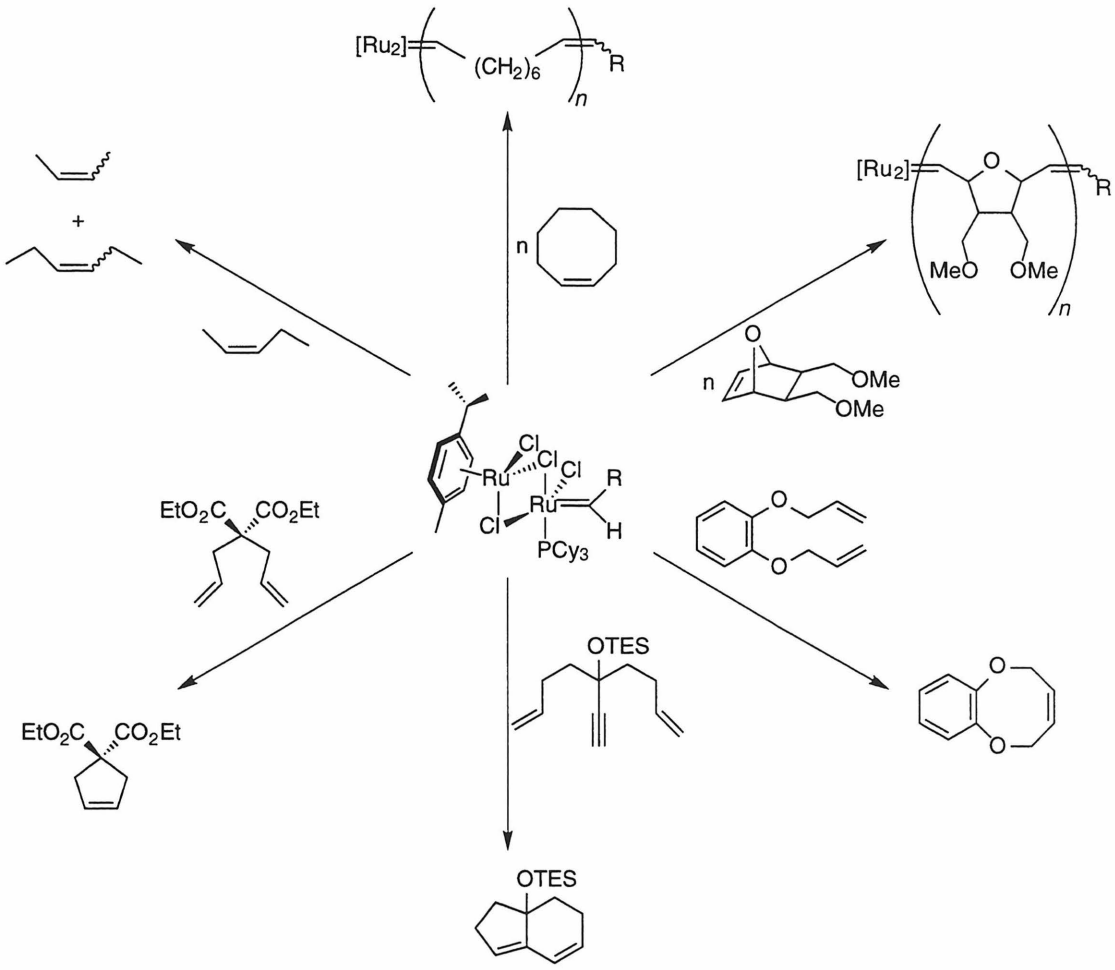
Comparing k_{rel} for **1a** and **1b** (Table 1), it is once again demonstrated that the vinyl alkylidene suffers from poorer initiation. Initiation is also found to be poorer for the vinyl alkylidenes **2a**, **4a**, and **6a** when compared to the benzylidenes **2b**, **4b** and **6b** respectively ; however, the differences in k_{rel} for the bimetallic catalysts are not nearly as large as that for **1a** and **1b**.

Reactivity of Bimetallic Ruthenium Alkylidenes. The bimetallic catalysts **2a,b**, **4a,b**, and **6a,b** perform all of the standard olefin metathesis reactions that are catalyzed by **1a,b** (Scheme 2). The RCM of diethyl diallylmalonate and the *ene-yne-ene* substrate proceed to quantitative conversion in less than 5 minutes at room temperature using 5 mol % of catalyst **2b**. The metathesis of *cis*-2-pentene (0.38 M in benzene) by **6b** (0.5 mol %) proceeds with an initial rate of 10 turnovers *per minute*, as compared with **1a** which exhibits a rate of 26 turnovers *per hour* under similar conditions.[7] Furthermore, because of their enhanced activities, it is often the case that much lower catalyst loadings can be used. For example, in the previously studied RCM of diallyl catechol to form the eight-membered cycloolefin[11] (Scheme 2), as little as 0.5 mole percent of **2b** can be used with no decrease in the yield of cyclized product.

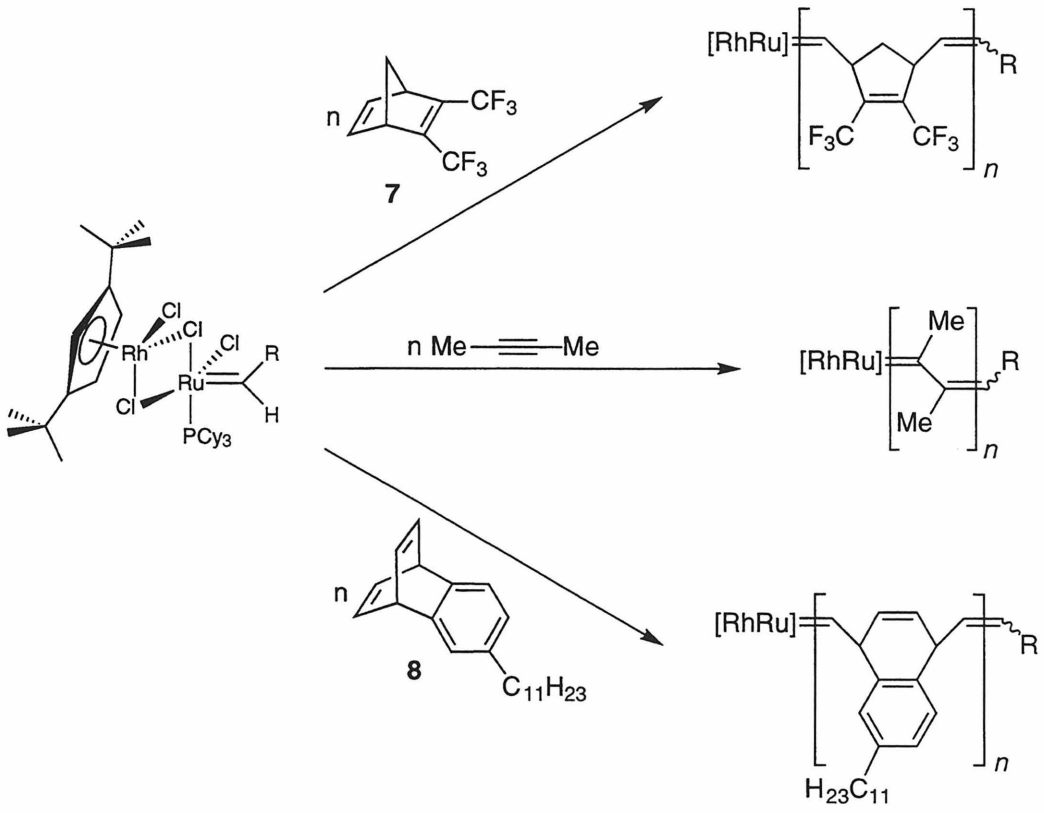
The bimetallic catalysts can also be used for reactions that proceed too slowly to make them feasible using catalysts **1a** and **1b**. For instance, when attempts are made to polymerize hexafluorodimethyl norbornadiene (**7**) or the alkyl substituted benzobarrelene (**8**) with catalysts **1a,b**, the reactions proceed so slowly (on the order of days to weeks) at

room temperature that catalyst decomposition becomes a problem. Furthermore, heating

Scheme 2



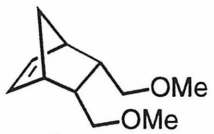
Scheme 3


n
CF3
CF3
7
[RhRu]
R
F3C
CF3
n
Cl
Cl
Cl
Rh
Ru
R
Cl
H
PCy3
n Me
Me
[RhRu]
Me
R
Me
n
n
8
C11H23
[RhRu]
R
n
H23C11

these reactions results in a faster rate of catalyst decomposition. When catalysts **2a,b**, or especially **6a,b**, are employed, the rate of polymerization is sufficient to make these reactions much more practical (Scheme 3). Even 2-butyne can be polymerized to an appreciable extent when catalyst **6a** or **6b** is used.

Mechanism of Olefin Metatethesis by Bimetallic Ruthenium Alkylidenes. For the bimetallic catalysts discussed above, the structures and resulting activities suggest that the ancillary metal center may be acting as a hemilabile chelating group, such that the tricyclohexylphosphine may not dissociate during olefin metathesis. Furthermore, the pseudo-first order kinetics observed for the ROMP of 1,5-cyclooctadiene by these catalysts also suggest a mechanism that is associative in nature.

During the activity studies summarized in Table 1, small deviations from first-order behavior were observed in a few cases. This can be attributed to bimolecular decomposition of the propagating species during the reaction, presumably due to the lack of steric bulk adjacent to the ruthenium metal center upon initiation with COD. It should be noted that even in these cases, the kinetics did not deviate far from ideal first-order behavior. However, in order to decrease such decomposition, substrate **9** was used in the following studies.



9

The polymerization of **9** with catalyst **2b** shows good pseudo-first order kinetics with respect to substrate concentration, as shown in Figure 3. A plot of k_{obs} vs. catalyst concentration exhibits a linear relationship (Figure 4), and the plot of $\ln(k_{obs})$ vs. $\ln[Ru_2]$ (not shown) has a slope of one, indicating that the rate expression is first-order in catalyst concentration. Dependence of the rate upon phosphine concentration could not be tested

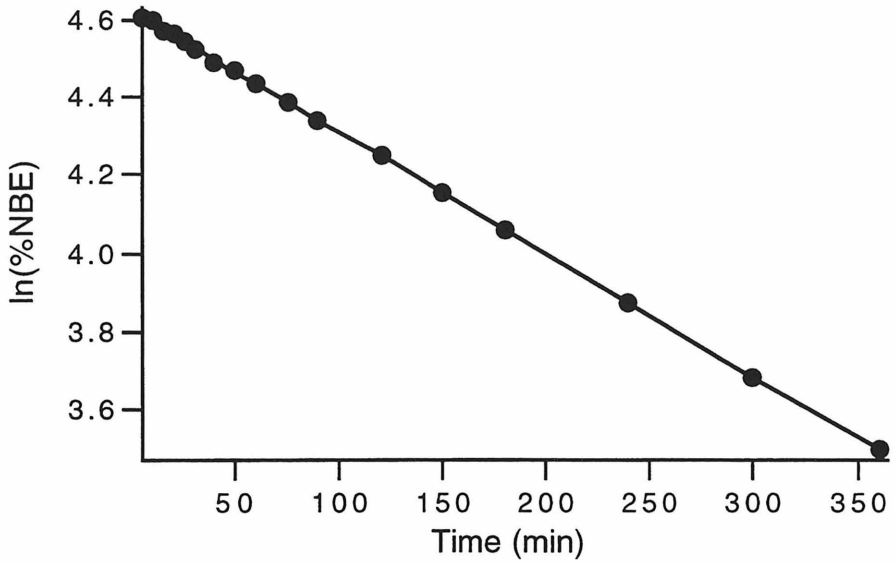


Figure 3: Plot of ln[**9**] vs time for catalyst **2a** in the polymerization of **9** in CD_2Cl_2 at 20°C, where [**2a**] = 3.54 mM. The monomer concentration was expressed in terms of percentage remaining. The filled circles are the data points and the solid line is the linear fit. Slope = (3.13±0.01) x 10^{-3}, intercept = 4.62±0.01, linear correlation coefficient = 1.000.

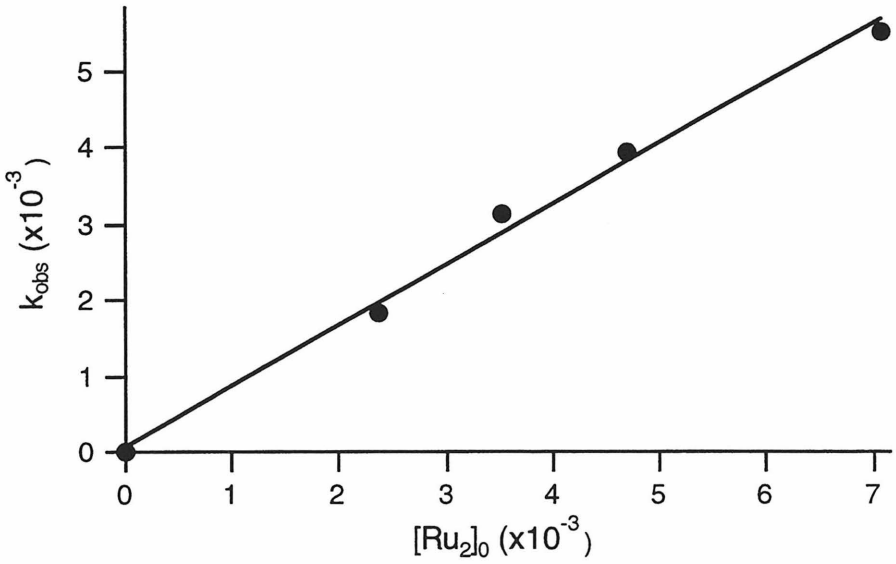
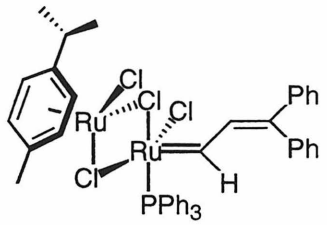


Figure 4: Plot of k_{obs} vs catalyst concentration for catalyst **2a** in the polymerization of **9** in CD_2Cl_2 at 20°C. The filled circles are the data points and the solid line is the linear fit. Slope = 0.793±0.040, intercept = (8.07±16.9) x 10^{-5}, linear correlation coefficient = 0.996.

because tricyclohexylphosphine slowly reacts with **2b** to produce **1b** and **3**. However, there is nothing in the kinetics to suggest that any phosphine dependence exists.

The resulting rate equation, $-d[\mathbf{9}]/dt = k[\text{Catalyst}][\mathbf{9}]$ is consistent with an associative mechanism for olefin metathesis by these catalysts. This is supported experimentally by the fact that the compound **10**, employing a triphenylphosphine ligand, does *not* show activity for the metathesis of low ring-strain cyclic or acyclic olefins, similar to the triphenylphosphine analogs of **1a** and **1b**. If phosphine dissociation is required to produce the active catalytic species, as in the case of **1**, compounds **2a** and **10** would be expected to have similar reactivities.

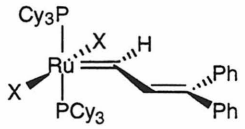


10

Explanation of Bimetallic Catalyst Activities. One source of the enhanced activity of the bimetallic catalysts is the associative mechanism of olefin metathesis. For the parent catalysts **1a,b**, dissociation of a phosphine ligand results in a rate expression that has an *effective* catalyst order of 1/2. By introducing the second metal fragment as a chelating ligand, the absence of phosphine dissociation produces a rate expression that is first-order in catalyst concentration. However, because there are substantial differences in the activities of the bimetallic catalysts as the ancillary metal center is varied, other effects must be present as well.

A possible explanation for the observed trend, Ru < Os < Rh in order of increasing activity, is that coordination of the second metal center to the bound chloride ligand (M···Cl—Ru) makes the chloride more electron withdrawing—similar effects have been observed by Estruelas et al. in bimetallic compounds containing bridging

imidazolide and pyrazolide ligands.[12] Investigation of the relative metathesis activities of **1a** and its derivatives **11a** and **11b** indicate that more electron withdrawing halogens produce more active catalysts, such that I < Br < Cl in order of increasing activity.[8] While the higher oxidation state Rh(III) is expected to coordinate more strongly to the bound chloride than Ru(II) and Os(II), the difference between Ru(II) and Os(II) is less obvious. Because Ru(II) is more electronegative than Os(II), it might be expected to coordinate better to the bound chloride; however, because third-row transition metals generally form stronger bonds, the Os···Cl bond is expected to be stronger than the Ru···Cl bond.



1a: X = Cl
11a: X = Br
11b: X = I

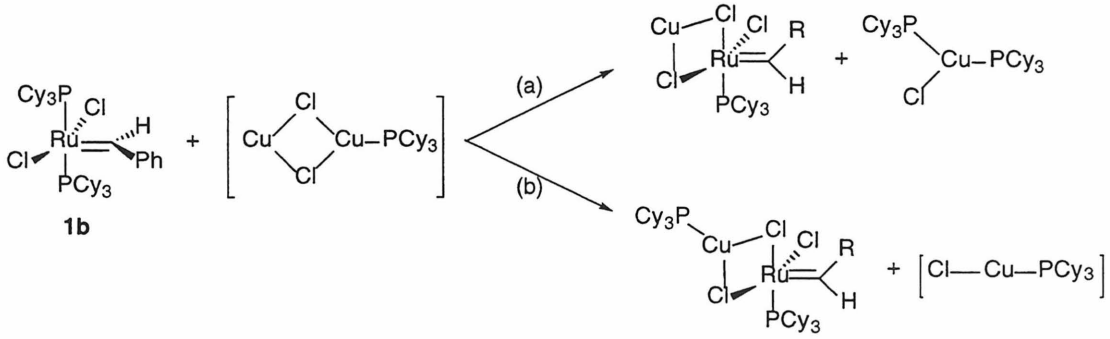
It has been observed that the chemical shift of the carbene H_α proton correlates well with the relative electron donating or withdrawing ability of the halogens for catalyst such as **1a**, **11a,b**. For example, the chemical shift of the carbene H_α in **1a** is 19.07 ppm. The signal appears upfield at 18.88 ppm for **11a**, and even further upfield at 18.54 ppm for **11b**. This trend is observed for other derivatives as well—more electron withdrawing halogens shift the H_α resonance downfield.[8] From the ^{1}H NMR spectra of the bimetallic compounds, it is apparent that the chemical shifts for the osmium-ruthenium catalysts **4a,b** (18.60 and 19.62 ppm) are downfield of those for the corresponding ruthenium catalysts **2a,b** (18.55 and 19.58 ppm), while the chemical shifts for the rhodium-ruthenium catalysts **6a,b** are the furthest downfield (18.70 and 19.69 ppm). Following the trend observed for **1a**, **11a,b**, the electron withdrawing ability of the chlorides in the bimetallic catalysts increases in the order Ru < Os < Rh, consistent with the observed activities.

Mechanism of CuCl Activation of 1a and 1b. Due to the observed tendency for **1a** and **1b** to form bimetallic complexes when one of the phosphines is removed from the metal center, the activation of **1a** and its derivatives by CuCl was examined in further detail. The $CuCl•PR_3$ complex is ill-defined and oligomeric in solution—bridging of the chloride ligands leads to several types of higher-order structures.[9] It is therefore feasible that chloride-bridged complexes of copper and ruthenium may form as well.

A ^1H NMR study was conducted in which five equivalents of CuCl were added to a solution of **1b** in CD_2Cl_2. After 20 minutes, two small doublets appeared in the carbene α-proton region of the spectrum at 19.18 and 19.72 ppm, upfield of the singlet for **1b** at 20.02 ppm. At this time, *cis*- and *trans*- stilbene were also observed, indicative of bimolecular decomposition. After one hour, several minor peaks appeared between 19.60 and 20.00 ppm.

Because the carbene α-proton resonances for the bimetallic catalysts **2b**, **4b**, and **6b** all appear as doublets upfield of **1b** at 19.58, 19.62, and 19.69 ppm respectively, it is believed that the peaks at 19.72 and 19.18 ppm correspond to bimetallic copper-ruthenium complexes. The appearance of two species can be explained by reaction of **1b** with dimeric copper compounds having the formula "$Cu_2Cl_2•PCy_3$" which may form upon reaction of CuCl with PCy_3 (Scheme 4). The minor peaks that subsequently appear are most likely oligomeric species, which may form *via* path (a) in Scheme 4—the unsaturated copper center in the bimetallic alkylidene complex may accomodate other

Scheme 4



ligands (e.g. bridging chlorides). Due to the instability of these complexes, however, a more positive identification cannot be made at this time.

One-Pot Polymerization and Hydrogenation with 2b. It is well-documented that ruthenium dimers $[Ru(Ar)Cl_2]_2$ react with H_2 in the presence of triethylamine to form catalysts that hydrogenate olefins under mild conditions (1 atm H_2, 30°C).[13] Studies were undertaken to determine if catalysts such as **2a** and **2b** would show similar hydrogenation activities, such that ROMP polymers generated with these catalysts could be hydrogenated *in situ*.

In preliminary experiments, 500 equivalents of COD were polymerized with catalyst **2b** in benzene in a Fischer-Porter apparatus. After polymerization was complete, approximately 10 equivalents of triethylamine were added to the solution. Heating the reaction to 50°C under 30 psi of H_2 resulted in hydrogenation of the poly(butadiene) to polyethylene over 60 hrs, at which time the polymer became insoluble. It is estimated from the ^1H NMR spectrum that the resulting polyethylene contains <5% olefins, indicating an unoptimized yield of >90% for the hydrogenation reaction under what are relatively mild conditions.

Conclusions

A new strategy for synthesizing ruthenium-based olefin metathesis catalysts that exhibit a range of activities higher than those previously reported for ruthenium alkylidenes **1a** and **1b** has been developed. The reaction of 18-electron, chloride-bridged dimers of ruthenium, osmium, and rhodium with the ruthenium catalysts **1a** and **1b** proceeds cleanly and quantitavely to produce stable, bimetallic complexes that can be easily isolated. Although stoichiometric amounts of the corresponding piano-stool type complexes are generated in these reactions, it should be emphasized that they do *not* affect catalyst activity, and need not be separated for routine usage.

There are several indications that a sterically bulky environment is required to

stabilize the bimetallic complexes. Bimolecular decomposition is observed for compounds containing alkylidene substituents that are smaller than the diphenylvinyl and phenyl moieties in **1a** and **1b**. While reaction of **1a** or **1b** with [Ru(*p*-cymene)Cl_2]$_2$ produces stable compounds **2a,b**, reaction with [Ru(benzene)Cl_2]$_2$ produces compounds which decompose rapidly. Further evidence for the steric requirement at the ancillary metal center is provided by the heterobimetallic rhodium-ruthenium complexes, from which it was determined that stability increases in the order Cp* < ^{t}BuCp < ^{t}Bu$_2$Cp .

The bimetallic catalysts exhibit relative rate constants for the ROMP of 1,5-cyclooctadiene that range from approximately 25 for the homobimetallic ruthenium catalysts to 80 for the heterobimetallic rhodium-ruthenium catalysts, with respect to parent catalyst **1a**. One possible explanation for the observed trend in activity, Ru < Os < Rh, is that coordination of the ancillary metal center to the ruthenium-bound chloride makes the chloride more electron withdrawing—an idea that is supported by spectroscopic evidence. Both kinetic and experimental studies support the hypothesis that these bimetallic catalysts operate *via* an associative mechanism of olefin metathesis—i.e. the bound tricyclohexylphosphine does not dissociate during the course of reaction. With respect to the previously reported enhancement of the activity of catalyst **1a** by the addition of CuCl, there is spectroscopic evidence that at least two new bimetallic copper-ruthenium complexes are being generated in this system.

Preliminary experiments demonstrate that catalyst **2b** can also be used for the *in situ* hydrogenation of poly(butadiene) produced from the ROMP of 1,5-cyclooctadiene. The extension of this methodology to utilize the control over molecular weight and polydispersity provided by ROMP in the synthesis of polymers with saturated backbones is currently under investigation.

Experimental

All manipulations were performed using standard Schlenk techniques unless

otherwise specified. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). Solid organometallic compounds were transferred and stored in a nitrogen-filled Vacuum Atmospheres drybox. All ^{1}H and ^{31}P NMR spectra were recorded in CD_2Cl_2 on a JEOL JNM-GX400 (399.80 MHz ^{1}H). All NMR tubes and septa used were dried under vacuum and stored in a drybox.

All solvents were vacuum transferred from sodium-benzophenone ketyl, except for chlorinated solvents (including CD_2Cl_2) which were vacuum transferred from CaH_2. All solvents were degassed by several freeze-pump-thaw cycles.

$(PCy_3)_2Cl_2Ru(CHCHCPh_2)$ (**1a**) and $(PCy_3)_2Cl_2Ru(CHPh)$ (**1b**) were synthesized from $Ru(PPh_3)_3Cl_2$ according to published procedures.[7] [[Os(*p*-cymene)Cl_2]$_2$,[14] [Co(Cp*)Cl_2]$_2$,[15] lithium *tert*-butyl cyclopentadienide,[16] di-*tert*-butyl cyclopentadiene,[17] and substrates **7**,[18] **8**[5a] and **9**[19] were prepared according to literature procedures. [Ru(*p*-cymene)Cl_2]$_2$, [Ru(benzene)Cl_2]$_2$, [Rh(Cp*)Cl_2]$_2$, and [Ir(Cp*)Cl_2]$_2$ were purchased from Aldrich and used without further purification. $RhCl_3 \cdot xH_2O$ purchased from Alfa (Johnson Matthey) consistently gave the best results.

Mass spectral analysis was performed at the Southern California Mass Spectrometry Facility at the University of California at Riverside and the Caltech Mass Spectrometry Facility. Elemental Analyses were performed by the Caltech Analytical Facility.

Synthesis of [(*p*-cymene)(Cl)Ru(μ-Cl)$_2$Ru(Cl)(PCy$_3$)(CHCHCPh$_2$) (2a). Inside the drybox, 1.0 g (1.08 mmol) of $(PCy_3)_2Cl_2Ru(CHCHCPh_2)$ (**1a**) and 0.660 g (1.08 mmol) of [(*p*-cymene)$RuCl_2$]$_2$ were weighed into a 100 ml Schlenk flask equipped with a stirbar and dissolved in 60- 70 ml of C_6H_6. The flask was capped with a rubber septum, removed from the drybox, placed under argon on the Schlenk line, and stirred for 3.5 hrs at 45°C, during which time a yellow precipitate formed from the dark red-orange solution. The solvent was removed *in vacuo*, and the product was washed with a mixture of acetone (15 ml) and benzene (app. 5 ml) to remove the [(*p*-cymene)$Ru(Cl)_2(PCy_3)$]

by-product and any unreacted starting materials. The solid product was isolated by cannula filtration, the washing procedure was repeated two more times, and the product was dried *in vacuo*, yielding 0.621 g (0.65 mmol, 60%) of a yellow-orange powder which was isolated and stored inside of the dry box Alternatively, the product can be isolated directly from the reaction mixture by cannula filtration and washed with benzene or acetone/benzene to give pure product in slightly lower yield. ^{1}H NMR: δ 18.55 (dd, 1 H, Ru=C*H*, $^3J_{HH}$ = 11 Hz, $^3J_{HP}$ = 10 Hz), 8.91 (d, 1 H, C*H*=CPh$_2$, $^3J_{HH}$ = 11 Hz), 7.68 (d, 2 H, H_{ortho}, $^3J_{HH}$ = 7 Hz), 7.54 (t, 1 H, H_{para}, $^3J_{HH}$ = 7 Hz), 7.44 (t, 1 H, H_{para}, $^3J_{HH}$ = 7 Hz), 7.32 (pseudo q, 4 H, H_{meta}, $^3J_{HH}$ = 7 Hz), 7.23 (d, 2 H, H_{ortho}, $^3J_{HH}$ = 7 Hz), 5.60 (d, 1 H, H_{cymene}, $^3J_{HH}$ = 6 Hz), 5.51 (d, 1 H, H_{cymene}, $^3J_{HH}$ = 6 Hz), 5.34 (d, 2 H, H_{cymene}, $^3J_{HH}$ = 6 Hz), 2.95 (sept, 1 H, $H_{isopropyl}$, $^3J_{HH}$ = 6 Hz), 2.29 (s, H_{methyl}, 3 H), 1.87 (app q, 3 H, $H_{cyclohexyl}$), 1.75-1.41(br m, 21 H, $H_{cyclohexyl}$), 1.37 (app t, 6 H, H_{methyl}, $^3J_{HH}$ = 6 Hz), 1.33-1.00 (br m, $H_{cyclohexyl}$, 9 H). ^{31}P{^{1}H} NMR: δ 49.70 (s). FAB-HRMS: *m/z* calcd for $C_{43}H_{59}Cl_4PRu_2$ (M^+) 952.1155. Found 952.1166.

Synthesis of [(*p*-cymene)(Cl)Ru(μ-Cl)$_2$Ru(Cl)(PCy$_3$)(CHPh) (2b). Inside the drybox, 0.700 g (0.85 mmol) of $(PCy_3)_2Cl_2Ru(CHPh)$ (**1b**) and 0.521 g (0.85 mmol) of [(*p*-cymene)$RuCl_2$]$_2$ were weighed into a 100 ml Schlenk flask equipped with a stirbar and 50 ml of C_6H_6 were added. The flask was capped with a rubber septum, removed from the drybox, placed under argon on the Schlenk line, and stirred for 2 hrs at room temperature, during which time a yellow precipitate formed from the dark orange-brown solution. The solvent was removed *in vacuo*, and the product was washed with a mixture of acetone (30 ml) and benzene (app. 1 ml) to remove the [(*p*-cymene)Ru(Cl)$_2$(PCy$_3$)] by-product and any unreacted starting materials. The solid product was isolated by cannula filtration, the washing procedure was repeated two more times, and the product was dried *in vacuo*, yielding 0.621 g (0.46 mmol, 63%) of a yellow-green powder which was isolated and stored inside of the dry box Alternatively, the product can be isolated directly from the reaction mixture by cannula filtration and washed with benzene or

acetone/benzene to give analytically pure product in slightly lower yield. ^{1}H NMR: δ 19.58 (d, 1 H, Ru=C*H*, $^3J_{HP}$ = 10 Hz), 8.47 (d, 2 H, H_{ortho}, $^3J_{HH}$ = 7 Hz), 7.76 (t, 1 H, H_{para}, $^3J_{HH}$ = 7 Hz), 7.46 (t, 2 H, H_{meta}, $^3J_{HH}$ = 7 Hz), 5.57 (d, 1 H, H_{cymene}, $^3J_{HH}$ = 6 Hz), 5.41 (d, 1 H, H_{cymene}, $^3J_{HH}$ = 6 Hz), 5.28 (d, 1 H, H_{cymene}, $^3J_{HH}$ = 6 Hz), 5.17 (d, 1 H, H_{cymene}, $^3J_{HH}$ = 6 Hz), 2.91 (sept, 1 H, $H_{isopropyl}$, $^3J_{HH}$ = 6 Hz), 2.17 (s, H_{methyl}, 3 H), 2.04 (app q, 3 H, $H_{cyclohexyl}$), 1.80-1.55 (br m, 21 H, $H_{cyclohexyl}$), 1.37 (d, 3 H, H_{methyl}, $^3J_{HH}$ = 7 Hz), 1.33 (d, 3 H, H_{methyl}, $^3J_{HH}$ = 6 Hz), 1.27-1.15 (br m, $H_{cyclohexyl}$, 9 H). ^{31}P{^{1}H} NMR: δ 48.68 (s). Anal. Calcd for $C_{35}H_{53}Cl_4PRu_2$: C, 49.53; H, 6.29. Found: C, 49.42; H, 6.34.

Synthesis of [(*p*-cymene)(Cl)Os(μ-Cl)$_2$Ru(Cl)(PCy$_3$)(CHCHCPh$_2$) (4a). Inside the drybox, 100 mg (0.11 mmol) of $(PCy_3)_2Cl_2Ru(CHCHCPh_2)$ (**1a**) and 85 mg (0.11 mmol) of $[(p\text{-cymene})OsCl_2]_2$ were weighed into a 10 ml Schlenk flask equipped with a stirbar and dissolved in 5 ml of CH_2Cl_2. The flask was capped with a rubber septum, removed from the drybox, placed under argon on the Schlenk line, and stirred for 3 hrs at room temperature to yield a dark orange-brown solution. The solvent was removed *in vacuo*, the flask was placed in an ice/water bath and the solids were washed with 2 x 5 ml of 0°C toluene. The yellow solid was isolated from the orange filtrate by cannula filtration, and washed with an additional 2 x 5 ml of 0°C hexane to remove the residual toluene. The product obtained in this manner was dried *in vacuo*, yielding 37.5 mg (0.036 mmol, 33%) of a yellow powder which was isolated and stored inside of the dry box. ^{1}H NMR: δ 18.60 (dd, 1 H, Ru=C*H*, $^3J_{HH}$ = 11 Hz, $^3J_{HP}$ = 10 Hz), 8.98 (d, 1 H, C*H*=CPh$_2$, $^3J_{HH}$ = 11 Hz), 7.68 (d, 2 H, H_{ortho}, $^3J_{HH}$ = 7 Hz), 7.54 (t, 1 H, H_{para}, $^3J_{HH}$ = 7 Hz), 7.46 (t, 1 H, H_{para}, $^3J_{HH}$ = 7 Hz), 7.34 (app q, 4 H, H_{meta}, $^3J_{HH}$ = 7 Hz), 7.25 (d, 2 H, H_{ortho}, $^3J_{HH}$ = 7 Hz), 6.18 (d, 1 H, H_{cymene}, $^3J_{HH}$ = 6 Hz), 6.10 (, 1 H, H_{cymene}, $^3J_{HH}$ = 6 Hz), 5.92 (app t, 2 H, H_{cymene}, $^3J_{HH}$ = 6 Hz), 2.81 (sept, 1 H, $H_{isopropyl}$, $^3J_{HH}$ = 6 Hz), 2.29 (s, 3 H, H_{methyl}), 1.91 (dt, 3 H, $H_{cyclohexyl}$), 1.71-1.43(br m, 21 H, $H_{cyclohexyl}$), 1.35 (pseudo t, 6 H, H_{methyl}, $^3J_{HH}$ = 6 Hz), 1.28-1.03 (br m, 9 H,

$H_{cyclohexyl}$). $^{31}P\{^1H\}$ NMR: δ 51.30 (s).

Synthesis of [(*p*-cymene)(Cl)Os(μ-Cl)$_2$Ru(Cl)(PCy$_3$)(CHPh) (4b). Inside the drybox, 0.500 g (0.61 mmol) of $(PCy_3)_2Cl_2Ru(CHPh)$ (**1b**) and 0.480 g (0.61 mmol) of $[(p\text{-cymene})OsCl_2]_2$ were weighed into a 50 ml Schlenk flask equipped with a stirbar and 25 ml of C_6H_6 were added. The flask was capped with a rubber septum, removed from the drybox, placed under argon on the Schlenk line, and stirred for 2 hrs at room temperature to yield a dark green-brown solution. The solvent was removed *in vacuo*, and the product was dissolved in a minimum amount of toluene. Pentane was slowly added until a green solid began to precipitate, and the flask was stoppered and placed in the freezer at -10°C overnight to selectively precipitate the product. The solid product was isolated by cannula filtration, washed with a mixture of pentane/toluene (app. 1 ml toluene in 20 ml pentane), and twice more with pentane (2 x 15 ml) to remove the residual toluene. The product was dried *in vacuo*, yielding 0.225 g (0.24 mmol, 40%) of a light green analytically pure powder which was isolated and stored inside of the dry box. ^1H NMR: δ 19.62 (d, 1 H, Ru=C*H*, $^3J_{HP}$ = 10 Hz), 8.47 (d, 2 H, H_{ortho}, $^3J_{HH}$ = 7 Hz), 7.76 (t, 1 H, H_{para}, $^3J_{HH}$ = 7 Hz), 7.48 (t, 2 H, H_{meta}, $^3J_{HH}$ = 7 Hz), 6.12 (d, 1 H, H_{cymene}, $^3J_{HH}$ = 6 Hz), 5.99 (d, 1 H, H_{cymene}, $^3J_{HH}$ = 6 Hz), 5.85 (d, 1 H, H_{cymene}, $^3J_{HH}$ = 6 Hz), 5.73 (d, 1 H, H_{cymene}, $^3J_{HH}$ = 6 Hz), 2.75 (sept, 1 H, $H_{isopropyl}$, $^3J_{HH}$ = 6 Hz), 2.16 (s, H_{methyl}, 3 H), 2.08 (app q, 3 H, $H_{cyclohexyl}$), 1.85-1.56 (br m, 21 H, $H_{cyclohexyl}$), 1.33 (app t, 6 H, H_{methyl}, $^3J_{HH}$ = 6 Hz), 1.27-1.16 (br m, $H_{cyclohexyl}$, 9 H). $^{31}P\{^1H\}$ NMR: δ 51.57 (s). Anal. Calcd for $C_{35}H_{53}Cl_4POsRu$: C, 44.82; H, 5.70. Found: C, 44.80; H, 5.93.

Synthesis of [(^{t}Bu$_2$Cp)RhCl$_2$]$_2$ (5). $RhCl_3 \cdot xH_2O$ (x≈3) (0.500 g, 1.90 mmol) was weighed into a 50 ml Schlenk flask, which was evacuated and filled with argon. 25 ml of degassed methanol were added, followed by 0.500 g (2.8 mmol) of di-*tert*-butyl cyclopentadiene . The flask was fitted with a reflux condenser with bubbler outlet and purged with argon for 15 min. The argon flow was adjusted to one bubble every 2-3

seconds, and the reaction was heated to reflux for 36 hrs. The reaction was allowed to cool to room temperature, the reflux condenser was replaced with a stopper, and the solvent was removed *in vacuo*. The solids were scraped out onto a Buchner funnel and washed liberally with hexanes until the washings were colorless. The resulting red solid was recrystallized from boiling ethanol, yielding 0.250 g (0.71 mmol, 37%) of a red crystalline solid. ^{1}H NMR: δ 5.62 (s, 2 H), 5.36 (s, 1 H), 1.33 (s, 18 H). FAB-HRMS: *m/z* calcd for $C_{26}H_{42}Cl_3Rh_2$ (M-Cl$^+$) 665.0467. Found 665.0467.

Synthesis of [(^{t}Bu$_2$Cp)(Cl)Rh(μ-Cl)$_2$Ru(Cl)(PCy$_3$)(CHCHCPh$_2$) (6a). Inside the drybox, 66 mg (0.071 mmol) of $(PCy_3)_2Cl_2Ru(CHCHCPh_2)$ (**1a**) and 50 mg (0.071 mmol) of $[(^tBu_2Cp)RhCl_2]_2$ were weighed into a 10 ml Schlenk flask equipped with a stirbar and dissolved in 5 ml of CH_2Cl_2. The flask was capped with a rubber septum, removed from the drybox, placed under argon on the Schlenk line, and stirred for 5 hrs at room temperature to produce a red-orange solution. The solvent was removed *in vacuo*, and the product was washed with acetone (3 x 5 ml) to remove the $(^tBu_2Cp)RhCl_2(PCy_3)$ by-product and any unreacted starting materials. The product was isolated by cannula filtration and dried *in vacuo* to yield 10 mg (0.010, 15%) of a yellow powder. ^{1}H NMR: δ 18.70 (dd 1 H, Ru=C*H*, $^3J_{HH}$ = 11 Hz, $^3J_{HP}$ = 10 Hz), 9.01 (d, 1 H, C*H*=CPh$_2$, $^3J_{HH}$ = 11 Hz), 7.70 (d, 2 H, H_{ortho}, $^3J_{HH}$ = 7 Hz), 7.53 (t, 1 H, H_{para}, $^3J_{HH}$ = 7 Hz), 7.45 (t, 1 H, H_{para}, $^3J_{HH}$ = 7 Hz), 7.35 (t, 2 H, H_{meta}, $^3J_{HH}$ = 7 Hz), 7.31 (t, 2 H, H_{meta}, $^3J_{HH}$ = 7 Hz), 7.26 (d, 2 H, H_{ortho}, $^3J_{HH}$ = 7 Hz), 5.51 (s, 1 H, H_{Cp}), 5.48 (s, 2 H, H_{Cp}), 1.91 (app q, 3 H, $H_{cyclohexyl}$), 1.71-1.43(br m, 21 H, $H_{cyclohexyl}$), 1.42 (s, 18 H, $H_{t\text{-}butyl}$), 1.30-1.03 (br m, 9 H, $H_{cyclohexyl}$). ^{31}P{^{1}H} NMR: δ 49.03 (s).

Synthesis of [(^{t}Bu$_2$Cp)(Cl)Rh(μ-Cl)$_2$Ru(Cl)(PCy$_3$)(CHPh) (6b). Inside the drybox, 173 mg (0.21 mmol) of $(PCy_3)_2Cl_2Ru(CHPh)$ (**1b**) and 150 mg (0.21 mmol) of $[(^tBu_2Cp)RhCl_2]_2$ were weighed into a 25 ml Schlenk flask equipped with a stirbar and dissolved in 10 ml of CH_2Cl_2. The flask was capped with a rubber septum, removed from the drybox, placed under argon on the Schlenk line, and stirred for 30 min at room

temperature to produce a red-orange solution. The solvent was removed *in vacuo*, and the product was washed with acetone (3 x 10 ml) to remove the (^{t}Bu$_2$Cp)RhCl$_2$(PCy$_3$) by-product and any unreacted starting materials. The product was isolated by cannula filtration and dried *in vacuo* to yield 100 mg (0.11 mmol, 53%) of analytically pure red-orange powder. ^{1}H NMR: δ 19.69 (d, 1 H, Ru=C*H*, $^3J_{HP}$ = 10 Hz), 8.52 (d, 2 H, H_{ortho}, $^3J_{HH}$ = 7 Hz), 7.76 (t, 1 H, H_{para}, $^3J_{HH}$ = 7 Hz), 7.46 (t, 2 H, H_{meta}, $^3J_{HH}$ = 7 Hz), 5.45 (s, 1 H, H_{Cp}), 5.30 (s, 2 H, H_{Cp}), 2.08 (app q, 3 H, $H_{cyclohexyl}$), 1.83-1.62 (br m, 21 H, $H_{cyclohexyl}$), 1.37 (s, 18 H, $H_{t\text{-}butyl}$), 1.27-1.18 (br m, $H_{cyclohexyl}$, 9 H). ^{31}P{^{1}H} NMR: δ 47.75 (s). Anal. Calcd for $C_{38}H_{60}Cl_4PRhRu$: C, 51.07; H, 6.77. Found: C, 50.80; H, 6.74.

Ring-opening metathesis polymerizations of 1,5-cyclooctadiene and 9. Reactions for kinetic studies were performed in screw-cap NMR tubes available from Wilmad, sealed with septum-fitted screw caps. Polymer formation and diene disappearance were measured against a blank (no catalyst) solution of either COD or **9** as an external standard.

(1) Relative catalyst activity experiments. A 10X stock solution of the each catalyst **2a,b**, **4a,b**, and **6a,b** was made by dissolving 0.0162 mmol of catalyst in 5 ml CD_2Cl_2. Inside the dry box, 50 µl of the catalyst solution was diluted with 405 µl of CD_2Cl_2 in a screw-top NMR tube. The NMR tube was then capped with a septum-fitted screw cap and removed from the dry box. A sample of COD was prepared in the dry box in a vial and capped with a septum-fitted screw cap.

The NMR probe was equilibrated to 16.0°C (ambient temperature), and 45 µl of COD were injected via syringe immediately before the sample was placed in the probe. The final concentrations are: [catalyst] = 3.25 mM, [COD] = 0.73 M. Ratio of [COD]/[catalyst] = 225/1.

(2) Catalyst dependence experiments. A catalyst stock solution was made by dissolving 25 mg (0.0295 mmol) of **2b** in .5 ml CD_2Cl_2. Inside the dry box, 20, 30, 40,

and 50 μl of catalyst stock solution were syringed into a screw-cap NMR tube and diluted with CD_2Cl_2 in to bring the volume to 480 μl. The NMR tube was capped with a septum-fitted screw cap and removed from the dry box. A sample of **9** was prepared in the dry box in a vial and capped with a septum-fitted screw cap.

The NMR probe was equilibrated to 20.0°C (ambient temperature in summer), and 20 μl of **9** were injected via syringe immediately before the sample was placed in the probe. The final concentrations of catalyst are 2.36, 3.54, 4.72, and 5.90 mM.

One-Pot Polymerization/Hydrogenation. Inside the dry box, 30 mg (.035 mmol) of **2b** were weighed into a Fischer-Porter bottle w/stirbar and dissolved in approximately 20 ml benzene. 2g (18.5 mmol, 530 eq) of COD were added to the solution, which subsequently turned orange. The bottle was fitted with a regulator top, sealed, and removed from the dry box. The polymerization was stirred for 5 hrs at room temperature, after which a hydrogen inlet was fitted to the apparatus. Under flowing H_2, approximately 50 μl of NEt_3 (10 eq) were added *via* syringe, and the apparatus was placed in an oil bath preheated to 50°C and pressured up to 30 psi H_2. After 24 hrs, an addition 10 ml of benzene were added *via* syringe under flowing H_2 to dilute the solution, which was pale yellow in color. After 60 hrs, the polymer became insoluble and the solution became a thick gel. The apparatus was removed from the oil bath, quickly opened, and toluene was added to loosen the gel. The resulting mixture was poured into stirring methanol to precipitate the polymer as a fluffy white solid, which was collected by filtration and dried *in vacuo*, yielding 1.65 g of poly(ethylene).

Acknowledgments. Financial support has been provided by Rohm and Haas and the National Institute of Health.

References and Notes

[1]For recent reviews, see (a) Hashimi, A. S. K. *J. Prakt. Chem.* **1997**, *339*, 195-199. (b) Schmalz, H.-G. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1833-1836. (c) Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446-552.

[2](a) Kim, S.-H.; Zuercher, W. J.; Bowden, N. B.; Grubbs, R. H. *J. Or.g. Chem.* **1996**, *61*, 1073-1081. (b) Kim, S.-H.; Bowden, N.; Grubbs, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 10801-10802.

[3]Zuercher, W. J.; Hashimoto, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 6634-6640.

[4](a) Maughon, B. R.; Grubbs, R. H. *Macromolecules* **1997**, *30*, 3459-3469. (b) Hillmyer, M. A.; Nguyen, S. T.; Grubbs, R. H. *Macromolecules* **1997**, *30*, 718-721. (c) Fraser, C.; Hillmyer, M. A.; Gutierrez, E.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 7256-7261. (d) Hillmyer, M. A.; Laredo, W. R.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 6311-6316. (e) Stumpf, A. W.; Saive, E.; Demonceau, A.; Noels, A. F. *J. Chem. Soc. Chem. Commun.* **1995**, 1127-1128.

[5]For recent examples, see (a) Wagaman, M. W.; Grubbs, R. H. *Syn. Met.* **1997**, *84*, 327-328. (b) Boyd, T. J.; Geerts, Y.; Lee, J. K.; Fogg, D. E.; Lavoie, G. G. et al. *Macromolecules* **1997**, *30*, 3553-3559. (c) Tasch, S.; Grapner, W.; Leising, G.; Pu, L.; Wagaman, M. W. et al. *Adv. Mat.* **1996**, *8*, 125. (c) Pu, L.; Wagaman, M. W.; Grubbs, R. H. *Macromolecules* **1996**, *29*, 1138-1143. (d) Schattenmann, F. J.; Schrock, R. R. *Macromolecules* **1996**, *29*, 8990-8991. (e) Baigent, D. R.; Friend, R. H.; Lee, J. K.; Schrock, R. R. *Syn. Met.* **1995**, *71*, 2171-2172. (f) Lee, J. K.; Schrock, R. R.; Baigent, D. R.; Friend, R. H. *Macromolecules* **1995**, *28*, 1966-1971.

[6]For recent examples, see (a) Maughon, B. R.; Weck, M.; Mohr, B.; Grubbs, R. H. *Macromolecules* **1997**, *30*, 257-265. (b) Arehart, S. V.; Pugh, C. *J. Am. Chem. Soc.* **1997**, *119*, 3027-3037. (c) Pugh, C.; Liu, H.; Arehart, S. V.; Narayanan, R. *Macromol.*

Symp. **1995**, *98*, 293-310. (d) Ungerank, M.; Winkler, B.; Eder, E.; Stelzer, F. *Macromol. Chem. Phys.* **1995**, *196,* 3623. (e) Pugh, C. *Macromol. Symp.* **1994**, *77,* 325.

[7](a) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100-110. (b) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2039-2041. (c) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858-9859. (d) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3974-3975.

[8]Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887-3897.

[9](a) *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: New York, 1987; Vol. 5. (b) *Advanced Inorganic Chemistry*, Cotton, F. A.; Wilkinson, G.; Wiley: New York, 1988; 757-766.

[10]Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233.

[11]Miller, S. J.; Kim, S.-H.; Chen, Z.-R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 2108-2109.

[12](a) Esteruelas, M. A.; Garcia, M. P.; Lopez, A. M.; Oro, L. A. *Organometallics* **1991**, *10*, 127-133. (b) Garcia, M. P.; Lopez, A. M.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A. *J. Chem. Soc. Dalton Trans.* **1990**, 3465-3472. (c) Garcia, M. P.; Lopez, A. M.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A. *J. Chem. Soc., Chem. Commun.* **1988**, 793-795. (d) Garcia, M. P.; Lopez, A. M.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A. *J. Organomet. Chem.* **1990**, *388*, 365-377.

[13](a) Hinze, A. G. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 542-552. (b) Iwata, R.; Ogata, I. *Tetrahedron* **1973**, *29*, 2753-2758. (c) Ogata, I.; Iwata, R.; Ikeda, Y. *Tetrahedron Lett.* **1970**, *34*, 3011-3014.

[14]Cabeza, J. A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1985**, 573-578.

[15]Koelle, U.; Fuss, B. *Chem. Ber.* **1984**, *117*, 743-752.

[16]Sullivan, M. F.; Little, W. F. *J. Organomet. Chem.* **1967**, *8*, 277.

[17]Venier, C. G.; Cassarly, E. W. *J. Am. Chem. Soc.* **1990**, *112*, 2808.

[18]Bazan, G. C.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C. et al. *J. Am. Chem. Soc.* **1990**, *112*, 8378-87.

[19]Lynn, D. M.; Kanaoka, S.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 784-790.

Chapter 3:

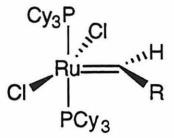
Synthesis of Ruthenium Alkylidenes Containing Pyridine and β-Diketonate Ligands

Abstract

Reaction of excess pyridine with $(PCy_3)_2(Cl)_2Ru(CHPh)$ (**1b**) produces the stable, bis(pyridine) adduct $(PCy_3)(pyr)_2(Cl)_2Ru(CHPh)$ (**3**) which can be isolated as a light yellow-green solid. In solution, an equilibrium is established between **3** and the mono(pyridine) adduct $(PCy_3)(pyr)(Cl)_2Ru(CHPh)$ (**4**). Reaction of thallium salts of β-diketonates with **1b** or the vinylcarbene **1a** produces the complexes $(PCy_3)(L)_2Ru(CHR)$ (L = acac, $^tBu_2$acac; R = $CHCPh_2$, Ph) (**5**, **6**) cleanly and quantitatively. While the pyridine complexes are stable and completely initiate RCM, the propagating methylidene is very unstable, decomposing as fast as, or faster than, it is formed. The β-diketonate complexes initiate ROMP in the presence of HCl and RCM in the presence of CuCl.

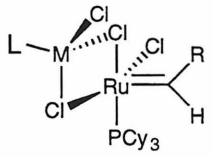
Introduction

Although the ruthenium catalysts **1** and the bimetallic catalysts **2** exhibit activities and reactivities that make them suitable for most practical applications of olefin metathesis, introducing a diverse array of ligands at the metal center should allow for a better understanding of ruthenium alkylidenes in general. In particular, it would be interesting to synthesize complexes containing nitrogen and oxygen donor ligands for comparison with **1** and **2**, which contain only phosphine and halogen ligands. In addition to studying the relationship between the ligand sphere and catalyst activity, reactivity, and stability as discussed in the previous chapters, the types of ligands that produce viable catalysts should also be determined.



1

R = $CHCPh_2$ (**1a**)
R = Ph (**1b**)



2

R = $CHCPh_2$, Ph
M = Ru, Os, Rh
L = *p*-cymene, $^tBu_2Cp$

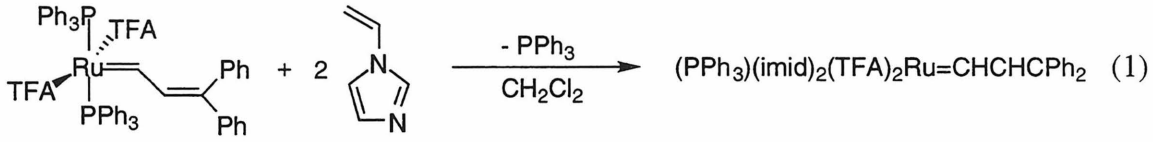
The development of catalyst systems with different electron counts is also of further interest. In Chapter 1, it was determined that during the course of metathesis, a phosphine dissociates from the 16-electron complex **1a**, such that the reactive species can be considered to be a 14-electron intermediate. Recoordination of the phosphine to form a 16-electron complex stabilizes the propagating species towards bimolecular decomposition. It would therefore be interesting to develop an 18-electron system, such that the reactive species is a 16-electron complex, and determine if the same factors are required for catalyst stability and activity.

In this chapter, the synthesis and reactivity of several ruthenium alkylidenes containing pyridine and β-diketonate ligands is presented. Both 16- and 18-electron complexes have been synthesized, and the differences in stability and reactivity are

discussed. The development of stable complexes that can be activated by addition of co-catalysts is also reported, providing a new methodology for ROMP in solution and bulk systems.

Results and Discussion

Reaction of 1b with pyridine. While catalyst **1** is tolerant of several different types of functionality, attempts at the RCM or ROMP of substrates containing amines often result in catalyst deactivation or decomposition. Previous attempts to synthesize analogs of **1** containing amines as ligands were also unsuccessful,[1] probably because they do not coordinate well enough to prevent bimolecular decomposition of the alkylidenes. However, it was demonstrated that the reaction of *N*-vinyl imdidazole with $(PPh_3)_2(TFA)_2Ru{=}CHCHCPh_2$ produced a stable, bis(imidazole) complex (eq. 1),[2] suggesting that cyclic imines, in particular pyridine, would coordinate strongly enough to provide stable ruthenium alkylidenes derived from **1b**.



(1)

Initial NMR scale experiments were conducted in which approximately 50 equivalents of d_5-pyridine were added to a solution of **1b** in a mixture of CD_2Cl_2/C_6D_6. Upon addition, the solution immediately changed from pinkish/purple to green, and the ^1H NMR spectrum showed a single resonance in the carbene H_α region at 20.75 ppm (doublet). The ^{31}P NMR showed two resonances at 11.12 ppm (free PCy_3) and 28.50 ppm, indicating that only one phosphine remained bound to the metal center, and a pyridine complex had been generated.

On a larger scale, 25-30 equivalents of pyridine were added to a solution of **1b** in toluene at room temperature, and the reaction was stirred for 30 minutes. The solution was then transferred *via* cannula filtration to a separate flask containing hexanes cooled to

0°C to precipitate the product . The light green solid obtained in this manner was isolated by cannula filtration and dried *in vauo*. The ^{1}H NMR spectrum of the product in CD_2Cl_2 showed a doublet in the carbene H_α region at 20.00 ppm, characteristic of a complex in which only one phosphine is present. Surprisingly, the aromatic region integrated to 15 protons, indicating that two equivalents of pyridine were present in the product. The ^{31}P NMR spectrum showed a single, sharp peak at 37.71 ppm. Due to the limited solubility of pyridine in hexanes, however, it could not be readily determined if the actual product of the reaction was a bis(pyridine) complex, or if an extra equivalent of pyridine was "sticking" to the product as a result of the workup procedure.

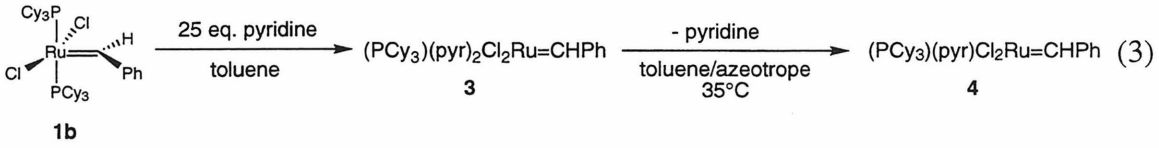
VT-NMR studies were conducted to provide further insight into the nature of this product. At lower temperatures (- 50°C), the carbene H_α resonance shifted downfield to 20.5 ppm. Conversely, at higher temperatures (60°C), the signal shifted upfield to 19.8 ppm. Such a large change in chemical shift as a function of temperature is consistent with a dynamic equilibrium between two species—in this case, a bis(pyridine) complex and a mono(pyridine) complex (eq. 2).

$$(PCy_3)(pyr)Cl_2Ru{=}CHPh + \text{pyridine} \underset{\text{high T}}{\overset{\text{low T}}{\rightleftharpoons}} (PCy_3)(pyr)_2Cl_2Ru{=}CHPh \qquad (2)$$

For the reaction of a mono(pyridine) complex with one equivalent of pyridine to produce the corresponding bis(pyridine) complex (eq. 2), ΔH is expected to be less than zero, exothermic due to the formation of an additional ruthenium-nitrogen bond. ΔS for this transformation is expected to negative as well, because two molecules condense to a single complex. As a result, the free energy, ΔG, is composed of two opposing factors: while ΔH is negative, $-T\Delta S$ is positive. At lower temperatures, the entropic contribution is reduced such that the enthalpic term dominates—ΔG becomes negative for this reacion, favoring formation of the bis(pyridine) complex (ca. 20.5 ppm). At higher temperatures, the situation is reversed—the entropic term dominates, such that ΔG is positive and the mono(pyridine) complex is favored (ca. 19.8 ppm).

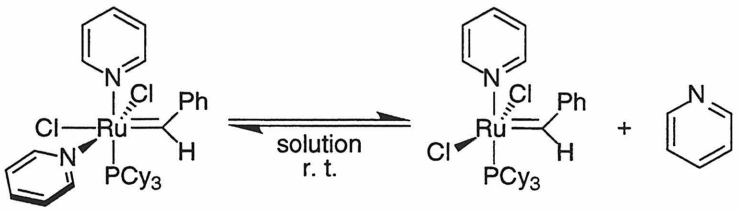
To verify this conclusion, the light green product was dissolved in toluene, and the solvent was removed *in vacuo* at 35°C in an attempt to azeotrope the extra equivalent of pyridine with the toluene. The product obtained by this method was a dark green solid (after washing with pentane)—the ^{1}H NMR spectrum showed a doublet in the carbene H_α region at 19.8 ppm, indicative of a mono(pyridine) complex, and the ^{31}P NMR spectrum showed a single, sharp resonance at 38.40 ppm. The aromatic region of the ^{1}H NMR spectrum likewise showed that only one equivalent of pyridine was present. Addition of d_5-pyridine to the NMR sample produced an immediate change in the color of the solution from dark green to light green, along with a shift in the carbene H_α resonance from 19.8 to 20.4 ppm, indicating formation of the bis(pyridine) complex. Likewise, the phosphorous resonance shifted from 38.40 ppm to a broad resonance at 30 ppm.

Thus, while the procedure outlined above provides a solid in which two equivalents of pyridine are present (**3**), the second equivalent can be removed by azeotroping with toluene, yielding a mono(pyridine) complex (**4**) (eq. 3). After **3** is isolated, a dynamic



(3)

equilibrium between **3** and **4** is established when **3** is re-dissolved (eq. 4). Unfortunately, due to difficulty in removing *all* of the excess pyridine to form the mono(pyridine) complex, the degree to which this equilibrium is established could not be accurately determined; however, it can be estimated from the ^{31}P NMR chemical shifts that **3** is approximately 90% dissociated in solution at room temperature.



3 4 (4)

Proposed structures for **3** and **4** are shown in eq. (4). For both **3** and **4**, the size of $^3J_{HP}$ (ca. 12 Hz) suggests that the P-Ru-Cα-Hα dihedral angle is approximately 0°,[3] since steric interactions between the tricycloyexylphosphine and the phenyl group would preclude a dihedral angle of 180°. By analogy with **1**, the structure of **4** is proposed to be pseudo-square pyramidal, with the pyridine ligand *trans* to the tricyclohexylphosphine, as shown. Complex **3** must have an octahedral geometry, allowing for two possible structures, in which either a pyridine or a chloride occupies the position *trans* to the carbene. Based upon the proposed intermediates in the catalytic cycle of **1**,[3] it is believed that the second pyridine ligand coordinates *cis* to the carbene, providing the structure shown in eq. (4).

Similar reactions were performed using 2-picoline (2-methyl pyridine), 2,6-lutidine (2,6-dimethyl pyridine), and quinuclidine. Unfortunately, even in the presence of a gross excess of these reagents, the equilibrium for phosphine displacement was very poor (< 10%). In the case of 2-picoline and 2,6-lutidine, addition of the methyl groups in the *ortho* position(s) must weaken the ruthenium-nitrogen bond strength significantly. For quinuclidine, a bicylic, tertiary amine, the cone angle may be too large or the ligand may be too "hard" to produce a sufficient ruthenium-nitrogen bond strength.

Metathesis Activity of Pyridine Complexes. The RCM activity of **4** was investigated using diethyl diallylmalonate, with the expectation that it would be more active than **1** due to the increased lability of the pyridine ligand compared to PCy_3. Upon addition of 25 equivalents of substrate to a solution of **4** in CD_2Cl_2/C_6D_6, the color immediately changed from green to orange. After 15 minutes, approximately 20% of the substrate was ring-closed as determined by ^1H NMR. No carbene signals were visible at

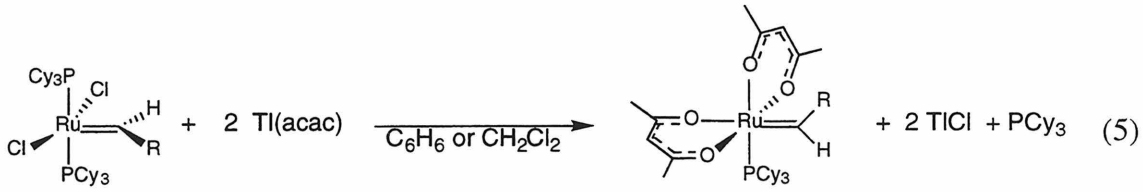
this time. Upon standing, the solution darkened to a reddish color, and the ^{1}H NMR spectrum indicated that the reaction did not proceed further.

In an effort to stabilize the propagating methylidene in this reaction, the experiment was repeated several times with the addition of excess pyridine. In the presence of excess pyridine, the 16-electron, mono(pyridine) complex (cf. **4**) could be the reactive species, while the 18-electron, bis(pyridine) (cf. **3**) species is expected to be stable. When 10 equivalents of pyridine were added, the ^{1}H NMR spectrum after 35 minutes showed approximately 10% conversion. The doublet for **3** (or the average of **3** and **4**) was visible, although no propagating species was apparent. Upon heating to 38°C for 30 minutes, the solution turned red and no carbene signals were visible. Approximately 20% of the ring-closed product was observed.

Thus, while **4** initiates very quickly, the propagating methylidene is very unstable and decomposes quite rapidly. Addition of excess pyridine slows down initiation (presumably by forming **3**), but does not stabilize the propagating methylidene sufficiently toward decomposition. For RCM, therefore, these catalysts may be useful only in cases were at least one of the olefins is 1,2-disubstituted with a group that is bulky enough to slow down or prevent catalyst decomposition. For ROMP, the catalysts may be useful for substrates that produce bulky propagating carbenes; however, the polymerization activities of **3** and **4** have not been investigated at this time.

Synthesis and Reactivity of β-Diketonate Complexes. The synthesis of ruthenium alkylidenes containing β-diketonate ligands was accomplished by reacting **1a** or **1b** with the thallium salt of the β-diketonate. Salts of alkali metals such as lithium and sodium were largely ineffective, resulting in decomposition of the alkylidene without observable formation of a new carbene species. On the other hand, the reaction of **1a** and **1b** with Tl(acac) in benzene or dichloromethane proceeded to give **5a** and **5b** as orange and green solids respectively, as shown in eq. (5). In general, the reactions in dichloromethane proceeded much faster; however, an excess of Tl(acac) (app. 6 eq.) was

required for the reaction to go to completion, resulting in decomposition of the product at longer reaction times. Although slower, the reactions performed in benzene were much cleaner: little or no product decomposition was observed, and only two equivalents of the thallium salt were required for quantitative conversion. Under both sets of conditions, it



(5)

1a: R = $CHCPh_2$
1b: R = Ph

5a: R = $CHCPh_2$
5b: R = Ph

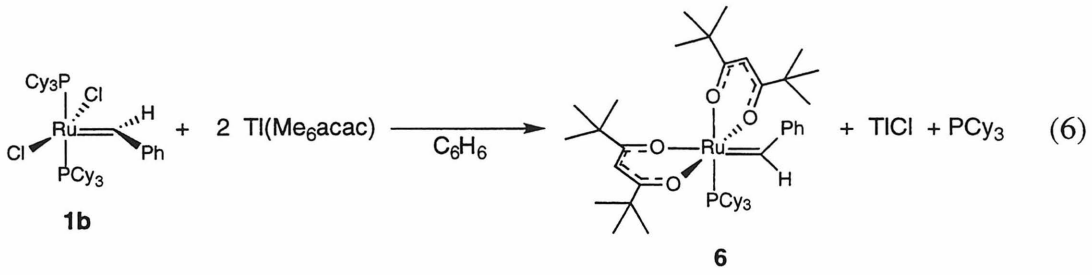
appeared that the second substitution proceeded faster than the first, making a complex containing only one (acac) ligand difficult to isolate.

The products **5a,b** are exceedingly soluble in organic solvents, including pentane. CuCl was therefore added to remove the one equivalent of tricyclohexylphosphine that is produced in this reaction, and the product was extracted from the $CuCl{\bullet}PCy_3$ polymer with cold pentane or hexane. The carbene H_α signal appears as a triplet at 18.61 ppm (CD_2Cl_2) for **5a** , and a doublet at 19.35 ppm (C_6D_6) for **5b**, indicating a P-Ru-C_α-H_α dihedral angle of approximately 0°.[3] The inequivalent methyl groups (four singlets) and vinyligous protons (two singlets) in the ^1H NMR spectra of **5a** and **5b** provide further evidence for the geometry shown in eq. (5).

Investigations of the metathesis activity of **5a,b** indicated that these 18-electron, coordinatively saturated, compounds do not react directly with diethyl diallylmalonate, 1,7-octadiene, 1,5-cyclooctadiene, or cyclobutenes. Because a vacant coordination site is required for olefin metathesis, a ligand must dissociate before any reaction can occur. It has been observed that the ruthenium-phosphine bond strengths in β-diketonate complexes are often quite strong, such that the phosphine does not easily dissociate from the metal center—a factor which may be responsible for the lack of catalytic activity. Attempts to remove the phosphine by oxidation with pyridine-*N*-oxide resulted in

decomposition of the carbene, with no observable production of tricyclohexylphosphine oxide.

Reaction of two equivalents of thallium 1,1,1,5,5,5-hexamethyl acetylacetonate (Tl(Me_6acac)), synthesized from thallium ethoxide and 2,2,6,6-tetramethyl heptane-3,5-dione, with **1b** proceeded in twenty-four hours at room temperature in benzene to produce **6** as a light-green solid (eq. 6). It was believed that the increased steric bulk of the (Me_6acac) ligands would possibly aid in dissociation of the tricyclohexylphosphine from the ruthenium center, thereby opening up a coordination site; however, compound **6** was as unreactive as **5a** and **5b**.



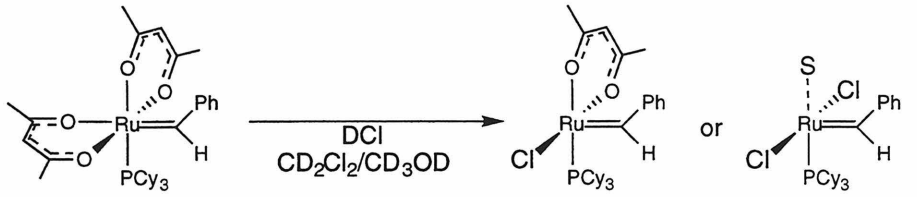
(6)

Activation of β-Diketonate Complexes. It has recently been shown that addition of Bronsted acids, mainly HCl, to water-soluble analogs of **1b** activates them *via* protonation of one of the phosphines to generate a highly active species.[4] In a preliminary experiment, approximately 0.5-1.0 equivalent of DCl in d_4-methanol were added to a solution containing **5b** and approximately 100 equivalents of the substituted 7-oxanorbornene (**7**) in CD_2Cl_2 (eq. 7). After 10 minutes, the polymerization was complete, and a propagating carbene was visible as a broad triplet at 18.54 ppm. The PDI of the resulting polymer was 3.5, and the low molecular weight tail indicated that there was a significant amount of catalyst termination.

(7)

Attempts at the RCM of diethyl diallylmalonate with 5 mol % of **5b** showed limited success. After the addition of DCl, the ^{1}H NMR spectrum after 15 minutes showed approximately 30% cyclization and no visible carbene signal. The reaction did not proceed further at longer reaction times.

Unlike the water-soluble catalysts, the acid in this case protonates either one or both of the (acac) ligands to generate *in situ* either $(PCy_3)(acac)(Cl)Ru{=}CHPh$ or $(PCy_3)(Cl)_2Ru{=}CHPh$ respectively—possibly as solvated complexes in the presence of CD_3OD (eq. 8), as determined by an NMR experiment in which a solution of DCl in CD_3OD was added to a solution of **5b** in CD_2Cl_2.

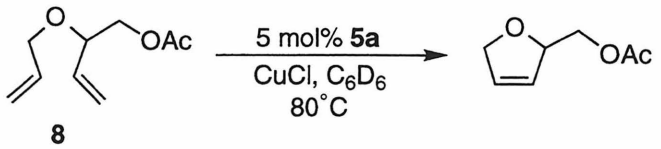


5b S = solvent (8)

Approximately 30 minutes after the addition of 0.5 equilvalent of DCl, it was clear from the ^{1}H NMR spectrum that the vinylogous hydrogens on the (acac) ligands were being exchanged for deuterium atoms, with no other observable changes. Furthermore, there was no observable resonance corresponding to a tricyclohexyl phosphonium salt in the ^{31}P NMR spectrum. Because the vinylogous carbon is expected to be the most basic site on the complex, protonation with DCl most likely generates the diketone and the corresponding ruthenium chloride complex. Stronger acids, such as triflic acid and *p*-toluenesulfonic acid, did not work nearly as well, most likely because the weakly coordinating counterions cannot stabilize the active species generated in this manner.

It has been determined that CuCl can also be used to activate catalysts **5a** and **5b**. When a mixture of 10 eq.of CuCl, **5a** , and aporoximately 50 eq. of diethyl diallylmalonate was heated to 80°C in a sealed NMR tube in C_6D_6 , ethylene was

observed to bubble rapidly out of the solution. After 1.5 hours, the reaction had gone to > 95% completion. Under similar conditions, RCM of the substituted diallyl ether (**8**) went to approximately 90% conversion after 8 hours (eq. 9). No propagating carbene was evident in either reaction, however, suggesting that the active species is not stable under these conditions. While it is possible that the CuCl simply reacts with the tricyclohexylphosphine to make the



8 (9)

$CuCl{\bullet}PCy_3$ complex as in the case of **1a**,[3] creating an open coordination site, it is also likely that the CuCl is undergoing a transmetallation with the the catalysts to produce Cu(acac) and the corresponding ruthenium chlorides (cf. eq. 8).

Attempts at ROMP with catalysts **5a,b** were not as successful. Addition of norbornene (app. 50 eq.) to a solution of **5a** in C_6D_6 resulted in the formation of poly(norbornene), but no propagating species could be observed. In addition, the high viscosity of the resulting solution suggests that only a small portion of the catalyst was responsible for the turnover, such that initiation by a catalyst impurity cannot be ruled out. Heating a solution of **5a** and 1,5-cyclooctadiene (COD) to 80°C in C_6D_6 produced no observable reaction. Prolonged heating after the addition of 10 equivalents CuCl only resulted in isomerization of 1,5-COD to 1,4-COD and 1,3-COD. Similar attempts to ROMP several cyclobutenes were also unsuccessful.

Conclusions

The reaction of excess pyridine with ruthenium benzylidine **1b** has been shown to proceed quantitatively to produce the light green, 18-electron compound **3**, in which one of the tricyclohexylphosphines has been displaced by *two* pyridine molecules. In solution, there is a dynamic equilibrium for dissociation of one of the pyridine molecules

to produce the 16- electron complex **4**, which can be isolated as a dark green solid by a toluene azeotrope to remove the second equivalent of pyridine. Both pyridine complexes **3** and **4** inititate the RCM of diethyl diallylmalonate, but the reaction does not reach completion due to the instability of the propagating methylidene species.

The synthesis of ruthenium complexes containing β-diketonates can be accomplished by reaction of either **1a** or **1b** with the thallium salt of the ligand. In general, substitution of the second equivalent of ligand is faster than the first equivalent, such that the monosubstituted product cannot be isolated. The complexes **5a**, **5b**, and **6** synthesized in this manner are not active for olefin metathesis without addition of a cocatalyst. The addition of CuCl to a solution of **5a** or **5b** initiates RCM at elevated temperatures, while HCl can be added to initiate ROMP at room temperature. Although some catalyst termination occurs in the solution polymerization of **7**, the solubility of these compounds in non-polar media makes them attractive candidates for bulk polymerizations.

Experimental

All manipulations were performed using standard Schlenk techniques unless otherwise specified. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). Solid organometallic compounds were transferred and stored in a nitrogen-filled Vacuum Atmospheres drybox. All ^{1}H spectra were recorded on a GE-QE300 (300 MHz ^{1}H) or JEOL JNM-GX400 (399.80 MHz ^{1}H) spectrometer, and ^{31}P NMR spectra were recorded on a JEOL JNM-GX400 (161.9 MHz ^{31}P). All NMR tubes and septa used were dried under vacuum and stored in a drybox.

All solvents were vacuum transferred from sodium-benzophenone ketyl, except for chlorinated solvents (including CD_2Cl_2) which were vacuum transferred from CaH_2. All solvents were degassed by several freeze-pump-thaw cycles.

$(PCy_3)_2Cl_2Ru(CHCHCPh_2)$ (**1a**) and $(PCy_3)_2Cl_2Ru(CHPh)$ (**1b**) were synthesized from $Ru(PPh_3)_3Cl_2$ according to published procedures.[5] Tl(OEt) and Tl(acac) were purchased from Strem and used without further purification. 2,2,6,6-tetramethyl heptane-3,5-dione was purchased from Aldrich and used without further purification.

Synthesis of $(PCy_3)(pyr)_2(Cl)_2Ru(CHPh)$ (3). Inside the dry box, 200 mg (0.243 mmol) of **1b** were weighed into a Schlenk flask and dissolved in approximately 5 ml toluene. The Schlenk flask was capped with a rubber septum, removed from the dry box and placed under argon on a Schlenk line. 500 µl of pyridine (6.18 mmol, 25 eq) were added *via* syringe, and the solution immediately turned from violet to green. The reaction was stirred for 30 min at room temperature, and the green solution was transferred *via* cannula filter to a separate Schlenk flask containing approximately 20 ml of 0°C hexanes to precipitate the product as a light green solid. The solid was isolated *via* cannula filtration and dried *in vacuo*. ^{1}H NMR: δ 19.90 (d, 1 H, Ru=C*H*, $^3J_{HP}$ = 12 Hz), 8.76 (br s, 2 H, Ru-pyrH_{ortho}), 8.38 (br s, 2 H, Ru-pyrH_{ortho}), 7.93 (d, 2 H, Ru=CHPhH_{ortho}, $^3J_{HH}$ = 7.2 Hz), 7.64 (br m, 2 H, Ru-pyrH_{para}), 7.54 (t, 1 H, Ru=CHPhH_{para}, $^3J_{HH}$ = 7.2 Hz), 7.29 (br s, 2 H, Ru-pyrH_{meta}), 7.18 (t, 2 H, Ru=CHPhH_{meta}, $^3J_{HH}$ = 7.2 Hz), 7.09 (br s, 2 H, Ru-pyrH_{meta}), 2.34 (app q, 3 H, $H_{cyclohexyl}$), 2.01 (br m, 6 H, $H_{cyclohexyl}$), 1.78-1.67 (br m, 15 H, $H_{cyclohexyl}$), 1.24 (br m, 9 H, $H_{cyclohexyl}$). ^{31}P{^{1}H} NMR: δ 37.71 (s).

Synthesis of $(PCy_3)(pyr)(Cl)_2Ru(CHPh)$ (4). 100 mg of **3** were weighed into a Schlenk flask inside the dry box and dissolved in toluene. The flask was capped, removed from the dry box, and placed in an oil bath preheated to 35°C. The toluene was removed *in vacuo* to azeotrope away the extra equivalent of pyridine, leaving an oily, yellow-green solid. The product was washed with hexanes to remove the yellow-orange color and the product was isolated *via* cannula filtration and dried *in vacuo*, leaving a dark green solid. ^{1}H NMR: δ 19.81 (d, 1 H, Ru=C*H*, $^3J_{HP}$ = 12 Hz), 8.41 (br s, 2 H, Ru-

pyrH_{ortho}), 7.90 (d, 2 H, Ru=CHPhH_{ortho}, $^3J_{HH}$ = 7.2 Hz), 7.65 (br s, 1 H, Ru-pyrH_{para}), 7.51 (t, 1 H, Ru=CHPhH_{para}, $^3J_{HH}$ = 7.2 Hz), 7.18 (t, 2 H, Ru=CHPhH_{meta}, $^3J_{HH}$ = 7.2 Hz), 7.14 (br s, 2 H, Ru-pyrH_{meta}), 2.34 (app q, 3 H, $H_{cyclohexyl}$), 2.01 (br m, 6 H, $H_{cyclohexyl}$), 1.78-1.67 (br m, 15 H, $H_{cyclohexyl}$), 1.24 (br m, 9 H, $H_{cyclohexyl}$). $^{31}P\{^1H\}$ NMR: δ 38.40 (s).

Synthesis of $(PCy_3)(acac)_2Ru(CHCHCPh_2)$ (5a). Inside the dry box, 100 mg (0.11 mmol) of **1a** were weighed into a Schlenk flask and dissolved in approximately 10 ml of CH_2Cl_2 and 200 mg of Tl(acac) (0.66 mmol, 6 eq) were added. The flask was capped with a rubber septum, removed from the dry box, and stirred for 3 hrs under argon on a Schlenk line, during which time the solution turned orange. The solvent was removed *in vacuo*, and the solids were washed with hexanes (3 x 5 ml) to extract the product and PCy_3. The filtrate was collected *via* cannula filtration in another Schlenk flask, and the solvent was removed *in vacuo*.

Inside the dry box, the product mixture was dissolved in benzene, and 100 mg of CuCl (1.01 mmol, 9 eq) were added. The suspension was placed back on the Schlenk line and stirred for 2 hrs, and the solvent was removed *in vacuo*. The product was extracted from the CuCl•PCy_3 polymer with cold hexanes (3 x 5 ml). The filtrate was collected *via* cannula filtration, and the solvent removed *in vacuo*, leaving an orange powder. The product was freeze-dried from benzene for easier isolation. ^1H NMR: δ 18.61 (app t, 1 H, Ru=C*H*, $^3J_{HP}$ = $^3J_{HH}$ =12 Hz), 8.48 (d, 1 H, Ru=CH-C*H*, $^3J_{HH}$ =12 Hz), 7.20-7.70 (m, 10 H), 5.41 (s, 1 H), 5.00 (s, 1 H), 2.12 (s, 3 H), 1.99 (s, 3 H), 1.85 (s, 3 H), 1.78 (s, 3 H), 1.00-1.85 (m, 33 H). $^{31}P\{^1H\}$ NMR: δ 39.45 (s). FAB-HRMS: *m/z* calcd for $C_{43}H_{59}O_4PRu$ (M^+) 772.3194. Found 772.3167.

Synthesis of $(PCy_3)(acac)_2Ru(CHPh)$ (5b). Inside the dry box, 200 mg (0.243 mmol) of **1b** were weighed into a Schlenk flask and dissolved in approximately 10 ml of C_6H_6 and 150 mg of Tl(acac) (0.494 mmol, 2.03 eq) were added. The flask was capped with a rubber septum, removed from the dry box, and stirred for 1-2 hrs under argon on a

Schlenk line, during which time the solution turned green. The solvent was removed *in vacuo*, and the solids were washed with hexanes (3 x 5 ml) to extract the product and PCy_3. The filtrate was collected *via* cannula filtration in another Schlenk flask, and the solvent was removed *in vacuo*.

Inside the dry box, the product mixture was dissolved in benzene, and 100 mg of CuCl (1.01 mmol, 4 eq) were added. The suspension was placed back on the Schlenk line and stirred for 2 hrs, and the solvent was removed *in vacuo*. The product was extracted from the $CuCl{\bullet}PCy_3$ polymer with cold hexanes (3 x 5 ml). The filtrate was collected *via* cannula filtration, and the solvent removed *in vacuo*, leaving a green powder. ^1H NMR (C_6D_6): δ 19.35 (d, 1 H, Ru=C*H*, $^3J_{HP}$ =12 Hz), 8.59 (d, 2 H, H_{ortho}, $^3J_{HH}$ = 8.0 Hz), 7.47 (t, 1 H, H_{para}, $^3J_{HH}$ = 7.3 Hz), 7.37 (app t, 2 H, H_{meta}, $^3J_{HH}$ = 8.0, 7.3 Hz), 5.58 (s, 1 H), 4.76 (s, 1 H), 2.18 (s, 3 H), 2.12 (s, 3 H), 1.80 (s, 3 H), 1.67 (s, 3 H), 1.20-2.00 (m, 33 H). $^{31}P\{^1H\}$ NMR: δ 38.86 (s).

Synthesis of Tl(^{t}Bu$_2$acac). Inside the dry box, 1 g of Tl(OEt) (4.01 mmol) was weighed into a Schlenk flask. The flask was capped with a rubber septum, removed from the dry box, placed on a Schlenk line under argon, and suspended in approximately 20 ml pentane. In a separate flask, 0.85 ml of 2,2,6,6-tetramethyl heptane-3,5-dione (4.07 mmol, 1.01 eq) was added to approximately 10 ml pentane *via* syringe. The Tl(OEt) solution was stirred until it appeared homogeneous, and added to the 2,2,6,6-tetramethyl heptane-3,5-dione solution *via* cannula filtration (to remove any black precipitate from the TlOEt). After stirring for 1 hr, the pentane was removed *in vacuo*. Upon concentration, the product precipitated as a fine, white, crystalline solid. The solid was washed with cold pentane to remove excess starting material, isolated by cannula filtration, and dried *in vacuo*.

Synthesis of (PCy$_3$)(^{t}Bu$_2$acac)$_2$Ru(CHPh) (6). Inside the dry box, 100 mg (0.12 mmol) of **1b** were weighed into a Schlenk flask and dissolved in approximately 10 ml of C_6H_6 and 94 mg of Tl(^{t}Bu$_2$acac) (.24 mmol, 2 eq) were added. The flask was capped

with a rubber septum, removed from the dry box, and stirred for 2 days under argon on a Schlenk line, during which time the solution turned green. The solvent was removed *in vacuo*, and the solids were washed with hexanes (3 x 5 ml) to extract the product and PCy_3. The filtrate was collected *via* cannula filtration in another Schlenk flask, and the solvent was removed *in vacuo.*

Inside the dry box, the product mixture was dissolved in benzene, and 100 mg of CuCl (1.01 mmol, 8 eq) were added. The suspension was placed back on the Schlenk line and stirred for 2 hrs, and the solvent was removed *in vacuo*. The product was extracted from the $CuCl{\bullet}PCy_3$ polymer with cold hexanes (3 x 5 ml). The filtrate was collected *via* cannula filtration, and the solvent removed *in vacuo*, leaving a light green powder. ^{1}H NMR: δ 19.04 (d, 1 H, Ru=C*H*, $^3J_{HP}$ =12 Hz), 8.28 (d, 2 H, H_{ortho}, $^3J_{HH}$ = 8.0 Hz), 7.56 (t, 1 H, H_{para}, $^3J_{HH}$ = 8.0 Hz), 7.31 (t, 2 H, H_{meta}, $^3J_{HH}$ = 8.0 Hz), 5.75 (s, 1 H), 5.11 (s, 1 H), 1.15 (app s, 18 H), 1.10 (s, 9 H), 0.82 (s, 9 H), 1.10-2.10 (m, 33 H). $^{31}P\{^1H\}$ NMR: δ 37.90 (s).

References and Notes

[1]Nguyen, S. T.; Grubbs, R. H. Unpublished results.

[2]Wu, Z.; Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 5503-5511.

[3]Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887-3897. See also Chapter 1 of this thesis.

[4]Lynn, D. M.; Grubbs, R. H. Unpublished results.

[5](a) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100-110. (b) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2039-2041. (c) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858-9859. (d) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3974-3975.

Summary and Conclusions

electron donating have a greater *trans* influence, further facilitating phosphine dissociation. These effects therefore combine to favor the overall equilibrium for olefin binding and phosphine dissociation, increasing the rate of metathesis. Additionally, it is proposed that the more electron donating phosphines facilitate formation of the Ru(IV) metallacyclobutane intermediate, which is believed to be the rate determining step. The sum of these two effects accounts for the large variations in catalyst activity that result from small changes in the electronic donating abilities of the phosphines.

Productive cleavage of the metallacyclobutane regenerates a carbene and bound olefin, which is displaced *via* recoordination of the phosphine to generate the bis(phosphine) propagating alkylidene that is observed by NMR. No unbound phosphine or mono(phosphine) intermediates are observed by NMR during the course of reaction, indicating that they are present only in very small concentrations (less than 5%). This large equilibrium constant for phosphine binding to the metal center, or rather the small equilibrium constant for olefin-phosphine substitution, has direct consequences upon the activities and stabilities of these ruthenium carbenes. *Because less than 5% of the phosphine is dissociated, less than 5% of the active species is in solution at any given time.*

It is exactly this aspect of these systems that permits the living polymerization of strained olefins, fitting nicely within the classic model for other living polymerizations in which the active species is highly reactive, *e.g.* living cationic and free-radical polymerizations. Because the active chain ends are highly reactive, a "trap" is required to sequester the propagating species in an unreactive form—the "trap" being a reaction with a very large equilibrium constant, such that there is only a very small concentration of active chain ends at any given time (see Figure 1 below). In the case of metal alkylidenes, bimolecular decomposition pathways can be facile, and the rate of decomposition is proportional to the square of the concentration of the active species. Thus, reducing the concentration of active species in solution has a dramatic effect upon the rate of catalyst termination. For the titanacyclobutane catalysts, shown to polymerize norbornene in a

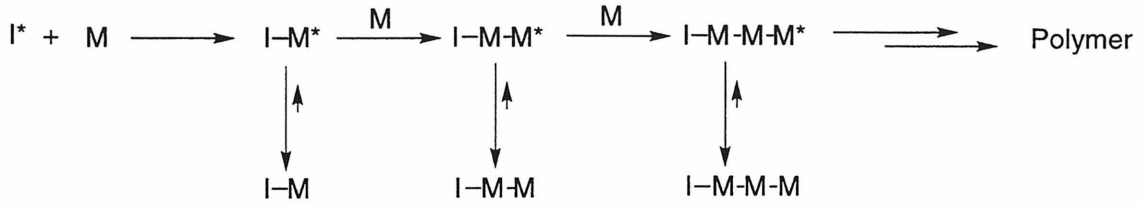
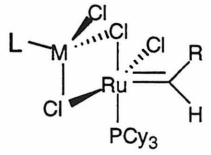


Figure 1. Model for living polymerizations.

living manner, it is the large equilibrium for formation of the metallacyclobutane *vs.* the carbene that provides the required stability.

Although the equilibrium for phosphine dissociation has several attractive features, one unavoidable aspect of this system is the limit that is placed upon catalyst activity. For example, it is often desirable to have more active catalysts for applications other than living ROMP. In addition to faster reaction rates, the catalyst loading can often be decreased if the catalyst is more active, resulting in substantial savings when these relatively expensive catalysts are used for preparative or industrial-scale reactions.

Because the mechanism for **2** involves a pre-equilibrium for olefin binding and phosphine dissociation, the rate of metathesis is effectively proportional to the square-root of the catalyst concentration. The addition of a phosphine scavenger such as CuCl accelerates olefin metathesis, but does not serve to stabilize the active species well enough to guarantee that the reactions will proceed to completion. The search for other phosphine scavengers led to the discovery of the bimetallic catalysts **3**, discussed in Chapter 2. Surprisingly, it was found that transition metal chloride dimers could be used to remove



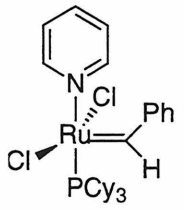
3

R = $CHCPh_2$, Ph
M = Ru, Os, Rh
L = *p*-cymene, $^tBu_2Cp$

one equivalent of phosphine from the ruthenium center, while stabilizing the remaining complex *via* bridging chloride ligands.

These bimetallic catalysts **3** were all more active than the parent catalysts **2**, with the order of activity increasing as M = Ru < Os < Rh. It was determined that the phosphine does *not* dissociate from the ruthenium center during metathesis, such that the rate of reaction is first order with respect to catalyst concentration (as opposed to the square-root dependence observed for **2**). Additionally, it is believed that coordination of the ancillary metal center to the chlorides makes them more electron withdrawing. Observing the trend for **2**, this should enhance catalyst activity. Spectroscopic evidence supports this hypothesis, as the chemical shifts observed in the ^{1}H NMR spectrum corellate well with the observed trend in activities.

Although the bimetallic catalysts (**3**) are more active than **2**, they are also more fragile. Similar to the catalysts developed by Schrock *et al.*, bulky ligands around the metal center are required to prevent rapid bimolecular decomposition of the alkylidenes. Additionally, the stability of these complexes is *more* sensitive to the steric bulk of the carbene substituent. Bulky groups such as the phenyl or diphenyl vinyl moieties are required for the stability of **3**, and for **1** and **4** as well; however, this is *not* the case for **2**.



4

One particular feature that **1**, **3**, and **4** (but not **2**) have in common is the orientation of the alkylidene. In **2**, which is by far the most robust of these complexes, the carbene lies in the Cl-Ru-Cl plane. The carbene is *perpendicular* to the Cl-Ru-Cl plane in **1**, **3**, and **4**, suggesting that this orientation may be responsible, in some fashion, for the rapid decomposition that occurs when the carbene substituent is not very bulky.

One of the more intriguing steps in the proposed mechanism for **2** involves rotation of the carbene by ninety degrees. When the carbene is in the Cl-Ru-Cl plane, the catalyst remains unreactive because there is little or no overlap between the pi-orbitals of the carbene and bound olefin. After rotation, the carbene is parallel to the plane of the olefin, allowing metallacyclobutane formation to occur. The extension of this reasoning leads to the conclusion that, in **2**, the carbene is in an unreactive orientation, providing additional stability regardless of the steric bulk of the carbene substituent. Conversely, because bimolecular decomposition of metal alkylidenes is often thermodynamically favorable, the reactive orientation of the carbene in **1**, **3**, and **4** facilitates decomposition when the carbene substituent is not bulky enough to prevent the formation of dimeric intermediates.

The fact that there are two bulky tricyclohexylphosphines ($\theta = 170°$) coordinated to **2** cannot be ignored, athough it has been shown that analogs of **2** containing smaller phosphines, *e.g.* the diisopropyl phenyl phosphine ($\theta < 160°$) catalyst synthesized in Chapter 1, show the same characteristic stability. The effects of the orientation of the carbene and the steric environment provided by the phosphines cannot be completely separated from one another, however, and it is likely that contributions from both are responsible for the observed stability.

Overall, the original class of ruthenium alkylidenes represented by **2** provides the required activity and versatility for a broad spectrum of reactions. The combination of subtle geometric features in both the ligand sphere and the carbene orientation have interesting consequences. The geometry of these complexes allows for apparently contradictory effects as the steric and electronic properties of the ligands are varied, while the orientation of the carbene appears to provide additional stability towards bimolecular decomposition. Due to the dissociative mechanism that predominates for these catalysts, and also the small equilibrium constant for phosphine dissociation, polymerizations with these systems are often living. Other reactions, such as RCM, may also be considered living as well, due to the *unique* stability of the resulting propagating species.

By effectively removing one equivalent of phosphine, bimetallic catalysts could be synthesized that exhibit activities up to 80 times that of **2**, although they tend to decompose faster. However, these bimetallic catalysts may have other applications, as they can also be used for hydrogenation under relatively mild conditions. This provides a potentially useful method for the synthesis of functionalized polymers with saturated backbones, *via* ROMP, in a one-pot reaction.

The development of 18-electron ruthenium alkylidenes for olefin metathesis was also briefly explored. These compounds were shown to be entirely unreactive towards olefins other than norbornene, although the addition of CuCl or HCl to these catalysts *in situ* generates highly reactive species for RCM and ROMP. Unlike reactions with **2**, the phosphine remains bound to the metal center, and the mechanism for activation in this case is believed to involve exchange of a β-diketonate ligand for a chloride.

In conclusion, a variety of ruthenium olefin metathesis catalysts have been synthesized which exhibit an extremely wide range of activities. Because it is the ligands that ultimately determine the properties of the catalysts—stability, activity, and reactivity—it is essential to understand which ligands are compatible with the ruthenium alkylidenes, as well as to predict the manner in which they will affect the catalyst properties. This research has focused not only on the synthesis, but also on the understanding of these systems, and it is hoped that this will provide a firm basis for future catalyst design.