The Designs, Syntheses, and Applications of Well-Defined, Single Component Group VIII Olefin Metathesis Catalysts

Thesis by

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to the people who shape my life:

those who gave me life and those who are my family,
those who taught me, and
those who are my friends

Acknowledgments

I would like to thank my advisors, Bob Grubbs and Nate Lewis for their supports and mentorships during the past several years. They have taught me how to carry out rigorous scientific research, provided clear guidance for my research, and have been very patient when I am struggling or making mistakes. One could not hope for two better research mentors who are both excellent scientists and good teachers. Together Bob and Nate created an ideal research environment for me and gave me the encouragements and freedom to pursue knowledge.

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I thank Dean Gregory Geoffroy of the Pennsylvania State University for taking me into his laboratory when I was a very "green" college freshman and teaching me the abc of organometallic chemistry. It was his encouragements and supports that steered me into chemistry after undergraduate schools. Many thanks also to the faculties of Caltech and Penn State who taught me the fundamentals of the sciences and the arts.

The research presented in this thesis is the results of collaborations with many people and I thank them for their contributions. Lynda Johnson suggested to me that perhaps the cyclopropene chemistry can be extended to the synthesis of ruthenium(II) carbenes and that ruthenium(II) may behave like tungsten(IV) in carbene-transfer chemistry. This suggestion marks the beginning of the well-defined late transition metal metathesis chemistry and I would not have been able to accomplish all the organometallic work for this chemistry without her intellectual contributions. Her friendship and encouragements and her remarkable knowledge and intuition about transition metal chemistry have helped a struggling first-year graduate student turned his career around.

Greg Fu carried out the lion's share of the early ring-closing metathesis (RCM) chemistry using ruthenium that popularized this catalyst within the synthetic community. His expertise in organic synthesis and RCM chemistry helped to demonstrate the usefulness of ruthenium vinylcarbene in a very short time and I was privileged to collaborate with him on the synthetic part of this project. I also want to thank Konstantinos Litinas and Ned Bowden for their inputs during the early days of the ruthenium-catalyzed RCM chemistry.

Zhe Wu and Alto Benedicto performed the early ROMP experiments to demonstrate the living nature of the ruthenium catalysts. Zhe also synthesized many heteroatom-substituted ruthenium carbenes from which important conclusions about the nature of the carbene substituents can be inferred. Marc Hillmyer and Bob Maughon are the principal people behind the experiments that demonstrated the utilities of the ruthenium metathesis catalysts in making large quantities of fine polymers. Bob is also responsible for the synthesis of the 3-Methyl-3-Phenylcyclopropene that was used in the experiments of chapter 4 of this thesis. Jeff Moore put together a viable synthesis of the 3,3-diphenylcyclopropene that is used throughout my research.

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This thesis was hastily put together during the Christmas season of 1994 and thus is very incomplete. Scott Miller was especially kind to volunteer his holiday time to proofread the first three chapters for me in record time. To him go all the credits for helping to make those chapters readable. All the other blunders and mistakes are mine.

When I arrived at Caltech, I was able to start doing organometallic synthesis right away on my own. This was because Han Sung-Hwan had taught me all the basic techniques when I was at Penn State. Subsequently, I was fortunate to be able to learn from Henry Bryndza, Ron McKinney, Chad Mirkin, Rocco Paciello, and Lynda Johnson. I wish to thank these people for teaching me the "tools of the trade" so that I can become independent.

Synthetic chemistry can't survive without analytical and technical supports. I wish to thank Dr. Robert Lee and the NMR GLA's—Nat Finney, Bryan Coughlin, Zhe Wu, Scot Cohen, Rob Li, Tommy Chen, Tamara Hendrickson, and Curt Hastings—for their help and their patience with my naive NMR questions. Dr. Joseph Ziller of the University of Irvine was responsible for all the crystal structure reported in this thesis—without Joe's amazing skills, my job would have been a lot more difficult. I want to thank Kraig Anderson and Michael Murray for keeping the GC/MS humming. Tom Dunn and Jack Guledjian have done an excellent job to keep the electronic network and the NMR instruments functioning perfectly. Fenton Harvey of the Caltech Analytical Facility and Oneida Research Laboratory carried out all the elemental analysis. I want to thank Rick Gerhart and Gabor Faludi for the beautiful and timely glass blowing/repair. Guy Duremberg, Ray Garcia, and Tony Stark helped me with all the machine shop works. Fran Bennett, Ruth de Pineda, Dan Fralin worried about chemical orders so that I can concentrate on my work. I thank Chris Smith and Paul Carroad for always being very helpful and for taking care of all my various maintenance requests.

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An old Vietnamese proverb states: "After drinking the water, one should remember the source." I am writing these words today because there are other people who believed in my when I was growing up. My parents gave me life and love and were willing to let me go to find freedom and an education. My aunt and uncle, the Carmans, raised my younger brother and me when we arrived as refugees in the United States. The faculty at Williamsport Area High School and the community of Williamsport took me in, educated me, and helped in sending me off to college. It is to these people that I am partially dedicated this thesis.

Caltech is a very special place because of its people . I am at home at Caltech during the last five years and I have made many friends here. It has been difficult for me to let go but it is time to move on. I want to thank all of my friends at Caltech, in and out of the lab for making my life a little bit easier. Thanks to the MJ staff and fellow residents for making a five-year mission in a Caltech dorm a good experience.

Abstract

This thesis reports the synthesis and reactivity studies of a series of $X_2(PR_3)_2M=CHR$ complexes (X is an anionic ligand, L represents a neutral, two-electron donor ligand, M is either Ru or Os, and CHR represents a carbene moiety). These complexes are olefin metathesis catalysts and is remarkable in their stability toward a variety of functional groups, including protic species such as water and acid.

Chapter 2 describes the synthesis, stability, and mechanism of formation of the forementioned $X_2(PR_3)_2M=CHR$ catalysts from a strained 3,3-disubstituted cyclopropene. Their metathesis activities as functions of the anionic ligands and the metal center will be discussed together with the mechanism of cyclopropene-vinylcarbene rearrangement at Group VIII metal centers . In chapter 3 and chapter 4, the modification of the metathesis activity of these catalysts as functions of the ancillary phosphine ligands and the carbene substituents, respectively, will be presented. Chapter 5 describes the applications of this new catalyst system in the self metathesis and ethenolysis of oleic acid and its methyl ester. The acyclic diene metathesis polymerization and polyolefin depolymerization reactions catalyzed by these new catalysts are the subjects of chapter 6. Chapter 7 reports the results of resin-immobilization experiments and Chapter 8 is a collection of the author's personal impressions of the development in this area of chemistry over the last decade.

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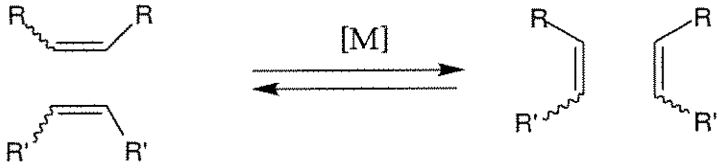
Chapter I

Introduction

Background

The olefin metathesis reaction in its simplest form is a thermoneutral reaction where two new olefins are formed from two other olefinic bonds in the presence of a transition metal catalyst (eq 1). Being discovered almost at the same time as Ziegler-Natta polymerization, olefin metathesis chemistry has remained an active field of research during the past forty years.[1-4] During this time, the catalyst development in this area has progressed continuously through three distinct generations of catalysts. The first generation of catalysts, the so-called classic systems, involved ill-defined, multi-component mixtures of a transition metal salt, an alkylating agent and a hydroxylic proton source. Catalysis is often difficult to initiate and control.[1] (Indeed, it has been estimated that less than a few percent of the transition metal centers in these catalyst mixtures are active at any one time).



(1)

The evolution to the second generation of catalyst represents a classic example of the intimate interplay between mechanistic studies and catalyst development. In the early 1970's, Chauvin and coworkers put forth a proposal that the two most important catalytic intermediates in the olefin metathesis reaction (and its cyclic variation, the Ring-Opening Metathesis Polymerization (ROMP[a]) reaction) are a metal carbene and a metallacyclobutane species (Scheme I).[5,6] Following this proposal, a set of exhaustive mechanistic studies then overwhelmingly supported the involvement of the Chauvin intermediates.[7-13] The early 1980's saw a number of studies involving the syntheses of

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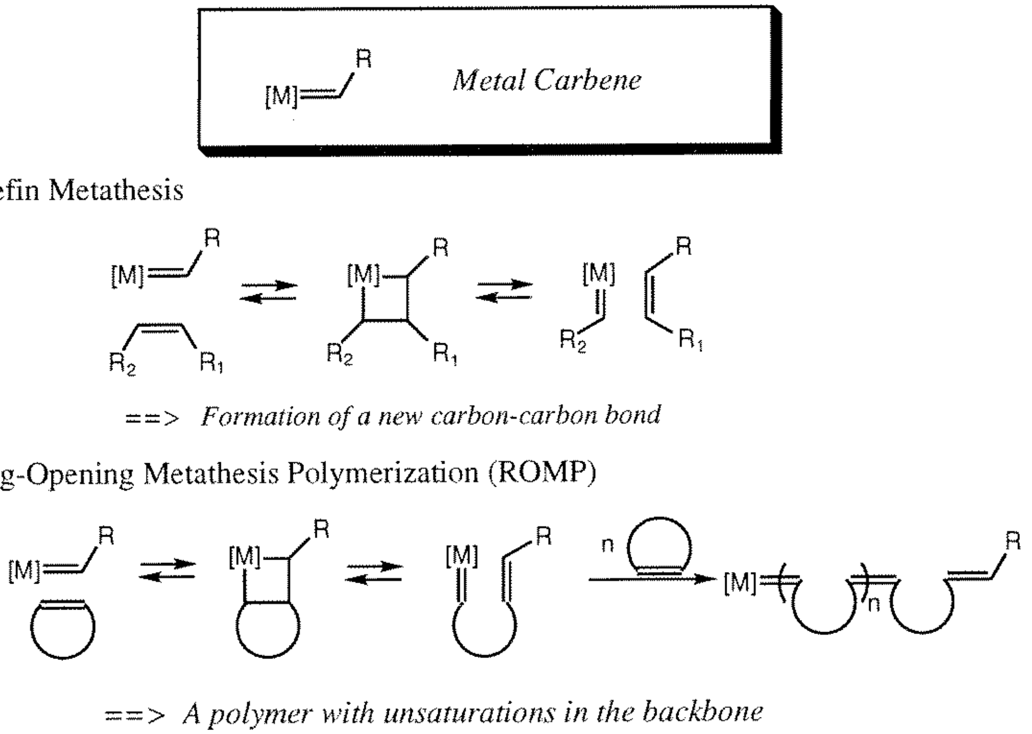
[a] The acronym ROMP was coined by Dr. Timothy Swager, a former member of the Grubbs group, who now holds an academic position at the University of Pennsylvania.

several high oxidation state, early transition metal carbene catalysts for the olefin metathesis reaction.[14-20] Despite their high activities, the catalysts of this second generation are still multicomponent; that is they often require the activation by a Lewis acid catalyst to achieve their best activity.

Scheme I. Transition Metal Carbenes and Their Roles in Olefin Metathesis and ROMP.



It was not until the mid 80's that the third phase in the development of olefin metathesis catalysts began with the discovery of single-component, well-defined, highly active metallacyclobutane and metal carbene catalysts based on Ti, Ta, Mo, W, and Re (Figure 1).[21-27] In these cases, the activity of the metal centers can be modified at will using a variety of techniques available to the organometallic chemist. As the results, the past decade has witnessed numerous developments aimed at obtaining an in-depth understanding of the olefin metathesis reaction as catalyzed by early transition metal complexes. Structural descriptions of active intermediates, structure-function analysis, and ligand-activity relations have all been probed and described in considerable details.[23-25,27]

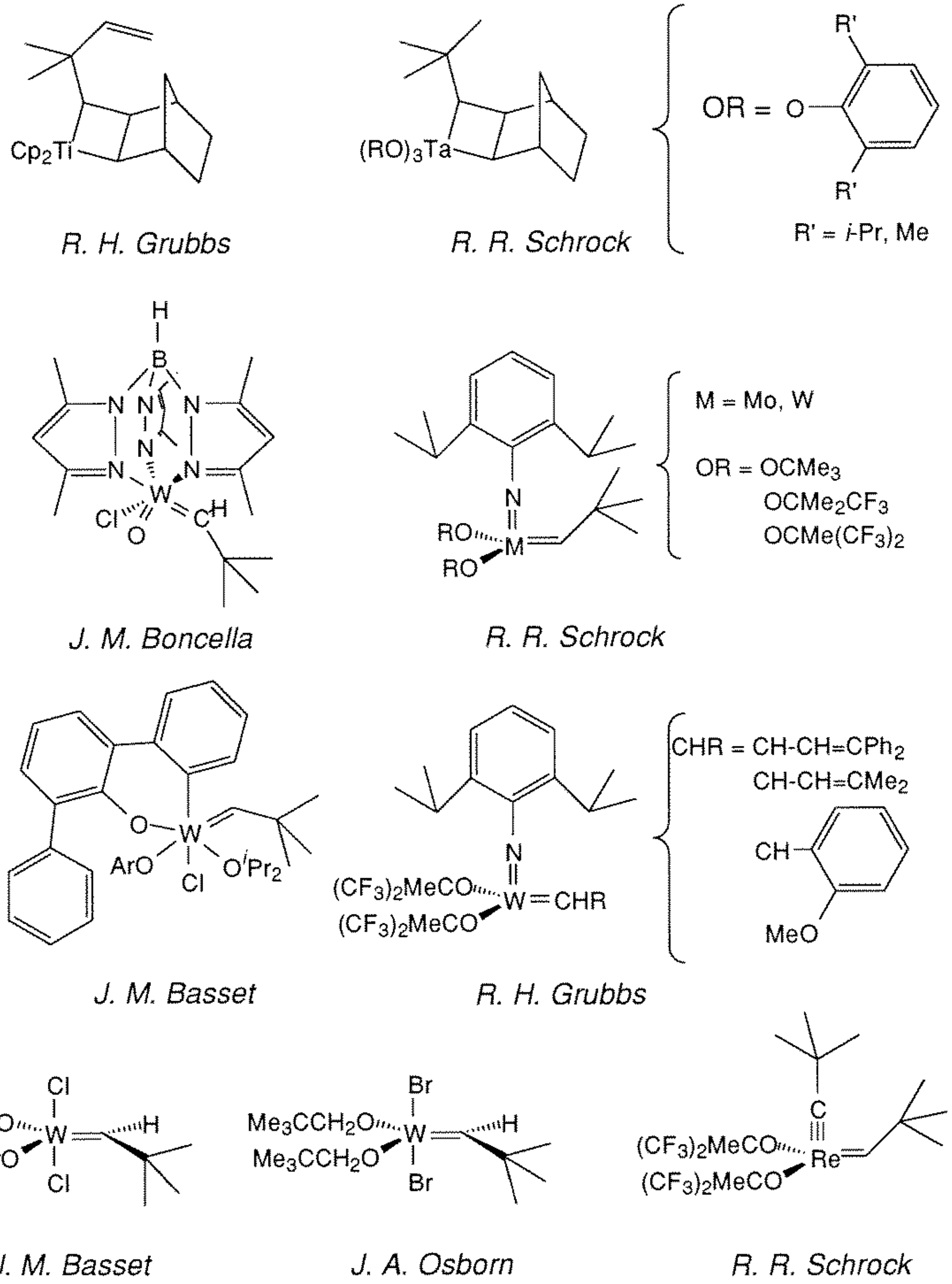


Figure 1. Representative examples of metallacyclobutane and alkylidene olefin metathesis catalysts.[21,28-44] Reprint with modification from reference 45.

The arrivals of olefin metathesis catalysts of the second and third generation have also prompted several efforts to utilize these complexes in controlled polymerizations and organic synthesis.[3,23,24,46,47] Unfortunately, the high oxidation state nature of these early transition metal catalysts and the rigorous synthetic regimens in which they are derived have rendered them inaccessible to the majority of chemists who are not trained in the ways of inert atmosphere chemistry.[b] Indeed, with the possible exception of the Tebbe-Grubbs reagent, the use of carbene-based olefin metathesis catalyst in synthetic applications have been limited to a few research groups. In addition, the high oxophilicity of these carbene-based early metal catalysts have limited their utilities in applications in which functional groups are involved. Figure 2 illustrates the reactivities of the three most popular catalysts shown in Figure 1—the titanacycle developed by Grubbs,[21] and the Schrock alkylidenes based on tungsten and molybdenum[24,25,27]—toward an olefin containing a carbonyl functional groups Fn. The titanium catalyst is the most reactive; it will react with all the carbonyl functionalities such as aldehydes, ketones, esters, and amides before reacting with the olefins. The tungsten-based catalyst is tolerant of esters and amides but still will react with aldehydes and ketones before reacting with the olefins. The molybdenum complex is the most tolerant catalyst in the group in the sense that it will only prefer aldehydes over olefins. With carbonyl compounds being among the mildest functionalities, it is no surprise that these catalysts will not tolerate all the common protic species such as amines, primary alcohols, water, and acids.

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[b] A well-known metathesis chemist have written the following words as a testimony to the long synthetic sequence and the high sensitivities of these well-defined early transition metal catalysts: "There is a penalty to be paid for the intending participant in this activity in as much as the synthesis and use of these newer catalysts places experimental skill at a premium". See: Feast, W. J. In *Comprehensive Polymer Science*; Allen, G; Bevington, J. C., Eds.; Pergamnon Press: New York, 1989; Vol. 4, Chapter 7, pp 135-142.

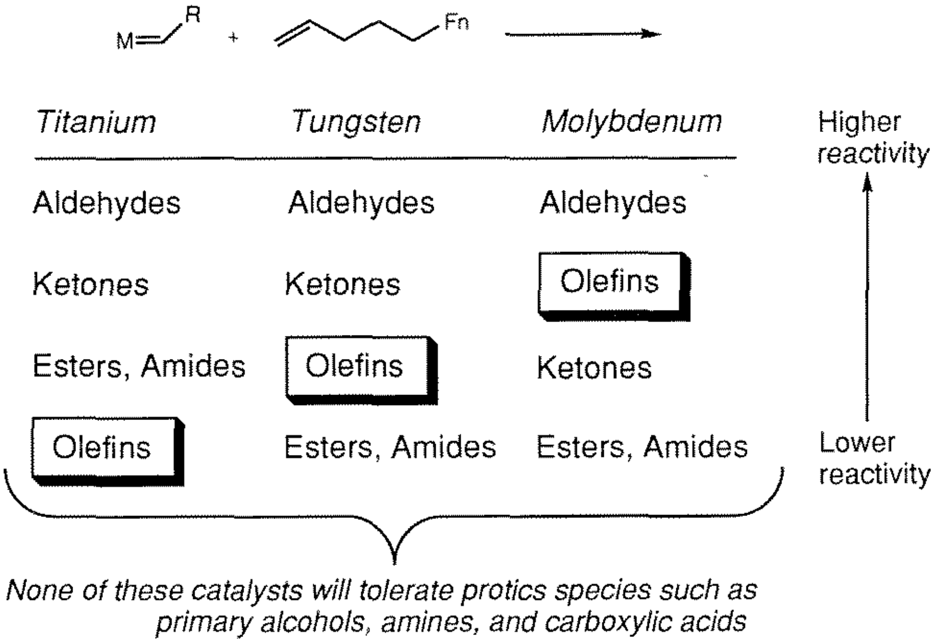

Figure 2. Relative reactivities of well-defined Ti, W, and Mo olefin metathesis catalysts toward an olefin containing a carbonyl functionality.

Although transition metals of all groups are known to catalyze the olefin metathesis reaction in classical systems, the development of late transition metal olefin metathesis catalysts has been trailing behind that of the early transition metals. In my opinion, this phenomenon may be attributed to three reasons: 1) Historical influences. Olefin metathesis was discovered as an unexpected reaction during the early days of Ziegler-Natta chemistry which primarily based on early transition metals. The readily available knowledge from this Ziegler-Natta technology has helped speed up the development of early transition metal-based olefin metathesis chemistry relative to that based on late transition metals.[c] 2) Specialization. Early research efforts in other types of chemistry such as oxidative coupling, hydroformylation, etc... have shown that late

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[c] Indeed, comprehensive surveys of the olefin metathesis literature often reflected a dominance of publications involved early transition metals over those involved late transition metals, see references 1-3.

transition metals are better than early transition metals as catalysts for these processes. Coupled with 1), this observation might have lead to subsequent developments in which early and late transition metals became exclusively "specialized" in the type of chemistry that they catalyzed. In the case of olefin metathesis, this meant that early transition metals catalysts became greatly preferred over late transition metal catalysts. 3) Cost. The diminishing appeals of late transition metal olefin metathesis catalysts in the presence of less expensive (thus, more attractive in terms of costs, especially in industry where most of the early olefin metathesis chemistry was discovered) and often more active (in terms of metathesis rate) early transition metal catalysts. Hence, it is no surprise that the first well-defined olefin metathesis catalysts are those based on early transition metals. Although late transition metal carbene chemistry has remained an active research area to date, their development most often proceed in exclusion of olefin metathesis as the immediate goal.

At the outset of this work the intermediates and the reaction mechanism for Group VIII transition metal metathesis catalysts remained elusive. Such knowledge is important in view of the promise Group VIII metals have shown in polymerizing a wide variety of functionalized cyclic olefins via ROMP in protic solvents.[1,2,48-50] Well-defined, highly active, single-component late transition metal catalysts were desired to open the way to the controlled metathesis of functionalized acyclic olefins, a goal that has eluded early transition metal systems to a certain degree (*vide supra*). Previous studies in the Grubbs group had focused on the chemistry of highly active, functional-group-tolerant catalysts prepared from aquoruthenium(II) olefin complexes.[48-53] In these systems, characterization of the catalytic intermediates has been difficult due to their very low concentrations and high activity in the reaction mixtures. Although it is reasonable to assume that the active species are ruthenacyclobutanes and ruthenium carbenes, the oxidation state and ligation of these intermediates are not known. Furthermore, the discrete ruthenium carbene complexes that have been isolated to date exhibit neither metathesis activity nor are they stable to protic/aqueous solvents[54-56] (see also Chapter 2 and 5).

Given this background, well-defined, single-component ruthenium carbene complexes which posses metathesis activity while functioning in a protic/aqueous media were the objective at the beginning of this work. It was hypothesized that the synthesis of such complexes will help in elucidating some of the outstanding mechanistic questions involving classical late transition metal metathesis system. Furthermore, these complexes may open up new applications in polymer chemistry and organic synthesis by virtue of their functional group tolerance, indication of which was hinted by previous works (*vide supra*). With ruthenium being the least expensive among the late transition metals that possess olefin metathesis activities,[1] the possibilities of these new complexes being used in conventional catalysis was indeed a very exciting prospect.

Thesis Research

This thesis reports the synthesis and reactivity studies of a series of $X_2(PR_3)_2M{=}CHR$ complexes (X is an anionic ligand, L represents a neutral, two-electron donor ligand, M is either Ru or Os, and CHR represents a carbene moiety). These complexes are olefin metathesis catalysts and is remarkable in their stability toward a variety of functional groups, including protic species such as water and acid.

Chapter 2 describes the synthesis, stability, and mechanism of formation of the forementioned $X_2(PR_3)_2M{=}CHR$ catalysts from a strained 3,3-disubstituted cyclopropene. Their metathesis activities as functions of the anionic ligands and the metal center will be discussed. In chapter 3 and chapter 4, the modification of the metathesis activity of these catalysts as functions of the ancillary ligands and the carbene moiety, respectively, will be presented. Chapter 5 describes the applications of this new catalyst system in the self metathesis and ethenolysis of oleic acid and its methyl ester. The acyclic diene metathesis polymerization and polyolefin depolymerization reactions catalyzed by these new catalysts are the subjects of chapter 6. Chapter 7 reports the results of resin-immobilization experiments and Chapter 8 is a collection of the author's personal impressions of the development in this area of chemistry over the last decade.

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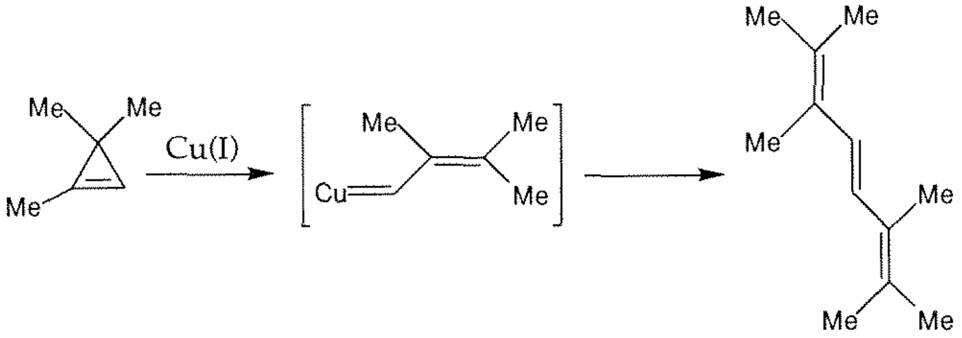
Chapter 2

Well-defined, Single-Component Group VIII Olefin Metathesis Catalysts: Syntheses, Mechanism of Formation, and Effect of the Anionic Ligands on Metathesis Activities

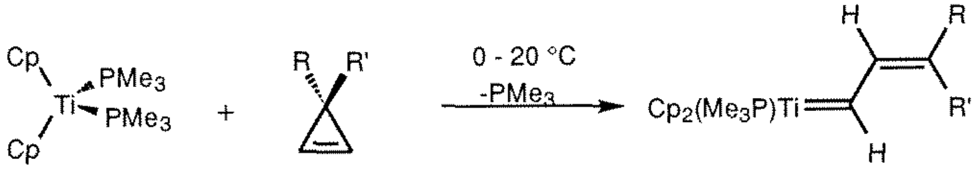
Introduction

The ring-opening rearrangements of cyclopropenes as catalyzed by transition metals is a well-known reaction.[1-3] In the early 1970's, it was suggested that vinylcarbenoid intermediates are often involved in these reactions. For example, the dimerization of 1,3,3-trimethylcyclopropene to 1,1,2,5,6,6-hexamethyl-1,3,5-hexatriene catalyzed by Cu(I) was proposed to proceed through a Cu(I) vinylcarbene complex (eq 1).[4] Other metals complexes such as Hg(II), Tl(III), Ni(0), Pd(0), and Ag(I) also catalyzed related processes where the involvement of metal carbenoid species was implicated.



(1)

Given this background and the explosive development of organotransition metal carbene chemistry during the 70's and 80's, it is surprising that the use of cyclopropenes as a carbene source in the synthesis of transition metal carbenes remained unexplored. Indeed, it was not until 1989 that Binger and coworkers reported the syntheses of vinylcarbene complexes of titanium and zirconium from 3,3-disubstituted cyclopropenes (eqs 2 and 3).[5]



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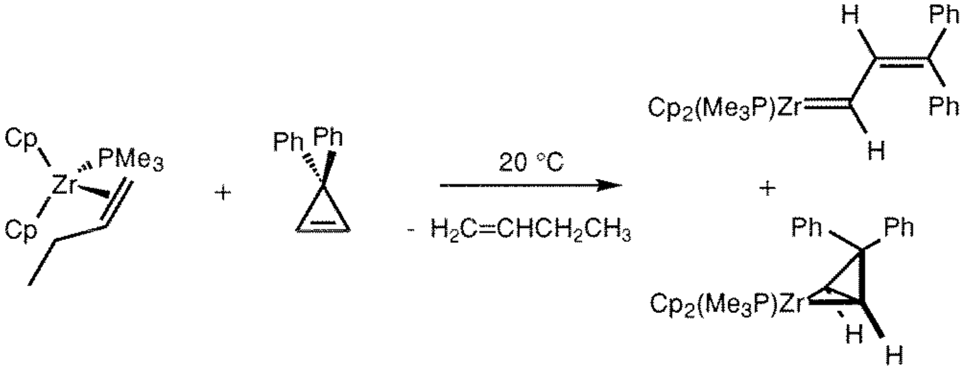
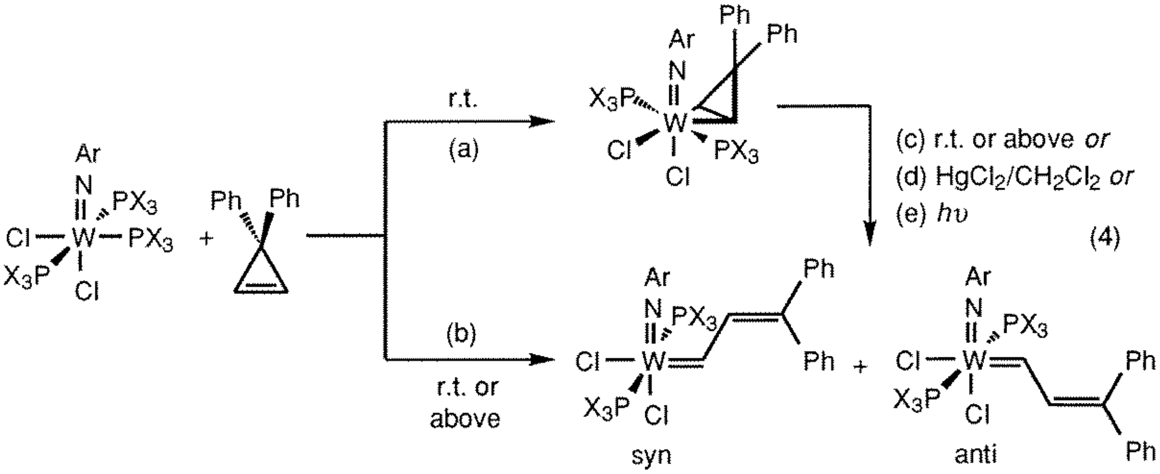
R, R' = Ph, Ph; Ph, Me



(3)

Subsequently, Johnson and Grubbs extend this chemistry to synthesize a series of high oxidation state tungsten imido alkylidene complexes (eq 4).[6,7] Their work offers the first indication that the cyclopropene ring-opening chemistry may be further generalized to include other transition metal centers. Since then, the generality of this reaction has been demonstrated in the syntheses of a wide range of transition metal vinylcarbene complexes ranging from Re(VII)[8] to Ru(II),[9,10] Os(I),[9] Ir(I),[11] and Rh(I).[11] Recent works have indicated that this methodology is also compatible with a W(VI) oxo complex[12] and a Mn(I) metal center.[13]



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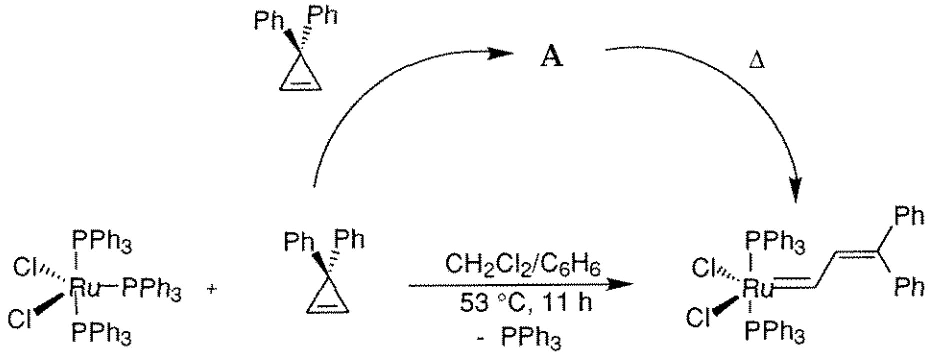
This chapter focuses on the first extension of the cyclopropene ring-opening chemistry toward the syntheses of late transition metal vinylcarbene complexes, in particular those of Ru(II) and Os(II) metal centers. The discussion will center around the syntheses, mechanism of formation, reactivities, and the effect of the anionic ligands on the olefin metathesis activities exhibited by these complexes.

Results and Discussion

Synthesis of *trans*-$(PPh_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$, 1. The reaction of 3,3-diphenylcyclopropene with either $RuCl_2(PPh_3)_3$ or $RuCl_2(PPh_3)_4$ in a 1:1 mixture of CH_2Cl_2/C_6H_6 produces the vinylcarbene complex **1** in good yield (eq 5). The use of a solvent mixture is necessary to ensure the complete homogeneity of the reaction mixture. In addition, temperature and time control are very important: extended reaction time or temperature > 60 °C tends to decompose the product while maintaining reaction at a temperature < 50 °C results in incomplete reaction. In pure powder form, complex **1** is a green solid with a yellow tint; however, microcystalline form of **1** appears as a deep black solid. Complex **1** is most soluble in chlorinated organic solvents such as methylene chloride, 1,2-dicholoroethane, and chlorobenzene. It is moderately soluble in benzene, THF, and ether and is almost insoluble in saturated hydrocarbons.



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(5)

Key to the structural assignment of **1** from the ^1H NMR spectrum are a) the characteristic pseudo-quartet (two overlapping triplets: H_α couples to 2 equivalent phosphorous and H_β) at 17.94 ppm (J_{HH}= 10.2 Hz,J_{PH}= 9.7 Hz) and b) the doublet at 8.7 ppm (J_{HH}= 10.2 Hz) due, respectively, to H_α and H_β of the vinylcarbene moiety. Similar ^1H NMR patterns have been observed for the analogous vinylcarbene complexes

$Cp_2(PMe_3)Ti{=}CH{-}CH{=}CPh_2$,[5] $Cp_2(PMe_3)Zr{=}CH{-}CH{=}CPh_2$[5] and $(ArN)(P(OMe)_3)_2Cl_2W{=}CH{-}CH{=}CPh_2$,[6,7] which were prepared by the addition of 3,3-diphenylcyclopropene to the corresponding reduced precursors. Although not directly comparable, the ^{13}C chemical shift of C_a of **1** at 288.9 ppm is in the same range as those found for a variety of known bis(triphenylphosphine)Ru(II) and -Os(II) carbene complexes.[14-17] The ^{31}P chemical shift at 28.2 ppm for the coordinated triphenylphosphines is similar to that observed at 27.2 ppm for the phosphorous ligands of the recently reported vinylidene complex $(PPh_3)_2Cl_2Ru{=}C{=}CH^tBu$.[18]

The definitive structural determination for **1** comes from an X-ray diffraction experiment (Figure 1). The most notable feature of this structure is the almost coplanar orientation of the vinylcarbene moiety to the P_1-Ru-P_2 plane (Figure 2) (the dihedral angle $\angle$ P-Ru-C1-C2 is 8.46°) which supports the fairly large coupling between H_α and P.[a] The Cl_1-Ru-Cl_1' angle is 148.4(1)°, much smaller than that observed for the Cl_1-Ru-Cl_2 angle in the parent $Cl_2(Ph_3P)_3Ru$ complex 157.2(2)°.[19] Unfortunately, the vinylcarbene moiety is disordered about a two-fold axis (Figure 3), thus preventing an accurate determination of bond lengths and bond angles for this fragment.[b] Selected bond angles and bond distances are listed in Table I.

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[a] In general, $^3J_{HP}$ obeys the Karplus relationship., see: Bentrude, W. G.; Setzer, W. N. in *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis--Organic Compounds and Metal Complexes*; Verkade, J. G.; Quin, L. D. Eds.; VCH Publishers, Inc.: Deerfield Beach, FL, 1987; Methods in Stereochemical Analysis Vol. 8, pp. 365-389. Although not a direct comparison, for $(N\text{-}2,6\text{-}C_6H_3\text{-}Me_2)(PEt_2Ph)_2Cl_2W{=}CHR$ where the C-H bond is almost 90° with the W-P bond, $^3J_{HP}$ is about 2.13 Hz for both the anti and syn isomers, see reference 6.

[b] This disorder is intrinsic to the molecule, see Appendix 2.

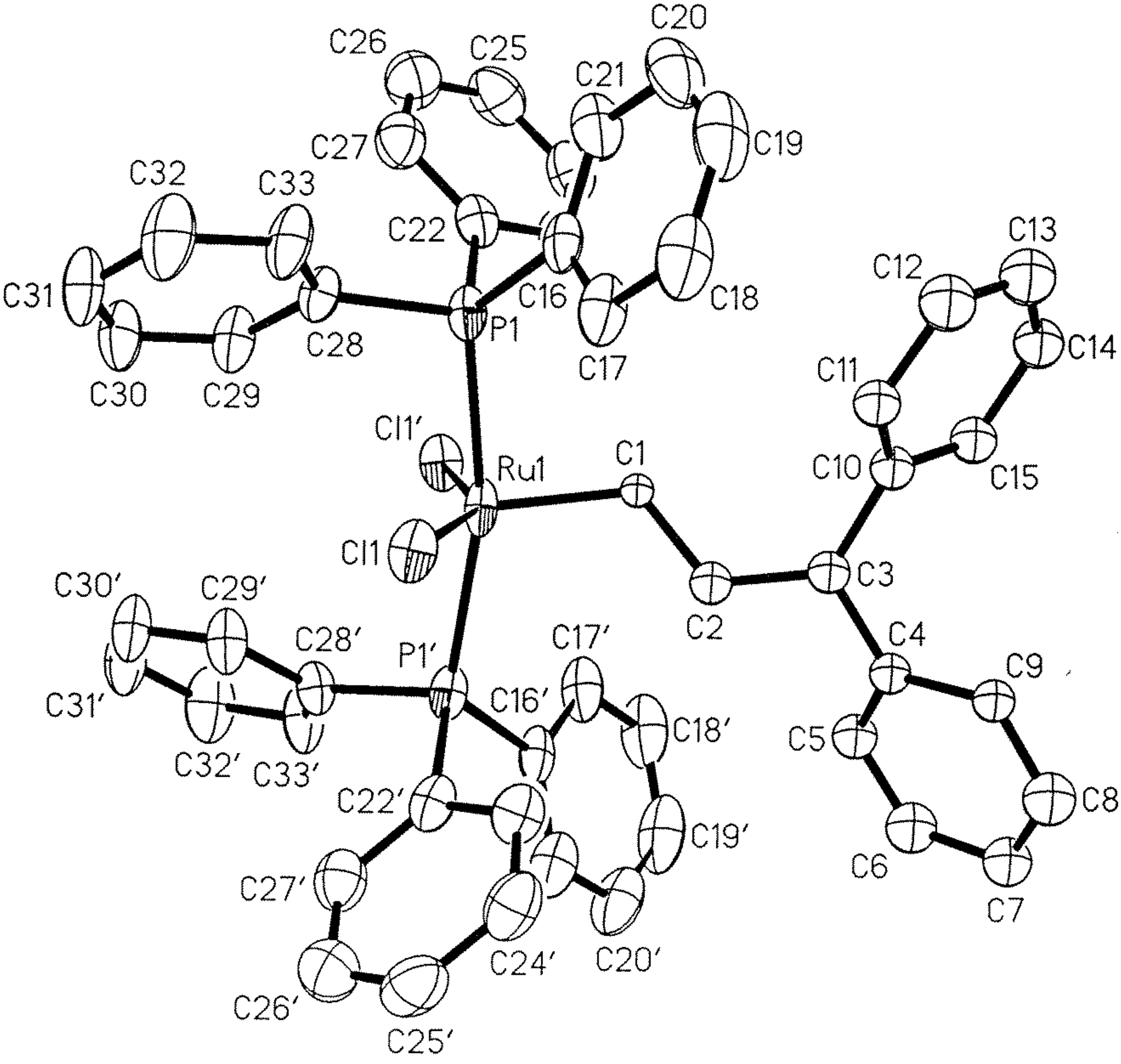


Figure 1. A molecular drawing of **1**. Thermal ellipsoids are drawn at 50% probability levels.

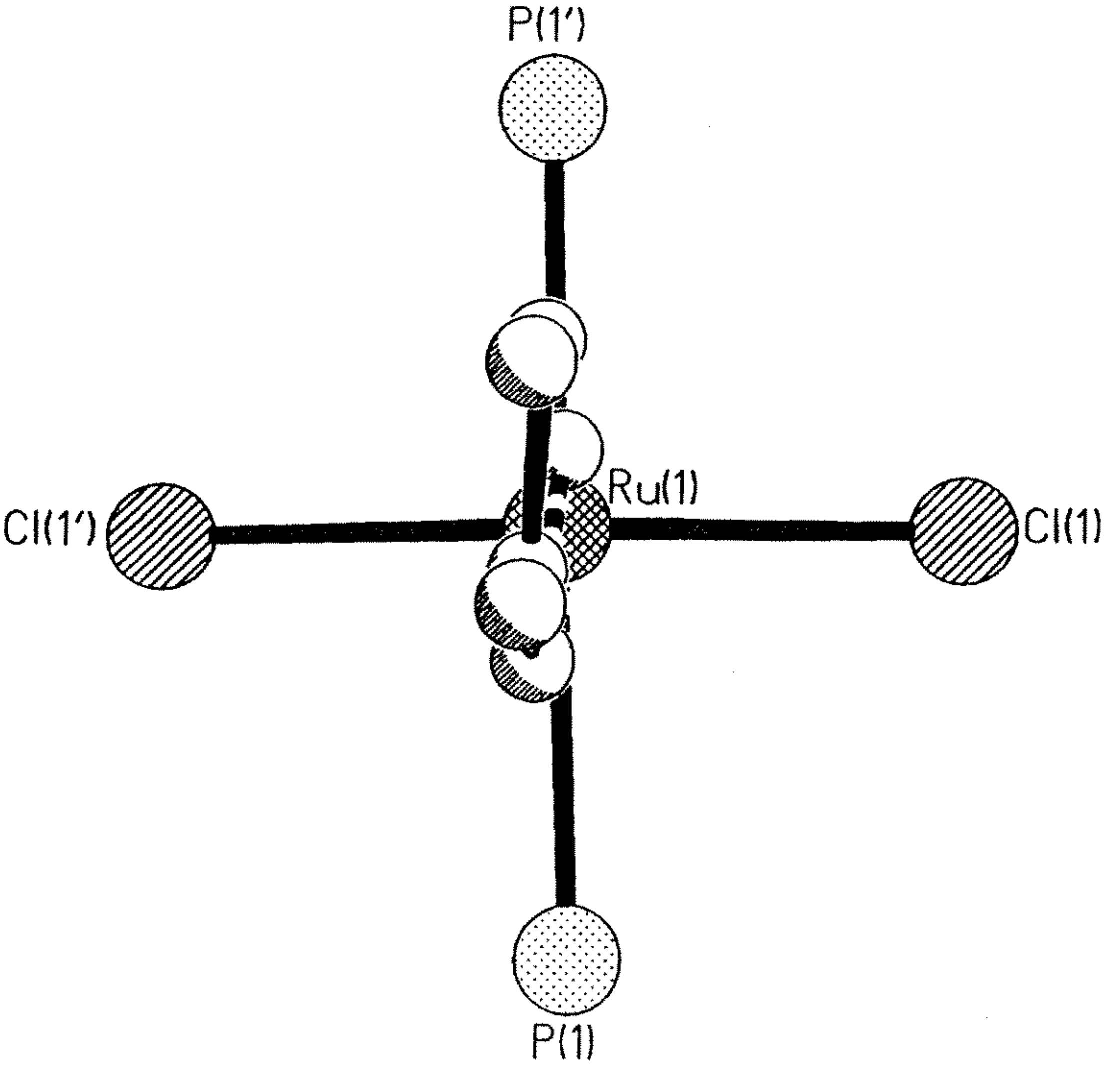


Figure 2. A skeleton drawing of **1**. The view is looking down the C_3-C_2-C_1-Ru fragment of the vinylcarbene moiety.

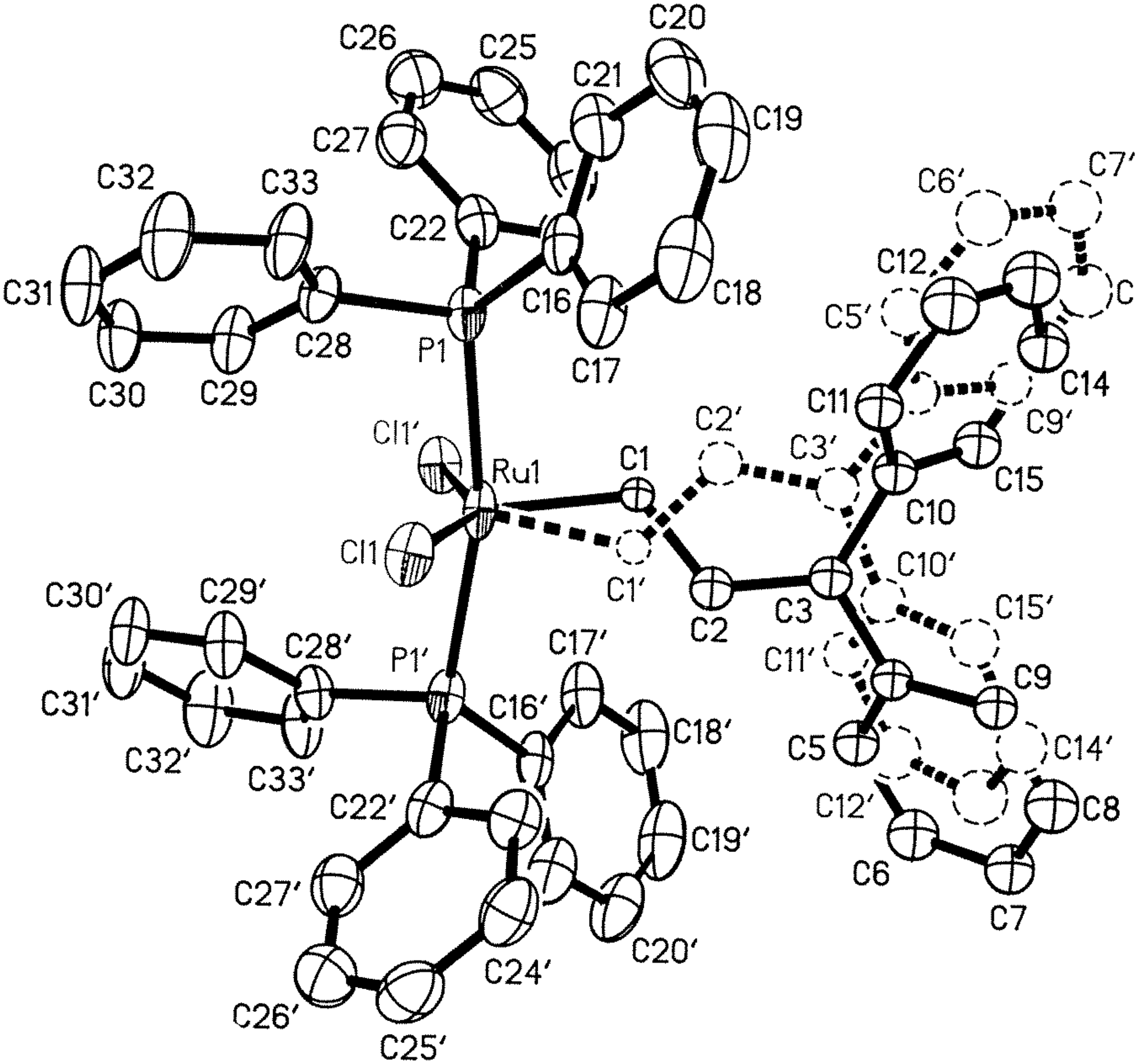


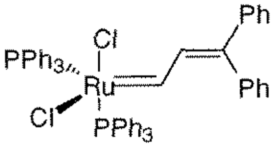
Figure 3. A molecular drawing of **1** showing the nature of the disorder of the crystal structure.

Table I. Selected Bond Lengths and Angles for *trans*-$(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$, **1**.

	Bond lengths (Å)		
Ru(1)-P(1)	2.387(2)	C(1)-C(2)	1.444(11)
Ru(1)-Cl(1)	2.338(2)	C(2)-C(3)	1.419(13)
Ru(1)-C(1)	1.887(7)	C(3)-C(4)	1.485(12)
P(1)-C(16)	1.841(5)	C(3)-C(10)	1.489(12)
P(1)-C(28)	1.823(5)	P(1)-C(22)	1.824(6)
	Bond Angles (deg)		
Ru(1)-C(1)-C(2)	122.6(5)	C(1)-C(2)-C(3)	123.1(7)
P(1)-Ru(1)-P(1')	166.5(1)	Cl(1)-Ru(1)-Cl(1')	148.4(1)
P(1)-Ru(1)-Cl(1)	87.2(1)	P(1)-Ru(1)-Cl(1')	89.1(1)
P(1)-Ru(1)-C(1)	87.5(2)	P(1)-Ru(1)-C(1')	106.0(2)
Cl(1)-Ru(1)-C(1)	108.3(3)	Cl(1)-Ru(1)-C(1')	102.8(3)
Ru(1)-P(1)-C(16)	121.1(2)	Ru(1)-P(1)-C(22)	117.1(2)
C(16)-P(1)-C(22)	103.1(2)	Ru(1)-P(1)-C(28)	104.5(2)
C(16)-P(1)-C(28)	105.3(2)	C(22)-P(1)-C(28)	104.0(2)
C(2)-C(3)-C(10)	125.0(8)	C(2)-C(3)-C(4)	115.4(7)
C(4)-C(3)-C(10)	119.6(8)		

Observation of *cis*-$(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$, 1-cis. If reaction 5 is carried out at room temperature in C_6D_6 (0.035 M solution in Ru) and monitored by both ^1H and ^{31}P NMR spectroscopy, the initial product formed after 3 h at room temperature is a bisphosphine vinylcarbene species, **A**, (H_a = 16.38 ppm (q), H_b = 9.44 ppm (d), J_{HH} = 12.90 Hz) different than **1**. The 36.2 MHz ^{31}P NMR spectrum of this complex shows two resonances at 47.3 ppm and 37.9 ppm corresponding with two inequivalent phosphines on a metal center; free PPh3 is also observed, consistent with loss of one PPh_3 from the starting material. After 10 h, complex **1** begins to appear and continues to grow at the expense of the initial complex **A**. After three days at room temperature, the reaction has gone to completion to give **1** as the single product. At 50° C, the reaction proceeds to completion within 11 h. The conversion of **A** to **1** seems to require the presence of excess PPh_3. For example, an isolated mixture of **A** and **1** converts to pure **1** faster in the presence of one equiv of free PPh_3 than without PPh_3 present.

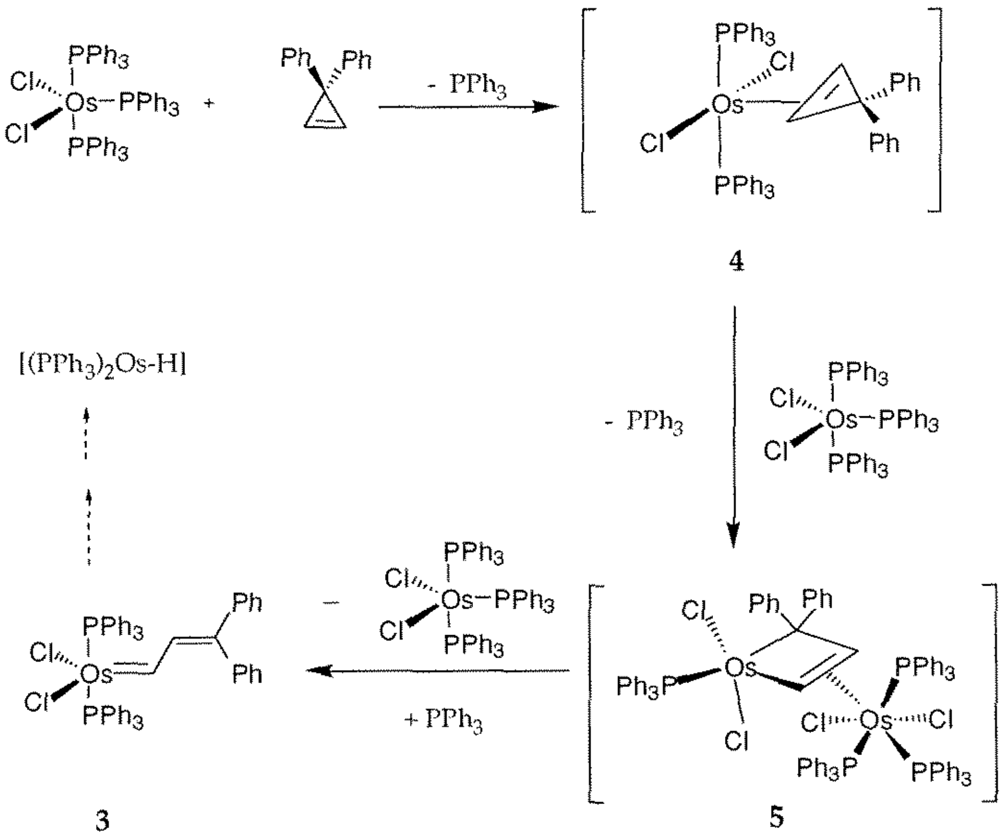
Based on the above observations, we suggest that **A** is the *cis*-phosphine isomer of **1**, **1-cis**. Complex **1-cis** is the kinetically formed isomer in the initial displacement of PPh_3 from $RuCl_2(PPh_3)_3$ to form the vinylcarbene moiety of $(PPh_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$. The thermodynamic product **1** is formed from an PPh_3-assisted associative isomerization of **1-cis**.



A = 1-cis

Observation of $(PPh_3)_2Cl_2Os{=}CH\text{-}CH{=}CPh_2$ and the Mechanism of Vinylcarbene Formation. The precursor $OsCl_2(PPh_3)_3$, **2**, also undergoes a reaction with 3,3-diphenylcyclopropene at room temperature in a 2:1 mixture of C_6D_6:CD_2Cl_2 to give $(PPh_3)_2Cl_2Os{=}CH\text{-}CH{=}CPh_2$, **3**, the Os analog of **1**, as a major product (H_α = 19.67 ppm (q) and H_β = 7.94 ppm (d), J_{HH} = 9.90 Hz). However, when the reaction is carried out at 75°C for an hour, formation of a triplet at -5.7 ppm (J_{HP} = 15.72 Hz) attributed to a $[(PPh_3)_2Os\text{-}H]$ species is observed together with the vinylcarbene product. When the reaction is carried out at room temperature in a 2:1 mixture of C_6D_6:CD_2Cl_2 and monitored by both ^1H and ^{31}P NMR spectroscopy, a gradual color change from green (for $OsCl_2(PPh_3)_3$) to inky blue with some temporary precipitate, dirty green, dirty brown, yellow brown, and finally yellow brown with some insoluble precipitate is observed over several days. From simultaneous spectroscopic observation we propose that this color change process is consistent with the following general mechanism (Scheme I): 1) Displacement of PPh_3 from $OsCl_2(PPh_3)_3$ to from the olefin complex

$(PPh_3)_2Cl_2Os(\eta^2$-3,3-diphenylcyclopropene), **4**. 2) Insertion of another $OsCl_2(PPh_3)_3$ molecule into the C-C bond of the complexed olefin in **4** to generate a bimetallic species **5** which is heavy and thus, temporarily precipitates out of solution . 3) Break down of **5** to generate the final product **3**. 4) Product **3** is then decomposed into the insoluble $[(PPh_3)_2Os\text{-}H]$ byproduct which precipitates out of the solution. The details of this final decomposition step are not well understood at the moment.



Scheme I. Proposed Mechanism for the Formation of $(PPh_3)_2Cl_2Os{=}CH\text{-}CH{=}CPh_2$, **3**.

The ^1H NMR spectrum of the reaction mixture between $OsCl_2(PPh_3)_3$ and 3,3-diphenylcyclopropene in a 2:1 mixture of C_6D_6:CD_2Cl_2 shows two different olefinic resonances for **4** (H_1 = 5.87 ppm (dd) and H_2 = 6.32 ppm (dd), J_{HH} = 8.66 Hz). The ring protons of complex **5** are observed significantly upfield relative to those of **4** (H_1 = 2.82

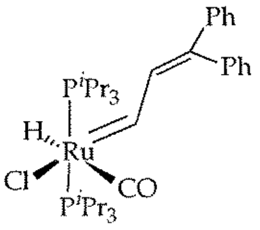
ppm (m) and H_2 = 3.17 ppm (m)), consistent with a metallacylic nature. The 36.2 MHz ^{31}P NMR spectrum of the reaction mixture before the vinylcarbene formation shows a ratio of 2:4:3 for PPh_3:**5**:**4**, further supporting this formulation. Longer reaction time will yield **3** but unfortunately, the isolation of **3** has been problematic due to the onset of decomposition to $[(PPh_3)_2Os\text{-}H]$ which occurs before the complete conversion of **5** to **3**, even at room temperature. The assignment of the bisphosphine stoichiometry for the Os-H species is based solely on a triplet resonance -5.73 ppm (J_{PH} = 15.72 Hz) in the ^1H NMR spectra of both the reaction mixture and the isolated precipitate at the end of the reaction.

A small amount of an η^2-3,3-diphenylcyclopropene complex could be observed at the initial stage of the reaction between $RuCl_2(PPh_3)_3$ and 3,3-diphenylcyclopropene in CD_2Cl_2. Concurrent with the appearance of Complex **A**, a sharp doublet (4.56 ppm, J_{HH} = 11.56 Hz) and a broad doublet (3.29 ppm, J_{HH} = 11.56 Hz)can be observed in the H NMR spectrum of the reaction mixture. These resonances may be attributed to the olefinic proton of the ruthenium analog of **4**, $(PPh_3)_2Cl_2Ru(\eta^2$-3,3-diphenylcyclopropene). The lack of ^{31}P coupling in this complex is very similar for that in $(PR_3)_2Cl_2Ru(\eta^2$-3,3-diphenylcyclopropene) (see Chapter 3), (R = Cy, ^iPr, Cps) and may be explained by a rapid rotational exchange on the ^1H NMR time scale (300 MHz). As the reaction approach completion, this complex eventually disappear from the reaction mixture.

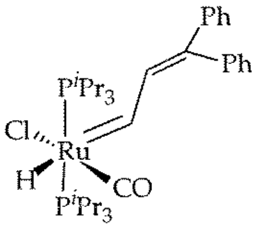
Although no clear evidences for an bimetallic complex was observed in the reaction of $RuCl_2(PPh_3)_3$ with 3,3-diphenylcyclopropene, it is conceivable that a ruthenium analog of **5** could be formed but is not observable from the reaction of $RuCl_2(PPh_3)_3$ with $(PPh_3)_2Cl_2Ru(\eta^2$-3,3-diphenylcyclopropene). Indeed, because Os is a third-row metal and has more electron density on the metal for π-backbonding it has a higher affinity for olefin than its second-row analog Ru analog thus its olefin complexes are more stable than ruthenium olefin complexes. This is the case observed by Taube and coworkers between analogous Os(II) and Ru(II) coordination complexes.[20,21]

A related mechanism to that shown in Scheme I has been proposed in a recent paper by Grubbs and coworkers where a bimetallic intermediate similar to **5** was observed from the reaction of $(PMe_3)_2Cl(CO)Ir(\eta^2$-3,3-diphenylcyclopropene) and $IrCl(CO)(PMe_3)_2$.[22] Given the isoelectronic nature of both $RuCl_2(PPh_3)_3$ and $OsCl_2(PPh_3)_3$, it is reasonable to speculate that the mechanism proposed in Scheme I may also operate in the formation of complex **1**.

The Rearrangement of 3,3-Diphenylcyclopropene at other Ruthenium(II) Centers. A majority of ruthenium(II) derivatives does not react with 3,3-diphenylcyclopropene to yield ruthenium vinylcarbene. In our hand, $(DMSO)_4RuCl_2$, $RuHCl(PPh_3)_3$, $RuH_2(PPh_3)_4$, and $Ru(PPh_3)_3(OAc)_2$ do not give the corresponding vinylcarbene complexes when being exposed to 3,3-diphenylcyclopropene. The two exceptions are $RuBr_2(PPh_3)_3$ (*vide infra*) and $RuHCl(CO)(P^iPr_3)_3$. The latter complex reacts with 3,3-diphenylcyclopropene in C_6D_6 to give a dark red solution whose ^1H NMR spectrum shows, in addition to the starting material, two new complexes **B** and **C** in 5:1 ratio. Characteristic to **B** in the ^1H NMR spectrum are resonances at 16.93 ppm (dq, H_α, $J_{H\alpha H\beta} = 15.5$ Hz, $J_{H\alpha HRu} = 3.0$ Hz, $J_{HP} = 3.4$ Hz), 9.56 ppm (d, H_β, $J_{H\alpha H\beta} = 15.5$ Hz), and -3.58 ppm (dt, $J_{H\alpha HRu} = 3.0$ Hz, $J_{HP} = 26.6$ Hz). Characteristic to **C** in the ^1H NMR spectrum are resonances at 16.69 ppm (dq, H_α, $J_{H\alpha H\beta} = 14.3$ Hz), 10.82 ppm (d, H_β, $J_{H\alpha H\beta} = 14.3$ Hz), and -3.86 ppm (dt, $J_{HP} = 25.6$ Hz). The ^{31}P NMR spectrum of the reaction mixture exhibits two singlet resonances at 81.5 ppm and 80.2 ppm for **B** and **C**, respectively. Based on these spectral data and that reported for the related complex $(P^iPr_3)_2(CO)Cl_2Ru{=}Ch{-}CH{=}CPh_2$,[23] we assigned isomeric structures for **B** and **C** where the vinylcarbene is trans to Cl in **B** and cis to Cl in **C**.



B

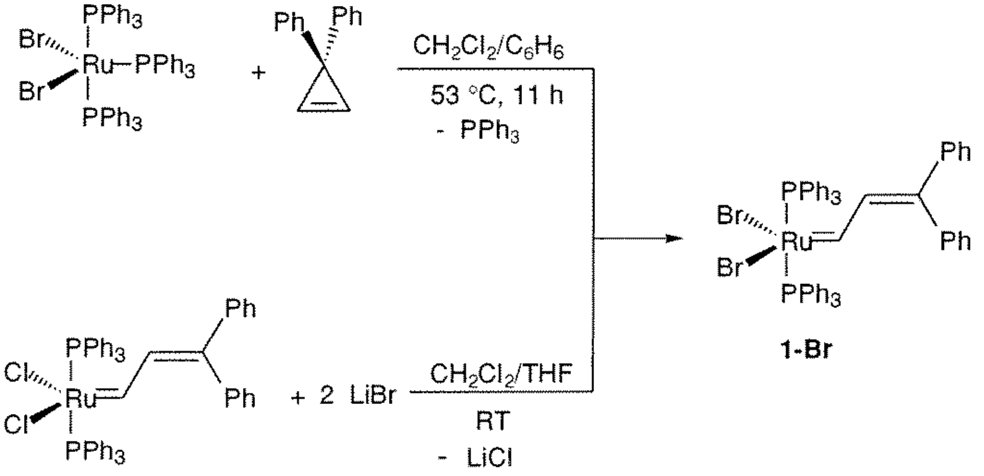


C

Derivatives of 1 with Anionic Ligands Other than Cl. Several derivatives of **1** can be synthesized from simple metathetical exchange of the chloride ions in **1** with other anions. For example, $(PPh_3)_2Br_2Ru{=}CH{-}CH{=}CPh_2$, **1-Br**, can either be synthesized from the metathesis of **1** and LiBr or directly from $RuBr_2(PPh_3)_3$ (eq 6). Similarly, $(PPh_3)_2I_2Ru{=}CH{-}CH{=}CPh_2$, **1-I**, is best obtained from **1** and NaI (eq 7). The direct synthesis from $RuI_2(PPh_3)_3$ was not attempted due to the difficulties in preparing this starting material from RuI_3. In addition, metathetical exchange from $RuCl_2(PPh_3)_3$ and NaI proved to be somewhat problematic. Finally, the synthesis of $(PPh_3)_2TFA_2Ru{=}CH{-}CH{=}CPh_2$ (TFA = CF_3COO), **1-TFA2**, is most efficient with 2 equiv of AgTFA as the TFA-transfer agent (eq 7). Careful controlling the addition of 1 equiv of AgTFA to $(PPh_3)_3Cl_2Ru{=}CH{-}CH{=}CPh_2$ gives rise to $(PPh_3)_2(TFA)ClRu{=}CH{-}CH{=}CPh_2$, **1-TFACl**. Other carboxylate anions such as acetate and benzoate can also be exchanged with the chlorides in **1** in similar manners. However, attempts to replace the chlorides in **1** with other anions such as alkoxides and non-coordinating counterions has so far been unsuccessful.

Complexes **1-Br** and **1-I** are brown green solids in powder form and dissolves in CH_2Cl_2 to give green solutions with yellow tint. Complex **1-TFA2** is a bright green solid and **1-TFACl** is a fluorescent green solid. Both of these dissolves in CH_2Cl_2 to give solution with color corresponding to the solid state color. The structure of **1-TFACl** is depicted in eq 9 as an ionic complex due to its lowest solubility in organic solvents within the series. There may exist an alternate structure where the both the Cl and TFA ligands are covalently bound to the metal center. In solution, **1-TFACl** dissociates to gives **1-**

TFA2 and **1** over time. Selected spectroscopic data for these derivatives are listed in Table II.



1-Br

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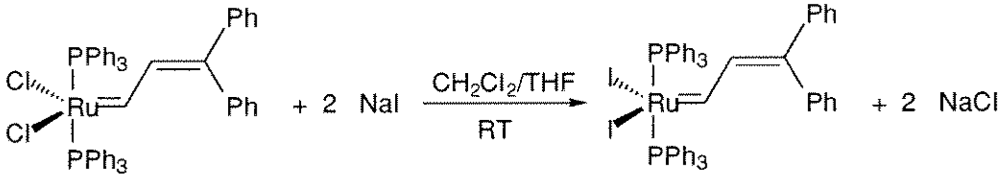

1-I

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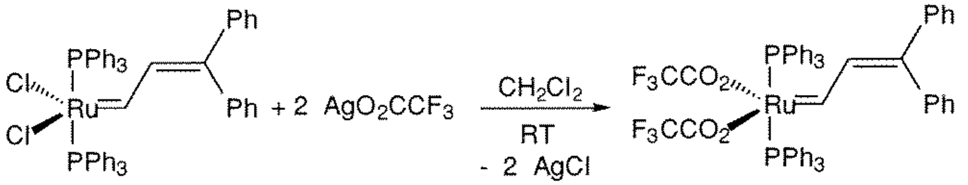

1-TFA2

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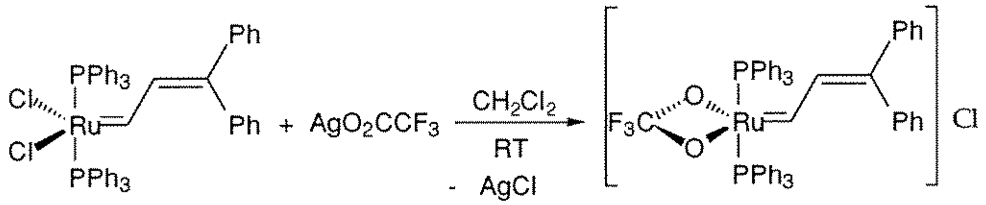

1-TFACl

(9)

Stability of 1 and Its Derivatives. In the solid state, complex **1** is stable indefinitely under an inert atmosphere and for several days in air. In a test experiment, a powder sample of **1** was exposed to atmospheric conditions over one month and then examined using ^{1}H NMR spectroscopy[c] at which time the carbene resonances were still detectable. The complex is stable for weeks in organic solvents in the absence of oxygen. Surprisingly, **1** is also stable for several days in CH_2Cl_2/C_6H_6 in the presence of water, alcohol, or a diethyl ether solution of HCl. This unusual stability is consistent with the desired functional-group tolerance of Group VIII metathesis catalysts (*vide supra*). As expected, **1** does not undergo Wittig-type reactions with either a ketone or an aldehyde.

Table II. Selected Spectroscopic Data for **1** and Its Derivatives.[a]

Complex	H_α		H_β		δP	C_α		
	δ(ppm)	J_{HP}	δ(ppm)	J_{HH}	(ppm)	δ(ppm)	J_{PC}	J_{CH}
1-I	16.27 (q)	9.5	7.81(d)	10.1	34.6	284.6(t)	10.6	152.2
1-Br	17.26 (q)	9.6	8.07(d)	10.3	30.4	289.0(t)	10.2	152.7
1	17.67 (q)	10	8.28(d)	10.2	28.3	288.9(t)	10.0	153.5
1-TFA2	19.02 (dt)	4.7	7.92(d)	11.6	29.0	317.3(t)	11.4	147.7
1-TFACl	18.69 (dt)	7.9	8.26(d)	11.6	29.6	311.9(t)	10.6	151.0

[a] Chemical shifts are in ppm, coupling constants are in Hz. Solvents = CD_2Cl_2.

ROMP Activity of 1 and Its Derivatives. Four basic characteristics distinguish complex **1** and its derivatives from other Ru carbenes existing in the literature: 1) It is formally a Ru(II) metal center.[d] 2) It is a 16-electron complex.[e] 3) It is 5-coordinate. 4) The carbene moiety is not a cumulene (i. e. vinylidene or allenylidene). We believe this combination of attributes is responsible for the metathesis activities of this class of

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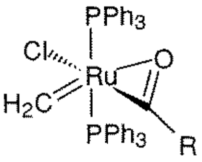
[c] The NMR sample was prepared under inert atmosphere conditions.

[d] In assigning the formal oxidation state of the metal center, the carbene moiety is considered to be a neutral, 2-electron donor ligand. This convention is set in accordance with previous literature reports, see also references 14-17.

[e] The electron count is 16 regardless of formal oxidation state assignments.

ruthenium carbene complexes. For examples, we[24] and others[25] have shown that Roper-type carbenes such as **6**, **7**, and **8** (which are formally 18-electron, 6-coordinate, Ru(II) carbenes) or **9** and **10** (which are formally 18-electron, 5-coordinate, Ru(0) carbenes) are inactive for the ROMP of norbornene. Complex **11**,[18] which is very similar to **1** except for the fact that it is a vinylidene[f] is also inactive for the ROMP of norbornene.[26]



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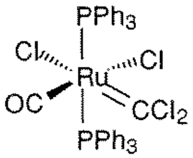

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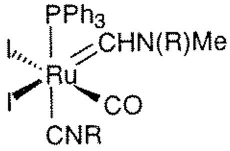

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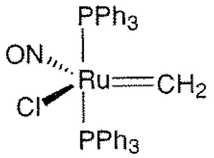

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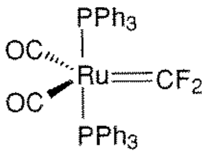

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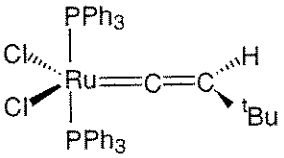

11

Complex **1** polymerizes norbornene in a 1:8 mixture of CD_2Cl_2/C_6D_6 at room temperature to yield polynorbornene. When the reaction is monitored by ^1H NMR spectroscopy, a new signal, attributed to H_α of the propagating carbene, was observed at 17.79 ppm (q). Its identity and stability was confirmed by preparing a block polymer with 2,3-*dideuterio*norbornene and *perprotio*norbornene. When 2,3-*dideuterio*norbornene was added to the propagating species, the new carbene signal vanished and then reappeared when *perprotio*norbornene was added for the third block (Scheme II). Even more remarkable is the fact that this process can be stopped and repeated at will over a period of several weeks as long as the reaction mixture is kept cold (-20° C) under inert atmosphere during the resting period. These experiments

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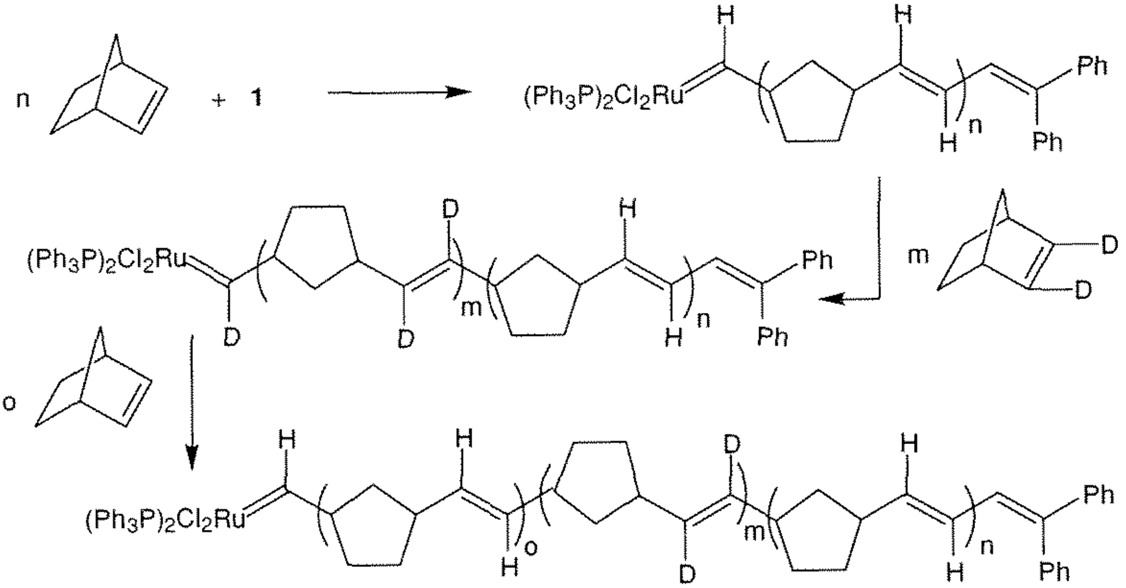
[f] The detailed examination of the role of the carbene moiety in the metathesis activity of this class of ruthenium complexes is reserved for Chapter 4.

demonstrate that the active polymer is stable and that chain termination and transfer are extremely slow relative to propagation, thus satisfying the sole criteria for a "living polymer".[g] In addition, extensive kinetic studies have been carried out by Benedicto and Grubbs to rigorously verify the living nature of this polymerization reaction.[27]

Scheme II. The Block Copolymerization of 2,3-*Dideuterio*norbornene and *Perprotio*norbornene by **1**.



Although initiation is slower than propagation at room temperature,[28] complete conversion of the parent vinylcarbene to the propagating carbene can be achieved. At 40°C in dichloromethane, complete initiation is achieved quickly.[27] The propagating carbene, generated from the reaction of **1** with norbornene, is quite stable in the presence

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[g] This system is living because the propagating alkylidene is stable on the time scale of the reaction and, as was demonstrated by the blocking experiment, will continue to polymerize quantitatively on addition of further aliquots of monomer several hours after the original amount of norbornene has been consumed. See: (a) Szwarc, M. *Carbanions, Living Polymers and Electron Transfer Processes*; Wiley-Interscience: New York, 1968. (b) Van Beylen, M.; Bywater, S.; Smets, G.; Szwarc, M.; Worsfold, D. J. *Adv. Polym. Sci.* **1988,** *86*, 87-143.

of water or ethanol (up to 1000 equivalents per catalyst molecule in a 1:9 mixture of CH_2Cl_2/THF; unfortunately, **1** is not soluble in either pure water or alcohol). Protic solvents do not slow down the polymerization activity of the catalyst.

The modification of **1** with other anionic ligands has a tremendous effect on the norbornene ROMP activity of the vinylcarbene parent catalyst. In essence, putting more electron donating anionic ligands on the ruthenium center in **1** results in a slower propagation rate and a corresponding qualitative decrease in the relative k_p/k_i ratio. Thus under the same monomer concentration and monomer/catalyst ratio (140:1), **1-I** will effect ROMP of norbornene the slowest while **1-TFACl** will ROMP norbornene the fastest. Correspondingly, the polynorbornene obtained using **1-TFACl** catalyst will have very high molecular weight (225 K) and broad PDI (2.91) while that obtained using **1-I** will have the lowest molecular weight (30 K) and PDI (1.23).

The effect of the anionic ligand variation can be observed visually. For a series of simultaneous experiments in five different test tubes, each contains one of the five derivatives from **1-I** to **1-TFACl** (0.5 mL of a 4.5 mM solution) and norbornene (140 equiv), the appearance of the reaction mixture at completion can serve as a qualitative indicator of the change k_p/k_i ratio. At completion, the reactions containing **1-TFACl** and **1-TFA2** retain the original color of the starting catalyst (bright and fluorescent green, respectively) due to incomplete initiation. The reaction solutions for these tubes are also the most viscous, evidence of high-molecular-weight polymer ($k_p >> k_i$). On the other hand, the tubes containing **1-I** rapidly change its color from dark green to bright yellow, a sign of total initiation (complete lost of the original conjugated carbene). The solution in the tube **1-I** is also more free-flowing, indication of low-molecular-weight polymers ($k_p \sim k_i$). Tube **1-Br** and **1-Cl** would be of intermediate viscosity although their color also would have changed to bright yellow from dark green. Table III lists the complete physical data of the polymer samples obtained from this experiments.

Table III. The Polymerization of Norbornene by **1** and Its Derivatives.[a]

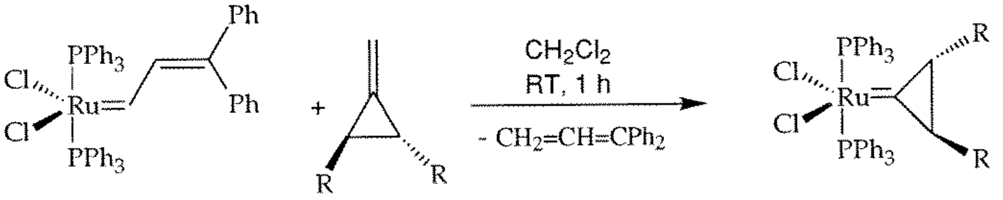
Catalyst	M_w[b]	PDI	
1-I	30K	1.23	$k_i \sim k_p$
1-Br	45K	1.32	
1-Cl	51K	1.32	$k_i < k_p$
1-TFA2	73K	3.04	
1-TFACl	225K	2.91	$k_i << k_p$

k_p/k_i increases ↓

[a]Conditions: [Ru] = 4.5 mM, Norbornene = 140 equiv, 20% CH_2Cl_2 in benzene.
[b] From GPC in CH_2Cl_2 vs. polystyrene standards.

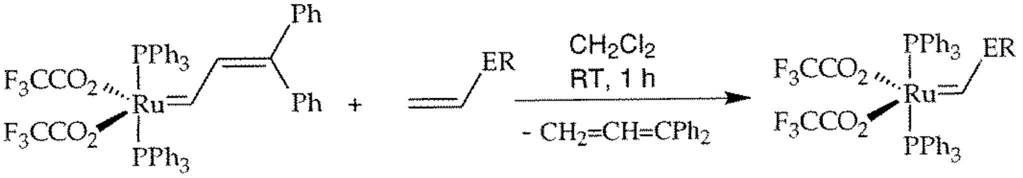
Although the ROMP of norbornene by **1** and its derivatives represents a conceptual advance in the area of well-defined, late transition metal metathesis catalyst at the time of observation (ca 1991), these catalysts are not very active in the polymerization of cyclic monomers less strained than norbornene (calculated SE = 27.2 kcal/mol[29]). Grubbs and coworkers have reported the use of **1** in the polymerization of bicyclo[3.2.0]hept-2-ene[30] (calculated SE = 37 kcal/mol[31]), bicyclo[4.2.0]oct-2-ene[32] and *trans*-cyclooctene[32] (calculated SE = 16.7 kcal/mol[29]). However **1** and its derivatives reported in this chapter does not polymerize *cis*-cyclooctene (calculated SE = 7.4 kcal/mol[29]) or cyclopentene (calculated SE = 6.8 kcal/mol[29]).

Acyclic Olefin Metathesis Activity of 1. Complex **1** and its anionic derivatives are not active for the metathesis of normal acyclic olefins such as *cis*-2-pentene. In the case of strained terminal olefins and electron-rich vinyl-functionalized olefins the metathesis reaction does occur stoichiometrically to give the functionalized ruthenium carbene in good yield (eqs 10 and 11).[32,33]



(10)

R = H, CO_2H, CO_2Me



(11)

E = O; R = Et, COMe
E = S; R = CH_2Ph
E = NR'; NRR' =Carbazole, Pyrolidinone, Imidazole

The only instances where **1** and its derivatives catalyze the productive metathesis of acyclic olefins is with highly conjugated terminal olefins such as 1,1-dimethyl-1,3-butadiene and vinylferrocene (Chapter 4), perhaps due to the low energy cost involved in the activation of such conjugated olefins (i. e. the final product is also a conjugated ruthenium carbene). Nevertheless, these examples have offered the first clues that the metathesis of normal acyclic olefins such as *cis*-2-pentene might be achieved.

Conclusion

The above observations demonstrate that carbene complexes are viable intermediates in the olefin metathesis reactions with Group VIII metals, since an isolated, well-characterized ruthenium carbene complex shows all the characteristic reactions that are required for such intermediates. We have shown the first examples of ROMP and productive acyclic olefin metathesis using **1** and explored the ability to tune the catalytic activity of the ruthenium vinylcarbene center through the modification of its anionic ligands. The potential for solvent variation and other ligand modifications held great promise for further fine-tuning the reactivity of the catalyst. These are the subjects of the next chapters in this thesis.

Experimental

General Considerations. All manipulations were performed using standard Schlenk techniques or drybox procedures. 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. ^{31}P NMR spectra were recorded with either a JEOL FX-90Q (89.60 MHz ^{1}H; 22.53 MHz ^{13}C; 36.2 MHz ^{31}P) spectrometer (locking on a static ^{7}Li lock sample and reference to an external 85% H_3PO_4 sample where a 10 mM solution of PPh_3 in $CDCl_3$ will exhibit a resonance at -5.4 ppm) or when indicated, with a JEOL GX-400 (399.65 MHz ^{1}H; 140 MHz ^{13}C; 161.85 MHz ^{31}P) spectrometer (locking on the ^{2}D solvent signal and reference to an external 85% H_3PO_4 sample where a 10 mM solution of PPh_3 in $CDCl_3$ will exhibit a resonance at -4.9 ppm). ^{1}H and ^{13}C NMR spectra were recorded with either a QE-300 Plus (300.10 MHz ^{1}H; 75.49 MHz ^{13}C) spectrometer or a Bruker AM-500 (500.138 MHz ^{1}H; 125.759 MHz ^{13}C) spectrometer at ambient temperature. NMR data are reported as follows: chemical shifts (multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration, assignment, and coupling constant (Hz)). ^{1}H NMR chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) (δ scale) with TMS employed as the internal standard. ^{13}C NMR chemical shifts are reported in ppm downfield from tetramethylsilane (δ scale) with the solvent resonance employed as the internal standard (CD_2Cl_2 at δ 53.8) and are obtained from complete proton-decoupled spectra while coupling constants are measured from coupled spectra with full NOE enhancement.

Materials. Benzene and tetrahydrofuran (THF) were distilled or vacuum-transferred from sodium-benzophenone ketyl. Methylene chloride (CH_2Cl_2) was dried over CaH_2, vacuum-transferred, and then degassed by three continuous freeze-pump-thaw cycles.. Pentane was stirred over concentrated H_2SO_4, dried over $MgSO_4$ and CaH_2, and then transferred onto sodium-benzophenone ketyl solubilized with tetraglyme.

Methanol was distilled over $Mg(OMe)_2$ and degassed by three continuous freeze-pump-thaw cycles. Water was obtained from the in-house deionized water source at Caltech and degassed by bubbling a stream of argon through the solvent for 15 minutes. Benzene-d_6 and THF-d_8 were distilled over sodium-benzophenone ketyl. Methylene chloride-d_2 was dried over CaH_2, vacuum-transferred, and then degassed by three continuous freeze-pump-thaw cycles. Deuterium oxide was degassed by bubbling a stream of argon through the solvent for 15 minutes. Ethanol-d_6 was dried over activated neutral alumina, vacuum-transferred and degassed by three continuous freeze-pump-thaw cycles. $RuCl_2(PPh_3)_3$,[34] $RuCl_2(PPh_3)_4$,[34] $RuHCl(CO)(P^iPr_3)_2$,[35] $RuBr_2(PPh_3)_3$,[34] and $OsCl_2(PPh_3)_3$[36] were synthesized according to literature procedures. 3,3-Diphenylcyclopropene was prepared following the procedure described in Appendix 1. Reagent grade LiBr and NaI were obtained from Mallinkrodt and used as received. Silver trifluoroacetate (AgTFA) is obtained from Aldrich Chemical Company, grounded into a fine powder and dried under vacuum in the dark until dry. Norbornene is obtained from Aldrich, dried over sodium, and vacuum-transferred into a storage flask before use. All other chemicals were obtained from Aldrich Chemical Co. and used as received.

Synthesis of $(PPh_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$, 1. In a typical reaction, a 200 mL Schlenk flask equipped with a magnetic stirbar was charged with $RuCl_2(PPh_3)_4$ (6.00 g, 4.91 mmol) inside a nitrogen-filled drybox. Methylene chloride (40 mL) was added to dissolve the complex followed by 100 mL of benzene to dilute the solution. 3,3-Diphenylcyclopropene (954 mg, 1.01 equiv) was then added to the solution via pipet. The reaction flask was capped with a stopper, removed from the box, attached to a reflux condenser under argon and heated at 53 °C for 11 h. After allowing the solution to cool to room temperature, all the solvent was removed *in vacuo* to give a dark yellow-brown solid. Benzene (10 mL) was added to the solid and subsequent swirling of the mixture broke the solid into a fine powder. Pentane (80 mL) was then slowly added to the mixture via cannula while stirring vigorously. The mixture was stirred at room temperature for 1 h and allowed to settle before the supernatant was removed via cannula filtration. This washing procedure was repeated two more times to ensure the complete removal of all phosphine by-products. The resulting solid was then dried under vacuum overnight to afford 4.28 g (98%) of **1** as a green powder with a yellow tint.

^{1}H NMR (C_6D_6): δ 17.94 (pseudo-quartet = two overlapping triplets, 1 H, Ru=C*H* , J_{HH}= 10.2 Hz, J_{PH}= 9.7 Hz), 8.70 (d, 1 H, C*H*=CPh$_2$, J_{HH}= 10.2 Hz); ^{31}P NMR (C_6D_6): δ 28.5 (s).

^{1}H NMR (CD_2Cl_2): δ 17.62 (pseudo-quartet = two overlapping triplets, 1 H, Ru=C*H* , J_{HH}= 9.9 Hz, J_{PH}= 9.7 Hz), 8.22 (d, 1 H, C*H*=CPh$_2$, J_{HH}= 9.9 Hz); ^{31}P NMR (CD_2Cl_2): δ 28.2 (s); ^{13}C NMR (CD_2Cl_2): δ 288.9 (t, Ru=*C*, J_{CP} = 10.4 Hz), 149.9 (t, *C*H=CPh$_2$, J_{CP} = 11.6 Hz).

X-ray Data Collection, Structure Determination and Data Refinement for $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$, 1. Please see Appendix 2 for a complete write up of the X-ray diffraction experiment.

Observation of the Reaction Between $OsCl_2(PPh_3)_2$ and 3,3-Diphenylcyclopropene. The Rearrangement from 4 to 5 to 3. In the drybox, $OsCl_2(PPh_3)_2$ (23 mg, 2.23 x 10 $^{-2}$ mmol) was weighed into a 5 mm NMR tube equipped with a Teflon-lined screw cap. CD_2Cl_2 (0.2 mL) was then added to dissolve the green solid following by C_6D_6 (0.4 mL). 3,3-Diphenylcyclopropene (5.2 mg, 1.2 equiv), weighed on the tip of a disposable pipet, was added to the mixture. The tube was capped, shaken vigorously, and then taken out of the drybox to be monitored by NMR spectroscopy.

Spectrosccopic data for **4**. ^{1}H NMR (1:2 :: CD_2Cl_2:C_6D_6): δ 6.32 (dd, 1 H, CH=C*H* , J_{HH}= 8.7 Hz), 5.87 (dd, 1 H, C*H*=CH, J_{HH}= 8.7 Hz); ^{31}P NMR (1:2 :: CD_2Cl_2:C_6D_6): δ -11.0 (s).

Spectrosccopic data for **5**. ^{1}H NMR (1:2 :: CD_2Cl_2:C_6D_6): δ 2.82 (m, 1 H, CH=C*H*), 3.17 (dd, 1 H, C*H*=CH); ^{31}P NMR (1:2 :: CD_2Cl_2:C_6D_6): δ -24.2 (s, 3P), -32 (s, 1P).

Spectrosccopic data for **3**. ^{1}H NMR (1:2 :: CD_2Cl_2:C_6D_6): δ 19.67 (pseudo-quartet = two overlapping triplets, 1 H, Os=C*H* , J_{HH}= 9.9 Hz), 7.94 (d, 1 H, C*H*=CH, J_{HH}= 9.9 Hz); ^{31}P NMR (1:2 :: CD_2Cl_2:C_6D_6): δ 4.71 (s).

Observation of Reaction of 3,3-Diphenylcyclopropene with Other Ru (II) Centers. In a typical reaction, the ruthenium(II) complex (20 mg) was weighed into a 5 mm NMR tube *and dissolved with* C_6D_6 *(0.6 mL) inside the drybox.* Next, ,3,3-Diphenylcyclopropene was weighed on tip of a glass pipet and added to the NMR tube. The tube was then capped, shaken vigorously, taken out of the drybox, and monitored by NMR spectroscopies.

Spectrosccopic data for **B**. ^{1}H NMR (C_6D_6): δ 16.93 (dq, H_α, $J_{H\alpha H\beta}$ = 15.5 Hz, $J_{H\alpha HRu}$ = 3.0 Hz, J_{HP} = 3.4 Hz), 9.56 ppm (d, H_β, $J_{H\alpha H\beta}$ = 15.5 Hz), -3.58 ppm (dt, $J_{H\alpha HRu}$ = 3.0 Hz, J_{HP} = 26.6 Hz); ^{31}P NMR (C_6D_6): δ 81.5 .

Spectrosccopic data for **C**. ^{1}H NMR (C_6D_6): δ 16.69 ppm (dq, H_α, $J_{H\alpha H\beta}$ = 14.3 Hz), 10.82 ppm (d, H_β, $J_{H\alpha H\beta}$ = 14.3 Hz), -3.86 ppm (dt, J_{HP} = 25.6 Hz); ^{31}P NMR (C_6D_6): δ 80.2.

Synthesis of $(PPh_3)_2Br_2Ru$=CH-CH=CPh_2, 1-Br. In the drybox, **1** (790 mg, 0.888 mmol) was added to a 100 mL Schlenk flask equipped with a magnetic stirbar. containing LiBr (1.16g, 15 equiv). Methylene chloride (70 mL) was then added. The reaction was taken outside of the box, attached to an argon line, and allowed to stir at room temperature for 10 h under argon and then filtered into another flask. The mixture was then evaporated to dryness, washed with degassed water (2 x 20 mL) and MeOH (3 x 20 mL), redissolved in methylene chloride (5 mL) and precipitated out with pentane (40 mL). The brown supernatant was discarded and the remaining green solid was finally washed with pentane (2 x 20 mL) and then dried under vacuo for 18 h. Yield = 608 mg (70 %).

^{1}H NMR (CD_2Cl_2): δ 17.26 (pseudo-quartet = two overlapping triplets, 1 H, Ru=C*H* , J_{HH}= 9.6 Hz, J_{PH}= 10.3 Hz), 7.81 (d, 1 H, C*H*=CPh_2, J_{HH}= 9.6 Hz); ^{31}P NMR (CD_2Cl_2): δ 30.4 (s).

Synthesis of $(PPh_3)_2I_2Ru$=CH-CH=CPh_2, 1-I. In the drybox, **1** (790 mg, 0.888 mmol) was added to a 100 mL Schlenk flask equipped with a magnetic stirbar. containing NaI (1g, 8 equiv). Methylene chloride (70 mL) was then added. The reaction was taken outside of the box, attached to an argon line, and allowed to stir at room temperature for 10 h under argon and then filtered into another flask. The mixture was then evaporated to dryness, washed with degassed water (2 x 20 mL) and MeOH (3 x 20 mL), redissolved in methylene chloride (5 mL) and precipitated out with pentane (40 mL). The brown supernatant was discarded and the remaining green solid was finally washed with pentane (2 x 20 mL) and then dried under vacuo for 18 h. Yield = 705 mg (74 %).

^{1}H NMR (CD_2Cl_2): δ 16.27 (pseudo-quartet = two overlapping triplets, 1 H, Ru=C*H* , J_{HH}= 9.9 Hz, J_{PH}= 9.7 Hz), 8.28 (d, 1 H, C*H*=CPh_2, J_{HH}= 10.11 Hz, J_{HP} = 9.47 Hz); ^{31}P NMR (CD_2Cl_2): δ 34.6(s).

Synthesis of $(PPh_3)_2TFA_2Ru$=CH-CH=CPh_2, 1-TFA2. In the drybox, **1** (1 g, 1.125 mmol) was dissolved in methylene chloride (40 mL) in a 100 mL Schlenk flask equipped with a magnetic stirbar. In another flask was dissolved AgTFA (522 mg, 2 equiv) in THF (10 mL). Both flasks were then taken out of the drybox and attached to an argon line. The ruthenium solution was cooled down to 0° C in an ice-water bath and the solution of the silver salt was added dropwise via double cannula into the stirring ruthenium solution over a period of ten minutes during which time the solution turned bright green and white precipitate began to appear. The reaction was allowed to warm up to room temperature slowly over the next 2 h under argon and then filtered into another flask. The mixture was then evaporated to dryness, redissolved in methylene chloride (4 mL) and precipitated out with pentane (40 mL). The brown supernatant was discarded and the remaining green solid was finally washed with pentane (2 x 20 mL) and then dried under vacuo for 18 h. Yield = 1.1 g (94 %).

^{1}H NMR (CD_2Cl_2): δ 19.02 (dt, 1 H, Ru=*CH* , J_{HH}= 11.6 Hz, J_{PH}= 4.7 Hz), 7.92 (d, 1 H, C*H*=CPh_2, J_{HH}= 11.6 Hz); ^{31}P NMR (CD_2Cl_2): δ 29.01 (s); ^{13}C NMR (CD_2Cl_2): δ 311.93 (t, Ru=*C*, J_{CP} = 10.6 Hz, J_{CH} =151.0 Hz), 164.34 (q, CF_3CO_2, J_{FC} = 38.5 Hz), 113.52 (q, CF_3CO_2, J_{FC} = 287.1 Hz).

Synthesis of $(Ph_3P)_2TFA_2Ru$=CH-CH=CPh_2, 1-TFACl. In the drybox, **1** (1 g, 1.125 mmol) was dissolved in methylene chloride (40 mL) in a 100 mL Schlenk flask equipped with a magnetic stirbar. In another flask was dissolved AgTFA (253 mg, 2 equiv) in THF (10 mL). Both flasks were then taken out of the drybox and attached to an argon line. The ruthenium solution was cooled down to 0° C in an ice-water bath and the solution of the silver salt was added dropwise via double cannula into the stirring ruthenium solution over a period of ten minutes during which time the solution turned bright green and white precipitate began to come out of solution. The reaction was allowed to warm up to room temperature over the next 15 minutes under argon and then filtered into another flask. The mixture was then evaporated to dryness, redissolved in methylene chloride (4 mL) and precipitated out with pentane (40 mL). The brown supernatant was discarded and the remaining green solid was dried quickly and redissolved in methylene chloride (15 mL). Pentane was then added until precipitate began to form. The flask was capped and put into a freezer at -20°C overnight . The green precipitate was isolated during the next day, washed with pentane (2 x 20 mL), and then dried under vacuo for 18 h. Yield = 0.652 g (60 %). The remaining supernatant is a mixture of **1-TFA**, **1-TFA2**, and **1**. A second crop may be obtained using the same procedure.

^{1}H NMR (CD_2Cl_2): δ 18.69 (dt, 1 H, Ru=*CH* , J_{HH}= 11.6 Hz, J_{PH}= 7.9 Hz), 8.26 (d, 1 H, C*H*=CPh_2, J_{HH}= 11.6 Hz); ^{31}P NMR (CD_2Cl_2): δ 29.6 (s); ^{13}C NMR (CD_2Cl_2): δ 317.3 (t, Ru=*C*, J_{CP} = 11.4 Hz, J_{CH} =147.7 Hz), 163.83 (q, CF_3CO_2, J_{FC} = 37.24 Hz), 113.40 (q, CF_3CO_2, J_{FC} = 288.83 Hz).

Polymerization of Norbornene Catalyzed by 1. At room temperature, 2 mg of **1** polymerized 70 equiv of norbornene in 0.5 mL of a 1:8 CD_2Cl_2/C_6D_6 solvent mixture in 3 h. The polymer was about 90% trans by ^1H NMR spectroscopy. The classical $RuCl_3$ systems also give high (>90%) trans polymer.[37,38]

Comparing the Polymerization of Norbornene Catalyzed by 1 and its Derivatives. In the drybox and into five different NMR tubes was carefully weighed the following: **1-I** (2 mg, 2.25 x 10^{-3} mmol), **1-Br** (2 mg, 2.25 x 10^{-3} mmol), **1** (2 mg, 2.25 x 10^{-3} mmol), **1-TFA** (2 mg, 2.25 x 10^{-3} mmol), **1-TFACl** (2 mg, 2.25 x 10^{-3} mmol). CD_2Cl_2 (0.1 ml) was then added to each tube followed by C_6D_6 (0. 4 mL). Next, norbornene (0.13 mL of a stock solution (made up from 230 mg norbornene in enough C_6D_6 to make 1 mL of solution)) was added each tube. The tube was then capped, shaken and taken out of the box to be monitored by ^1H NMR.

On the Stability of 1. Complex **1** showed no detectable decomposition in a 2:3 CD_2Cl_2/C_6D_6 solvent mixture after 2 weeks, was stable in the presence of 3 equiv of 1N HCl in diethyl ether for more than 3 days, and did not react with excess (> 5 equiv) acetone or propionaldehyde after several days at room temperature.

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Chapter 3

Well-defined, Single-Component Group VIII Olefin Metathesis Catalysts: Effects of Phosphine Ligands on Metathesis Activities

Introduction

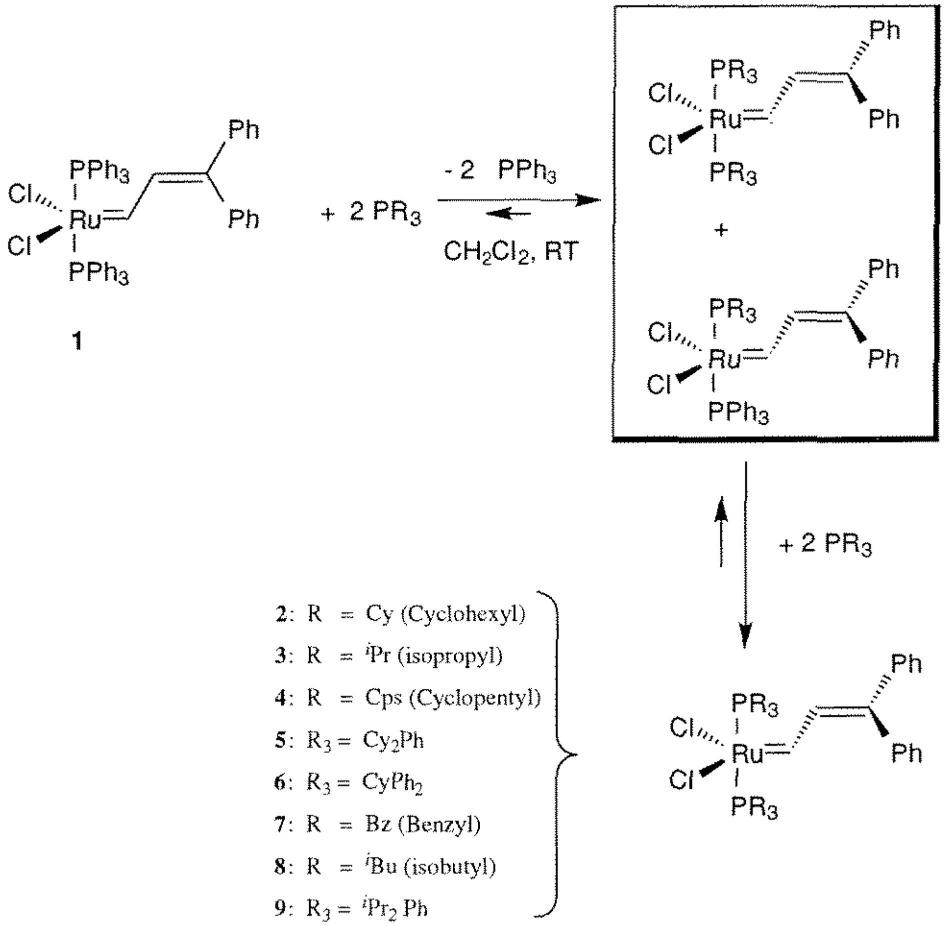
In chapter 2, the synthesis of the first well-defined ruthenium-based olefin metathesis catalyst, $(Ph_3P)_2Cl_2Ru=CH\text{-}CH=CPh_2$, **1**, and its activity in the ROMP of norbornene were discussed.[1] Although **1** is also a good catalyst for the Ring-Opening Metathesis Polymerization (ROMP) of other highly strained cyclic olefins, such as bicyclo[3.2.0]hept-6-ene,[2] bicyclo[3.3.0]oct-2-ene[3] and *trans*-cyclooctene,[3] it is not an efficient catalyst for the ROMP of low-strain cyclic olefins or the metathesis of acyclic olefins. Furthermore, attempts at replacement of the chloride ions in **1** with more electron-withdrawing groups, following examples in early transition metal metathesis chemistry,[4,5], have not lead to significant increases in olefin metathesis activity. Although these modifications increase the electrophilicity of the metal center (and modulate the propagation rate for norbornene polymerization), they do not facilitate either the ROMP of *cis*-cyclooctene or the metathesis of *cis*-2-pentene.

In this chapter, we discuss the modification of **1** by replacing the original triphenylphosphine ligands with electron-rich alkylphosphines. The result of this study is a series of highly active ruthenium vinylcarbene catalysts for general olefin metathesis.

Results and Discussions

Syntheses of $(PR_3)_2Cl_2Ru=CH\text{-}CH=CPh_2$ Catalysts by Direct Phosphine Exchange. The direct substitution of the triphenylphosphine ligands in $(PPh_3)_2Cl_2Ru=CH\text{-}CH=CPh_2$, **1**, with better σ-donating alkylphosphines led to several new $(PPh_3)_2Cl_2Ru=CH\text{-}CH=CPh_2$ complexes. For example, the reaction of tricyclohexylphosphine (PCy_3) with **1** in CH_2Cl_2 produces the corresponding metal carbene complex **2** in 90% yield after two consecutive exchange reactions (Scheme I). Other phosphines such as triisopropylphosphine (P^iPr_3), tricyclopentylphosphine($PCps_3$), dicyclohexylphenylphosphine (PCy_2Ph), cyclohexyldiphenylphosphine ($PCyPh_2$), and tribenzylphosphine (PBz_3), etc... also works in this exchange scheme. Since the direct

Scheme I. The Syntheses of $(PR_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ Catalysts by Direct Phosphine Exchange.



exchange of the triphenylphosphine ligands in **1** with the external alkylphosphines PR_3 is governed by an equilibrium, a single exchange with only two equivalents of PR_3 is often not sufficient to generate the desired $(PR_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ complexes in pure form. Rather, mixed-$(PPh_3)(PR_3)Cl_2Ru{=}CH{-}CH{=}CPh_2$ species remains in the reaction mixture.[a] The amount of this mixed-phosphine species relative to the desired

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[a] *In a preliminary account of this chemistry* (Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858-9859) this mixed phosphine compound is incorrectly assigned as the *cis*-$(PR_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ complex based on a

$(PR_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ complex correlates to the electron donating ability of the alkyl phosphine.[b] For example, after a single exchange of 2 equiv of PCy_3 with **1**, the isolated product contains 16% of $(PPh_3)(PCy_3)Cl_2Ru{=}CH{-}CH{=}CPh_2$, **Mix-2**, and 84% of **2**. The analogous exchange of 2 equiv of P^iPr_3 with **1** gives a product mixture of 20% **Mix-3** and 80% **3**. Less electron rich phosphine such as $PCyPh_2$ will yields product mixtures that contain even more of the mixed-phosphine component.

In contrast to the case of **1** where the α-proton of the metal carbene moiety appears as a pseudo-quartet in the ^{1}H NMR spectrum, showing clear spin-coupling to the two equivalent phosphine ligands (Chapter 2), the α-proton of the vinylcarbene moiety of **2** appears only as a doublet at 19.09 ppm, showing no P-H coupling, even at 500 MHz. Similar ^{1}H NMR coupling pattern can be observed for the vinylcarbene moiety of **3**. This lack of $^3J_{PH}$ coupling is rather surprising but is consistent with a change in the dihedral angle between the Ru-P bond and carbene C-H bond. The Karplus relationship then predicts that $^3J_{PH}$ is minimum when the dihedral angle $\angle$P-Ru-C_α-H_α is 90°.[6] We note that the carbene moiety in **1** is almost coplanar to the P_1-Ru-P_2 axis (Chapter 2) which results in a large $^3J_{PH}$ coupling constant. A zero $^3J_{PH}$ for **2** and **3** necessarily requires that the carbene moiety for these two compounds be perpendicular to the P_1-Ru-P_2. Table I lists selected spectroscopic data for these new phosphine complexes.

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precedent in the $(Ph_3P)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ case (Chapter 1). However, a control experiment had since then correctly identified the true nature of this mixed-phosphine species.

[b] A complete thermodynamic study of this phosphine exchange process have been carried out in collaboration with Prof. Stephen P. Nolan of the University of New Orleans. Interested reader should refer to Appendix 3 of this thesis for a condensed account of this work.

Table I. Selected Spectroscopic Data for $(PR_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$ Complexes.[a]

Complex	H_α		H_β		δP	C_α		
	δ(ppm)	J_{HP}	δ(ppm)	J_{HH}(Hz)	(ppm)	δ(ppm)	J_{PC}(Hz)	J_{CH}(Hz)
2	19.04 (d)	0	8.67(d)	11.3	36.8	290.9(t)	7.5	150.8
3	19.24 (d)	0	8.83(d)	11.2	45.9	290.7(t)	7.0	152.6
4	19.35(d)	0	8.68(d)	11.0	28.5	294.4(t)	8.4	152.6
5	19.14(d)	0	8.85(d)	11.0	44.4	291.2(t)	7.6	151.5
6	19.08(dt)	2.2	8.58(d)	11.0	47.6			
7	16.81(q)				22.4			
8	18.51(dt)		8.12	11.0	16.3			
9	19.10 (d)		8.55	11.1	40.2			

[a] Chemical shifts are in ppm, coupling constants are in Hz. Solvents = CD_2Cl_2.

An X-ray diffraction experiment carried out on a single crystal of **2** further confirmed the structural assignment (Figure 1). The geometry of **2** is that of a square pyramid with the phosphines and the chlorides forming the base. Indeed, the carbene moiety in **2** is orthogonal to the P_1-Ru-P_2 axis (the dihedral angle ∠P-Ru-C_α-H_α is almost 90°) (Figure 2) which further implies that the proposed solution structure is also retained in the solid state. This geometry where the vinylcarbene moiety is perpendicular to the P_1-Ru-P_2 axis has also been observed recently in the crystal structure of [*trans*-$Cl(CO)(P^iPr_3)_2Ru{=}C(OMe)\text{-}CH{=}CPh_2]^+$.[7] Notable also is the very large ∠Cl_1-Ru-Cl_2 angle (173.4(2)°) compared to that in **1** (157.2(2)°) and that observed for $Cl_2(PPh_3)_2$Ru(Cyclobutylidene)[8] (150.4(1)°), indicating that a widening of the angle has occurred upon phosphine exchange, making the molecule more square-pyramidal. This large ∠Cl_1-Ru-Cl_2 angle is more comparable to the ∠Cl_1-Ru-CO angle in $Cl(CO)(P^iPr_3)_2Ru{=}C(OMe)\text{-}CH{=}CPh_2]^+$[7] (169.16(9)°). Unfortunately, the vinylcarbene moiety in the structure of **2** is disordered about a two-fold axis, preventing an accurate determination of bond lengths and bond angles for this fragment.[c] Selected bond lengths and bond angles are listed in Table II.

Table II. Selected Bond Lengths and Angles for $(PCy_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$, **2**.

Bond lengths (Å)			
Ru(1)-P(1)	2.413(6)	Ru(1)-P(2)	2.423(7)
Ru(1)-Cl(1)	2.391(5)	C(1)-C(2)	1.436(28)
Ru(1)-Cl(2)	2.401(6)	C(2)-C(3)	1.332(20)
Ru(1)-C(1)	1.851(21)	C(3)-C(4)	1.452(30)
P(1)-C(16)	1.844(22)	C(3)-C(10)	1.516(30)
P(1)-C(28)	1.866(20)	P(1)-C(22)	1.856(20)
Bond Angles (deg)			
Ru(1)-C(1)-C(2)	129.2(16)	C(1)-C(2)-C(3)	127.3(20)
P(1)-Ru(1)-P(2)	162.2(2)	Cl(1)-Ru(1)-Cl(2)	173.4(2)
P(1)-Ru(1)-Cl(1)	89.2(2)	P(1)-Ru(1)-Cl(2)	89.5(2)
P(2)-Ru(1)-Cl(1)	88.3(2)	P(2)-Ru(1)-Cl(2)	91.0(2)
P(1)-Ru(1)-C(1)	98.7(7)	P(2)-Ru(1)-C(1)	98.9(7)
Cl(1)-Ru(1)-C(1)	88.8(6)	Cl(2)-Ru(1)-C(1)	97.8(6)
Ru(1)-P(1)-C(16)	113.7(7)	Ru(1)-P(1)-C(22)	114.7(7)
C(16)-P(1)-C(22)	110.6(9)	Ru(1)-P(1)-C(28)	111.2(7)
C(16)-P(1)-C(28)	101.1(9)	C(22)-P(1)-C(28)	104.2(9)
Ru(1)-P(2)-C(34)	106.6(7)	Ru(1)-P(2)-C(40)	114.7(8)
C(34)-P(2)-C(40)	100.8(10)	Ru(1)-P(2)-C(46)	117.1(7)
C(34)-P(2)-C(46)	104.7(10)	C(40)-P(2)-C(46)	110.9(10)
C(2)-C(3)-C(4)	123.9(20)	C(2)-C(3)-C(10)	120.0(19)
C(4)-C(3)-C(10)	116.1(19)		

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[c] As in **1**, this disorder is intrinsic to the molecule, see Appendix 4.

In comparison to **1**, the new $(PR_3)_2Cl_2Ru=CH\text{-}CH=CPh_2$ catalysts are more soluble in organic solvents. For example, **1** is only sparingly soluble in benzene and THF, but **2** is quite soluble in these solvents. Also, **1** is not soluble in alcohols but **2** is slightly soluble in alcohols. In certain cases, such as that of $(P^iBu_3)_2Cl_2Ru=CH\text{-}CH=CPh_2$, the considerable solubility in saturated hydrocarbons have made the isolation of this compound problematic.

Stability of 2 and 3. Complexes **2** and **3** are fairly stable to air in the solid state. After a microcrystalline sample of **2** was exposed to air for two months, the vinylcarbene resonance could still be detected via ^1H NMR spectroscopy upon solvation (the sample was prepared under inert atmosphere). In addition, we have reported that **2** can be dissolved in the presence of air using commercial, reagent-grade organic solvent on the bench top and still retain metathesis activity for at least one hour.[9] If a solution of **2** is exposed to air, very slow oxidation of the catalyst can be observed visually as a green layer diffusing from the surface downward into the orange-red solution over a period of hours. As in the case of **1**, **2** is stable in organic solvents in the presence of water, alcohol, acetic acid, or a diethyl ether solution of HCl. These observations indicate that the modification of **1** with alkylphosphines does not increase the susceptibility of the ruthenium carbene center to attack by electrophilic species.

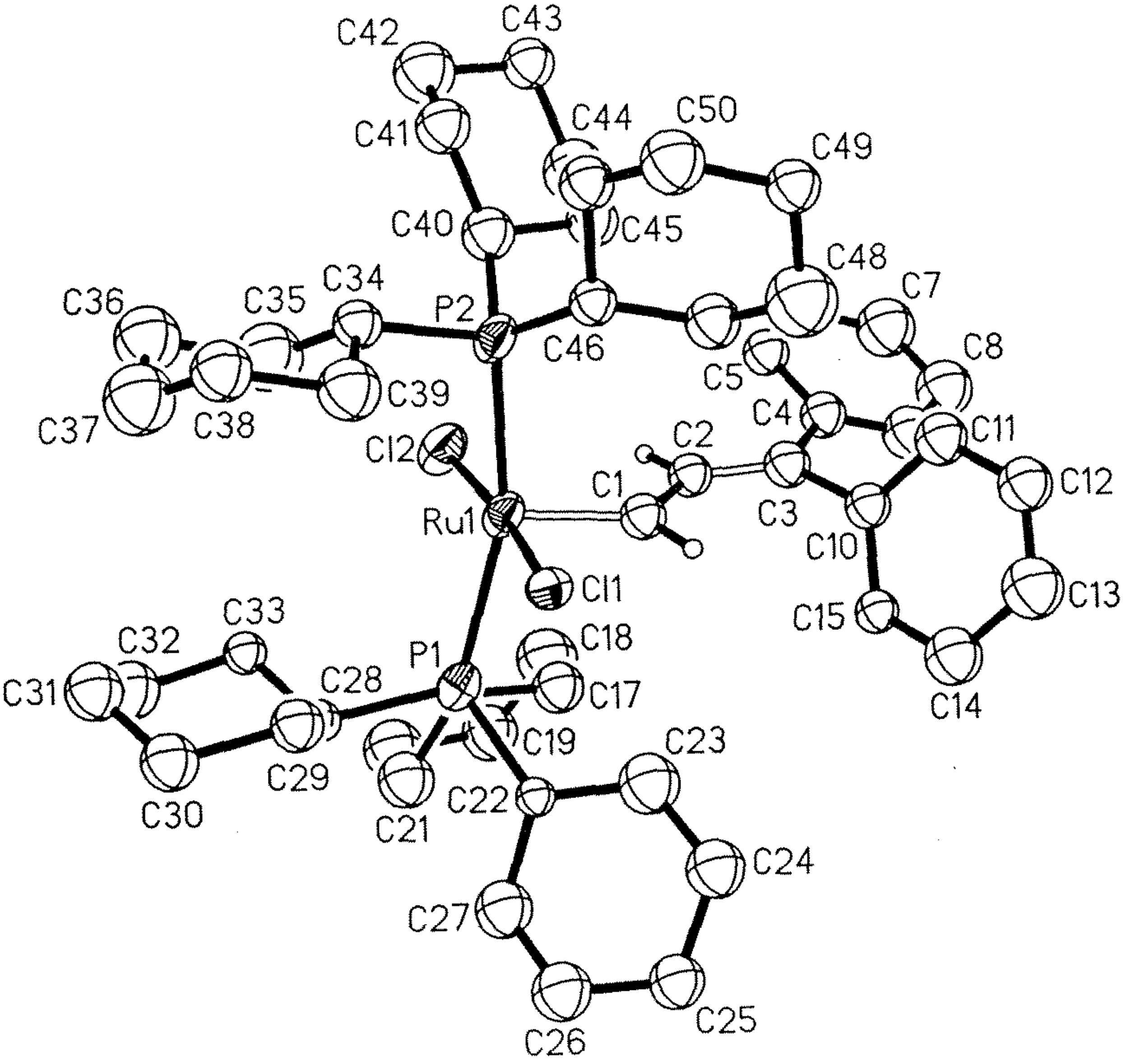

Figure 1. A molecular drawing of **2**. Thermal ellipsoids are drawn at 50% probability levels.

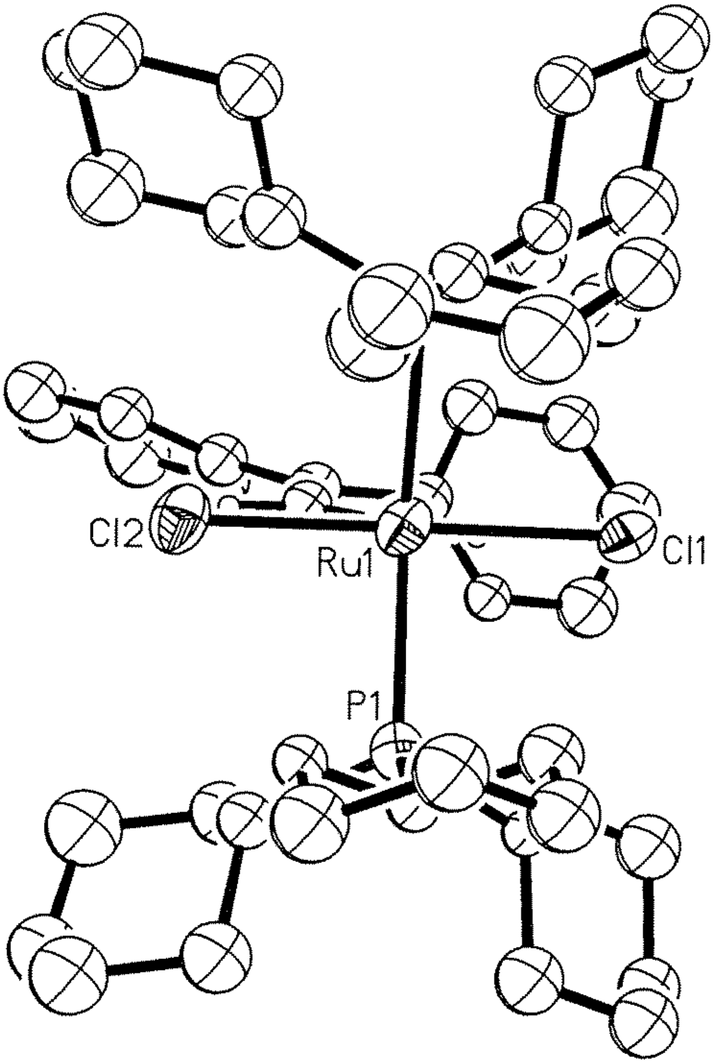

Figure 2. A molecular drawing of **2**. The view is looking down the Cl_1-Ru-Cl_2 wedge of the molecule.

Interestingly, the stability of **2** is not a limitation of the carbene moiety. Rather it is the phosphine ligands that are responsible for certain decomposition mode of **2**. With the electron-rich PCy_3 as ligands, one possible decomposition mode of **2** results from the quaternization or oxidation of PCy_3 itself. For example, PCy_3 will react with CCl_4 to give $Cy_3P{=}CCl_2$ and $[Cy_3PCl]Cl$.[10,11] With $CDCl_3$, PCy_3 will quarternize to give both the corresponding monomeric and dimeric phosphonium salts.[12,13] This quarternization also occurs between CD_2Cl_2 and PCy_3 albeit at a slower rate.[13] These exact reactions are observed to occur when **2** is dissolved in the forementioned halogenated solvents and leads to the eventual decomposition of **2**. By continually removing some PCy_3 from the solution, the halogenated solvents strip away the protecting ligand sphere of the metal vinylcarbene center and leave the latter vulnerable to either bimolecular decomposition or hydride formation, both of which can be observed. In addition, it is well known that alkylphosphines are more prone to air oxidation than PPh_3—it is this reactivity that makes a solution of **2** more susceptible to air oxidation (of the phosphine ligand) than that of **1**.

ROMP Activities of 2. Complex **2** polymerizes norbornene at room temperature to yield polynorbornene. Because the rate of propagation is much faster than the rate of initiation, very little of the catalyst reacts and the resulting polymer possesses both high molecular weight and broad molecular weight distribution (entry 1, Table III). In contrast to **1**, **2** catalyzes the ROMP of 1,5-cyclooctadiene, a 7- oxanorbornene derivative, *cis*-cyclooctene, and cyclopentene (entries 2-6, Table III). In each of these cases, a propagating species can be observed via ^1H NMR spectroscopy.[d] This propagating species is stable through out the polymerization reaction although the polymerization is

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[d] Except for cyclopentene where the polymerization has to be done neat, *cis*-Cyclooctene, 1,5-cyclooctadiene, and 7-oxonorbornene could be polymerized in deuterated organic solvents and the corresponding propagating species can be observed.

not truly living due to possible chain transfer to acyclic olefin double bonds of the polymer chain.

Table III. The Polymerization of Various Cyclic Monomer by **2**.[b]

Entry	Monomer	[Mon]/[**2**]	M_w[a]	PDI	Yield (%)
1	Norbornene	140	216 k	2.65	95
2	1,5-Cyclooctadiene	228	88.8 k	2.42	74
3	Exo-5,6-dimethoxymethyl-7-oxabicyclo[2.2.1]hept-2-ene	134	270.2 k	1.7	72
4	Cyclooctene (95% cis)	224	73.9	2.62	89
5	Cyclopentene	362	110.8	1.95	89

[a] Obtained using GPC in CH_2Cl_2 against polystyrene standard. [b] All polymerization was carried out near neat (only 0.1 mL of CH_2Cl_2 was used to dissolve 15 mg of the catalyst) over a 24 h period

Olefin Metathesis Catalyzed by 2 and 3. Complexes **2** and **3** also catalyze the metathesis of unstrained acyclic olefins such as *cis*-2-pentene. The reaction proceeds at room temperature, and both propagating species (ruthenium ethylidene and ruthenium propylidene) can be observed by ^1H NMR spectroscopy. The data from Table IV indicate that CH_2Cl_2 is the best solvent for metathesis by **2** (entries 1-3). Although the turn over number[e] at room temperature is modest compared to that observed for the most active catalysts in the tungsten- and molybdenum-based systems,[4,5] this is the first time that the

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[e] The turn-over number is defined as the ratio of the number of substrate molecules to the number of metal centers and is obtained by monitoring the first part of the *cis*-2-pentene metathesis reaction where the rate of metathesis is approximately pseudo-first order; it is taken as the point at which 40% of the initial *cis*-2-pentene is consumed. Because of the nature of the kinetics and the slow initiation of the parent catalyst, the reported turn-over numbers are only lower-limit values.

Table IV. Turn-Over Numbers[c] (TON) and Conditions for the Metathesis of *Cis*-2-pentene Catalyzed by $(PR_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$.

Entry	Catalyst	Solvent and Catalyst Concentration	TON.[c] (equiv/h)
1	$(PCy_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$, **2**	6.06 mM in C_6D_6[a]	26
2	$(PCy_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$, **2**	6.06 mM in THF-d_8[a]	11
3	$(PCy_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$, **2**	6.06 mM in CD_2Cl_2[a]	103
4	$(PCy_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$, **2**	5.19 mM in (0.29:1) CD_3OD/CD_2Cl_2[b]	67
5	$(P^iPr_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$, **3**	6.06 mM in C_6D_6[a]	22
6	$(PCy_2Ph)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$, **5**	6.06 mM in CD_2Cl_2[a]	15
7	$(PCyPh_2)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$, **6**	6.06 mM in CD_2Cl_2[a]	0

[a] Conditions: 0.5 ml of solution, 100 equiv of *cis*-2-pentene, room temperature. The reaction is carried out in an NMR tube with mesitylene as an internal standard. [b] Conditions: 0.59 ml of solution, 100 equiv of *cis*-2-pentene, room temperature. [c]The turn over number (TON) is obtained by monitoring the first part of the *cis*-2-pentene metathesis reaction where the rate of metathesis is approximately pseudo-first order; it is taken as the point at which 40% of the initial *cis*-2-pentene is consumed.

metathesis of a normal acyclic olefin has been reported with well-defined ruthenium carbene complexes.[14] Among other factors, the modest turn-over number for complexes **2a-b** can be attributed to the slow initiation of the parent vinylcarbene complex and the small equilibrium constant for the interconversion of the parent catalyst to the "propagating" species.[f] Under the conditions described for entries 1-5 of Table IV, the parent catalysts can be observed throughout the metathesis reaction, together with both

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[f] The reluctance of the parent vinylcarbene complex to initiate may be attributed in part to the extra stability imparted on these compounds by the conjugated vinylcarbene moiety. At very high concentrations of olefin it is possible to eventually convert all of **2** into the "propagating" species.

ruthenium propylidene and ruthenium ethylidene even after two days. (Under similar circumstances, both the W[4] and Re[15] neopentylidenes react completely with *cis*-3-hexene to generate the corresponding propylidene.) Both propagating ruthenium carbene species are quite stable under these conditions. After 12 h, ~ 85% of the total starting ruthenium carbene is still present in various forms (Figure 3).

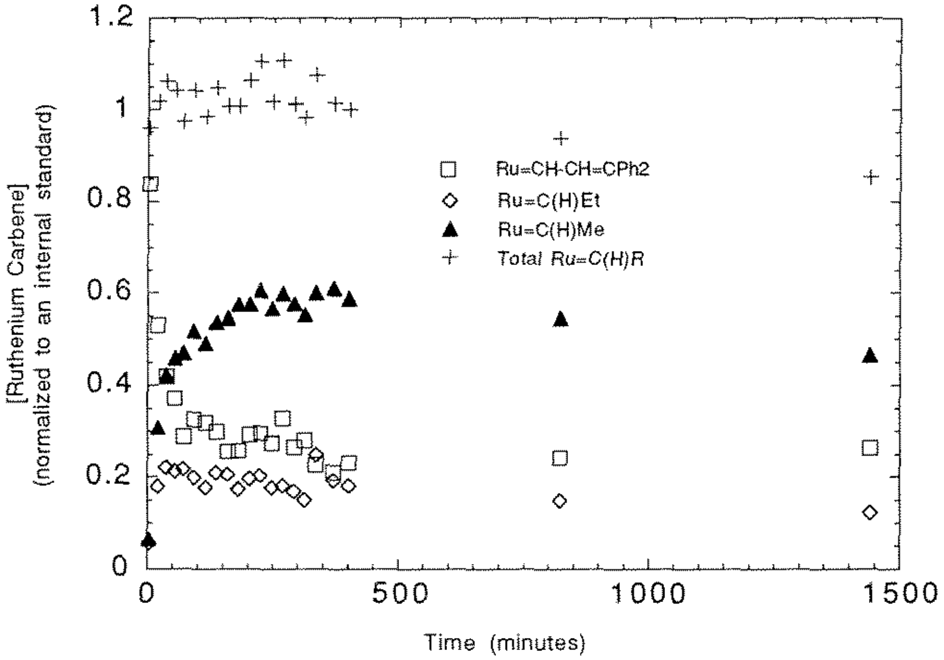

Figure 3. The concentration of Ru=C(H)R during the metathesis of *cis*-2-pentene.

In contrast to early transition metal metathesis catalysts, where functional group tolerance is limited, **2** is an extremely robust catalyst. Furthermore, neither a protic solvent (entry 4, Table IV and reference 9) nor a coordinating solvent (entry 2, Table IV) significantly affected the metathesis rate of *cis*-2-pentene. Complex **2** also catalyzes the metathesis of functionalized substrates such as allyl ether, 3-butene-1-ol, methyl oleate, and oleic acid[g] and the ring-closing metathesis of functionalized dienes.[9,16,17] In neat monomer, **2** will catalyze the diolefin metathesis polymerization of α,ω-dienes.[h]

At first consideration, the effect of varying the phosphine ligand in activating the catalytic activity of the vinylcarbene moiety appears to be mainly electronic, not steric, in origin. Complex **1** (cone angle PPh_3 = 145° [18]) does not metathesize acyclic olefins (entry 4, Table V) while complexes **2** and **3**, with bulky, electron-rich, alkylphosphine ligands, catalyze the metathesis of *cis*-2-pentene (entries 1 and 3, Table V). Although PCy_3 (cone angle 170° [18]) and P(*i*-Pr)$_3$ (cone angle 160° [18]) are sterically somewhat different,[i] **2** and **3** are almost equally active in acyclic olefin metathesis (Entries 1 and 5, Table IV). On the other hand, the vinylcarbene derivative resulting from the reaction of $P(CH_2Ph)_3$ with **1** does not metathesize unfunctionalized acyclic olefins (entry 2, Table V).[6] This result clearly suggests that electronic factors are more important than steric effects since the cone angle of $P(CH_2Ph)_3$ (165° [18]) is intermediate between that of P(*i*-Pr)$_3$ and PCy_3 but the phosphine is much less electron-rich. In addition, sequential replacement of the phosphorus cyclohexyl groups of $(PCy_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ with phenyl group leads to decreasing metathesis activity (Table IV, entries 1, 6 and 7).

In contrast to the catalysts developed from d^0, early transition metal centers,[5] where increasing the electron-withdrawing ability of the ancillary ligands leads to increased turn-over numbers, it appears that the d^6 Ru^{II} metal center[j] requires electron-rich ancillary ligands for increased metathesis activity (Figure 4). There are two

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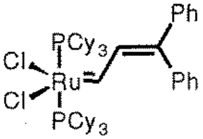
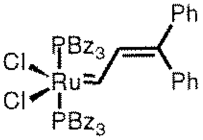
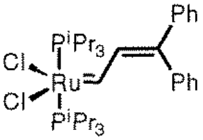
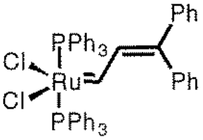
[g] The metathesis of methyl oleate and oleic acid is the subject of chapter 5 in this thesis.

[h] The Diolefin Metathesis Polymerization (DOMP) catalyzed by **2** is the subject of chapter 6 in this thesis.

[i] The difference between P^iPr_3 and PCy_3 is more steric than electronic. See reference

[j] In assigning the oxidation state for the ruthenium center, the vinylcarbene moiety was considered to be neutral. See: Bohle, D. S.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1988**, *358*, 411-447.

Table V. Electronic Effects of the Phosphine Ligands on Metathesis Activity

Entry	Catalyst	Phosphine cone angles[a]	cis-2-pentene metathesis
1		170°	Yes
2		165°	No
3		160°	Yes
4		145°	No

[a] Values for phosphine cone angles were obtained from reference.[18]

complementary explanations for this observation. 1) If the formation of a metallacyclobutane is assumed to be the rate-determining step in the metathesis cycle then during the metallacyclobutane intermediate, the metal center becomes formally Ru(IV) and better σ-donor ligands will stabilize this intermediate better (Figure 5). 2) If the main mechanism for the metathesis is of a dissociative nature (i. e. going through a 14-electron $(PR_3)Cl_2Ru{=}CH\text{-}CH{=}C(H)R$ intermediate) then the presence of an electron-rich, sterically bulky phosphine such as PCy_3 would be more effective in enhancing this pathway (stabilizing the 14-electrons $(PR_3)Cl_2Ru{=}CH\text{-}CH{=}CPh_2$ intermediate) than an electron-poor, sterically small phosphine such as PPh_3. Indeed, there are accumulated kinetic evidences to support the dissociative pathway for olefin metathesis catalyzed by **2**.[2,19]

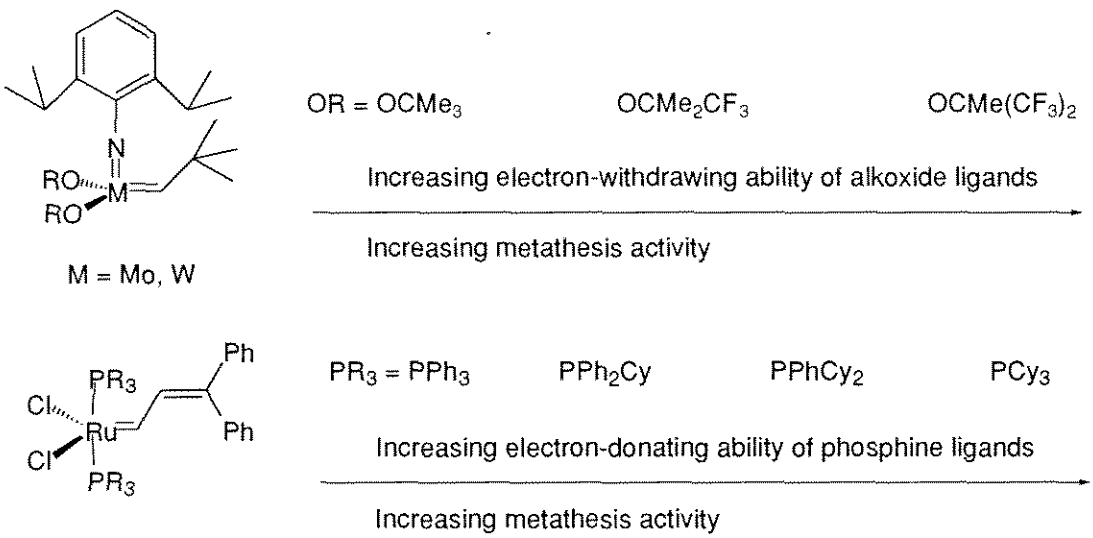


Figure 4. Comparison of ligand activity trends between $(OR)_2(N\text{-}2,6\text{-}{}^iPr_2)M{=}CH^tBu$ (M = Mo, W) and $(PR_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$.

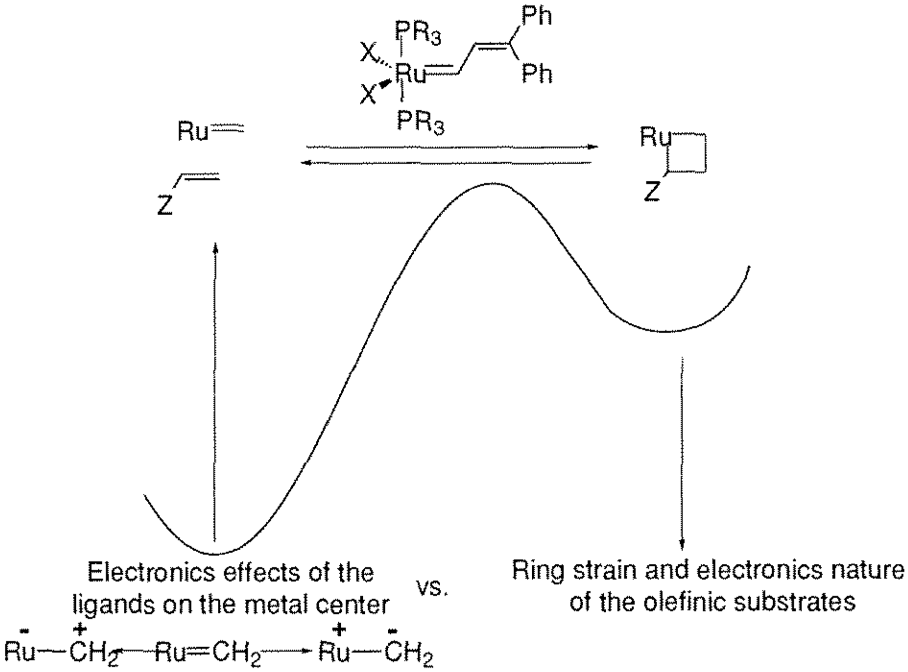


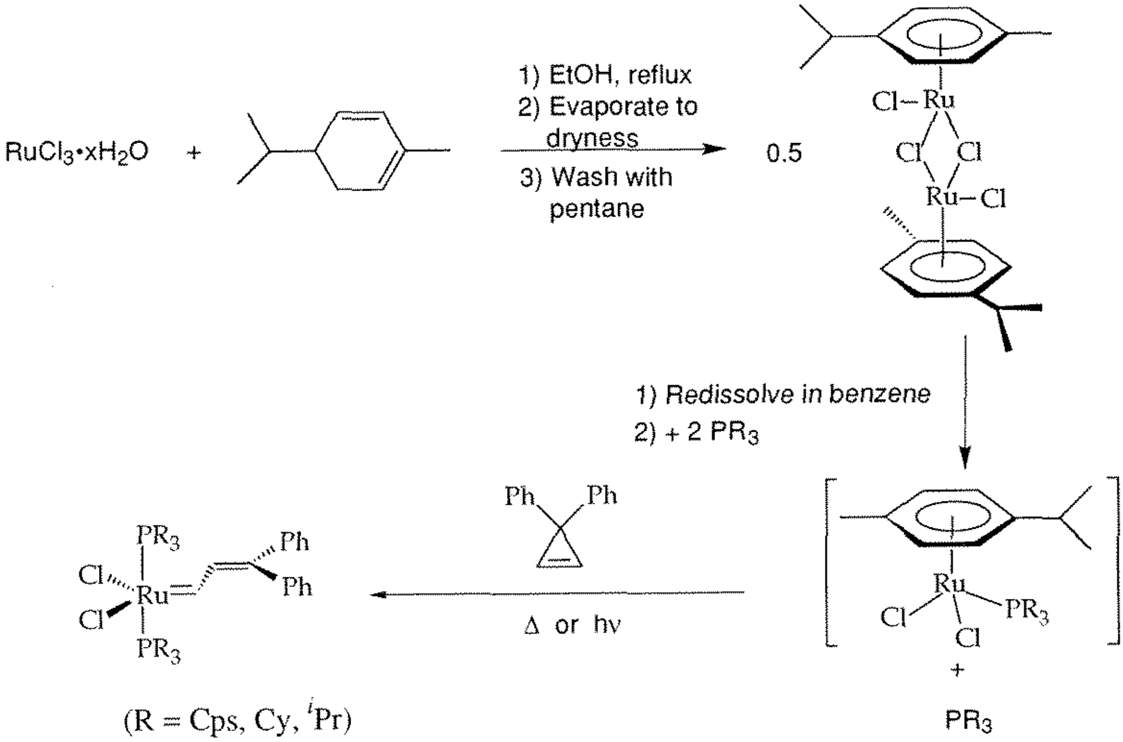
Figure 5. A simple model to explain the enhancement of metathesis activity for $(PR_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$ complexes. Increasing the σ-donor ability of the ancillary ligand should lead to the relative stabilization of the Ru(IV) metallacycle vs. the Ru(II) carbene/olefin mixture and should enhance the metathesis activity.

A One-Pot Synthesis of $(PR_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$. Since the first report of the syntheses of **2** and **3** in 1993,[20] these catalysts have found many applications in polymer chemistry[2,21,22] and organic synthesis.[9,16,17,23-25] The direct exchange procedures for the syntheses of theses catalysts (*vide supra*), although simple and easy, still involves a number of separate steps. We have developed a simple and high yield one-step synthesis from readily available starting materials to several olefin metathesis catalyst $(PR_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$ (R = Cy, Cps, ^{i}Pr) (Scheme 2). This procedure is advantageous in the sense that in one step we can spontaneously assemble all the components (a Cl_2Ru center, two phosphines, and a carbene source) into the desired product. Such ease of synthesis, to the best of our knowledge, is unprecedented in the well-defined olefin metathesis catalyst literature and can be cited as example of the high accessability of these $(PR_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$ derivatives.

This procedure is applicable to electron-rich bulky phosphines such as PCy_3, $PCps_3$, P^iPr_3. Less bulky phosphines such as P^iBu_3 do not work well due to the formation of insoluble Cl-bridging oligomers and PPh_3 does not work due to the insolubility of the (η^6-cymene)$RuCl_2(PPh_3)$ intermediate. Unfortunately, the procedure described here does not work for the $[(Cymene)OsCl_2]_2$ analog, perhaps due to the tendency of Os(II) to bind more strongly to the arene moiety.[26,27]

The one-pot procedure described above suffers a small problem, however. There is always a side product, $(PR_3)_2Cl_2Ru(\eta_2$-3,3-diphenylcyclopropene), which could not be separated from the desired carbene product. From simultaneous spectroscopic observation (^{1}H and ^{31}P NMR) this product appear to be an intermediate through which the final vinylcarbene product is formed. At the beginning of the reaction, this olefin complex exists in large quantities which went away as the reaction proceed to completion. However, toward the end of the reaction, the amount of this olefin complex remains fairly constant (10-15%). Attempts to convert this side product further to the

Scheme II. A One-Pot Synthesis for $(PR_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ (R = Cps, Cy, ^{i}Pr).



desired vinylcarbene by extended reflux of reaction mixture have so far lead only to decreased yield. These observations can be explained by considering a bimetallic mechanism such as that depicted in Scheme I, Chapter 2. Toward the end of the reaction, the majority of the metal centers is tied up as olefin or phosphine complexes, the concentration of free metal complex available to act as catalyst for the ring opening of cyclopropene is reduced and thus there is very little conversion to the vinylcarbene.

Table VI lists selected spectroscopic data for these $(PR_3)_2Cl_2Ru(\eta_2\text{-}3,3\text{-}$diphenylcyclopropene) complexes. Assignment for structures was made based on spectroscopic data and based on the inertness of these species towards olefin metathesis.

Table VI. Selected Spectroscopic Data for $(PR_3)_2Cl_2Ru(\eta_2\text{-}3,3\text{-diphenylcyclopropene})$ Complexes.[a]

$(PR_3)_2Cl_2Ru(\eta_2$-3,3-diphenylcyclopropene)	H_α		H_β			δP
	δ(ppm)	J_{HH}(Hz)	δ(ppm)	J_{HP}(Hz)	J_{HH}(Hz)	(ppm)
10, R = Cy	5.09 (d)	11.5	8.67(d)	0	11.5	28.1
11, R = ^{i}Pr	4.97(d)	11.6	8.83(d)	3.3	11.6	29.0
12, R = Cps	4.95(d)		8.68(d)			16.9

[a] Chemical shifts are in ppm, coupling constants are in Hz. Solvents = $CDCl_3$

Conclusions

Complexes **2-10** represent the first examples of a new generation of robust, well-defined, single-component catalysts for the metathesis of acyclic olefin. Given their ease of synthesis, unique activities, and remarkable functional group tolerance, catalyst **2-10** are becoming attractive tools in the synthesis of a variety of useful polymers and organic intermediates.

Experimental

General Considerations. All manipulations were performed using standard Schlenk techniques or drybox procedures. 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. ^{31}P NMR spectra were either recorded with a JEOL FX-90Q (89.60 MHz ^1H; 22.53 MHz ^{13}C; 36.2 MHz ^{31}P) spectrometer (locking on a static ^7Li lock sample and reference to an external 85% H_3PO_4 sample where a 10 mM solution of PPh_3 in $CDCl_3$ will exhibit a resonance at -5.4 ppm) or with a JEOL GX-400 (399.65 MHz ^1H; 140 MHz ^{13}C; 161.85 MHz ^{31}P) spectrometer (locking on the ^2D solvent signal and reference to an external 85% H_3PO_4 sample where a 10 mM solution of PPh_3 in $CDCl_3$ will exhibit a resonance at -4.9 ppm). ^1H and ^{13}C NMR spectra were recorded with either a QE-300 Plus (300.10 MHz ^1H; 75.49 MHz ^{13}C) spectrometer or a Bruker AM-500 (500.138 MHz ^1H; 125.759 MHz ^{13}C) spectrometer at ambient temperature. NMR data are reported as follows: chemical shifts (multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration, assignment, and coupling constant (Hz)). ^1H NMR chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) (δ scale) with TMS employed as the internal standard. ^{13}C NMR chemical shifts are reported in ppm downfield from tetramethylsilane (δ scale) with the solvent resonance employed as the internal standard (CD_2Cl_2 at δ 53.8) and are obtained from complete proton-decoupled spectra while coupling constants are measured from coupled spectra with full NOE enhancement.

Materials. Benzene and tetrahydrofuran (THF) were distilled or vacuum-transferred from sodium-benzophenone ketyl. Methylene chloride was dried over CaH_2, vacuum-transferred, and then degassed by three continuous freeze-pump-thaw cycles. Pentane was stirred over concentrated H_2SO_4, dried over $MgSO_4$ and CaH_2, and then transferred onto sodium-benzophenone ketyl solubilized with tetraglyme. Benzene-d_6

and THF-d_8 were distilled from sodium-benzophenone ketyl. Methylene chloride-d_2 was dried over CaH_2, vacuum-transferred, and then degassed by three continuous freeze-pump-thaw cycles. Methanol-d_4 was dried over activated neutral alumina, vacuum-transferred and degassed by three continuous freeze-pump-thaw cycles. PCy_3 was obtained either from Aldrich Chemical Co. or Strem Chemical Company and recrystallized under argon from ethanol (distilled from $Mg(OEt)_2$ under argon) if containing $OPCy_3$ as determined by ^{31}P NMR spectroscopy. $PCps_3$ was a gift from Cytec Chemicals. P^iPr_3 was obtained from Strem Chemicals, all other phosphines were obtained from Organometallics Inc. (East Hampstead, NH) and used as received. $Cl_2(PPh_3)_2Ru{=}CH{-}CH{=}CPh_2$, **1**,[1] $[(Cymene)RuCl_2]_2$,[28] and *Exo*-5,6-dimethoxymethyl-7-oxabicyclo[2.2.1]hept-2-ene[29] were synthesized according to literature procedures. 3,3-Diphenylcyclopropene is prepared according to the procedure described in Appendix 1. Cyclooctadiene, *cis*-cyclooctene (95%), *cis*-2-pentene, and cyclopentene were obtained from Aldrich, distilled over CaH_2 and degassed through three freeze-pump-thaw cycles. For the polymer work up: 2,6-Di-*tert*-butyl-4-methylphenol (BHT) and ethyl vinyl ether were obtained from Aldrich; Silica gel, CH_2Cl_2, methanol, and CCl_4 were obtained from EM Science; all were used as received.

Synthesis of $(PCy_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$, 2, by Direct Phosphine Exchange. In a typical reaction, a 100 mL Schlenk flask equipped with a magnetic stirbar was charged with $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ (3.624 g, 4.08 mmol) and PCy_3 (2.4 g, 2.1 equiv) inside a nitrogen-filled drybox. Methylene chloride (50 mL) was added to dissolve the mixture. The reaction flask was capped with a stopper, removed from the box, and allowed to stir under argon for three hours during which time the reaction turns red. The reaction mixture was then concentrated to a slush. Pentane (60 mL) was then slowly added to the mixture via cannula while stirring vigorously. The red supernatant was quickly filtered away using cannula filtration The remaining red solid was washed with pentane (3 x 40 mL). To ensure the complete removal of all phosphine by-products, each wash was stirred at room temperature for at least 30 minutes before the supernatant was cannula-filtered away . The final red solid was dried quickly on the vacuum line, redissolved in methylene chloride (50 mL), treated with a second portion of PCy_3 (2.4 g, 2.1 equiv) and then allowed to stir for 3 h more at room temperature. Again, the reaction mixture was concentrated to a slush, precipitated out with pentane, and the remaining solid was washed with pentane as above. The resulting product was then dried under vacuum overnight to afford 2.90 g (ca. 79 %) of a red powder which consists of mostly **2** and a very small amount of **mix-2**. Total removal of **mix-2** is rather difficult due to the similar solubilities of **mix-2** and **2**. However, very pure samples of **2** can be obtained by a third treatment of the product mixture with PCy_3 to drive the phosphine exchange to completion. In addition, the amount of **mix-2** can be reduced significantly by selective crystallization. For all practical purposes, the concentration of **mix-2** does not affect the results of the experiments reported herein (i.e., **mix-2** is essentially inert compared to **2** under the conditions of the experiments).

^{1}H NMR (CD_2Cl_2): δ 19.09 (d, 1 H, Ru=C*H* , J_{HH} = 11.1 Hz, J_{PH} = 0 Hz), 8.70 (d, 1 H, C*H*=CPh_2, J_{HH} = 11.1 Hz); ^{31}P NMR (CD_2Cl_2): δ 36.5 (s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 290.9 (t, Ru=*C*, J_{PC} = 7.5 Hz, J_{CH} = 150.8 Hz).

Synthesis of $(P^iPr_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$, 3, by Direct Phosphine Exchange. A similar procedure to that for **2** above, starting with $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ (500 mg, 0.56 mmol) and two treatments of P^iPr_3 (each 184 mg, 2.04 equiv) gave 336 mg (ca. 87%) of a red powder which consists mostly of **3**.

^{1}H NMR (CD_2Cl_2): δ 19.24 (d, 1 H, Ru=C*H* , J_{HH} = 11.2 Hz, J_{PH} = 0 Hz), 8.83 (d, 1 H, C*H*=CPh_2, J_{HH} = 11.2 Hz), 2.84 (m, 2 H, PC(*H*)$(CH_3)_2$), 1.27 (pseudo-quartet = 2 overlapping triplets, 12 H, PC(H)$(CH_3)_2$, J_{HH} = 7.2 Hz, J_{PH} = 6.2 Hz); ^{31}P NMR (CD_2Cl_2): δ 45.9 (s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 290.65 (t, Ru=*C*, J_{PC} = 7.0 Hz, J_{CH} = 152.6 Hz), 22.52 (s/br, P-*C*(H)$(CH_3)_2$, J_{CH} = 131.4 Hz), 19.55 (s, P-C(H)$(CH_3)_2$, J_{CH} =

127.1 Hz).

Synthesis of $(PCps_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$, 4, by Direct Phosphine Exchange. A similar procedure to that for **2** above, starting with $(PPh_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$ (500 mg, 0.56 mmol) and two treatments of $PCps_3$ (each 274 mg, 2.04 equiv) gave 388 mg (ca. 82%) of a red powder which consists mostly of **4**.

^1H NMR (CD_2Cl_2): δ 19.35 (d, 1 H, Ru=C*H* , J_{HH} = 11.0 Hz, J_{PH} = 0 Hz), 8.68 (d, 1 H, C*H*=CPh_2, J_{HH} = 11.0 Hz). ^{31}P NMR (CD_2Cl_2): δ 28.5(s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 294.4 (t, Ru=*C*, J_{PC} = 8.4 Hz, J_{CH} = 152.6 Hz)

Synthesis of $(PCy_2Ph)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$, 5, by Direct Phosphine Exchange. A similar procedure to that for **2** above, starting with $(PPh_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$ (500 mg, 0.56 mmol) and two treatment of $P(Cy_2Ph)_3$ (each 315 mg, 2.04 equiv) gave 436 mg (ca. 85%) of a red powder which consists mostly of **5.**

^1H NMR (CD_2Cl_2): δ 19.14 (d, 1 H, Ru=C*H* , J_{HH} = 11.0 Hz, J_{PH} = 0 Hz), 8.85 (d, 1 H, C*H*=CPh_2, J_{HH} = 11.0 Hz). ^{31}P NMR (CD_2Cl_2): δ 44.4 (s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 291.2 (t, Ru=*C*, J_{PC} = 7.62 Hz, J_{CH} = 151.5 Hz)

Synthesis of $(PCyPh_2)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$, 6, by Direct Phosphine Exchange. A similar procedure to that for **2** above, starting with $(PPh_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$ (500 mg, 0.56 mmol) and two treatment of $P(CyPh_2)_3$ (each 184 mg, 2.04 equiv) gave 380 mg (ca. 75%) of a green powder which consists mostly of **6.**

^1H NMR (CD_2Cl_2): δ 19.08 (dt, 1 H, Ru=C*H* , J_{HH} = 11.0 Hz, J_{PH} = 2.2 Hz), 8.58 (d, 1 H, C*H*=CPh_2, J_{HH} = 11.0 Hz). ^{31}P NMR (CD_2Cl_2): δ 47.6 (s).

Synthesis of $(PBz_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$, 7, by Direct Phosphine Exchange. A similar procedure to that for **2** above, starting with $(PPh_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$ (500 mg, 0.56 mmol) and two treatments of PBz_3 (each 465 mg, 2.04 equiv) gave 336 mg (ca. 87%) of a green powder which consists mostly of **7**.

^1H NMR (CD_2Cl_2): δ 16.81 (q, 1 H, Ru=C*H*). ^{31}P NMR (CD_2Cl_2): δ 22.4 (s).

Observation of $(P^iBu_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$, 8, by Direct Phosphine

Exchange. A similar procedure to that for **2** above, starting with $Cl_2(PPh_3)_2Ru=CH-CH=CPh_2$ (500 mg, 0.56 mmol) and one treatment of P^iBu_3 (184 mg, 4.04 equiv). However, the green sludge remained does not lend itself to isolation of pure **8** due to its extreme solubility in a lot of solvents.

^1H NMR (CD_2Cl_2): δ 18.51 (dt, 1 H, Ru=C*H* , J_{HH} = 11.0 Hz), 8.12 (d, 1 H, $C\underline{H}=CPh_2$, J_{HH} = 11.0 Hz). ^{31}P NMR (CD_2Cl_2): δ 16.3 (s).

Synthesis of $(P^iPr_2Ph)_2Cl_2Ru=CH-CH=CPh_2$, 9, by Direct Phosphine Exchange. A similar procedure to that for **2** above, starting with $Cl_2(PPh_3)_2Ru=CH-CH=CPh_2$ (500 mg, 0.56 mmol) and two treatments of $P(^iPr_2Ph)_3$ (each 223 mg, 2.04 equiv) gave 369 mg (ca. 87%) of a red powder which consists mostly of **9.**

^1H NMR (CD_2Cl_2): δ 19.10 (d, 1 H, Ru=C*H* , J_{HH} = 11.1 Hz, J_{PH} = 0 Hz), 8.55 (d, 1 H, C*H*=CPh_2, J_{HH} = 11.1 Hz). ^{31}P NMR (CD_2Cl_2): δ 40.2 (s).

Polymerizations of Cycloolefins catalyzed by 2. In a typical experiment, **2** (15 mg, 0.016 mmol) was dissolved in CH_2Cl_2 (100 μL) in a 4 mL vial in the drybox. The cyclic olefin (400 mg) was next added neat to the catalyst solution. The vial was capped, shaken vigorously to ensure homogeneity and then left at room temperature inside the drybox.

(a) Cyclooctadiene: The reaction mixture gels within 2 hours. The mixture was allowed to stand at room temperature for 24 h before working up.

(b) *Exo*-5,6-dimethoxymethyl-7-oxabicyclo[2.2.1]hept-2-ene: The mixture gels within 15 minutes. The mixture was allowed to stand at room temperature for an additional 2 h before working up.

(c) Cylopentene: The reaction mixture gels within 30 minutes. The mixture was allowed to stand at room temperature for 24 h before working up.

(d) Commercial 95% *cis*-cyclooctene (remainder trans): The reaction mixture gels within 1h. The mixture was allowed to stand at room temperature for 24 h before working up.

Work Up: The reaction vial was taken out of the drybox and to it was added a solution consisting of: methylene chloride (4 mL), ethyl vinyl ether (0.8 mL), and BHT (200 mg). This mixture was then left at room temperature for 2 h during which time the gel dissolved into a viscous solution and the color changes from red to brownish yellow. This solution was then passed through a 1" x 1" cylindrical plug of silica gel, eluted with methylene chloride (containing 0.1% BHT). The combined eluants was concentrated on a rotary evaporator, redissolved in CCl_4 (5 mL, containing 0.1% BHT) and precipitated into a vigorously stirred methanol solution (40 mL, containing 0.1% BHT). The resulting polymer is then washed with methanol (5 mL, containing 0.1% BHT) and dried under vacuum overnight.

(a) Cyclooctadiene: Yield = 295 mg (73.8%) of a white, tacky solid. GPC (*vs.* polystyrene standard) : M_w = 88.75K, PDI = 2.42.

(b) *Exo*-5,6-dimethoxymethyl-7-oxabicyclo[2.2.1]hept-2-ene: Yield = 286 mg (71.5%) of a white, tacky solid. GPC (*vs* polystyrene standard) : M_w = 270.24K, PDI = 1.70.

(c) Cyclopentene: Yield = 267 mg (66.8%) of a white, tacky solid. GPC (*vs* polystyrene standard) : M_w = 110.84K, PDI = 1.95.

(d) Commercial 95% *cis*-cyclooctene (remainder trans): Yield = 354 mg (88.5%) of a white, tacky solid. GPC (*vs* polystyrene standard) : M_w = 73.94K, PDI = 2.62.

Observations of The Propagating Species in ROMP and Olefin Metathesis Catalyzed by 2a.

(a) *cis*-2-pentene: 5 mg of **2a** in 500 μL CD_2Cl_2 + 20 μL of *cis*-2-pentene: (a)*trans*-$(PCy_3)_2Cl_2Ru{=}C(H)Et$: ^1H NMR (CD_2Cl_2): δ 19.13 (t, J_{HH} = 5.1 Hz); (b) *trans*-$(PCy_3)_2Cl_2Ru{=}C(H)Me$: ^1H NMR (CD_2Cl_2): δ 19.25 (q, J_{HH} = 5.1 Hz).

(b) Cyclooctadiene: 5 mg of **2a** in 500 μL CD_2Cl_2 + 20 μL of cyclooctadiene: Propagating species : ^1H NMR (CD_2Cl_2): δ 19.25 (t, J_{HH} = 6.2 Hz).

(c) *Exo*-5,6-dimethoxymethyl-7-oxabicyclo[2.2.1]hept-2-ene: 3 mg of **2a** in 500 μL CD_2Cl_2 + 20 μL of *Exo*-5,6-dimethoxymethyl-7-oxabicyclo[2.2.1]hept-2-ene: (a) Propagating species #1: ^1H NMR (CD_2Cl_2): δ 18.82 (t); (b) Propagating species #2: ^1H NMR (CD_2Cl_2): δ 18.52 (t).

(d) Commercial 95% *cis*-cyclooctene (remainder trans): 8 mg of **2a** in 200 μL CD_2Cl_2 + 250 μL C_6D_6+ 20 μL of cyclooctene: Propagating species : ^1H NMR (CD_2Cl_2/C_6D_6, referenced to internal TMS signal at 0 ppm): δ 19.47 (t).

Synthesis of $(PCy_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$, 2, by a One-Pot Synthesis. In a typical reaction, [(Cymene)$RuCl_2]_2$ dimer complex (0.53g, 1.73 mmol Ru) and PCy_3 (0.91g, 2 equiv) were loaded under inert atmosphere into a 100 mL Schlenk flask equipped with a magnetic stirbar. Next, benzene (40 mL) was added followed by 3,3-diphenylcyclopropene (0.33g, 1 equiv). The reaction flask was then attached to a water-cooled reflux condenser under an inert atmosphere and heated in an oil bath at 83-85°C for 6 h (i.e., to reflux--benzene refluxes at a temperature that is slightly higher than 80°C under a positive pressure; lower temperature will result in the preferred formation of an olefin complex. Alternatively, toluene can be used as a substitute solvent although care need to be taken so that the solution is not heated to too high a temperature, especially during the first stage of the reaction. Also, the use of toluene tends to lengthen the final removal of solvent during work-up). The solvent is then removed to complete dryness in *vacuo* and the remaining red solid is washed with pentane (4 x 25 mL) under inert atmosphere. The remaining red powder is dried under vacuum for 12 h and stored under an inert atmosphere. Yield = 1.4 g (88 %); higher yield are obtained with larger scale--we have carried this reaction at a scale up to 8g [(Cymene)$RuCl_2]_2$ dimer. The solid isolated in this manner consist of about 90% of the desired product and 10% of the olefin complex which cannot be completely removed from the product by fractional crystallization. For all practical purposes, however, the olefin complex is inert under most metathesis conditions and the product mixture can be used as obtained.

Synthesis of $(P^iPr_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$, 3, by a One-Pot Synthesis. From a procedure similar to that for **2** above, starting with $[(\mathrm{Cymene})\mathrm{RuCl}_2]_2$ dimer complex (1.52 g, 4.96 mmol Ru), $\mathrm{P}^i\mathrm{Pr}_3$ (1.591g, 2 equiv), and 3,3-diphenylcyclopropene (0.953 g, 1 equiv) gave **3** at 61.3 % with a 25 % olefin complex content.

Synthesis of $(\mathrm{PCps}_3)_2\mathrm{Cl}_2\mathrm{Ru{=}CH{-}CH{=}CPh}_2$, 4, by One-Pot Synthesis. From a procedure similar to that for **2** above, starting with $[(\mathrm{Cymene})\mathrm{RuCl}_2]_2$ dimer complex (2 g, 6.53 mmol Ru), PCps_3 (3.11g, 2 equiv), and 3,3-diphenylcyclopropene (1.25g, 1 equiv) gave **4** at 61% with a 10% olefin complex content.

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Chapter 4

Well-defined, Single-Component, Group VIII Olefin Metathesis Catalysts: Effects of Ligand Environments and Carbene Substituents on Metathesis Activities

Introduction

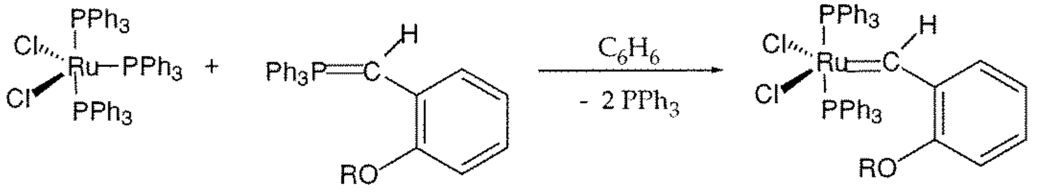
In Chapters 2 and 3 we have discussed the effects of the metal center, solvent, anionic ligands, and phosphines on the olefin metathesis activity of the group VIII metal vinylcarbene complexes $(PR_3)_2X_2M{=}CH\text{-}CH{=}CPh_2$. Two questions remain: (1) How important are the vinylcarbene moiety and the diphenylvinyl substituents in the overall olefin metathesis activity of these catalysts? (2) How important is the ligand environment (coordination numbers, π-acidity of ligands) in regards to the metathesis activity. This chapter attempts to address these questions.

Results and Discussion

In order to address the questions stated above, we have carried out a search for other non-cyclopropene methods to synthesize $(PR_3)_2X_2Ru{=}CH(R)$. Three promising *pathways were found: 1) The transfer of a carbene functionality from a phosphorous ylid* to a Ru(II) precursors and 2) The rearrangement of monosubstituted acetylenes to vinylidenes . 3) Direct metathesis of terminal olefins. In addition, efforts have been taken to expand the syntheses of $(PPh_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$, **1**, and $(PCy_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$, **2**, to include other 3,3-disubstituted cyclopropenes.

The Transfer of Carbene to Ru(II) from Phosphorous Ylids. Although the use of Wittig reagents as a carbene source has become a firmly established synthetic tool in organic chemistry, their use as carbene transfer agents for organometallic complexes remains limited. Indeed the publications concerning the synthesis of metal carbene complexes using phosphorus ylids during the past two decades can be counted on two hands.[1-6] Furthermore, these reports are all concerned with high-valent early transition metal centers. No examples have been reported for low-valent, late transition metal complexes. It was the works by Johnson and Grubbs on ylid transfer to a W(IV) complexes[2,3] and our observations of the similarities in cyclopropene ring-opening chemistry between W(IV) and Ru(II) that prompted us to investigate phosphoranes as carbene transfer reagents to Ru(II).

The reaction between $Ph_3P=CH(o\text{-}OR\text{-}C_6H_4)$ and $RuCl_2(PPh_3)_3$ results in $(PPh_3)_2Cl_2Ru=CH(o\text{-}OR\text{-}C_6H_4)$ (**3a**, R= Me; **3b**, R= Ph) in ca 80% yields (eq 1). Complexes **3a,b** are isolated as yellow brown powder. The ^1H NMR spectrum for **3a** shows a resonance at 16.25 ppm (t, J_{HP} = 7.26 Hz), significantly upfield from that observed for $(PPh_3)_2Cl_2Ru=CHPh$ (19.6 ppm),[7] perhaps due to the influence of the *o*-OR group on the phenyl group. The ^{31}P NMR spectrum for **3a** exhibits a broad resonance at 32 ppm, within normal range for these compounds. Interestingly, attempts to transfer the carbene group from other phosphoranes such as $Ph_3P=CH\text{-}CH=CMe_2$ and $Ph_3P=CHPh$ to the same ruthenium precursor have not been successful. This observation is somewhat surprising since it has been observed by Johnson and Grubbs that such ylids offers fairly good yield of tungsten(VI) carbene complexes in reaction with $WCl_2(NPh)(PMePh_2)_3$ due to their partially resonance-stabilized structures.[2,8] It appears that for the case of ruthenium(II) and $Ph_3P=CH(o\text{-}OR\text{-}C_6H_4)$, the best compromise is achieved with both resonance-stabilized carbene group and the help provided by the *o*-OR group in coordinating to the metal center in the transition state.



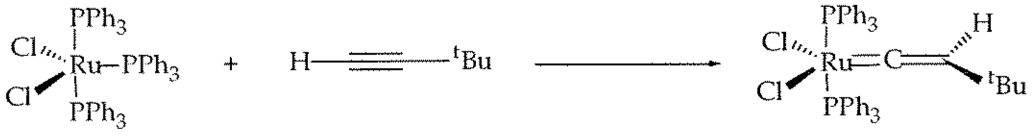
(1)

R = Me, Ph

3a: R = Me
3b: R = Ph

The Rearrangements of Terminal Acetylenes Ru(II) Metal Centers. The rearrangement of terminal acetylenes at transition metal centers to yield metal alkylidene is a well-known reaction.[9] Wakatsuki and coworkers have employed this methodology to synthesize the Ru(II) vinylidene complex $(PPh_3)_2Cl_2Ru=C=CH^tBu$, **3** (eq 2).[10] The analogous reaction between $RuCl_2(PPh_3)_3$ and phenylacetylene does not yield the desired products in our hand. In addition, although attempts to directly exchange the PPh_3

ligands in **4** with more electron-donating phosphine such as PCy_3 lead to the desired product $(PCy_3)_2Cl_2Ru{=}C{=}CH^tBu$, **5a**, this product could not be isolated away from the excess PPh_3 due to its extreme solubility.

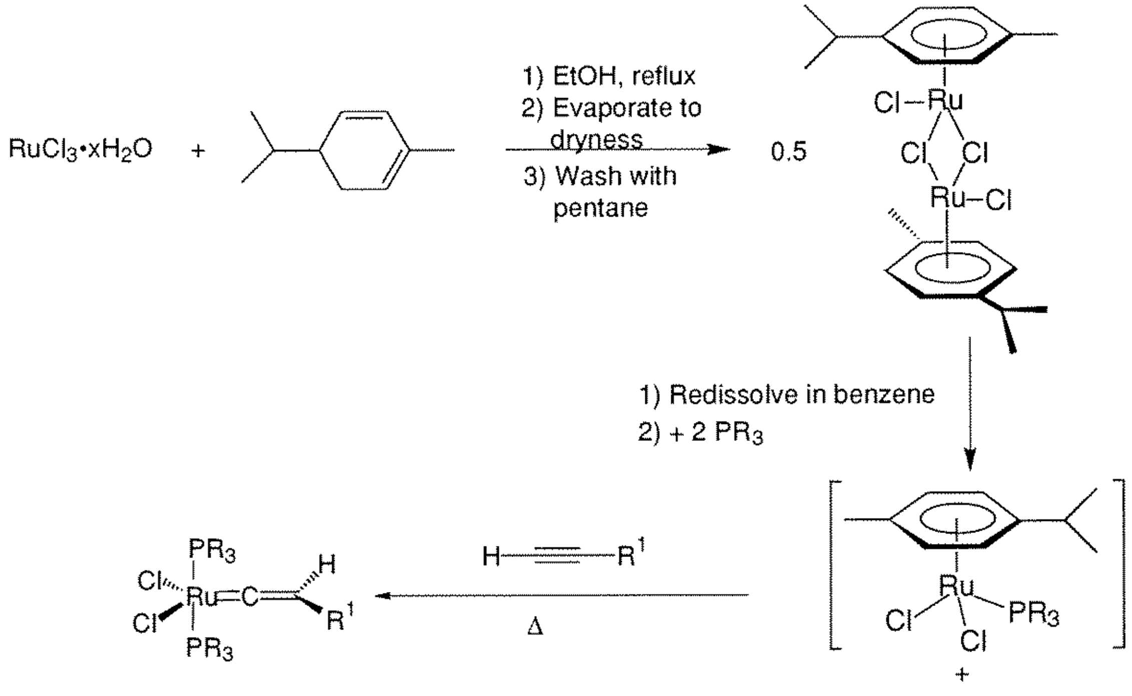


(2)

4

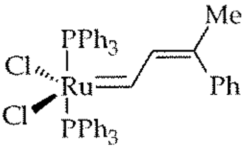
Using a one-pot procedure similar to that reported for the synthesis of **2** in Chapter 3 of this thesis (Scheme 1), we were able to obtain **5a** and $(PCps_3)_2Cl_2Ru{=}C{=}CHPh$, **6b** , in good yields. Although $(PCps_3)_2Cl_2Ru{=}C{=}CH^tBu$, **6a**, is formed and can be observed by ^1H and ^{31}P NMR spectroscopies , it could not be isolated in pure form due to extreme solubility problems.

Scheme 1. A one-pot synthesis for $(PR_3)_2Cl_2Ru{=}C{=}CHR^1$.

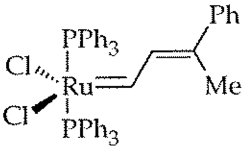


5a: R = Cy, $R^1 = {}^tBu$
6b: R = Cps, R^1 = Ph

Synthesis of $(PR_3)_2Cl_2Ru$=CH-CH=C(Me)Ph, 7, from 3-Methyl-3-phenylcyclopropene. Similar to the synthesis of **1** as reported in Chapter 2, the analogous reaction between $RuCl_2(PPh_3)_3$ with 3-methyl-3-phenylcyclopropene gives $(PPh_3)_2Cl_2Ru$=CH-CH=C(Me)Ph, **7**, in about 50 % yield after recrystallization as a green solid with a yellow tint. The low yield results from both the fragility of the cyclopropene under the thermal synthetic conditions and the higher solubility of the resulting product. The isolated product **7** exists in two isomeric forms **7a** and **7b** in ratio of 1:7. The isomer assignment were made based on spectroscopic data comparison to that of the model complexes $(PPh_3)_2Cl_2Ru$=CH-CH=CMe_2 (*vide infra*), **10**, and $(PPh_3)_2Cl_2Ru$=CH-CH=CPh_2, **1**.

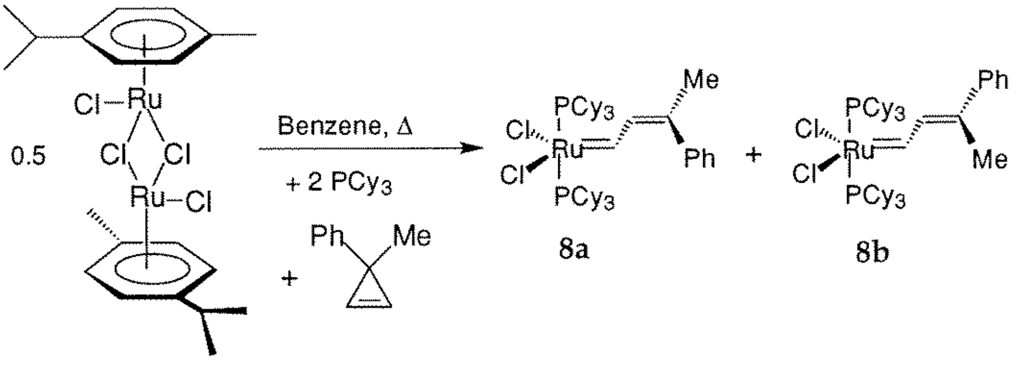


7a



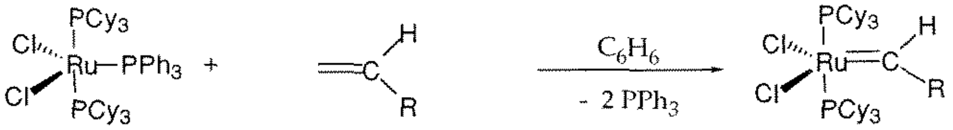
7b

The one-pot procedure described for **2** in chapter 3 can be used to synthesize $(PCy_3)_2Cl_2Ru$=CH-CH=C(Me)Ph, **8**, from $[(Cymene)RuCl_2]_2$, PCy_3, and 3-methyl-3-phenylcyclopropene (eq 3). Similar to **7**, **8** also exists in two isomeric forms: **8a** and **8b**.



(3)

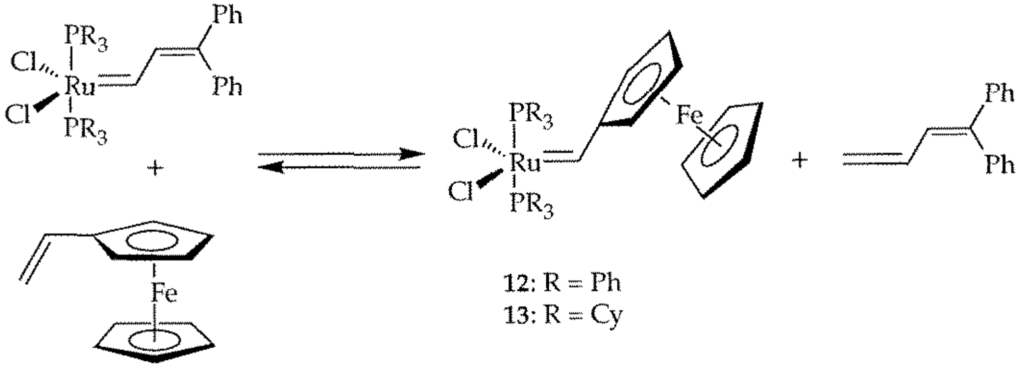
Synthesis of $(PPh_3)_2Cl_2Ru{=}CH(R)$ and $(PCy_3)_2Cl_2Ru{=}CH(R)$ by Direct Metathesis with Terminal Olefins. Grubbs and coworkers have shown that heteroatom-substituted carbene complexes of the form $(PPh_3)_2TFA_2Ru{=}CH(R)$ (where TFA = $CF_3C(O)O$ and R = OEt, SPh, and OC(O)Et) can be obtained from the direct reaction between $(PPh_3)_2TFA_2Ru{=}CH{-}CH{=}CPh_2$ and the appropriate vinyl olefins.[11] The analogous reactions between $(PCy_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ and several heteroatom-substituted vinyl olefins also yield stable $(PCy_3)_2Cl_2Ru{=}CH(R)$ complexes (eq 4). Similar to that observed by Grubbs and coworkers, C_6D_6 solutions of complexes **9a-c** will slowly decomposed over a period of 2 days. In the presence of an excess amount of an acyclic olefin such as *cis*-2-pentene these solutions become quite stable, however (*vide infra*).



(4)

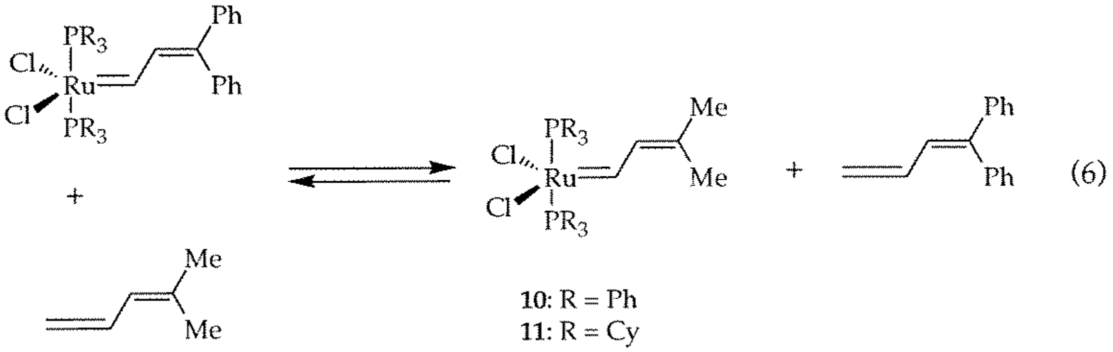
9a: R = OEt
9b: R = SPh
9c: R = OC(O)Et

Both **1** and **2** will catalyze the metathesis of acyclic conjugated olefins such as vinyl ferrocene and 1,1-dimethyl-1,3-butadiene (eqs 5 and 6). Both of these reactions are governed by equilibrium however, and we can only observed the resulting new carbenes by NMR spectroscopy.



(5)

12: R = Ph
13: R = Cy



10: R = Ph
11: R = Cy

Effect of the Vinylcarbene Conjugated Framework on the Stability of $(PR_3)_2X_2Ru{=}CH(R)$ Complexes and Their Initiation Rate in Olefin Metathesis. The equilibria depicted in eqs 5 and 6 offer a convenient means to qualitatively predict the thermodynamic stability of ruthenium vinylcarbene complexes. Both of these equilibria can be shifted with ease by the adjusting the concentration of the respective starting materials. Both 1,1-dimethyl-1,3-butadiene and vinylferrocene are special cases where true productive metathesis is observed for the $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$.[a] This is perhaps due to the low energy cost involved in the activation of such conjugated olefins (i. e. the final product is also a conjugated ruthenium carbene). Equilibrium studies of the reaction depicted in eq 5 and a similar reaction between **1** and styrene suggested that for a $(PR_3)_2Cl_2Ru$ center, the ruthenium diphenylvinylcarbene is more stable than the ruthenium ferrocenylcarbene which is more stable than the ruthenium benzylidene.

The diphenylvinyl substituents of the vinylcarbene moieties in **1** and **2** do impart an observable stability to the $(PR_3)_2Cl_2Ru{=}CH(R)$ complexes. Physically, complex **1** is more stable in solution than either **3a,b** or the $Cl_2(PPh_3)_2Ru{=}CHPh$ derivative. While **1** is stable in CD_2Cl_2 solution over several days, **3a,b** decomposes within 24 h and the $(PPh_3)_2Cl_2Ru{=}CHPh$ derivative significantly decomposes in solution in matter of hours.[7] The mode of decomposition for the benzylidene complexes appears to be of a

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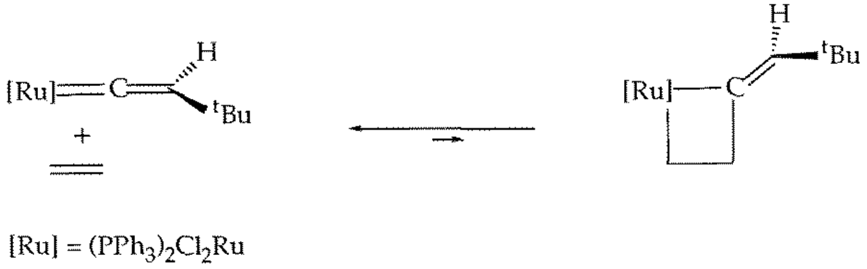
[a] Slightly "less conjugated" olefin such as styrene is not metathesized by **1** and its anionic derivatives.

bimolecular nature in which two carbene fragments are coupled together to form disubstituted ethylenes. This is also the case observed for high-valent early transition metal alkylidene complexes where very bulky ancillary ligands and carbene substituents are needed to protect the alkylidene complexes.[12-14]

Unfortunately, the stability provided by the vinylcarbene moiety is a trade-off for the ease of initiation that is sometimes needed in olefin metathesis chemistry. For example while $(PPh_3)_2Cl_2Ru{=}CHPh$ initiates completely to the propagating species after the consumption of 1 equiv of norbornene during the ROMP of 10 equiv of norbornene at room temperature,[7] under the same condition only 30% of **1** initiates. In another example, the metathesis of 100 equiv of *cis*-2-pentene by a 6.06 mM solution of $Cl_2(PCy_3)_2Ru{=}CH{-}CH{=}CPh_2$, **2**, will lead to only 70% initiation to the corresponding propagating species at equilibrium but the $(PCy_3)_2Cl_2Ru{=}CHPh$ catalyst initiated completely within the first 20 minutes of the reaction where only 10% of the *cis*-2-pentene was consumed. However, this slow initiation may be an advantage in some injection molding applications of ROMP where a period of time is needed for mixing and injecting before gelation occurs.

Other α-Substituents. Other substituents on the carbene carbon can also affect the metathesis activities of **1** a great deal. Grubbs and coworkers have shown that all heteroatoms-substituted ruthenium(II) carbene of the type $(PPh_3)_2TFA_2Ru{=}CH(ER)$, (E = O, S, NR), possess no metathesis activity compared to either the parent complex $(PPh_3)_2TFA_2Ru{=}CH{-}CH{=}CPh_2$, **1-TFA2**, or $(PPh_3)_2Cl_2Ru{=}C(CH_2CH_2)$.[11,15] In the same manner, complexes **9a,b,c** have no metathesis activity compared to **2**. The explanation for this inactivity in the $(PPh_3)_2TFA_2Ru{=}CH(ER)$, (E = O, S, NR), system have been published.[11]

Sometimes, the inactivity in metathesis is the result of a high barrier of initiation. In our hands, complex **4** does not catalyze the ROMP of norbornene and complexes **5a** and **6b** does not catalyze the metathesis of *cis*-2-pentene. These observations may be explained by potential initiation difficulties—formation of the exo-*tert*-butylmethylene metallacyclobutane necessary for the first insertion step is expected to have a high energy of activation (eq 7).



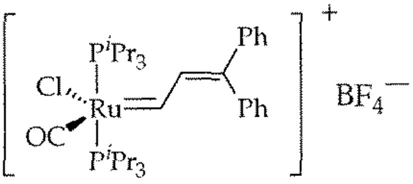
(7)

Effects of the Vinylcarbene C_γ-dialkyl Substituents on The Metathesis Activity of $(PR_3)_2Cl_2Ru{=}CH\text{-}CH{=}CR_2$. The dimethylvinylcarbene complexes $(PR_3)_2Cl_2Ru{=}CH\text{-}CH{=}CMe_2$, **10** and **11**, can be observed from the cross metathesis between 1,1-dimethyl-1,3-butadiene and **1** and **2** respectively. By studying the equilibrium described in equation 6 using **10**, **11**, **7a,b**, **8a,b**, **1**, **2**, and the appropriate olefins, a qualitative scale can be formed to evaluate the effects of the C_γ-dialkyl substituents on the stability of $(PR_3)_2Cl_2Ru{=}CH\text{-}CH{=}CR_2$ complexes. As expected from other results described above, the most significant effects of the C_γ-dialkyl substituents have are on the initiation rate and the stability of the vinylcarbene catalysts although the differences tends to be small in going from C_γ-dimethyl to C_γ-diphenyl. Qualitatively, **10** and **11** are slightly less stable than **1** and **2**, respectively and thus are predicted to initiate metathesis better than **1** and **2**, respectively. The complexes **7a,b** and **8a,b** were found to be intermediates between these two extremes, as expected.

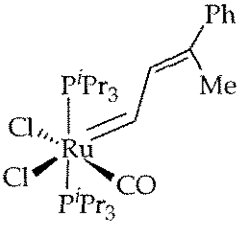
These observations raised an interesting question about the extend of conjugation along the Ru-C_1-C_2-C_3 vinylcarbene moiety. From the data we have available, it seems that this conjugation do contribute significantly to the observed stabilities of **1** and **2**. In catalysis, there is often a trade off between catalyst activity and stability. It appeared that the present ruthenium system is not an exception.

Ligand Environment and Metathesis Activity. In chapter 2 we distinguished complex **1** and its derivatives from other Ru carbenes existing in the literature by assigning **1** four basic characteristics: 1) It is formally a Ru(II) metal center. 2) It is a 16-electron complex. 3) It is 5-coordinate. 4) The carbene moiety is not a cumulene (i. e. vinylidene or allenylidene). Results to date appear to support these four basic characteristics as being the minimal requirements necessary for metathesis in the ruthenium system. However, there may be another restriction: that the ancillary in these systems should not be too acidic.

Recently, Esteruelas and coworkers reported the synthesis of two ruthenium(II) vinylcarbene complexes ,**13** and **14**,[16] which are very similar to our catalysts **1** and **2**.



13



14

In our hands, both **13** and **14** showed no metathesis activity. Given our requirements it is reasonable that 14 is not a metathesis catalyst. Complex **13**, however, is almost the same as catalyst 2 and thus should be a metathesis catalyst according to the aforementioned rules. Since **13** has an extra CO ligand and does not metathesize olefin, it may mean that strong π-acidic ligands should be avoided in our system as well.

Conclusions

The ylid transfer and acetylene rearrangement chemistry discussed herein offer new venues into the synthesis of new ruthenium(II) carbene complexes. We also have been able to extend the syntheses in chapters 2 and 3 toward 3-methyl-3-phenylcyclopropene.

In general vinyl-substituted $(PR_3)_2X_2Ru$ carbene complexes are the most stable and the slowest in metathesis initiation among the complexes considered in this chapter.

This effect may be explained by considering the ruthenium vinylcarbene moiety as a very stable extended π system that resists both decomposition and initiation in metathesis. The more conjugated the vinylcarbene moiety is, the more stable the catalyst become. Thus in essence we are trading off activity for stability and vice versa.

Carbene complexes having α-heterosubstituents appear to possess very little metathesis activity in comparison to alkylsubstituted counterparts. There are also indication that π-acidic ligand such as CO may not be good for the metathesis activity of our system.

Experimental

General Considerations. All manipulations were performed using standard Schlenk techniques or drybox procedures. 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. ^{31}P NMR spectra were either recorded with a JEOL FX-90Q (89.60 MHz ^1H; 22.53 MHz ^{13}C; 36.2 MHz ^{31}P) spectrometer (locking on a static ^7Li lock sample and reference to an external 85% H_3PO_4 sample where a 10 mM solution of PPh_3 in $CDCl_3$ will exhibit a resonance at -5.4 ppm) or with a JEOL GX-400 (399.65 MHz ^1H; 140 MHz ^{13}C; 161.85 MHz ^{31}P) spectrometer (locking on the ^2D solvent signal and reference to an external 85% H_3PO_4 sample where a 10 mM solution of PPh_3 in $CDCl_3$ will exhibit a resonance at -4.9 ppm). ^1H and ^{13}C NMR spectra were recorded with either a QE-300 Plus (300.10 MHz ^1H; 75.49 MHz ^{13}C) spectrometer or a Bruker AM-500 (500.138 MHz ^1H; 125.759 MHz ^{13}C) spectrometer at ambient temperature. NMR data are reported as follows: chemical shifts (multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration, assignment, and coupling constant (Hz)). ^1H NMR chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) (δ scale) with TMS employed as the internal standard. ^{13}C NMR chemical shifts are reported in ppm downfield from tetramethylsilane (δ scale) with the solvent resonance employed as the internal standard (CD_2Cl_2 at δ 53.8) and are obtained from complete proton-decoupled spectra while coupling constants are measured from coupled spectra with full NOE enhancement.

Materials. Benzene, toluene, and tetrahydrofuran were distilled or vacuum-transferred from sodium-benzophenone ketyl. Methylene chloride (CH_2Cl_2)was dried over CaH_2, vacuum-transferred, and then degassed by three continuous freeze-pump-thaw cycles. Pentane was stirred over concentrated H_2SO_4, dried over $MgSO_4$ and CaH_2, and then transferred onto sodium-benzophenone ketyl solubilized with tetraglyme.

Benzene-d_6 and THF-d_8 were distilled from sodium-benzophenone ketyl. Methylene chloride-d_2 was dried over CaH_2, vacuum-transferred, and then degassed by three continuous freeze-pump-thaw cycles. Deuterium oxide was degassed by bubbling a stream of argon through the solvent for 15 minutes. Ethanol-d_6 was dried over activated neutral alumina, vacuum-transferred and degassed by three continuous freeze-pump-thaw cycles. PCy_3 was obtained either from Aldrich Chemical Co. or Strem Chemical Company and recrystallized under argon from ethanol (distilled from $Mg(OEt)_2$ under argon) if containing $OPCy_3$ as determined by ^{31}P NMR spectroscopy. $PCps_3$ was a gift from Cytec Chemical. The phosphorous ylids used in this chapter were gifts from Dr. Lynda K. Johnson. 3-Methyl-3-phenylcyclopropene was prepared following the procedure described in Appendix 1. $RuCl_2(PPh_3)_3$[17],, {(Cymene)$RuCl_2]_2$,[18] $(PPh_3)_2Cl_2Ru{=}C{=}CH^tBu$[10] were synthesized according to literature procedures. $(PPh_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$ and $(PCy_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$ were synthesized as reported in Chapters 2 and 3. $[(P^iPr_3)_2(CO)ClRu{=}CH\text{-}CH{=}CPh_2][BF_4]$ and $(P^iPr_3)_2(CO)Cl_2Ru{=}CH\text{-}CH{=}CPh_2$ were synthesized according to a literature procedure.[16] All other chemicals were obtained commercially and purified by standard methods before use.

Synthesis of $(PPh_3)_2Cl_2Ru{=}CH(o\text{-}OMe\text{-}C_6H_4)$, 3a. In the drybox, $RuCl_2(PPh_3)_3$ (250 mg, 0.261 mmol) was weighed into a 50 mL Schlenk flask equipped with a magnetic stirbar. The ylid $Ph_3P{=}CH(o\text{-}OMe\text{-}C_6H_4)$ (105 mg, 1.05 equiv) was weighed into a separate flask. The flasks were capped with a rubber septa and brought out of the drybox. Next, both the ruthenium complex and the ylid were dissolved in toluene (10 mL each). The ruthenium solution was then cooled to ice water temperature and the ylid was added dropwisely to this stirring solution over a period of 30 minutes. The reaction mixture was allowed to warm up to room temperature and stir overnight. In the morning, the mixture was evaporated to dryness under vacuum. The remaining yellow solid was redissolved in methylene chloride (5 mL) reprecipitated with hexane, washed with hexane (3 x 20 mL x 30 min stirring), and dried *in vacuo* overnight. Yield = 170 mg (80%).

^{1}H NMR (C_6D_6): δ 16.25 (t, 1 H, Ru=C*H*, J_{PH}= 7.3Hz). ^{31}P NMR (C_6D_6): δ 32.3 (s) .

Synthesis of(PPh$_3$)$_2$ Cl$_2$Ru=CH(*o*-OPh-C$_6$H$_4$), 3b. From a procedure similar to that for **2a**, $RuCl_2(PPh_3)_3$ (250 mg, 0.261 mmol) and Ph_3P=CH(*o*-OPh-C_6H_4) (125 mg, 1.05 equiv) give **3b** = 178 mg (78 %).

One-Pot Synthesis of (PCy$_3$)$_2$Cl$_2$Ru=C=CH^{t}Bu, 5a. From a procedure similar to that described for the one-pot synthesis of **2** in Chapter 3, [(Cymene)$RuCl_2$]$_2$ (1 g, 3.28 x 10^{-3} mole Ru), PCy_3 (1.84 g, 2 equiv), *tert*-butylacetylene (0.269 g, 1 equiv), and benzene (60 mL) refluxed in a closed reaction vessel at 90 °C for 12 h give **5a** = 2.13g (80 %).

^{1}H NMR (C_6D_6): δ 3.4 (t, 1 H, Ru=C=C*H*^{t}Bu, J_{PH}= 3.7 Hz). ^{31}P NMR (C_6D_6): δ 17.4 (s)

One-Pot Synthesis of (PCps$_3$)$_2$Cl$_2$Ru=C=CHPh, 6b. From a procedure similar to that described for the one-pot synthesis of **2** in Chapter 3, [(Cymene)$RuCl_2$]$_2$ (1 g, 3.28 x 10^{-3} mole Ru), $PCps_3$ (1.56 g, 2 equiv), phenylacetylene (0.335 g, 1 equiv), and benzene (60 mL) refluxed in a closed reaction vessel at 90 °C give **6b** = 1.72g (70.2 %).

^{1}H NMR (C_6D_6): δ 4.59 (t, 1 H, Ru=C=C*H*Ph, J_{PH}= 3.7 Hz). ^{31}P NMR (C_6D_6): δ 18.6 (s)

Synthesis of (Ph$_3$P)$_2$Cl$_2$Ru=CH-CH=CMePh, 7a,b. In a typical reaction, a two-neck, 200 mL Schlenk flask equipped with a magnetic stirbar and a 25 mL dropping funnel was charged with $RuCl_2(PPh_3)_3$ (3.00 g, 3.13 mmol) inside a nitrogen-filled drybox. Methylene chloride (15 mL) was added to dissolve the complex followed by 60 mL of benzene to dilute the solution. 3-Methyl-3-phenylcyclopropene (418 mg, 1.01 equiv) was diluted in C_6H_6 and added to the solution via pipet. The reaction flask was capped with a stopper, removed from the box, attached to a reflux condenser under argon and heated at reflux while the cyclopropene solution was added dropwisely to the reaction mixture over a period of 30 minutes. After the addition, the reaction was kept at reflux for an additional 2.5 h. After the solution was cooled down to RT, all the solvent was removed *in vacuo* to give a dark yellow-brown solid. This solid was then washed with a 15% methylene chloride in hexanes. This washing procedure was repeated four more times to ensure the complete removal of all phosphine by-products. The resulting solid was then dried under vacuum overnight to afford 0.86 g (33 %) of **7a,b** as a green powder with a yellow tint.

trans-Me product:, **7a**: ^{1}H NMR (CD_2Cl_2): δ 17.714 (pseudo-quartet = two overlapping triplets, 1 H, Ru=C*H*); ^{31}P NMR (CD_2Cl_2): δ 28.6 (s).

cis-Me product, **7b**: ^{1}H NMR (CD_2Cl_2): δ 18.251 (pseudo-quartet = two overlapping triplets, 1 H, Ru=C*H* , J_{HH}= 9.9 Hz, J_{PH}= 9.35 Hz), 8.09 (d, 1 H, C*H*=CPhMe, J_{HH}= 9.9 Hz); ^{31}P NMR (CD_2Cl_2): δ 29.1 (s).

One-Pot Synthesis of $(PCy_3)_2Cl_2Ru$=CH-CH=CMePh, 8a,b. From a procedure similar to that described for the one-pot synthesis of **2** in Chapter 3, $[(Cymene)RuCl_2]_2$ (1 g, 3.28 x 10^{-3} mole Ru), PCy_3 (1.84 g, 2 equiv), 3-Methyl-3-phenylcyclopropene (436 mg, 1.01 equiv), and benzene (70 mL) give **8a,b** = 1.28 g (45.4 %).

trans-Me product:, **8a**: ^{1}H NMR (CD_2Cl_2): δ 18.835 (d, 1 H, Ru=C*H*, J_{HH} = 11.1 Hz), 8.113 (d, 1 H, Ru=CH=C*H*, J_{HH} = 11.1 Hz); ^{31}P NMR (CD_2Cl_2): δ 35.47 (s). ^{13}C NMR (CD_2Cl_2): δ 285.05 (t, Ru=*C*H, J_{CP} = 7.0 Hz).

cis-Me product, **8b**: ^{1}H NMR (CD_2Cl_2): δ 19.745 (d, 1 H, Ru=C*H*, J_{HH} = 11.0 Hz), 8.39 (d, 1 H, Ru=CH=C*H*, J_{HH} = 11.0 Hz); ^{31}P NMR (CD_2Cl_2): δ 36.34 (s). ^{13}C NMR (CD_2Cl_2): δ 290.89 (t, Ru=*C*H, J_{CP} = 7.5 Hz, J_{CH} = 150.8 Hz).

NMR-Scale Reactions between Complexes 1 or 2 and Terminal Olefins. In a typical reaction, the ruthenium vinylcarbene complex (1.125 x 10 $^{-2}$ mmole) was weighed into a 5 mm NMR tube inside the drybox. Next, C_6D_6 (0.6 mL) was added to dissolve the ruthenium complex. The terminal olefins was then added to the tube. The tube was capped, shaken vigorously, and taken out of the drybox to be monitored by NMR spectroscopy.

9a: ^{1}H NMR (C_6D_6): δ 14.76 (s, 1 H, Ru=C*H*); ^{31}P NMR (C_6D_6): δ 35.03 (s).

9b: ^{1}H NMR (C_6D_6): δ 18.24 (s, 1 H, Ru=C*H*); ^{31}P NMR (C_6D_6): δ 31.61 (s).

9c: ^{1}H NMR (C_6D_6): δ 15.96 (s, 1 H, Ru=C*H*); ^{31}P NMR (C_6D_6): δ 34.76 (s).

10: ^{1}H NMR (C_6D_6): δ 18.058 (q, 1 H, Ru=C*H*); ^{31}P NMR (C_6D_6): δ 29.68 (s).

11: ^{1}H NMR (C_6D_6): δ 18.893 (d, 1 H, Ru=C*H*, J_{HH} = 11.55 Hz), 8.345 (d, 1 H, Ru=CH-C*H*, J_{HH} = 11.55 Hz).

13: ^{1}H NMR (C_6D_6): δ 19.615 (s, 1 H, Ru=C*H*); ^{31}P NMR (C_6D_6): δ 35.29 (s).

Test of Metathesis Activity.

For those compounds which were isolated, a typical metathesis test involved NMR-scale reactions in C_6D_6 (0.6 mL) between the catalyst (11.125 x 10 $^{-2}$ mmole) and 10 equiv of an olefin (norbornene for PPh_3-based catalysts and *cis*-2-pentene for PCy_3-based catalysts). The reactions were monitored by ^{1}H NMR spectroscopy to check for metathesis progress.

For those compounds which were not isolated, such as **9a,b,c**, the NMR-scale reaction between **1** or **2** and the parent vinyl olefin was allowed to go to completion as monitored by ^{1}H NMR spectroscopy. The content of NMR tube was then quickly poured into a small Schlenk flask and evaporated to dryness *in vacuo* to remove excess olefin. The solid remained was taken into the drybox, redissolved in C_6D_6 in a 5 mm NMR tube, and taken outside to check for purity by ^{1}H NMR spectroscopy. *Cis*-2-pentene was then added through the septa via a gas-tight syringe and the reaction content was periodically monitored by ^{1}H NMR spectroscopy.

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Chapter 5

The Self Metathesis and Ethenolysis of Oleic Acid and Its Methyl Ester as Catalyzed by $(PCy_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$

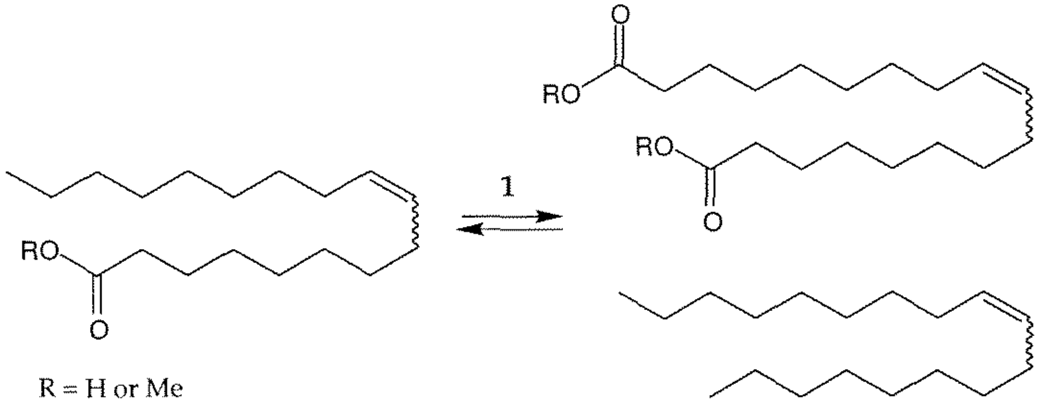
Introduction

One of the driving forces behind chemical catalysis research during the past two decades has been the need to find new ways to synthesize basic commodity chemicals from natural raw materials such as those derived from plants and grains. This motivation was put forth both from the realization that our limited reserve of petroleum-based feed stocks will eventually run out and from the incentive that natural raw materials are renewable resources that can be regenerated on an annual basis. The possibilities in this area of catalysis research have become more attractive in recent years given the current rising interests in biodegradable, environmental-friendly products. One of the most abundant and chemically usable natural raw materials is the family of natural oils and fats. With a world-wide production of 81 million tons in 1990 and only 14% of which were used for chemical and technical purposes,[1,2] there is still a lot opportunities to be explored in fully utilize this valuable resources. Commodity chemicals from natural oils and fats are easily available in a few numbers of steps and can be used in several consumer products as detergents, surfactants, plastic additives, cosmetics, and lubricants.[3-5]

The principal components of most vegetable oils are unsaturated fatty acids (>90% contains C=C bonds).[5] Yet surprisingly, current industrial oleochemical processes tend to rely heavily on traditional functional group conversions to produce commodity chemicals.[6] The chemistry of the olefinic bond is largely ignored in contrast to standard practices in petrochemistry.[5] Indeed, the fatty acid C=C bond is often considered a nuisance and have to be removed by hydrogenation in order to improve the shelf life of the commodity chemicals produced from these natural oils. However, Warvel and others have pointed out that the olefin bonds of fatty acids can be manipulated using olefin metathesis chemistry to open the door to a variety of new commodity products such as alpha olefins, polymer intermediates (Nylon 10 and Nylon 11, polyesters, polyurethanes), perfumes, fine chemicals, and new classes of surfactants and detergents.[5,7,8]

The large majority of existing literature on the olefin metathesis chemistry of vegetable oils have been focuses on either supported catalyst[5,7-10] or ill-defined, multi-component, first generation homogeneous catalysts.[7,8,10,11] In addition, most of the attention have been focused on the metathesis of unsaturated fatty acid ester and not of the fatty acids themselves, simply because most existing catalysts do not tolerate the carboxylic acid functionality.[7,10] Of the few reports concerning the use of well-defined, single component catalysts in the metathesis of unsaturated oil products,[12-16] all were focused on the ester of fatty acids.

In this chapter, we will discuss the use of the $(PCy_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$, **1**, catalyst developed in Chapter 3 to catalyze the metathesis of methyl oleate (eq 1). To our pleasant surprise, **1** also catalyze the self metathesis of the parent acid, oleic acid. Discussion concerning the cross metathesis of both methyl oleate and oleic acid with ethylene, the so-called ethenolysis reaction, will also be presented.



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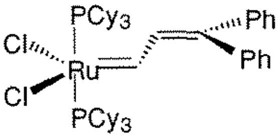


Results and Discussion

The Self Metathesis of Methyl Oleate Catalyzed by 1. When 550 equiv of methyl oleate is added to a solution of **1** (5 mg in 0.2 mL of *o*-dichlorobenzene) the reaction reaches equilibrium in about 20 h at room temperature (Figure 1). Although not rigorously comparable due to concentration differences, this activity is qualitatively similar to that reported for $\mathrm{Re(C^{t}Bu)(CH^{t}Bu)(OR_{F6})_2}$ (17 equiv/h[12]), $\mathrm{Mo(NAr)(CH^{t}Bu)(OR_{F6})_2}$ (30 equiv/h[15]), and $\mathrm{W(NAr)(CH^{t}Bu)(OR_{F6})_2}$ (100 equiv/h[13]) but somewhat slower than that observed for the Basset catalyst (500 equiv/h[14]). This comparison is quite interesting since **1** is several orders of magnitude slower than any of the above catalysts in catalyzing the metathesis of *cis*-2-pentene (Chapter 3). One potential explanation for this observation is that in contrast to the four-coordinate, high oxidation state catalysts mentioned above, the low valent Ru(II) center is not very oxophilic and thus is not slowed down significantly by the competitive binding of the ester functionality. Indeed, this competitive binding has been shown to inhibit the productive metathesis of alkyl-3-alkenoate by $\mathrm{Mo(NAr)(CHCMe_2Ph)(OR_{F6})_2}$.[17]

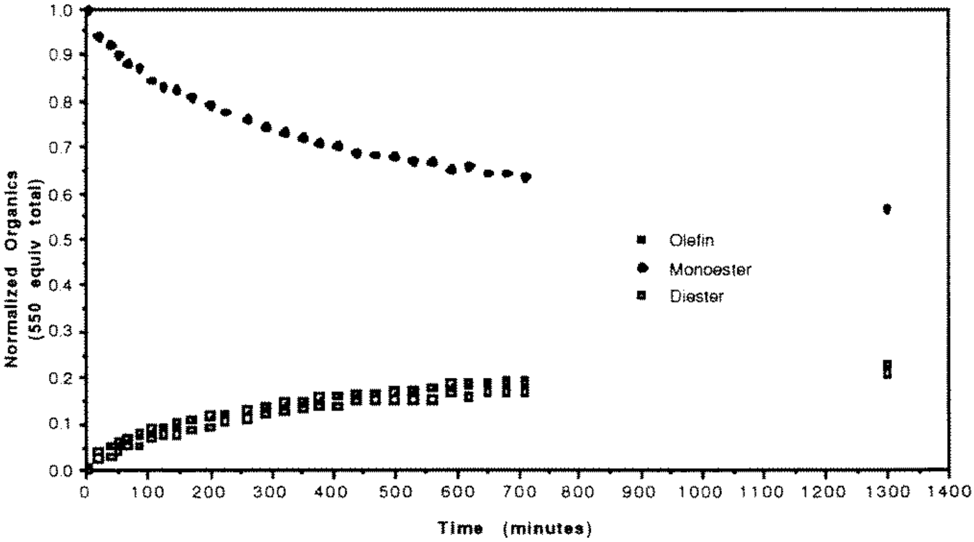
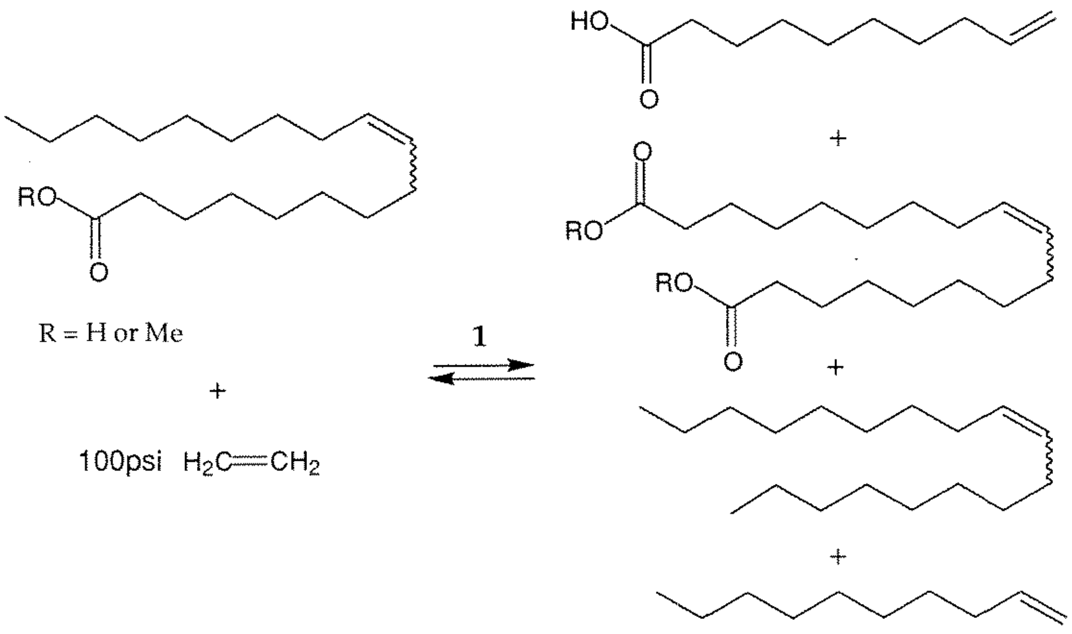


Figure 1. The self metathesis of methyl oleate catalyzed by **1**.

Even larger amount of methyl oleate can be metathesized by **1** successfully. Up to 5000 equiv of commercial-grade methyl oleate has been metathesized to completion by **1**, either at one time or spread out as successive 1000 equiv additions over a period of several days. This is perhaps the record turn over number reported to date and further illustrates the stability of **1** and the propagating species.

The Self Metathesis of Oleic acid Catalyzed by 1. Even more remarkable is the ability of **1** to catalyzed the self metathesis of oleic acid. In a typical reaction, 200 equiv of oleic acid is completely metathesized after 20h at room temperature by a solution of **1** (5 mg in 0.1mL CH_2Cl_2). Given the stability of **1** in the presence of protic species (Chapter 3), this observation is perhaps not surprising in retrospect. However, to the best of our knowledge, no catalyst system, either homogeneous or heterogeneous, has been reported to be capable of self-metathesizing COOH-containing olefins.[7]

The Ethenolysis of Methyl Oleate and Oleic Acid Catalyzed by 1. Complex **1** readily catalyzed the ethenolysis of both methyl oleate and oleic acid under 100 psi of $CH_2{=}CH_2$ (eq 2) . Although the cross metathesis of fatty acid esters with ethylene is fairly common,[5,7] there are only two reported instances of the cross metathesis of internal olefins such as 4-octene with the fatty acids themselves.[18,19] In addition, it is a unique ability of the ruthenium-based catalyst to tolerate fairly high pressure of ethylene. This is not the case for many of the well-defined, single-component, high-valent early transition metal catalysts report to date. Although we lacked the necessary equipment to directly measure the rate of ethenolysis of the oleic acid and its methyl ester, a qualitative estimate suggest that this rate is much faster than that of the self metathesis, consistent with the observation that the propagating species $(PCy_3)_2Cl_2Ru{=}CH_2$ is more active than the parent catalyst **1**.[20]



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Conclusion

We have demonstrated that the exceptional functional group tolerance of **1** is responsible for it being an effective catalyst in the self metathesis of methyl oleate. We also shown the first example of self metathesis of oleic acid by a well-defined, single-component catalyst. Due to its unique stability under high pressure ethylene, complex **1** is also very efficient in the cross metathesis of this olefin with oleic acid and its ester.

Experimental

General Considerations. All experiments were set up and (except for those involve ethylene) carried out in a nitrogen-filled glove box. The ethenolysis experiments were carried out using a medium-pressure Fisher-Porter type glass vessel designed by Ace Glass. All kinetic data and compositional analysis was perfomed using GC integration against an internal standard. Oleic acid and its diacid metathesis product were converted to the methyl ester ($MeOH/H_2SO_4$) before analysis by GC.

Catalyst **1** was synthesized according to the one-pot procedure described in chapter 3 of this thesis. Both methyl oleate and oleic acid were obtained from Aldrich Chemical Company and were degassed by three cycles of vacuum and refill with N_2 before use. All solvents were degassed with nitrogen and stored over 3Å molecular sieves before use. Ethylene (polymer grade) was obtained from Matheson Gas product and used as received.

General Procedure for the Self Metathesis of Methyl Oleate and Oleic Acid. In a typical experiment, catalyst **1** (5 mg) was dissolved in *o*-dichlorobenzene (0.2 mL) in a 2 mL vial equipped with a magnetic stirbar. The fatty acid derivative was then added neat. The vial was sealed and allow to stir at room temperature. Aliquots were then taken out periodically to monitor the progress of the reaction (the catalyst was quenched with ethyl vinyl ether before analysis by GC).

General Procedure for the Ethenolysis of Methyl Oleate and Oleic Acid. In a typical experiment, catalyst **1** (20 mg, 2.16×10^{-2} mmol) and *o*-dichlorobenzene (0.2 mL) were combined in the glove box with dichloromethane (30mL) in a 100 mL Fisher-Porter type glass vessel equipped with a magnetic stirbar. The fatty acid derivative was then added neat. The vessel was sealed quickly, taken out of the box, purged with ethylene (2 x 40 psi, each time allowed to stand for 5 minutes before venting to equilibrate with the solution phase). Finally, the vessel was pressurized to 40 psi and allowed to stir at room temperature for 4 h. After venting, the catalyst was quenched with ethyl vinyl ether (100 equiv) before analysis was performed by GC.

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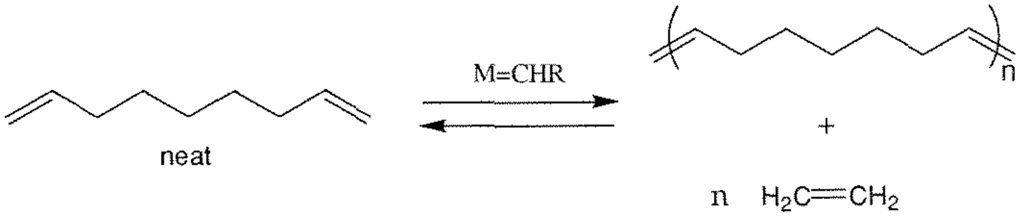
Chapter 6

The Diolefin Metathesis Polymerization (DOMP) Reaction and Polyolefin Depolymerization as Catalyzed by $(PCy_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$

Introduction

The Diolefin Metathesis Polymerization (DOMP) (or Acyclic Diene Metathesis Polymerization (ADMET)) reaction is essentially a metathesis-based condensation polymerization reaction where an α,ω-diene is polymerized neat in the presence of a metathesis catalyst to generate linear polyolefin chains with a total lost of one ethylene molecule per every incorporation of the α,ω-diene into the chain (eq 1).[1] Attempted during the early days of olefin metathesis[2-6] but was later abandoned due to the lack of a suitable catalyst, in recent years the DOMP reaction has seen a renaissance due to the availability of new well-defined, single component olefin metathesis catalysts based on high-valent Mo and W metal centers.[7-13]



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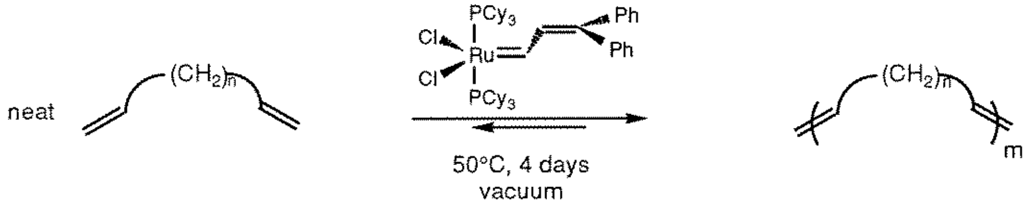
This chapter reports the results of our investigation into the use of the ruthenium catalyst $(PCy_3)_2Cl_2Ru=CH-CH=CPh_2$, **1**, for the DOMP reaction. Given the stability of **1** under a high pressure atmosphere of ethylene, we also carried out a depolymerization study where the reserve direction of eq 1 is accessed under high concentration of ethylene.

Results and Discussion

DOMP Chemistry Catalyzed by 1. We carried out DOMP polymerization using **1** for a series of simple α,ω-dienes. The results of this study are listed in Table I. In general, the DOMP polymer obtained by **1** have lower molecular weight than those obtained from $W(NAr)(OR_{F6})(CH^tBu)$.[7,8,14] The reaction takes much longer to complete and in certain instances, such as 1,5-hexadiene and 1,9-decadiene, the polymer yield is lower than obtained by Wagener and coworkers.[8] The PDI's of all isolated polymers are fairly narrow but probably is the consequence of low molecular weights and fractionation during work-up. Interestingly, for C_9-diene a large fraction of the products is cycloheptene.

Table I. The DOMP Reaction as Catalyzed by **1**.



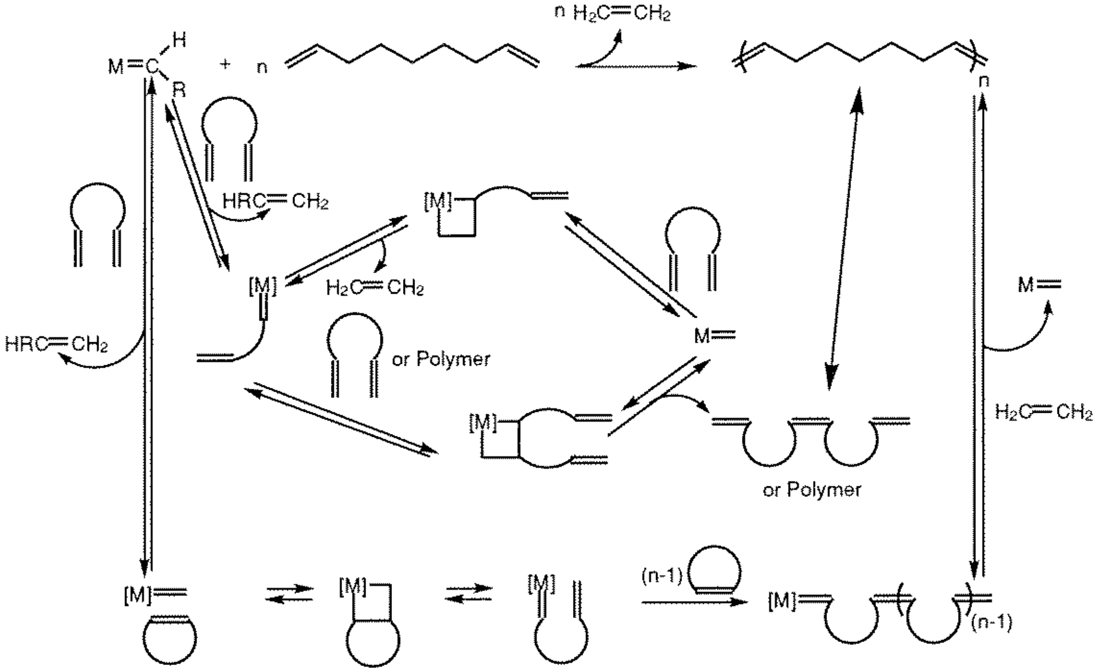
n	Cyclic Products and Oligomers[+]	Isolated Polymer[*]		
		Yield	M_n (vs. PS)	PDI
2	~ 41% of m =2-6 Oligomers	0	0	0
4	~ 7% Cyclohexene + 3% m =2 Oligomer	0	0	0
5	~ 40% Cycloheptene	47	4103	1.3
6	Mostly Oligomers	26	1835	1.13
7	Mostly Oligomers	50	2124	1.26
10	Mostly Oligomers	60	2888	1.34

[*] From MeOH Precipitation Only

[+] Soluble in MeOH

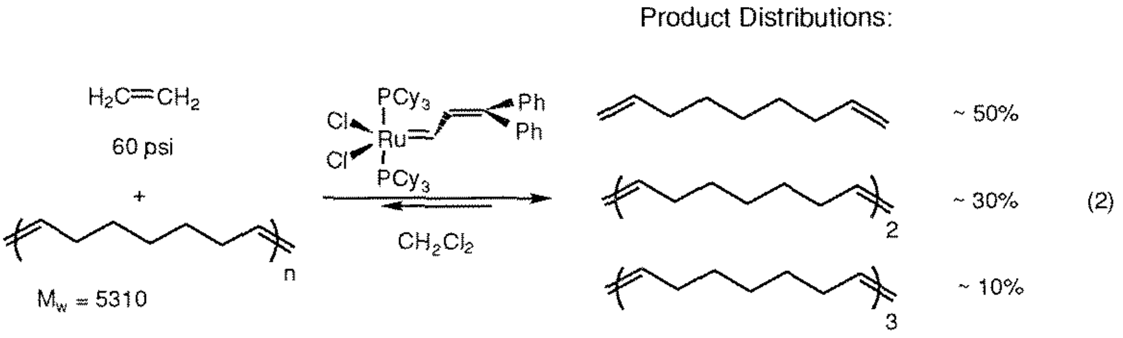
The mechanism of the DOMP reaction has been proposed as occurring through the continuous intermolecular coupling of terminal methylene bonds of α,ω-dienes to give the resulting polymer (Scheme 1, inner coupling cycle). This is based on the fact that the polymerization is carried out neat and there is a definite competition between intramolecular cyclization and intermolecular coupling. Indeed, proponents of the DOMP chemistry often strive to distinguish the DOMP cycle from the ROMP mechanism even to the point of excluding the possibilities that DOMP polymerization may occur by an intramolecular ring-closing reaction followed by a ROMP reaction (Scheme 1, outer coupling cycle).[1,8] The DOMP mechanism certainly makes sense for the dienes most often used in DOMP chemistry such as 1,5-hexadiene where the ring cyclization reaction will give cyclobutene, (or 1,9-decadiene where the ring cyclization will give cyclooctene) a high energy intermediates. For C_7 to C_9 α,ω-dienes, especially 1,7-octadiene where the thermodynamic of ring closing is most favorable, the possibility of polymerization occurring by an intramolecular ring-closing reaction follows by a ROMP reaction needs to be considered. Logically, there is no reason why, of the two processes depicted in Scheme 1, one process must occur with the exclusion of the other

Scheme I. The Complete DOMP Mechanism.



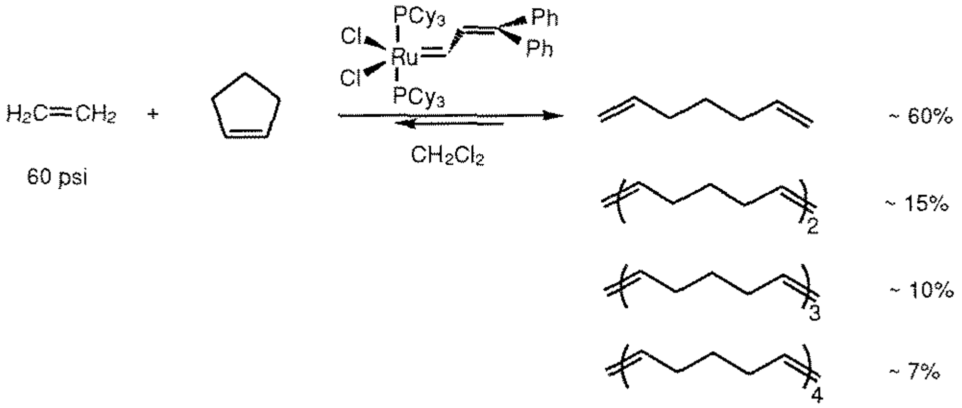
and it is experimentally impossible to rule out the possibilities of both pathways participating in the overall polymerization. It may be possible that in a typical DOMP experiment, the reaction mixture is a complex ring-chain equilibrium of polymer, oligomers both linear and cyclic, the starting dienes, and small cyclic rings resulting from the ring-closing reaction of the starting dienes. Given a catalyst and long enough reaction time (such as here), the reaction mixture will eventually reach this equilibrium. It is possible that in all the DOMP cases examined to date, due to the high activity of the catalysts, only the kinetically formed (linear high polymer) product have been isolated.

Depolymerization of a Polypentenamer with Ethylene as Catalyzed by 1. The use of ethylene to degrade polyunsaturated polymers in the presence of a metathesis catalyst have been previous reported.[15,16] This is basically the cross metathesis of ethylene and an internal olefins, similar to the ethenolysis of fatty acid esters reported in Chapter 5. We have been able to carried out the ethenolysis of a polypentenamer under a moderate pressure of ethylene and in the presence of **1** (eq 2). Under fairly moderate ethylene pressure (4 atm), the polypentenamer quickly reverts back to 1,6-heptadiene and oligomers.



(2)

In a related reaction, the ring-opening of cyclopentene to 1,6-heptadiene have been carried out (eq 3). The product distribution suggests that there may be competing ROMP process occurring during the reaction.



(3)

Conclusion

We have demonstrated that catalyst **1** can be used in DOMP and depolymerization reactions just as $W(NAr)(OR_{F6})(CH^{t}Bu)$. Although less active than the tungsten-based catalyst, **1** is more functional group tolerance and should be more useful in both the synthesis of DOMP functionalized polymers and the degradation of commercial polyunsaturated polymers such as vulcanized rubber.

Experimental

General Considerations. All manipulations involving catalyst **1** were performed using standard Schlenk techniques or drybox procedures. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). Solid samples of **1** were transferred and stored in a nitrogen-filled Vacuum Atmospheres drybox. ^{1}H and ^{13}C NMR spectra were recorded with a QE-300 Plus (300.10 MHz ^{1}H; 75.49 MHz ^{13}C) spectrometer at ambient temperature. Molecular weight was measured against polystyrene standards using GPC in CH_2Cl_2. Gas Chromatography was performed using a Hewlett-Packard HP 5890 Series II Gas Chromatography equipped with a 30 mm SE-30 (OV-1) capillary column and a HP 3396 Series II integrator.

Materials. Catalyst **1** was synthesized according to the one-pot synthesis procedure reported in Chapter 3. All the α,ω-diene were purchased from Wiley Organics, cyclopentene is purchased from Aldrich Chemical Co. All the olefins were passed through a plug of activated neutral alumina, degassed with three freeze-pump-thaw cycles and stored under nitrogen. The polypentenamer used in the depolymerization reaction was made from the DOMP reaction of 1,6-heptadiene (*vide infra*). Ethylene (polymer grade) is obtained from Matheson Gas Products and is used as received. Methylene chloride (CH_2Cl_2) to be used with the catalyst was dried over CaH_2, vacuum transferred and then degassed by three continuous freeze-pump-thaw cycles. For the polymer work up: ethyl vinyl ether were obtained from Aldrich; Silica gel, CH_2Cl_2, methanol, and CCl_4 were obtained from EM Science; all were used as received. All other solvents are standard reagent grade from EM Science and were used as received.

DOMP Polymerization of α,ω-Diene. In a nitrogen-filled glove box, catalyst **1** was dissolved in a minimal amount of a CH_2Cl_2 (0.05 mL) in a glass vessel equipped with a Kontes 4 mm Teflon valve and a magnetic stirbar. The monomer (2 mL, 800-1500 equiv) was then added to this catalyst. The mixture was then sealed, taken out of the glove box and subjected to three freeze-pump-thaw cycles. The reaction vessel was then lowered into an oil bath at 50° C and the reaction was subjected to vacuum to remove ethylene every three hours while the side of the reaction vessel was kept cold with a cloth band saturated with liquid nitrogen. Every 24 h, the reaction was backfilled with nitrogen and an aliquot was removed, quenched with ethyl vinyl ether, and analyzed by ^{1}H NMR spectroscopy to monitor the progress of the reaction.

Work-up: After the reaction has reached equilibrium, the reaction flask was cooled down to room temperature, quickly opened and to it was added a solution consisting of: CH_2Cl_2 (4 mL), ethyl vinyl ether (0.8 mL). This mixture was then left at RT for 2 h during which time the color changed from yellow to dark brown-yellow. This solution was then passed through a 1" x 1" cylindrical plug of silica gel, eluted with CH_2Cl_2. The combined eluants was evaporated on a rotary evaporator, redissolved in CCl_4 (5 mL)., and precipitated into a vigorously stirred methanol solution (40 mL). The resulting white polymer is then washed with methanol (5 mL) and dried under vacuum overnight. The methanol wash solutions were combined, evaporated to a minimum and *dried briefly (1 h) under vacuum before being analyzed by GC.*

Depolymerization of a Polypentenamer with Ethylene as Catalyzed by 1. In a nitrogen-filled glove box, catalyst **1** (23 mg, 2.49 x 10 $^{-2}$ mmol)was dissolved in CH_2Cl_2 (5 mL) in a Fisher-Porter medium pressure glass reaction vessel equipped with a magnetic stirbar. Next, the polymer (300 mg, $M_w = 5310$, 145 equiv linkage/catalyst) was added to this catalyst. The mixture was sealed, taken out of the glove box, and subjected to three freeze-pump-thaw cycles. The reaction vessel was then pressurized to 60 psi of ethylene and allowed to stir at room temperature. During the first two hours ethylene was added to the mixture occasionally to maintain the pressure. The mixture was then hold at 60 psi for 22 h more and then vented quickly. To it was then added a solution consisting of: CH_2Cl_2 (4 mL), ethyl vinyl ether (0.8 mL). This mixture was then left at RT for 2 h during which time the color changes from yellow to dark brown-yellow.

This solution was then passed through a 1" x 1" cylindrical plug of silica gel, eluted with CH_2Cl_2, and inject on the GC. A part of this solution was quickly pumped down and analyzed by GPC for trace of polymer; the remaining oligomers has a $M_w = 410$ and a PDI of 1.21, corresponding to at most a trimer.

Ring-Opening of Cyclopentene with Ethylene as Catalyzed by 1. In a nitrogen-filled glove box, catalyst **1** (20 mg, 2.155 x 10 $^{-2}$ mmol) was dissolved in CH_2Cl_2 (5 mL) in a Fisher-Porter medium pressure glass reaction vessel equipped with a magnetic stirbar. Next, cyclopentene (1g, 590 equiv) was added to this catalyst. The mixture was sealed, taken out of the glove box, and subjected to three quick pressure-vent cycles during which time the reaction has become viscous due to polymerization. The reaction vessel was then pressurized to 60 psi of ethylene and allowed to stir at room temperature. During the first two hours ethylene was added to the mixture occasionally to maintain the pressure. The mixture was then hold at 60 psi for 22 h more and then vented quickly. To it was then added a solution consisting of: CH_2Cl_2 (4 mL), ethyl vinyl ether (0.8 mL). This mixture was then left at RT for 2 h during which time the color changes from yellow to dark brown-yellow. This solution was then passed through a 1" x 1" cylindrical plug of silica gel, eluted with CH_2Cl_2, and inject on the GC. A part of this solution was quickly pumped down and analyzed by GPC for trace of polymer; the remaining oligomers has a $M_w = 556$ and a PDI of 1.21, corresponding at most to a trimer.

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Chapter 7

The Syntheses and Activities of Polystyrene-Supported Olefin Metathesis Catalysts based on $(PR_3)_2Cl_2Ru=CH-CH=CPh_2$

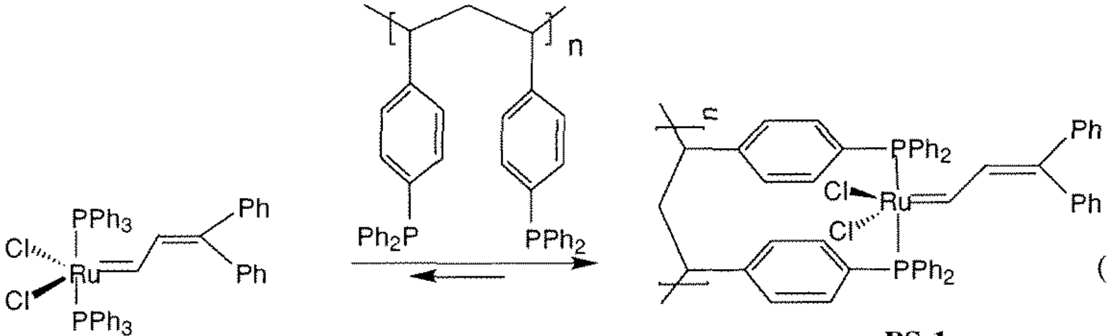
Introduction

The use of polymers as supports in organometallic catalysis is well-documented and have been extensively reviewed.[1,2] In contrast to the majority of traditional metal-oxide supports, lightly crosslinked (i. e. 2%) polymer substrates such as polystyrene-divinylbenzene (PS/DVB) offer a means to directly "heterogenize" well-defined, discrete, homogeneous organometallic complexes with the retention of all the ligand enviroment characteristics around the metal centers. As such, polymer-supported organometallic catalysts combine both the chemical activity and tunability of the homogeneous metal complexes and the stability and ease of separation/recovery afforded by traditional heterogeneous catalysts. Among the polymer-supported organometallic catalysts investigated, the most popular have been those based on the noble metals such as rhodium and platinum hydro-addition catalysts since in these cases the recovery and reuse of these expensive metal complexes are highly desirable. Although polymer-supported Mo and W catalysts of the first generation (i.e. non-carbene, multicomponent systems) have been found to possess olefin metathesis activities;[3,4] to the best of our knowledge, there has been no report of single-component, well-defined olefin metathesis catalysts being attached to a polymer support.

Recently, we reported the syntheses of the ruthenium vinylcarbenene metathesis catalysts $Cl_2(PR_3)_2Ru{=}CH\text{-}CH{=}CPh_2$ (**1**, R = Ph;[5] **2**, R= Cy[6]) which can catalyze the ring-opening metathesis polymerization (ROMP) of cyclic olefins and the metathesis of acyclic olefins. Subsequently, these catalysts have found a variety of applications in both polymer chemistry[7-10] and organic synthesis.[8,9,11-15] In particular, both **1** and **2** have been shown to catalyze the living ROMP of several cyclic monomers.[5,8,16] In the interest of developing methods to recover and reuse these noble metalcarbene catalysts as well as to prepare large quantities of monodispersed polymers on a support (much in the same manner that peptide synthesis is currently being carried out on Merrifield resins[17]), we synthesized a series of PS/DVB-supported ruthenium vinylcarbene catalyst and explored their metathesis activity. The results of this study are reported in this chapter.

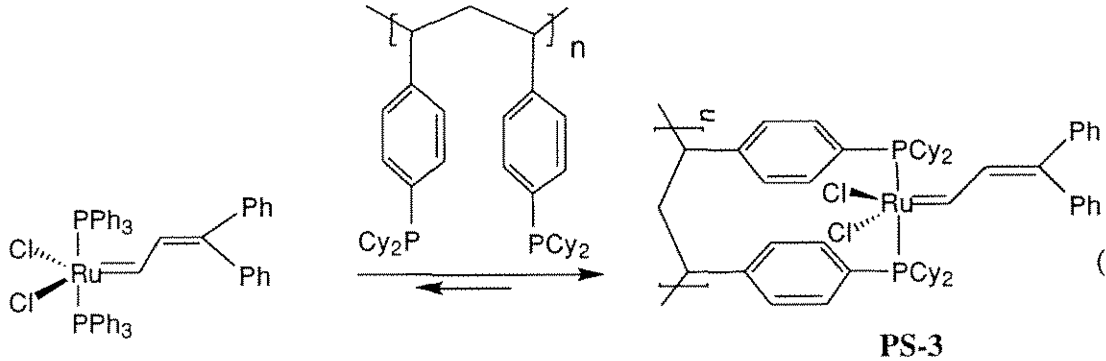
Results and Discussion

The Syntheses of PS/DVB-Supported Ruthenium Vinylcarbene Olefin Metathesis Catalysts. The ability of **1** to exchange its phosphine ligands with a variety of phosphines have enabled the convenient syntheses of several PS/DVB-supported ruthenium bis-phosphine vinylcarbene catalyst (eqs 1 to 3). Thus, a solution of **1** will *readily transferred the* $Cl_2Ru=CH\text{-}CH=CPh_2$ *moiety onto a variety of 2%-crosslinked* phosphine-functionalized PS/DVB resins to give the corresponding resin-supported ruthenium vinylcarbene catalysts **PS-1**, **PS-3**, and **PS-4**, presumably attached to the resin through bis-phosphine linkages. This assignment was made based on the similarities between the ^{31}P NMR chemical shifts of the PS/DVB-supported catalysts and their homogeneous counterparts.



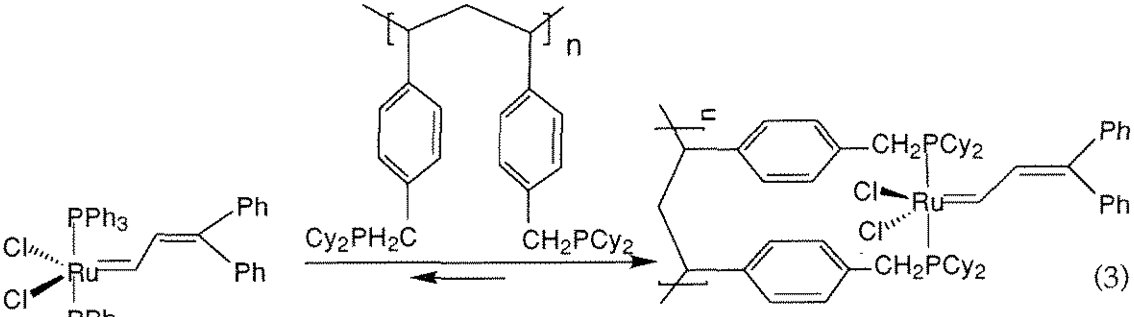
(1)

PS-1



(2)

PS-3



(3)

PS-4

The Activities and Recyclability of PS/DVB-Supported Ruthenium Carbene Olefin Metathesis Catalysts. Similar to their homogeneous analogs, catalysts **PS-1**, **PS-3**, and **PS-4** exhibit metathesis activities corresponding to the nature of the PS-linked phosphines. For example while **PS-1** catalyzes the ROMP of the highly strained norbornene, it does not metathesize acyclic olefin such as *cis*-2-pentene. On the other hand, **PS-3** and **PS-4** will catalyze both the metathesis of *cis*-2-pentene and the ROMP of less strained cyclic olefins such as cyclooctene. The more electron-rich catalyst **PS-4** metathesize *cis*-2-pentene with a turn-over number (TON) of 2 h^{-1}. The TON for the metathesis of *cis*-2-pentene in C_6D_6 by **PS-3** (0.1 h^{-1}) is slower than that of **PS-4** and is about 150 times slower than that of its homogeneous analog $PPhCy_2)_2Cl_2(Ru=CH-CH=CPh_2$, **3**.[18] This retardation in rate may be attributed to three reasons: (1) Incomplete substitution of phosphine: since the phosphine exchange reaction is governed *by an equilibrium and mixed-phosphine species* $(PR_3)(PPh_3)Cl_2Ru=CH-CH=CPh_2$ *can* be observed in the homogeneous exchange between PR_3 and $PPh_3)_2Cl_2(Ru=CH-CH=CPh_2$,[18] a large percentage of the total ruthenium complexes on the resin can potentially be mixed-phosphine species, which are very slow acyclic olefin metathesis catalysts. (2) Diffusion limit on metathesis rate: in contrast to the homogeneous metathesis reaction where both the catalyst and the olefin are dispersed throughout the solution, the heterogeneous olefin metathesis reaction as catalyzed by these PS/DVB-supported catalysts is limited by the diffusion of the olefin into the cavities of the crosslinked PS/DVB support. This diffusion limitation had been observed in PS/DVB-supported rhodium(I) hydrogenation catalysts.[19] (3) Phosphine chelation effect: if the main mechanism for the metathesis reaction is of a dissociative nature (i. e. going through a 14-electron $(PR_3)Cl_2Ru{=}CH{-}CH{=}CPh_2$) intermediate) then the presence of a local high concentration of phosphine such as that on the support will slow down the metathesis rate. Indeed, there are accumulated evidences to support the dissociative pathway for the olefin metathesis reaction catalyzed by **2**.[8,20]

The decrease in general acyclic metathesis rates of these PS/DVB-supported catalysts is offset by the extended lifetime of the supported catalysts and our ability to recycle and reuse the solid phase ruthenium vinylcarbene. A common decomposition mode of carbene-based olefin metathesis catalysts is of a bimolecular mechanism where two carbenes combined to yield an olefin and two unreactive metal center. Thus, spacing the catalyst molecules on the polystyrene support as reported herein should eliminate this decomposition pathway and enhance the lifetime of the catalyst. We have cycled catalyst **PS-4** through three complete metathesis of *cis*-2-pentene (100 equiv each) in C_6D_6 over a period of 30 days with a small lost of activity (20 % after each cycle). This experiment demonstrated that the PS-supported ruthenium carbene catalyst are long-lived and can be reused in practical circumstances.

For all polymerizations using these PS/DVB-supported catalysts, the polydispersity index (PDI) of the polymer products tends to be much higher than normally achieved with the homogeneous analog. For example, the ROMP of norbornene as catalyzed by **1** routinely gives polymers with PDI ranging 1.1 to 1.3[16] while the ROMP of norbornene catalyzed by **PS-1** yields a polymer with PDI = 5.5. Again, this phenomena can be attributed to both multiple-site and diffusion limitation problems.

Conclusion

This first generation of PS/DVB-supported ruthenium vinylcarbene metathesis catalyst represents the first time that a well-defined organometallic metathesis catalyst is attached to a polymeric support. This approach offers the promise that given the right conditions these PS/DVB-supported catalysts can be used in a manner analogous to solid phase peptide synthesis to generate several libraries of monodispersed ROMP-type block copolymers. Additionally, polymer back-biting problem such as in the case of homogeneous ROMP chemistry might be minimized by the sterically constrained nature of the crosslinked PS/DVB support and the synthesis of ROMP polymers with new stereochemical composition (for example, high-cis back bone) might be realized.

Although initial experiments with the first generation of PS/DVB-supported ruthenium metathesis catalysts have suggested that, in contrast to Merrifield resin chemistry where only one peptide link is formed at each reaction site during a single coupling, the ROMP chemsitry using these PS/DVB-supported ruthenium carbene catalysts is less selective in the sense that different number of links can be formed at different reaction sites depending on the time scale of the reaction and the location of the site. In addition, the slow initiation rate of the vinylcarbene catalyst can further contribute to the broad molecular weight distribution problem. Both of these problems can be avoided by using a different carbene complex and resins with a lower DVB crosslinked density.

Experimental Section

General Considerations. All manipulations were performed using standard Schlenk techniques or drybox procedures. 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. ^{31}P NMR spectra were recorded with a JEOL FX-90Q (89.60 MHz ^{1}H; 22.53 MHz ^{13}C; 36.2 MHz ^{31}P) spectrometer (locking on a static ^{7}Li lock sample and reference to an external 85% H_3PO_4 sample where a 10 mM solution of PPh_3 in $CDCl_3$ exhibits a resonance at -5.4 ppm). ^{1}H NMR spectra were recorded with a QE-300 Plus (300.10 MHz ^{1}H) spectrometer. NMR data are reported as follows: chemical shifts (multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration, assignment, and coupling constant (Hz)). ^{1}H NMR chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) (δ scale) with TMS employed as the internal standard. ^{31}P NMR spectra of the benzene-swollen PS/DVB-supported catalysts were carried out in a non-spinning mode with a 3-Hz line broadening applied during the processing of the FID. In general, the ^{31}P resonances of the polymeric catalysts measured in this manner are consistently broad due to restricted mobility of the ^{31}P nuclei and the chemical shifts positions are about ± 3 ppm different from that of a homogeneous sample.

Materials. Methylene chloride, methylene chloride-d_2, and N,N,N',N'-tetramethylene ethylenediamine (TMEDA) were dried over CaH_2, vacuum-transferred, and then degassed by three continuous freeze-pump-thaw cycles. Pentane was stirred over concentrated H_2SO_4, dried over $MgSO_4$ and CaH_2, and then further dried over sodium-benzophenone ketyl solubilized with tetraglyme. Tetrahydrofuran (THF), benzene, and benzene-d_6 were dried over sodium-benzophenone ketyl and vacuum-transferred into a storage flask. $ClPCy_2$ was obtained from Strem Chemical Company and was used as received. $LiPCy_2$ was collected as a pale yellow solid from the reaction of ^{n}BuLi in hexane (obtained from Aldrich) and $HPCy_2$ (obtained from Strem Chemical Company). $(Ph_3P)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$, **1**,[5] was synthesized according to literature procedures.

Triphenylphosphine-functionalized polystyrene ($PS\text{-}PPh_2$) *resin* (2% crosslinked PS/DVB, 200-400 mesh, 3 mmol P/g of resin) was obtained from Fluka (cat # 93093), chloromethylated polystyrene (PS-*p*-CH_2Cl) resin (2% crosslinked PS/DVB, 200-400 mesh, 0.43 mequiv Cl/g of resin) was obtained from Polyscience (cat #09011) and used as received. To obtain maximum para-substitution, lithiated polystyrene (PS-Li) resin (2% crosslinked PS/DVB, 25-60 mesh) is synthesized from brominated polystyrene (PS-Br) (which in turns is prepared from purified polystyrene[21] obtained as a gift from Dow Chemical Company) according to a procedure described by Farrall.[21] *Cis*-cyclooctene (95%) and *cis*-2-pentene were obtained from Aldrich, distilled over CaH_2 and degased through three freeze-pump-thaw cycles. Norbornene was obtained from Aldrich, dried over sodium benzophenone ketyl, vacuum transferred into a flask equipped with a Kontes 4 mm Teflon valve, and stored at -30°C before use.

For the polymer work up: 2,6-Di-*tert*-butyl-4-methylphenol (BHT) and ethyl vinylether were obtained from Aldrich; CH_2Cl_2 and methanol were obtained from EM Science and used as received.

The Synthesis of $(PS\text{-}PPh_2)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$, PS-1. In the drybox, complex **1** (200 mg, 0.225 mmol) and $PS\text{-}PPh_2$ resin (250 mg, Fluka cat # 93093, 2% crosslinked PS/DVB, 200-400 mesh, 3 mmol P/g of resin) were weighed into a 50 mL Schlenk flask equipped with a magnetic stirbar. CH_2Cl_2 (25mL) was then added and the mixture was allowed to stir at room temperature for 40 h during which time the amber beads turned deep green. The supernatant was filtered away and the remaining beads were washed with benzene (3 x 25mL x 30 min stirring during each wash) and CH_2Cl_2 (3 x 25mL x 30 min of stirring during each wash). The remaining resin beads were then dried under vacuum overnight.

^{31}P NMR (benzene-swollen sample of the catalyst): δ - 5 (br, residual PS-PPh_2), 30 (br, **PS-1**). ^{31}P NMR (C_6D_6 solution of $(PPh_3)_2Cl_2Ru$=CH-CH=CPh_2): δ 28.2 (s).

^{31}P NMR (benzene-swollen sample of PS-PPh_2 resin): δ - 8.4 (br, Fluka PS-PPh_2 *resin).* ^{31}*P NMR (C_6D_6 solution of PPh_3): δ - 5.4 (s).*

The combined filtrate was dried *in vacuo* to a greenish white powder mixture (100 mg) and analyzed by ^{31}P NMR to show a composition of 4:1 :: PPh_3 : complex **1** which corresponded to a total of 54 mg PPh_3 released and 46 mg of **1** remained. Based on this result, an estimated catalyst loading of 0.57 mmol [Ru]/g of resin was calculated.

The Synthesis of (PS-*p*-PCy_2) Resin. In the drybox, PS-Li freshly prepared from PS-Br (2g, 2% crosslinked PS/DVB, 25-60 mesh, 1 mequiv Br/g of resin) was suspended in THF (25 mL) in a 100 mL Schlenk flask equipped with a magnetic stirbar. $ClPCy_2$ (470 mg, 1.01 equiv) was then added dropwise to the reaction mixture over five minutes during which time the deep red color of the resin faded. The mixture was allowed to stirred at room temperature for 1 h more. The supernatant was filtered away and the beads were washed with THF (3 x 20 mL x 30 min of stirring during each wash). The remaining light amber-orange resin beads were then dried under vacuum overnight.

^{31}P NMR (benzene-swollen sample of PS-*p*-PCy_2 resin): δ 0.7 (br). ^{31}P NMR (C_6D_6 solution of $PPhCy_2$): δ 2.5 (s).

The Synthesis of (PS-*p*-PCy_2)$_2$$Cl_2$Ru=CH-CH=$CPh_2$, PS-3. In the drybox, the PS-*p*-PCy_2 resin prepared above (1.5 g) was swollen for 30 min in benzene (20 mL) in a 50 mL Schlenk flask equipped with a magnetic stirbar . A solution of complex **1** (650 mg, 0.731 mmol) in CH_2Cl_2 (10 mL) was then added and the mixture was allowed to stir at room temperature for 40 h during which time the beads turned deep red and the green solution became much lighter in color. The supernatant was filtered away and the remaining beads were washed with benzene (3 x 25mL x 30 min stirring during each wash) and CH_2Cl_2 (3 x 25mL x 30 min stirring during each wash). The remaining beads were then dried under vacuum overnight.

^{31}P NMR (benzene-swollen sample of the catalyst): δ - 0.4 (br, residual PS-*p*-PCy_2), 41.7 (br, **PS-3**). ^{31}P NMR (C_6D_6 solution of $(PPh_3)_2Cl_2Ru=CH\text{-}CH=CPh_2$): δ 44.8 (s).

The combined filtrate was dried under vacuo to a greenish white powder mixture (450 mg) and analyzed by ^{31}P NMR to show a composition of 1:1 :: PPh_3 : complex **1** which corresponds with a total of 167 mg PPh_3 released and 283 mg of **1** remained. Based on this result, an estimated catalyst loading of 0.22 mmol [Ru]/g of resin was calculated.

The Synthesis of (PS-*p*-CH_2PCy_2) Resin. In the drybox, the PS-*p*-CH_2Cl resin (1 g, Polyscience cat #09011, 2% crosslinked PS/DVB, 200-400 mesh, 0.43 mequiv Cl/g of resin) was slurried in THF (20 mL) in a 50 mL Schlenk flask equipped with a magnetic stirbar . $LiPCy_2$ (89 mg, 1.01 equiv) was then added as a solid followed by TMEDA (1 mL). The reaction mixture was then taken out of the drybox, attached to a reflux condenser and refluxed for 40 h. The supernatant was filtered away and the beads were washed with THF (3 x 20 mL x 30 min of stirring during each wash). The remaining pale yellow resin beads were then dried under vacuum overnight.

^{31}P NMR (benzene-swollen sample of *PS-p-*CH_2PCy_2 resin): δ 0.7 (br). ^{31}P NMR (C_6D_6 solution of $PPhCy_2$): δ 2.5 (s).

The Synthesis of (PS-*p*-$CH_2PCy_2)_2Cl_2Ru=CH\text{-}CH=CPh_2$, PS-4. In the drybox, the PS-*p*-CH_2PCy_2 resin prepared above (1 g) was swollen for 30 min in benzene (20 mL) in a 50 mL Schlenk flask equipped with a magnetic stirbar . A solution of complex **1** (160 mg, 0.18 mmol) in CH_2Cl_2 (5 mL) was then added and the mixture was allowed to stir at room temperature for 40 h during which time the beads turned dark orange yellow and the green solution became much lighter in color. The supernatant was filtered away and the remaining beads were washed with benzene (3 x 25mL x 30 min stirring during each wash) and CH_2Cl_2 (3 x 25mL x 30 min stirring during each wash). The remaining beads were then dried under vacuum overnight.

^{31}P NMR (benzene-swollen sample of the catalyst): δ 33.2 (br, **PS-4**).

The combined filtrate was dried under vacuo to a greenish white powder mixture (110 mg) and analyzed by ^{31}P NMR to show a composition of 1:1 :: PPh_3 : complex **1** which corresponds with a total of 41 mg PPh_3 released and 69 mg of **1** remained. Based on this result, an estimated catalyst loading of 0.1 mmol [Ru]/g of resin was calculated.

Monitoring the Acyclic Olefin Metathesis Activities of PS/DVB- supported Catalysts. In a typical experiment, the resin **PS-3** and **PS-4** (5 x 10^{-3} mmol of Ru) were weighed into a Teflon-lined screwcap 5 mm NMR tube inside the drybox. C_6D_6 (0.6 mL) was then added follwed by *cis*-2-pentene (42 mg, 100 equiv). The tube was then sealed, taken out of the box, and attached to a rotor to ensure complete mixing. The reaction content was then monitored periodically by ^1H NMR.

Experiments on the Recycling and Reuse of Catalyst PS-4. After the content of a *cis*-2-pentene metathesis reaction has reached equilibrium, the NMR tube wass taken back into the drybox. The liquid phase was drained off using a glass wool-packed pipet and the reamaining beads were washed with C_6D_6 (2 x 0.6 mL). A fresh sample of C_6D_6 (0.6 mL) was then added followed by another aliquot of *cis*-2-pentene (42 mg, 100 equiv). The tube was again sealed, taken out of the box, and attached to a rotor to ensure complete mixing. The reaction content was then monitored periodically by ^1H NMR.

Polymerization of Norbornene Catalyzed by PS-1. In a typical experiment, the resin **PS-1** (0.005 mmol) was swollen in C_6H_6 (0.5 mL) in a 10 mL vial equipped with a magnetic stirbar inside the drybox. Norbornene (70.62 mg, 150 equiv) in C_6H_6 (2.5 mL) was next added to the catalyst mixture. The vial was capped and allowed to stirred for 5 h inside the drybox during which time the mixture became viscous.

Work Up: The reaction vial was taken out of the drybox and to it was added a solution consisting of: CH_2Cl_2 (2 mL), ethyl vinylether (0.1 mL), and BHT (10 mg). This mixture was then allowed to stirred at RT for 2 h.. This solution was then removed using a glass wool-packed pipet and precipitated into a vigorously stirred methanol solution (40 mL, containing 0.1% BHT). The resulting polymer was then washed with methanol (5 mL, containing 0.1% BHT) and dried under vacuum overnight. Yield = 61 mg (87.8%) of a white solid. GPC (*vs* polystyrene standard) : M_W = 98.9 K, PDI = 5.5.

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Chapter 8

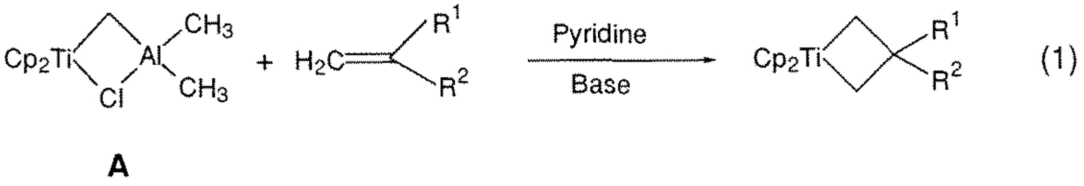
Epilogue

Introduction

This chapter is a collection of my personal impressions about the advances made in the area of well-defined olefin metathesis catalysts during the last decade. By pure *coincident, during the last five years I was fortunate enough to have the chance to* synthesize and work with most of the more popular well-defined metathesis catalysts ranging from the Grubbs-Tebbe reagent to all the Schrock alkylidenes based on tungsten, molybdenum, and rhenium to the recent Grubbs ruthenium vinylcarbene catalysts. This experience has given me a "hand-on" appreciation for the subtle differences between these different classes of catalysts that could not be learned from reading the scientific journals. The present thesis marks the end of my graduate career and since it is highly probable that I will not continue to do research in metathesis chemistry, I wish to leave here some personal notes about these well-defined catalysts. This chapter is also a semi-historical account of ruthenium-based metathesis research in the Grubbs group over the last several years. Events will be recounted as I remember them, some events will be described more vividly than others and I will attach more importance to certain facts than others. As such this chapter will not be free of personal bias, perhaps correctly describing the way I look at transition metal chemistry and catalysis over the years.

Discussion

Titanium. Perhaps the most famous of all the titanium alkylidene/metallacycles is the Tebbe-Grubbs reagent, **A**, from which a variety of Grubbs titanacycles can be generated (eq 1).[1]



Complex **A** is very sensitive to moisture and air. However, due to the high oxophilicity of the metal center and the high nucleophilicity of the methylene carbon it is a very useful synthetic reagent in Wittig-type reactions with organic carbonyls.[1] Since its discovery, the Tebbe-Grubbs reagent has become a standard tool in carbonyl olefination chemistry and a good complement to phosphorous ylid chemistry. Within the polymer community, **A** is important because the first well-defined living ring-opening metathesis polymerization (ROMP) catalyst was derived from it and norbornene.[2,3] From this discovery, a significant amount of fundamental information about the ROMP process and many novel applications of ROMP using titanium had been reported.[4] However, applications of **A** in catalytic metathesis of unstrained acyclic olefins remains limited.

Tungsten, Molybdenum and Rhenium. The catalysts based on tungsten, molybdenum, and rhenium developed by Schrock and coworkers (Figure 1)[5-11]still hold the records on olefins metathesis activity.[a] These oxophilic, highly unsaturated catalysts had been optimized

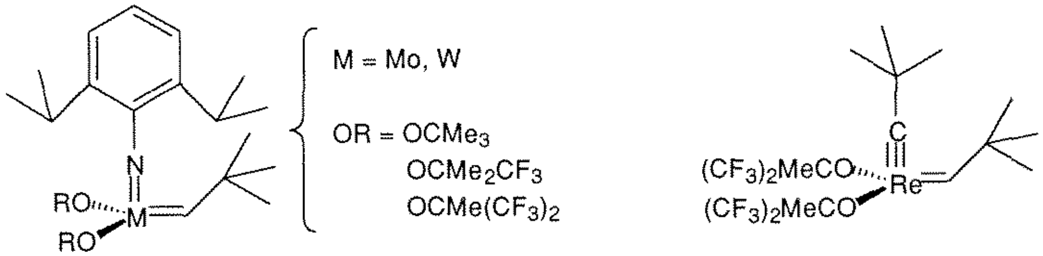


Figure 1. Schrock's molybdenum, tungsten, and rhenium catalysts.[5-11]

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[a] Although the metathesis rate is highly subjective to the carbene substituents, the concentrations of the olefin and the catalyst, and the solvent, some estimates can be placed on the lower limit of this rate. The lower limit of the *cis*-2-pentene metathesis rate for (NAr)((CF$_3$)$_2$MeCO)$_2$W=CH^{t}Bu is estimated to be 103 turn-overs/min; see:

and refined thoroughly to the point that it probably will be very difficult to improve their activity any further. The common basic structure of these catalysts is a picture of beauty in design with only the minimum number of ligands and with all the necessary steric crowding to protect the highly active metal center. Catalyst activity tuning is accomplished by adjusting the number of fluorine atoms on the alkoxide ligands. Yet it is this rigorous optimization for high activity that makes these catalysts difficult to handle and difficult to make. The use of fluorinated alkoxides is also not very convenient because their alcohol precursors are expensive, highly toxic, and difficult to handle. Since there have been numerous reviews on the chemistry of these catalysts,[12-16] I only recount here the story behind my exposure to these catalysts.

During the summer of 1990 I was working at Dupont before entering graduate school in the fall at Caltech. The project I was involved in required me to synthesize all of the Schrock catalysts from tungsten to molybdenum and rhenium. Beginning from the most basic starting materials, it took on average about three weeks to make each type of catalyst in all the possible derivatives (*tert*-butoxide, trifluoro-*tert*-butoxide, and hexafluoro-*tert*-butoxide). The learning curve was rather steep at the beginning but I eventually learned how to make these catalysts efficiently. The potentially most disappointing step is invariably the final recrystallization so one had to work with as large an amount of material as possible to obtain good yield. Also, it is critical to rigorously purify the starting materials at each step because impurities tend to decrease the yield of the reaction. I found out that the Schrock tungsten catalysts, while crystalline, are the most sensitive to handle. The rhenium catalysts are the most tolerant but have to be

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Schaverian, C. J.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2771-2773. That for the analogous molybdenum catalyst is 250 turn-overs/min; see reference 66. For $(CF_3)_2MeCO)_2(^tBuC)Re{=}CH^tBu$, that rate is 250 turn-overs/h; see: Toreki, R., Ph. D. Thesis, Massachusetts Institute of Technology, 1992, p 191.

handled in solution which is not very convenient. The molybdenum catalysts have just the right combination of crystallinity and tolerance that makes them the best materials to work with. Still, the synthetic routes to these catalysts are fairly lengthy because they invariably involve α-hydrogen abstraction and anionic ligand substitution as two main steps.[b]

Although my summer project did not work out too well due to the intrinsic oxophilicity and functional group intolerance of the Schrock catalysts, we realized then that it would be wonderful to have a metathesis catalyst which can be made easily, do not reacts with Lewis bases, and can tolerate a variety of functional groups. The problem of long synthetic sequence for the tungsten catalysts was solved that year by Johnson and Grubbs *with ylid transfer chemistry*[17,18] *and again two years later by cyclopropene* methodology (*vide infra*).[19,20]

The summer of 1990 ended and I went to Caltech for graduate school. At this time, the Novak-Grubbs aqueous ROMP chemistry and its clever application in polymer synthesis was almost two years old.[21] Although it was known that ruthenium-based metathesis catalysts can tolerate a wide variety of protic species,[22] the Novak-Grubbs papers[21,23] had rekindled within the olefin metathesis community the dormant interests in late transition metal metathesis chemistry .

Ruthenium, the First Steps. I came to Caltech, wanted to move away from organometallic chemistry and intended to work on the polyacetylene chemistry with Bob and Nate. However, by the time I arrived, a postdoc already beat me to the polyacetylene

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[b] Indeed, a well-known metathesis chemist have written the following words as a testimony to the long synthetic sequence and the high sensitivities of these well-defined early transition metal catalysts: "There is a penalty to be paid for the intending participant in this activity in as much as the synthesis and use of these newer catalysts places experimental skill at a premium". See: Feast, W. J. In *Comprehensive Polymer Science*; Allen, G; Bevington, J. C., Eds.; Pergamon Press: New York, 1989; Vol. 4, Chapter 7, pp 135-142.

project. For a while, I worked mostly with Nate on semiconductor surface chemistry while developing polystyrene resin immobilized versions of Schrock type catalysts on the side. After a year and several projects later, I finally concluded that a change of directions was needed. Bob agreed to let me work on the ruthenium chemistry and with Lynda Johnson's help, the work described in this thesis took shape in a month.

In retrospect, it is obvious that the chemistry discussed in the earlier parts of this thesis was bound to be discovered sooner or later by the Grubbs group since the stage was already set up by the time I begin the research. At that time, Lynda and Bob had already developed a general method for the synthesis of W(VI) vinylalkylidene complexes of the form $(ArN)L_2Cl_2W{=}CH{-}CH{=}CPh_2$, (L = phosphine or phosphite) by the addition of a 3,3-disubstituted cyclopropene[c] to the corresponding reduced W(IV) precursors.[19,20] In certain cases, they also observed the formation of isolable W(IV)-olefin complexes as an initial product from the reaction of the W(IV) precursors, $(ArN)WCl_2L_3$, with the cyclopropene. These olefin complexes can then be induced to rearrange to the W(VI) vinylalkylidene by a number of methods.[19,20]

After the initial Novak-Grubbs discovery,[21,23] the Grubbs group had been actively pursuing Ru(II) complexes as olefin metathesis catalysts for quite sometimes.[24-27] From this research, it was found that the coordinatively very labile Werner's complex $Ru(H_2O)_6(Tos)_2$ is one of the best initiators. It was then determined that the active ruthenium carbene catalysts in this systems are generated from the reaction of the metal precursors with the olefin substrates (eq 2).[28-30] However, no carbene intermediates have been observed in these systems.

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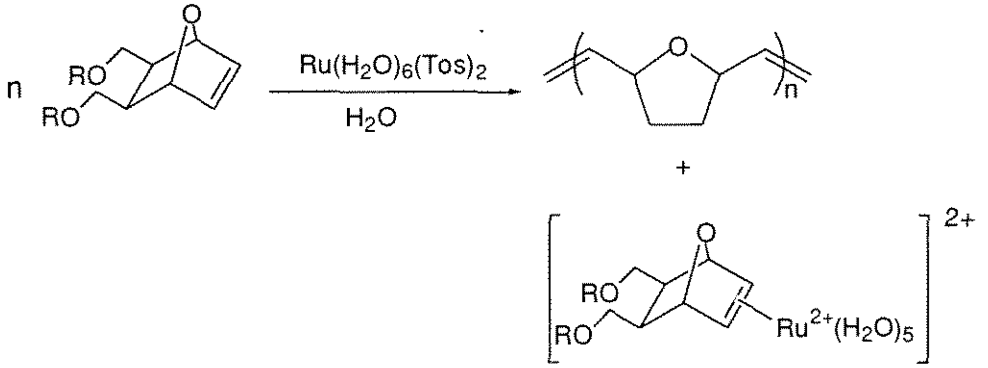
[c] The ring-opening rearrangement of a 3,3-disubstituted cyclopropene to give a metallavinylcarbene was first demonstrated by Binger for Ti(II) and Zr(II) metallocene phosphine complexes. see: Binger, P.; Muller, P.; Benn, R.; Mynott, R. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 610-611.



(2)

With expertise in both cyclopropene and ruthenium chemistry in the Grubbs group, it is highly suggestive that the reaction of a Ru(II) precursor with a cyclopropene may produce a Ru-olefin or Ru-carbene complex. When I first began the ruthenium project, Lynda suggested to me that in analogy to W(IV), perhaps a Ru(II) phosphine precursor will react with 3,3-disubstituted cyclopropene to generate an olefin complex which can be used as an intermediate toward a stable metallavinylcarbene.[d] I followed this suggestion and what happened is a example of "being at the right place at the right time". Shortly after the cyclopropene experiments turned out to be successful with $RuCl_2(PPh_3)_2$ (eq 3), the ylid-transfer chemistry worked successfully on this same precursor (eq 4). We found out that the analogous Os(II) starting material also yielded an osmium vinylcarbene when reacted with cyclopropenes but the reaction was not very clean so we decided to concentrate all of our efforts on Ru(II).

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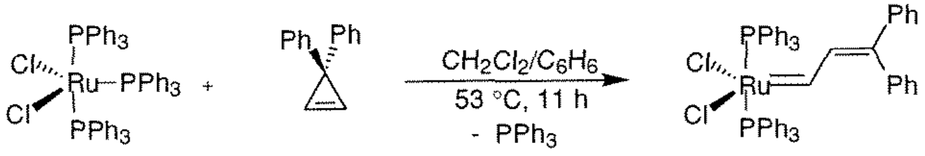
[d] I was told later that such a reaction was tried between 3,3-diphenylcyclopropene and $Ru(H_2O)_6(Tos)_2$ with no success. The moral here, in my opinion, is that sometimes it may be advantageous to step back and look at the problem from a different angle. Although it is true that $Ru(H_2O)_6(Tos)_2$ is the most active aqueous ROMP initiator, its very lability makes it a difficult target for synthetic studies. The $RuCl_2(PPh_3)_3$ precursor that we finally used has just the correct electronic saturation and ligand lability to make it a perfect carbene forming center.



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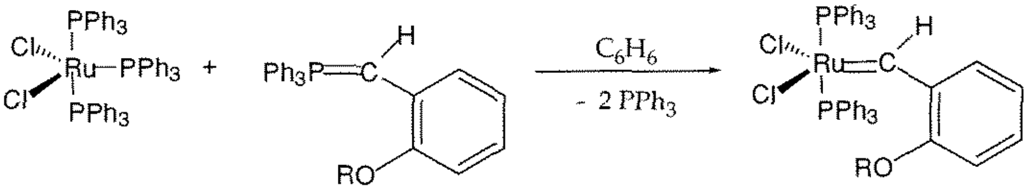

(4)

R = Me, Ph

In the six months following that initial discovery, it was an exciting time for me with many key experiments to do and ideas to explore. We were delighted to find out about the incredible stability and functional group tolerance of our first catalyst. We were even happier when the initial metathesis test showed a positive results.[31] Eventually however, things began to slow down because our $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ catalyst can only ROMP highly-strained olefins despite our rigorous efforts to modify its activity. We tried several olefins, many different electron-withdrawing anions and ancillary ligands with only limited success. The results are encouraging enough, however, that I kept working on this premise for another six months. During this period, we were influenced by the success-proven principle in early transition metal metathesis chemistry: the more electron-withdrawing the ligands are, the higher the metathesis activities.[12-14]

It took a leap of faith to make the next breakthrough. Frustrated by our unsuccessful attempts to modify the metathesis activity of the parent ruthenium vinylcarbene, I decided to ignore my early experience with the Schrock catalysts and tried the exact reverse. This was one crazy experiment that worked. I replaced the PPh_3 ligands of $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ with PCy_3, the most electron-donating phosphine that I could find in our stockroom. The resulting compound,

$(PCy_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$, was found to catalyze the metathesis of *cis*-2-pentene on September 28, 1992, almost one year since the initial observation of $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$.[e] It is obvious now why this is the case but at the beginning, we had very little to guide us on.

Ruthenium, the Applications. Having the ability to do acyclic metathesis with ruthenium, Bob suggested that we move quickly into ring closing metathesis (RCM) chemistry. At that time, Greg Fu had had considerable successes with RCM chemistry using the Schrock molybdenum catalysts[32-34] and thus had on hand several substrates to test the activity of the new ruthenium complex. After the initial positive results, we worked hard to produce several examples of cases where ruthenium catalyst is either better or comparable to molybdenum. The two communications on phosphine exchanges and RCM appeared together in print in July 1992.[35,36]

The application research using ruthenium-based RCM chemistry in the Grubbs group started to pick up. Greg and Ned Bowden worked on serial ene-yne-ene tandem cyclization and Konstantinous Litinas cyclized different types of lactones. Marc Hillmyer began to use ruthenium for telechelic polymer synthesis and ROMP of functionalized cyclooctenes. These large scale applications increased the demand for $(PCy_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$. To meet this need we developed the one-pot synthesis. Other applications such as fatty acid metathesis, Diolefin Metathesis Polymerization (DOMP), polyolefin depolymerization soon followed. In 1993, we developed the first water-soluble catalyst and several polystyrene resin-supported catalysts.

Applications in organic synthesis and polymer chemistry continued to expands within the Grubbs group. Parallel ene-yne-ene tandem cyclization to make fused bicyclic was completed in 1994.[37] The year 1995 saw the synthesis of eight-membered rings[38] and macrocyclization to cyclic peptides.[39] ROMP of functionalized cyclobutenes[40] and

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[e] The first observation of $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ was made on October 8, 1991.

polymerizations in biphasic media have also been carried out successfully.

It is perhaps the dream of every chemist to see his/her chemistry become useful to someone else. In the case of the Grubbs ruthenium catalyst, we are fortunate to see applications evolving quickly not only within but also without our group. For example Hoveyda and coworkers used the $(PCy_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ catalyst in a kinetic resolution of pyrans.[41] Pandit used the same catalyst to construct the macrocyclic ring D of Manzamine A.[42] Huwe and Blechert applied ruthenium-based RCM to construct aza-sugars.[43] Kinoshita and Mori used ruthenium catalyst in enyne cyclization.[44] These are just a few of published works. There are several other yet-to-be-published successes that we are aware of. We hope that given the ease of synthesis and handling of the well-defined ruthenium carbenes eventually they will become a regular tool in organic synthesis and polymer chemistry.

Metathesis Chemistry and the Transition Metals. I should note here that although the well-defined early transition metal catalysts are difficult to handle, they are important miles stones in olefin metathesis chemistry because it was with these compounds that we learned a great deal about the fundamental nature of carbenes and metallacycles in olefin metathesis.[4,12-14] Also, the first living ROMP reactions[2,3,6] and the first catalytic RCM experiments[32-34] were carried out with well-defined early transition metal catalysts.

Although the ruthenium carbene metathesis catalysts are the most functional group tolerant of all known, well-defined metathesis catalysts to date, they are not always the best catalysts for everything. For example, they do not catalyzed very well the ROMP of cyclooctatetraene to polyacetylene[45] which proceed very well with the tungsten catalysts.[46] In macrocyclic ring construction, sometimes ruthenium does not work as well as molybdenum.[47] Certainly, ruthenium(II) catalysts are not oxophilic enough to transfer carbene to organics carbonyls in the same manner as that of the Tebbe-Grubbs reagent[1] and the Schrock catalysts.[48]

Thus, the ruthenium catalyst should be thought of as being complement to and not as superseding the early transition metal catalysts in the arsenal of metathesis-based synthetic reagents . Each of the catalysts in Figure 2 has its own particular usefulness and is best at its own applications. It would be appropriate here to compare the reactivities of the well-defined titanium, tungsten, molybdenum, and ruthenium olefin metathesis catalysts. Figure 3 illustrates the reactivity profiles of these catalysts towards olefins and the organic carbonyls . Going from left to right on the periodic table, we have increased the preference of the metathesis catalysts toward olefins over the organic carbonyls. At ruthenium, the exclusive preference is for the carbon-carbon double bonds over the carbon-oxygen bonds and the protic species.

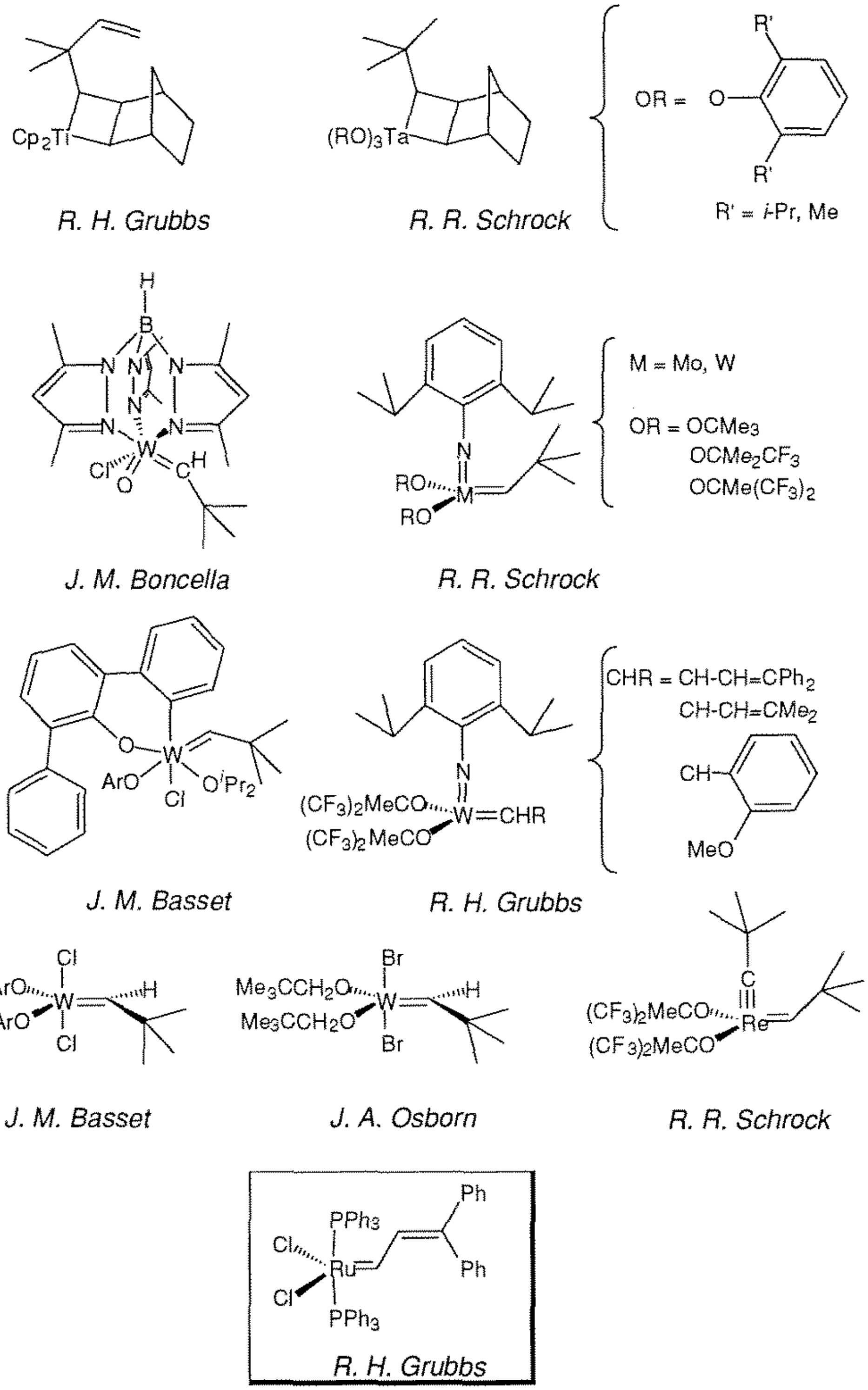
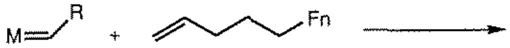


Figure 2. Representative examples of Groups IV-VIII metallacyclobutane and alkylidene olefin metathesis catalysts.[2,5-11,31,49-58] Reprint with modification from reference 19.



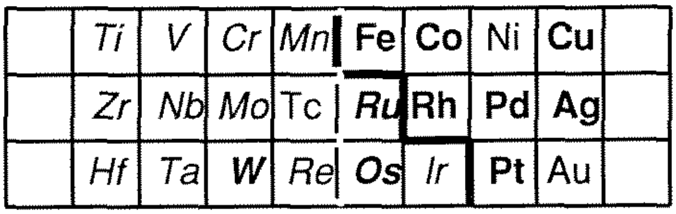
Titanium	Tungsten	Molybdenum	Ruthenium	
Aldehydes	Aldehydes	Aldehydes	Olefins	Higher reactivity
Ketones	Ketones	Olefins	Aldehydes	
Esters, Amides	Olefins	Ketones	Ketones	
Olefins	Esters, Amides	Esters, Amides	Esters, Amides	
			Acids, Amines	Lower reactivity
			Alcohols, Water	

Figure 3. Relative reactivities of well-defined Ti, W, Mo and Ru olefin metathesis catalysts toward an olefin containing a carbonyl functionality.

Late vs. Early in Transition Metal Chemistry. With ruthenium, we have completed the quest for well-defined olefin metathesis catalysts across most of the transition metals and it is interesting to reflect upon the progress of transition metal chemistry in this respect. In addition to olefin oxidation which is known for all metals,[59] two notable examples come to my mind where the development of well-defined catalysts have also made a complete traverse through the transition metals. 1) Ziegler-Natta olefin polymerization. Similar to metathesis, the development of well-defined Ziegler-Natta catalysts began with group IV metals[60-64] (and the lanthanides[65,66]) in the late 1970's and then moved across toward Co,[67,68] Ni,[69-71] and recently Pd.[72] 2) Asymmetric hydrogenation. Here, the progress is reverse—the initial literature started with Co, Rh, and Ru of group VIII[73-76] and moved toward the left to Ti of group IV in recent years.[77-79] Together with the recent developments in olefin metathesis, these trends suggest an interesting hypothesis: *a transition metal center can catalyze almost any of the known* *catalytic processes, provided that is at the right oxidation state and possess a ligand environment that is conductive to that particular catalytic process.* In other words, the classification of early and late transition metals begin to lose meanings when one consider general catalytic activities. This is a very sweeping statement that perhaps only time can verify.

Moving Forward in Metathesis Chemistry. Like Ziegler-Natta chemistry, research in olefin metathesis is driven by applications. This, in my opinion, is where a big part of future developments in metathesis will be. The creativity of Bob and the Grubbs group have shone through again and again through the ROMP and RCM chemistry. What lies ahead in the future is a very exciting time of discovery. For example, the synthesis of bioactive molecules/polymers by taking advantage of the functional group tolerance of the ruthenium catalyst should be possible. Natural products, specialty polymers, well-defined functionalized polymers and block copolymers, etc... by olefin metathesis are just some of the exciting applications waiting to be realized. One can even think about making libraries of bioactive block copolymers using resin-supported catalysts, much in the same manner that Merrifield resins are used for peptides synthesis.[80]

Fundamentally, much still remains to be discovered in the area of late transition metal metathesis catalysts. One can move further to the right hand side of the periodic table and address the issue of metathesis vs. cyclopropanation. The question why do the metals directly above and to the right hand of Ru tend to catalyze cyclopropanation rather than metathesis (Figure 4) is one of fundamental interests to carbene chemists. Furthermore, can changing ligand environments leads to a cross-over in reactivity profile for one metal? Closer to home is the continuing modification of the parent $(PCy_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$. Finding new and improved ways to make carbenes , modifying ligands environments, and accessing other oxidation states of the ruthenium center by redox modifications should further improve the existing catalysts.



	Ti	*V*	*Cr*	*Mn*	**Fe**	**Co**	Ni	**Cu**	
	Zr	*Nb*	*Mo*	Tc	***Ru***	**Rh**	**Pd**	**Ag**	
	Hf	*Ta*	***W***	*Re*	***Os***	*Ir*	**Pt**	Au	

Figure 4. A section of the periodic table. An italicized symbol denote an element that is known to catalyze olefin metathesis. A bold-faced symbol denote an element that is known to catalyze olefin cyclopropanation. An italicized bold-faced symbol denote an element that is known to catalyze both olefin metathesis and olefin cyclopropanation. The zigzag bold-faced line denotes an artificial separations between the two reactivity profiles.

As I am writing these final words, all of the ideas mentioned above are being actively pursued by members of the Grubbs group. I am looking forward to read about their results in the near future.

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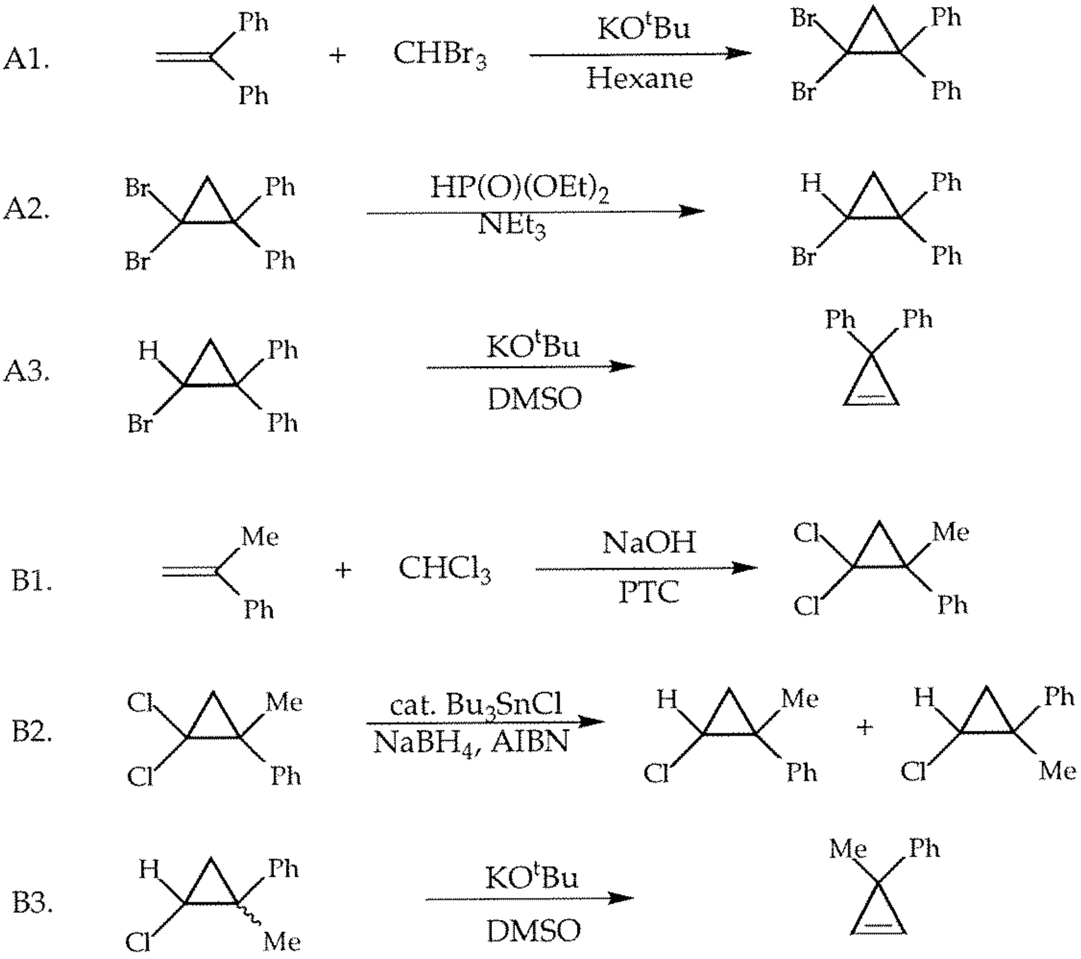
Appendix 1

The Syntheses of 3,3-Diphenylcyclopropene and 3-Methyl-3-phenylcyclopropene

Note: This appendix is a paper to be submitted to *Organic Synthesis*. The format presented here is that required by the Organic Synthesis Board of Editors.



Submitted by SonBinh T. Nguyen,[1] Bob R. Maughon,[1] Jeffrey S. Moore,[2] and Robert H. Grubbs.[1]

Checked by ____________________________

1. Procedure

A1. 1,1-Dibromo-2,2-diphenylcyclopropane. In a nitrogen-filled glovebag, Potassium *tert*-butoxide (KO^{t}Bu) (56 g, 499 mmol, 1.24 equiv) (Note 1) is weighed into a 1000 mL three-neck flask equipped with a magnetic stirbar. An inlet gas adapter and a 100 mL addition funnel capped with a rubber septa are then attached to two necks of the flask and a rubber septa is put on the remaining neck. The assembly is then sealed and taken out of the glove bag. To the flask is added hexane (600 mL) (Note 2) via cannula through the rubber septa. The suspension is stirred and cooled down to -10°C. Next, the 1,1-diphenylethylene (72.6 g, 402.8 mmol, 1 equiv) (Note 3) is added to the addition funnel under argon and then added dropwise from the addition funnel to the stirring reaction mixture over a period of 10 min. Hexane (25 mL) (Note 2) is used to rinse the addition funnel down into the reaction mixture. A 1:1 solution of $CHBr_3$ (104.86 g, 36.23 mL, 1.03 equiv) (Note 4) in hexane (Note 2) is added to the dropping funnel and then added dropwise from the addition funnel to the stirring reaction mixture over a period of 4 h. After this addition, the reaction mixture is warmed up slowly to room temperature (with stirring) over the next 2 h and then stirred at room temperature under argon for another 8 h. Next, the content of the reaction is poured into a 2000 mL separatory funnel. To this mixture is added deionized water (400 mL) (Note 5) and CH_2Cl_2 (600 mL) (Note 6). The funnel is shaken vigorously and the CH_2Cl_2 layer is collected in a 2000 mL Erlenmeyer flask. The aqueous layer is then extracted with CH_2Cl_2 (3 x 200 mL) (Note 6). All the CH_2Cl_2 extracts are combined and dried over anhydrous Na_2SO_4 (Note 7). This mixture is then filtered over a medium fritted funnel and the filtrate is concentrated to dryness on a rotovap. The yellow solid collected is then loaded onto a medium fritted funnel and washed successively with cold hexane (-10°C, 2 x 50 mL) (Note 6), cold 5% ethyl acetate/Hexane (-10°C, 50 mL) (Note 6), and cold hexane (-10°C, 2 x 50 mL) (Note 6). The resulting off-white solid is then dried under vacuum for 10 h (Note 8). Yield = 125.1 g (88.22 %). This material is sufficiently pure for the next step but alternatively, it can be further purified by recrystalization in hexane at -40 °C.

A2. 1-Bromo-2,2-diphenylcyclopropane. Into a 500 mL, two-neck flask equipped with a magnetic stirbar is added 1,1-dibromo-2,2-diphenylcyclopropane (42 g, 119.3 mmol, 1 equiv). A reflux condenser capped with an inlet gas adapter is attached to one neck of the flask and the other neck is capped with a rubber septa. The whole assembly is then evacuated and backfilled with nitrogen twice. Under a nitrogen atmosphere is successively added triethylamine (NEt_3) (36.21 g, 49.88 mL, 3 equiv) (Note 9) and diethylphosphite (45.31 g, 42.26 mL, 2.75 equiv) (Note 10) via a gastight syringe through the rubber septa. The reaction mixture is then heated at 90°C in an oil bath under argon while stirring vigorously for 10 h. At this point, an aliquot is taken for TLC analysis to make sure that all of the starting material has been consumed. The reaction is then taken off the oil bath and let cooled to RT. Next, diethyl ether (Et_2O) (150 mL) (Note 6) is added to the reaction mixture to precipitate out the tetraethylammonium bromide. The mixture is filtered through a medium fritted funnel and the solid salt is washed with Et_2O (2 x 50 mL) (Note 6). The combine filtrate and washes are then concentrated on a rotovap until all the ether is boiled off. The resulting yellow oil is then further dried on a vacuum line with stirring to remove all remaining NEt_3 (Note 11). This mixture is then carefully precipitated into 3000 mL of vigorously stirring deionized water (Note 5) in an Erlenmeyer flask to give an off-white precipitate which is collected over a medium fritted funnel. (An optional cold methanol wash of the precipitate will remove most of the yellowish color in the solid product.) This solid is then dried under vacuum overnight (Note 12). Yield = 25.16 g (77.2 %).

A3. 3,3-Diphenylcyclopropene. Into a 500 mL three-neck flask equipped with a magnetic stirbar is added 1-bromo-2,2-diphenylcyclopropane (27.6 g, 101 mmol, 1 equiv). A 100 mL addition funnel capped with a rubber septa is attached to one neck, a gas inlet adapter is attached to another neck and the remaining neck is capped with a rubber septa. The whole assembly is then evacuated and backfilled with argon twice. Under an argon atmosphere dimethyl sulfoxide (DMSO) (300 mL) (Note 13) is added to the cyclopropane via cannula and the solution is stirred vigorously in a room temperature bath until all the solid dissolve.

Potassium *tert*-butoxide (11.9g, 1.05 equiv) (Note 1) is weighed inside a drybox into a 100 mL Schlenk flask. The flask is then capped, taken out of the drybox, and dissolved in DMSO (80 mL) (Note 13) (with heating if necessary) under argon. This solution is loaded into the addition funnel via cannula and then slowly added to the stirring cyclopropane solution over a period of 2.3 h during which time the mixture turns to yellow, green, blue, and sometimes black. The addition funnel is then rinsed with DMSO (30 mL) (Note 13) and the rinse is added to the mixture also. The cooling bath is removed and the reaction mixture is stirred at room temperature for another 1 h. The reaction mixture is then poured into a 2000 mL separatory funnel loaded with pure ice (made from 400 mL of deionized or distilled water (Note 5) to give a cloudy yellow mixture upon mixing. To this mixture is then added a 2:1 petroleum ether/ether mixture (800 mL) (Note 6) to extract out the product. The remaining aqueous fraction is then extracted with a 2:1 petroleum ether/ether mixture (2 x 600 mL) (Note 6). The organic extracts are then combined, washed with saturated aqueous NaCl solution, and dried over anhydrous Na_2SO_4 (Note 7). The mixture is then filtered over a medium fritted funnel and then the filtrate is concentrated to a minimum on a rotovap. The resulting oily liquid is then loaded onto a chromatography column (Silica gel, 325 mesh, wet pack with hexane, column dimension = 26 cm length x 4 cm diameter) and eluted with petroleum ether. The elutions are collected in 200 mL fractions and tested with TLC to determine the presence of the product . The product fractions are then combined and concentrated on a rotovap to yield an off-white oily liquid which is stored at -30 °C (Notes 14 and 15). Yield = 19.1 g (98.4 %). (Alternatively, the chromatography step can be avoided by using a Kugelrohr distillation but one need to be careful since the product is heat sensitive.)

B1. 1,1-Dichloro-2-methyl-2-phenylcyclopropane. In a 500 mL Erlenmeyer flask equipped with an 1-inch Teflon-coated magnetic stirbar, α-methylstyrene (30 g, 254 mmol, 1 equiv) (Note 16), chloroform (60.7 g, 40.7 mL, 508 mmol, 2 equiv) (Note 17), 50 % aqueous NaOH solution (102 mL, 1.27 mol, 5 equiv), and cetyltrimethylammonium bromide (3 g, 8.2 mmol, 0.03 equiv) (Note 18) are combined and stirred vigorously for two hours. During this time, the reaction turns from a cloudy white mixture to a brown one and an exotherm occurs. After two hours the flask begins to cool, Et_2O (200 mL) (Note 6) is added and the mixture is stirred slowly for two minutes. The contents of the flask are then poured into a 1000 mL separatory funnel, and the organic layer is collected into a 1000 mL Erlenmeyer flask. The remaining aqueous layer is further extracted with diethyl ether (2 x 200 mL). The combined organics are successively washed with 0.5 M aqueous HCl (150 mL), deionized water (150 mL) (Note 5), and saturated aqueous NaCl (150 mL); dried over anhydrous $MgSO_4$ (Note 7); and filtered through a coarse fritted funnel. The filtrate is then concentrated to a minimum on a rotovap at 55 ^{0}C to give a brown liquid product (Note 19). Yield = 48.5g (95 %). Despite the colored impurities, this material is sufficiently pure to be used in the next step.

B2. 1-Chloro-2-methyl-2phenylcyclopropane. In a 2000 mL round bottom flask equipped with a 1-inch Teflon-coated magnetic stir bar, 1,1-dichloro-2-methyl-2-phenylcyclopropane (30 g,149 mmol, 1.0 equiv), tri-n-butyltin chloride (7.29 g, 22.4 mmol, 0.15 equiv) (Note 20), 2,2'-azobis(2-methylpropionitrile) (2 g, 12.2 mmol, 0.08 equiv) (Note 21), and *n*-propanol (600 mL) (Note 6) are combined and stirred vigorously. Next, sodium borohydride (8.47 g, 224 mmol, 1.5 equiv) (Note 22) is added in portions to the reaction mixture over five minutes. Once the addition is complete, the flask is capped with a water-cooled reflux condenser and placed in a 110 ^{0}C oil bath. The reaction is kept at reflux for 1 h during which time NaCl can be seen falling out of solution. At this point, the flask is removed from the oil bath and oxalic acid (3.0 g, 33.3 mmol, 0.22 equiv) (Note 23) is added in portions over five minutes. The reflux condenser is then replaced with a distillation head, and the flask is lowered back into the oil bath. *n*-propanol is then distilled away from the reaction mixture until the still head temperature drops below 50 ^{0}C. The flask is again removed from the oil bath and allowed to cool to room temperature. Petroleum ether (300 mL) (Note 6) is added and the mixture is transferred to a 1000 mL separatory funnel where the organic layer is washed with deionized water (3 x 200 mL). The organic layer is then dried over $MgSO_4$ (Note 7), filtered over a coarse fritted funnel, and concentrated to a minimum on a rotovap at 50 ^{0}C to give a yellow liquid. This crude material is then further purified by vacuum distillation (49-50 ^{0}C, 2.5 mmHg) to give a clear liquid product. The product isomeric distribution is ca 2:1 :: *cis*-Cl-*cis*-methyl / *cis*-Cl-*cis*-phenyl (Notes 24 and 25). Yield = 22.3 g (90 %). This material is pure enough to use in the next step.

B3. 3-Methyl-3-phenylcyclopropene. In a 500 mL round bottom flask equipped with a 1-inch Teflon-coated magnetic stirbar, 1-chloro-2-methyl-2-phenylcyclopropane (20 g, 120 mmol, 1.0 equiv) is combined with dry DMSO (150 mL) (Note 13). This flask is connected to a 250 mL addition funnel under argon. In a separate 250 mL round bottom flask, potassium *tert*-butoxide (27 g, 241 mmol, 2.0 equiv) (Note 1) is dissolved in dry DMSO (150 mL) (Note 13) under argon (with heating as necessary). This basic solution is then quickly poured into the addition funnel over the first flask and the argon inlet replaced. The reaction flask is then cooled to ca 15-20^{0}C, and the potassium *tert*-butoxide solution is added dropwise over 2 h. During the addition, the color changes to orange, then red, then green, then finally brown. The reaction is left stirring for another 2.5 h at the same temperature. The reaction mixture is then poured into a 2000 mL separatory funnel containing pure ice (300 mL) to give a cloudy yellow mixture upon addition. The aqueous layer is extracted with diethyl ether (3 x 500 mL). The combined organics are then washed successively with saturated aqueous NaCl solution (400 mL) and distilled water (2 x 400 mL), dried over anhydrous Na_2SO_4, and filtered over a coarse fritted funnel. This solution is then concentrated to a minimum on a rotovap. The resulting yellow liquid is then further purified by flash column chromatography (Silica gel, 325 mesh, wet pack w/ petroleum ether, column dimension = 26 cm length x 4 cm diameter) and eluted with petroleum ether. The elutions are collected in 100 mL frations and tested with TLC to determined the presence of the product ($R_f = 0.65$ with petroleum ether as the eluant). The product fractions are combined and concentrated on a rotovap to give a clear liquid (Notes 26 and 27). Yield = 7.02 - 10.14 g (45 - 65 %) (Note 28).

2. Notes

1. Potassium *tert*-butoxide is purchased from the Aldrich Chemical Company, handled under an dry nitrogen atmosphere, and used as received.

2. Hexane is distilled over calcium hydride and degassed with a stream of nitrogen.

3. 1,1-diphenylethylene can either be purchased from the Aldrich Chemical Company, made according to published procedures[3] or synthesized from benzophenone and methyl magnesium bromide at an unoptimized 82% yield.[4] In all cases, it is passed through a plug of activated neutral alumina (activated at 250 °C under vacuum overnight) and degassed with a stream of nitrogen before use.

4. $CHBr_3$ is purchased from the Aldrich Chemical Company, filtered through a plug of activated neutral alumina (activated at 250 °C under vacuum overnight), and then degassed with a stream of nitrogen before use.

5. Deionized water is obtained in-house at Caltech. Distilled water can be used as substitute.

6. CH_2Cl_2, ethyl acetate, petroleum ether, hexane, Et_2O, *n*-propanol used during worked up are reagent-grade solvents obtained from EM Science and used as received.

7. Anhydrous Na_2SO_4 and $MgSO_4$ are obtained from Mallinkrodt and used as received.

8. Spectral data for 1,1-dibromo-2,2-diphenylcyclopropane: ^1H NMR ($CDCl_3$): 2.48(s, 2H, CH_2), 7.22-7.53(3m, 10H, H_{Ar}). ^{13}C NMR ($CDCl_3$): 33.91 (s, CPh_2), 34.5 (s, CH_2), 45.08 (s, CBr_2), 127.29 (s, C_p), 128.40 (s, C_m), 129.18 (s, C_o), 141.88 (s, C_{ipso}).

9. NEt_3 is obtained from Mallinkrodt, distilled over CaH_2, degassed by a three cycle of freeze-pump-thaw and stored under nitrogen before use.

10. Diethylphosphite is obtained from either the Aldrich Chemical Company or Strem Chemicals Company, vacuum-distilled, degassed by a three cycle of freeze-pump-thaw, and stored under nitrogen before use.

11. It is necessary in this step to remove all the remaining NEt_3. If there is too much

NEt_3 left behind, the subsequent precipitation in water will oil out. Occasionally, some of the product may precipitate out of the yellow oil at this point in the work up as the NEt_3 is removed and the flask temperature drops below room temperature. This will not affect the rest of the work up.

12. Spectral data for 1-bromo-2,2-diphenylcyclopropane: ^1H NMR ($CDCl_3$): 1.84 (m, 2H, CH_2), 3.68 (dd, 1H, $CHBr$), 7.31 (m, 10H, H_{Ar}). ^{13}C NMR ($CDCl_3$): 23.84 (s, CH_2), 28.27 (s, CPh_2), 36.24 (s, $CHBr$), 126.6 and 127.05 (2s, C_p), 127.67 and 128.15 (2s, C_m), 128.53 and 130.41 (2s, C_o), 140.63 and 144.10 (s, C_{ipso}).

13. DMSO is obtained from Sigma Chemical Company, dried and distilled over CaH_2, degassed under full vacuum for 30 min while stirring, and stored under nitrogen before use.

14. Spectral data for 3,3-diphenylcyclopropene: ^1H NMR (C_6D_6): 6.90 (s, 2H, $CH{=}CH$), 7.03-7.19 (m, 10H, H_{Ar}). ^{13}C NMR (C_6D_6): 33.64 (s, CPh_2), 113.34 (s, $CH_2{=}CH_2$), 125.96 (s, C_p), 128.33 (s, C_m), 128.50 (s, C_o), 147.49 (s, C_{ipso}).

15. Physical properties: 3,3-Diphenylcyclopropene is an oily, thermally sensitive liquid that should be stored frozen. In our experience, it is stable for several months as a solid at -30°C.

16. α-methylstyrene is obtained from the Aldrich Chemical Company and is used as received.

17. Chloroform is obtained from EM Science and is used as received.

18. Cetyltrimethylammonium bromide is obtained from the Aldrich Chemical Company and is used as received.

19. Spectral data for 1,1-dichloro-2-methyl-2-phenylcyclopropane: ^1H NMR ($CDCl_3$): 1.57 (d, 1H, CH), 1.66 (s, 3H, CH_3), 1.94 (d, 1H, CH), 7.3 (m, 5H, H_{Ar}). ^{13}C NMR ($CDCl_3$): 25.49 (s, CH_3), 31.86 (s, CH_2), 36.40 (s, $CMePh$), 65.89 (s, CCl_2), 127.19 (s, C_p), 128.38 (s, C_m), 128.47 (s, C_o), 141.18 (s, C_{ipso}).

20. Tri-n-butyltin chloride is obtained from the Aldrich Chemical Company and is

used as received.

21. 2,2'-Azobis(2-methylpropionitrile) is obtained from Eastman Laboratory Chemicals and is used as received.

22. Sodium borohydride is obtained from the Aldrich Chemical Company and is used as received.

23. Oxalic acid is obtained from the Aldrich Chemical Company and is used as received.

24. Spectral data for *r*-1-chloro-*cis*-2-methyl-2-phenylcyclopropane (^{1}H spectral assignment is based on that reported by McKinney[5]): ^{1}H NMR ($CDCl_3$): 0.98 (dd, 1H, *H* cis to Me), 1.52 (overlapping dd, 1H, *H* cis to Ph), 1.58 (s, 3H, CH_3), 3.27 (dd, 1H, C*H*Cl). ^{13}C NMR ($CDCl_3$): 21.65 (s, CH_2), 22.94 (s, CH_3), 26.49 (s, *C*MePh), 40.86 (s, *C*HCl), 126.46 (s, C_p), 127.04 (s, C_m), 128.51 (s, C_o), 144.73 (s, C_{ipso}).

25. Spectral data for *r*-1-chloro-*trans*-2-methyl-2-phenylcyclopropane (^{1}H spectral assignment is based on that reported by McKinney[5]): ^{1}H NMR ($CDCl_3$): 1.27 (m, 2H, CH_2), 1.40 (s, 3H, CH_3), 3.14 (dd, 1H, C*H*Cl). ^{13}C NMR ($CDCl_3$): 21.94 (s, CH_2), 26.94 (s, CH_3), 28.11 (s, *C*MePh), 39.02 (s, *C*HCl), 126.73 (s, C_p), 128.16 (s, C_m), 129.49 (s, C_o), 141.19 (s, C_{ipso}).

26. Spectral data for 3-methyl-3-phenylcylopropene: ^{1}H NMR (C_6D_6): 1.57 (s, 3H, CH_3), 6.79 (s, 2H, C*H*=C*H*), 7.16-7.22 (4 m, 5H, H_{Ar}). ^{13}C NMR (C_6D_6): 22.1 (s, *C*MePh), 25.59 (s, CH_3), 115.60 (s, CH_2=CH_2), 125.29 (s, C_m), 126.42 (s, C_o), 127.38 (s, C_p), 149.97 (s, C_{ipso})

27. Physical properties: 3,3-Methylphenylcyclopropene is a thermally sensitive compound which will polymerize overnight at room temerature. Therefore, it should be stored at or below -50^{0}C at which temperature the compound only slowly decomposes during several weeks.

28. The yield is low in this case due to the inefficient elimination of HCl from the *r*-1-chloro-*trans*-2-methyl-2-phenylcyclopropane isomer which remains essentially

unchanged under the reaction conditions. Longer reaction time or higher temperature only leads to low yield from the decomposition of the product. The flash chromatography will effectively remove this unreacted starting material (TLC: $R_f = 0.45$ with hexane as the eluant).

3. Discussion

In recent years 3,3-disubstituted cyclopropenes have emerged as new and promising carbene sources. They are used both as reagents in the syntheses of metal vinylcarbene complexes[6-13] and as synthons in the catalytic generation of vinylcyclopropanes and vinylcyclopropenes.[6,13-15] The metal vinylcarbene complexes are active olefin metathesis catalysts and have found numerous applications in both polymer chemistry[7-12,16] and organic synthesis.[17-21] In addition, vinylcyclopropanes and vinylcyclopropenes are considered to be important intermediates in organic synthesis. These developments have stressed a need for easily accessible routes to 3,3-disubstituted cyclopropenes. 3,3-Diphenylcyclopropene was first isolated in 1969 from the photolysis of 3,3-diphenyl pyrazolenin.[22] Subsequently, the complete syntheses for both 3,3-diphenylcyclopropene and 3-methyl-3-phenylcyclopropene from the *gem*-disubstitued olefins were reported by Bovin and coworkers.[23]. These workers employed the expensive and toxic Bu_3SnH as a stoichiometric reducing agent to convert dihalocyclopropanes to the momocyclopropane intermediates. Our procedures, as reported herein, starts from inexpensive reagents, can be scaled up easily, are safer, simpler, and gives higher yield.

Our syntheses of both 3,3-diphenylcyclopropene and 3-methyl-3-phenylcyclopropene follows essentially the same sequence prescribed by Bovin:[23] (1) Dihalocarbene addition to an olefin to generate a *gem*-dihalocyclopropane. (2) Selective reduction of the *gem*-dihalocyclopropane to mono-halocyclopropane. (3) Base-induced elimination of the mono-halocyclopropane to the final cyclopropene. Despite the similarities in methodology, there are subtle differences in practical chemical manipulations of precursor C_3 rings with *gem*-diphenyl substituents vs those with *gem*-methylphenyl substituents (*vide infra*).

Dihalocarbene addition reaction to olefins to generate *gem*-dihalocyclopropanes is a well-known organic reaction . Procedure A1 follows essentially the Skattebol-modification[24] of the Doering and Hoffmann procedure[25] . Procedure B1 is a take-off from that described by Makosza[26] and illustrate the use of the simple, inexpensive, and high yield phase transfer condition employing NaOH and $CHCl_3$ in water (instead of KO^tBu and $CHBr_3$ in rigourously dried solvent). The phase transfer chemistry in procedure B1 can be extended to 1,1-diphenylethylene and bromoform although we generally observe a lower yield (ca 75 %) and dirtier product which prompted us to select the anhydrous condition of procedure A1 for the synthesis of 1,1-dibromo-2,2-diphenylcyclopropane. However, for very large scale synthesis, it is sometimes more convenience to sacrifice the yield and use the simpler phase transfer condition. Our decision to use bromoform in procedure A1 is determined by the chemistry of step 2 in the synthetic sequence. From an economical consideration, the best dihalocarbene source seems to be chloroform, however 1,1-dibromo-2,2-diphenylcyclopropane has generally given better yield and cleaner product during the selective reduction in step 2.

In step 2, the Bu_3SnH reduction of *gem*-dihalocyclopropanes to mono-halocyclopropanes reported by Bovin gives only moderate yield for both substrates.[23] Our procedure completely avoid the use of the toxic Sn reagent in the synthesis of 1-bromo-2,2-diphenylcyclopropane and reduce the use of Sn to a catalytic amount in the preparation of 1-chloro-2-methyl-2-phenylcyclopropane. It should be noted at this step that the reduction chemistry employed for 1-bromo-2,2-diphenylcyclopropane is not compatible with 1-chloro-2-methyl-2-phenylcyclopropane and vice versa. We tried the radical reduction of procedure B2[27] for 1,1-dibromo-2,2-diphenylcyclopropane with no success. In addition, the curious phoshite reduction in procedure A2 was reported to be difficult for *gem*-dichlorocylopropane substrates.[28,29] Interestingly, although the small-scale phosphite reduction of 1,1-dibromo-2-methyl-2-phenylcyclopropane has been reported to give 91 % yield of the desired product,[28] in our hand the large scale reaction of the same substrate does not go to completion--forcing conditions only leads to over-reduction.

The elimination step with KO^tBu in DMSO works very well for 1-bromo-2,2-

diphenylcyclopropane and gives excellent yield of the desired cyclopropene. In contrast, the yield is fairly low in procedure B3 due to the inefficient elimination of HCl from the *r*-1-chloro-*trans*-2-methyl-2-phenylcyclopropane isomer which remains essentially unchanged under the reported reaction conditions. Longer reaction time or higher temperature only leads to low yield from the decomposition of the product. It is interesting that the two isomers of 1-chloro-2-methyl-2-phenylcyclopropane have such different reactivity toward elimination by base. Perhaps the *trans*-phenyl group does play a role in assisting the elimination step. This observation fits well into the trend in which 1-chloro-2,2-diphenylcyclopropane eliminates easily at room temperature[30] and 1-chloro-2,2-dimethylcyclopropane eliminates at 90 °C over several hours.[31]

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Appendix 2

The X-Ray Diffraction Experiment for $(PPh_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$

X-Ray Diffraction Data for $C_{51}H_{42}P_2Cl_2Ru$: The crystals belong to the monoclinic system with unit cell parameters at 178 K: a = 13.466(5), b = 14.188(6), c = 22.62(2) Å, β = 104.50(6)°, and V = 4183(4) Å^3. The space group is C2/c with Z = 4 formula units/unit cell and D(calc.) = 1.41 Mg/m^3. Intensity data (2769 total) were collected on a Siemens R3m/V diffractometer system using monochromatized MoKα radiation ($\bar{\lambda}$ = 0.710730 Å) via a θ-2θ scan technique[1]. Those 2482 reflections with $|F_o| > 3.0\sigma(|F_o|)$ were considered observed.

The structure was solved by direct methods and refined by full-matrix least-squares techniques[2]. Hydrogen atoms were included using a riding model with d(C-H) = 0.96Å and U(iso) = 0.08Å^2. At convergence, R_F = 4.5%, R_{wF} = 5.9% and GOF = 1.43 for 246 variables. A final difference-Fourier map was featureless.

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Supplementary Material. Description of the X-ray diffraction experiment, tables of experimental data, atomic coordinates, thermal parameters, distances and angles (13 pages) and structure factor amplitudes (6 pages).

Acknowledgement. Funds for the purchase of the Siemens R3m/V diffractometer system were made available from the National Science Foundation under Grant CHE-85-14495.

The ORTEP plot is shown at the 50% probability level.

Collection of X-ray Diffraction Data. A dark redcrystal of approximate dimensions 0.20 × 0.23 × 0.33 mm was oil-mounted on a glass fiber and transferred to the Syntex $P2_1$ diffractometer which is equiped with a modified LT-1 low temperature system. Determination of Laue symmetry, crystal class, unit cell parameters and the crystal's orientation matrix were carried out by previously described techniques similar to those of Churchill[1]. Low temperature (178 K) intensity data were collected via a θ-2θ scan technique with MoKα radiation under the conditions given in Table 1.

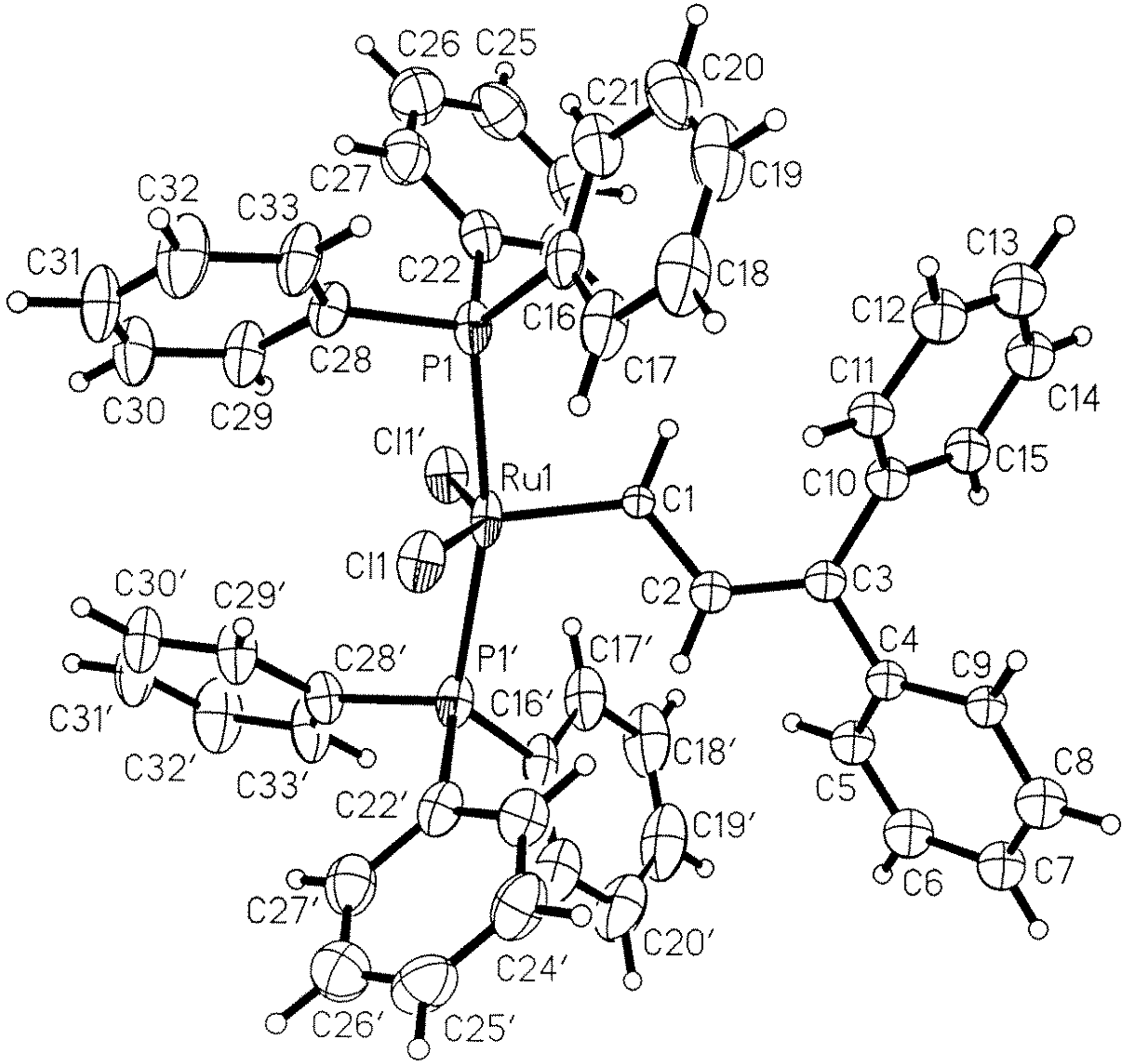
All 2769 data were corrected for absorption and for Lorentz and polarization effects and placed on an approximately absolute scale. Any reflection with I(net) < 0 was assigned the value $|F_o| = 0$. The systematic extinctions observed were *hk*l for *h*+*k* = 2n+1 and *h*0l for l = 2n+1; the diffraction symmetry was 2/m. The two possible monoclinic space groups are Cc [C_s^4; No. 9] or C2/c [C_{2h}^6; No. 15]. The centrosymmetric space was chosen and later shown to be the correct choice.

Solution and Refinement of the Crystal Structure. All crystallographic calculations were carried out using either the UCI modified version of the UCLA Crystallographic Computing Package[2] or the SHELXTL PLUS program set[3]. The analytical scattering factors for neutral atoms were used throughout the analysis[4a]; both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[4b] were included. The quantity minimized during least-squares analysis was $\sum w(|F_o|-|F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.001(|F_o|)^2$.

The structure was solved by direct methods (SHELXTL PLUS); and refined by full-matrix least-squares techniques.

The molecule is located about a two-fold rotation axis at 1/2, y, 1/4. The ruthenium atom lies on the two-fold axis and was assigned a site-occupancy-factor of 1/2. The carbene portion of the molecule is disordered about the symmetry axis resulting in the observed partial orientations shown in the ORTEP diagrams (Figures 1-3). Carbon atoms labelled C(1) through C(15), and their associated hydrogen atoms, were included in the refinement with site-occupancy-factors of 1/2. The carbene moiety was refined using isotropic temperature factors. Other disorder models were tried but proved less satisfactory resulting in larger discrepancies in interatomic distances and angles. (Other models tried were (a) C(1) and C(3) fixed on the two-fold axis, C(4)-C(9) included as the sole phenyl component with site-occupancies = 1.0, (b) C(1) fixed on the two-fold, C(2) and C(3) with s.o.f = 1/2 and C(4)-C(9) at full site-occupancy.) The non-centrosymmetric space group Cc was tried but, it was decided that the molecule was best described as presented.

Hydrogen atoms were included using a riding model with d(C-H) = 0.96Å and U(iso) = $0.08Å^2$. Refinement of positional and thermal parameters (isotropic for carbon atoms C(1) to C(15)) led to convergence with $R_F = 4.5\%$, $R_{wF} = 5.9\%$ and GOF = 1.43 for 246 variables refined against those 2482 data with $|F_o| > 3.0\sigma(|F_o|)$). A final difference-Fourier map was devoid of significant features, $\rho(\max) = 0.85$ eÅ^{-3}.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C11
C14
C30
C29
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Ru1
C15
C10
C1
Cl1
C2
C3
C30'
C29'
C4
C28'
P1'
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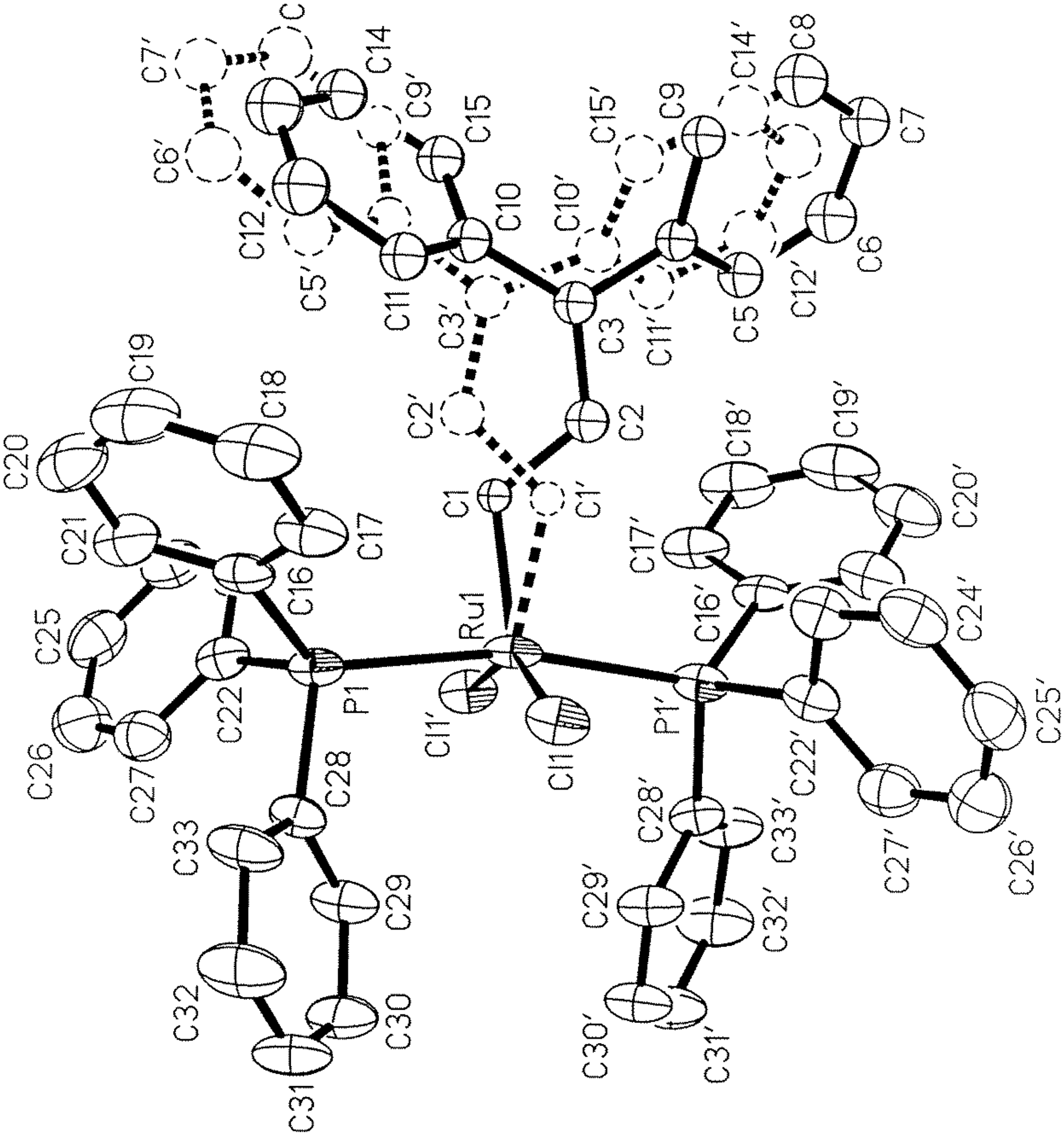
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C1
C1'
C21
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C16
C25
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C18'
C19'
C17'
C20'
C16'
C24'
C22
P1
C26
C27
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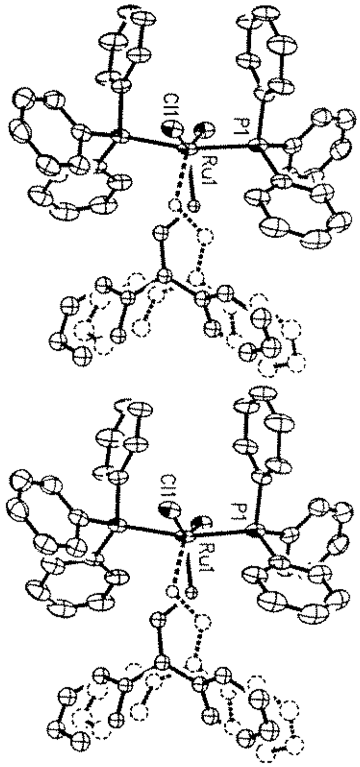
Cl1
Ru1
P1
Cl1
Ru1
P1

Table 1. Experimental Data for the X-ray Diffraction Study

Formula: $C_{51}H_{42}P_2Cl_2Ru$

Fw: 888.8

Temperature (K): 178

Crystal System: Monoclinic

Space Group: C2/c

$\underline{a}$ = 13.466(5) Å

$\underline{b}$ = 14.188(6) Å

$\underline{c}$ = 22.62(2) Å

β = 104.50(6)°

$\underline{V}$ = 4183(4) $Å^3$

Z = 4

$D_{calcd,}$ Mg/m^3 = 1.411

Diffractometer: Syntex $P2_1$ (Siemens R3m/V System)

Radiation: MoKα ($\bar{\lambda}$ = 0.710730 Å)

Monochromator: Highly oriented graphite

Data Collected: $+h,+k,\pm\ell$

Scan Type: θ–2θ

Scan Range: 1.20° plus Kα-separation

Scan Speed: 4.0 deg min^{-1} (in ω)

2θ Range: 4.0 to 45.0°

μ(MoKα), mm^{-1} = 0.605

Reflections Collected: 2769

Reflections with $|F_o| > 3.0\sigma(|F_o|)$: 2482

No. of Variables: 246

R_F = 4.5%, R_{wF} = 5.9%

Goodness of Fit: 1.43

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^4$)

	x	y	z	U(eq)	SOF
Ru(1)	5000	3537(1)	2500	273(2)	0.50
Cl(1)	6386(1)	3089(1)	2115(1)	345(4)	1.00
P(1)	6107(1)	3339(1)	3496(1)	296(4)	1.00
C(1)	5083(7)	4848(5)	2644(3)	171(19)	0.50
C(2)	4670(7)	5530(6)	2173(4)	277(20)	0.50
C(3)	4769(7)	6517(7)	2268(4)	270(21)	0.50
C(4)	4206(7)	7109(6)	1750(4)	255(20)	0.50
C(5)	3186(9)	6905(9)	1432(5)	325(29)	0.50
C(6)	2699(8)	7467(7)	943(5)	417(25)	0.50
C(7)	3151(8)	8262(7)	772(5)	382(24)	0.50
C(8)	4126(9)	8490(8)	1105(5)	422(26)	0.50
C(9)	4688(9)	7938(8)	1604(6)	269(27)	0.50
C(10)	5389(7)	6977(7)	2832(4)	289(22)	0.50
C(11)	6385(7)	6752(6)	3083(4)	309(21)	0.50
C(12)	6940(10)	7250(10)	3605(6)	445(36)	0.50
C(13)	6493(9)	7960(8)	3847(5)	462(27)	0.50
C(14)	5511(10)	8186(10)	3599(7)	383(33)	0.50
C(15)	4929(8)	7708(7)	3073(5)	335(23)	0.50
C(16)	7227(3)	4110(3)	3773(2)	356(17)	1.00
C(17)	7712(4)	4476(3)	3343(3)	450(20)	1.00
C(18)	8546(4)	5077(4)	3534(3)	595(25)	1.00
C(19)	8908(4)	5298(4)	4141(4)	646(27)	1.00
C(20)	8443(5)	4921(4)	4564(3)	621(24)	1.00
C(21)	7594(4)	4323(4)	4389(3)	495(21)	1.00
C(22)	5510(4)	3316(3)	4136(2)	347(17)	1.00
C(23)	4843(4)	4040(3)	4185(2)	404(18)	1.00
C(24)	4384(4)	4065(4)	4666(3)	478(21)	1.00
C(25)	4568(5)	3345(4)	5099(3)	548(23)	1.00
C(26)	5217(5)	2623(4)	5050(3)	558(23)	1.00
C(27)	5704(4)	2605(4)	4576(2)	461(20)	1.00
C(28)	6633(3)	2157(3)	3488(2)	306(16)	1.00
C(29)	5953(4)	1413(3)	3286(3)	411(19)	1.00
C(30)	6319(4)	524(3)	3222(3)	492(21)	1.00
C(31)	7354(4)	351(3)	3356(3)	515(23)	1.00
C(32)	8032(4)	1073(4)	3557(3)	587(24)	1.00

C(33)	7683(4)	1976(3)	3622(3)	458(20)	1.00

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 3. Interatomic Distances (Å) with Esd's

Ru(1)-Cl(1)	2.338(2)	Ru(1)-P(1)	2.387(2)
Ru(1)-C(1)	1.887(7)	P(1)-C(16)	1.841(5)
P(1)-C(22)	1.824(6)	P(1)-C(28)	1.823(5)

C(1)-C(2)	1.444(11)	C(2)-C(3)	1.419(13)
C(3)-C(4)	1.485(12)	C(3)-C(10)	1.489(12)
C(4)-C(5)	1.412(13)	C(4)-C(9)	1.421(15)
C(5)-C(6)	1.388(15)	C(6)-C(7)	1.383(15)
C(7)-C(8)	1.379(14)	C(8)-C(9)	1.425(16)
C(10)-C(11)	1.357(13)	C(10)-C(15)	1.387(15)
C(11)-C(12)	1.418(15)	C(12)-C(13)	1.357(19)
C(13)-C(14)	1.340(16)	C(14)-C(15)	1.423(17)

C(16)-C(17)	1.400(8)	C(16)-C(21)	1.389(8)
C(17)-C(18)	1.391(7)	C(18)-C(19)	1.372(10)
C(19)-C(20)	1.376(11)	C(20)-C(21)	1.400(8)
C(22)-C(23)	1.388(7)	C(22)-C(27)	1.395(7)
C(23)-C(24)	1.380(9)	C(24)-C(25)	1.394(8)
C(25)-C(26)	1.369(9)	C(26)-C(27)	1.389(9)
C(28)-C(29)	1.397(6)	C(28)-C(33)	1.393(7)
C(29)-C(30)	1.375(7)	C(30)-C(31)	1.371(8)
C(31)-C(32)	1.372(8)	C(32)-C(33)	1.386(8)

Table 4. Interatomic Angles (Deg.) with Esd's

Cl(1)-Ru(1)-P(1)	87.2(1)	Cl(1)-Ru(1)-C(1)	108.3(3)
P(1)-Ru(1)-C(1)	87.5(2)	Cl(1)-Ru(1)-Cl(1')	148.4(1)
P(1)-Ru(1)-Cl(1')	89.1(1)	Cl(1)-Ru(1)-C(1')	102.8(3)
P(1)-Ru(1)-P(1')	166.5(1)	P(1)-Ru(1)-C(1A)	106.0(2)
Ru(1)-P(1)-C(16)	121.1(2)	Ru(1)-P(1)-C(22)	117.1(2)
C(16)-P(1)-C(22)	103.1(2)	Ru(1)-P(1)-C(28)	104.5(2)
C(16)-P(1)-C(28)	105.3(2)	C(22)-P(1)-C(28)	104.0(2)
Ru(1)-C(1)-C(2)	122.6(5)	C(1)-C(2)-C(3)	123.1(7)
C(2)-C(3)-C(4)	115.4(7)	C(2)-C(3)-C(10)	125.0(8)
C(4)-C(3)-C(10)	119.6(8)	C(3)-C(4)-C(5)	121.7(9)
C(3)-C(4)-C(9)	118.6(8)	C(5)-C(4)-C(9)	119.6(9)
C(4)-C(5)-C(6)	119.6(11)	C(5)-C(6)-C(7)	122.6(9)
C(6)-C(7)-C(8)	117.6(9)	C(7)-C(8)-C(9)	123.3(11)
C(4)-C(9)-C(8)	117.1(9)	C(3)-C(10)-C(11)	122.6(9)
C(3)-C(10)-C(15)	117.0(8)	C(11)-C(10)-C(15)	120.2(9)
C(10)-C(11)-C(12)	119.4(10)	C(11)-C(12)-C(13)	120.7(11)
C(12)-C(13)-C(14)	120.0(11)	C(13)-C(14)-C(15)	121.0(13)
C(10)-C(15)-C(14)	118.6(10)		

P(1)-C(16)-C(17)	117.9(4)	P(1)-C(16)-C(21)	121.7(4)
C(17)-C(16)-C(21)	120.3(4)	C(16)-C(17)-C(18)	119.5(5)
C(17)-C(18)-C(19)	120.5(6)	C(18)-C(19)-C(20)	119.9(5)
C(19)-C(20)-C(21)	121.3(6)	C(16)-C(21)-C(20)	118.4(6)
P(1)-C(22)-C(23)	118.2(4)	P(1)-C(22)-C(27)	122.6(4)
C(23)-C(22)-C(27)	119.2(5)	C(22)-C(23)-C(24)	120.5(5)
C(23)-C(24)-C(25)	120.0(5)	C(24)-C(25)-C(26)	119.8(6)
C(25)-C(26)-C(27)	120.7(5)	C(22)-C(27)-C(26)	119.8(5)
P(1)-C(28)-C(29)	118.3(3)	P(1)-C(28)-C(33)	122.8(3)
C(29)-C(28)-C(33)	118.7(4)	C(28)-C(29)-C(30)	120.2(5)
C(29)-C(30)-C(31)	120.9(5)	C(30)-C(31)-C(32)	119.7(5)
C(31)-C(32)-C(33)	120.7(5)	C(28)-C(33)-C(32)	120.0(4)

Table 5. Anisotropic displacement coefficients ($\mathring{A}^2 x10^4$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru(1)	138(3)	156(3)	543(4)	0	118(2)	0
Cl(1)	201(6)	313(6)	554(8)	38(5)	158(6)	36(5)
P(1)	166(6)	217(6)	498(8)	11(5)	72(6)	-23(5)
C(16)	189(24)	212(24)	610(34)	27(20)	-6(24)	7(23)
C(17)	223(27)	301(27)	780(39)	-40(22)	41(26)	37(26)
C(18)	257(29)	404(32)	1055(55)	-71(25)	37(33)	57(33)
C(19)	290(33)	391(34)	1172(60)	-74(26)	23(38)	-71(36)
C(20)	392(33)	478(35)	838(46)	3(29)	-136(33)	-183(33)
C(21)	283(29)	380(30)	743(40)	12(23)	-18(28)	-89(27)
C(22)	231(26)	301(26)	494(30)	-15(20)	65(22)	-71(22)
C(23)	341(29)	383(28)	507(31)	7(24)	139(25)	-42(24)
C(24)	421(32)	423(31)	642(37)	-18(25)	229(29)	-132(27)
C(25)	624(40)	585(38)	507(34)	-106(31)	278(30)	-134(29)
C(26)	646(42)	520(36)	539(35)	-11(31)	206(32)	8(28)
C(27)	390(31)	391(30)	571(34)	-7(24)	64(27)	-18(26)
C(28)	220(25)	250(25)	465(28)	32(20)	117(21)	49(21)
C(29)	286(28)	262(27)	698(36)	5(21)	148(26)	34(24)
C(30)	490(36)	241(27)	748(39)	-50(24)	160(30)	-19(25)
C(31)	506(36)	252(27)	838(42)	111(25)	262(32)	-26(27)
C(32)	331(32)	405(32)	1048(50)	131(27)	212(33)	22(32)
C(33)	227(27)	279(27)	850(41)	63(22)	99(26)	76(26)

The anisotropic displacement exponent takes the form:
$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$

Table 6. H-Atom coordinates ($\times 10^4$) and isotropic displacement coefficients ($\AA^2 \times 10^4$)

	x	y	z	U	SOF
H(1A)	5412	5070	3046	800	0.50
H(2A)	4310	5304	1777	800	0.50
H(5A)	2832	6380	1553	800	0.50
H(6A)	2021	7296	715	800	0.50
H(7A)	2799	8642	433	800	0.50
H(8A)	4441	9048	997	800	0.50
H(9A)	5363	8118	1831	800	0.50
H(11A)	6710	6260	2908	800	0.50
H(12A)	7640	7084	3789	800	0.50
H(13A)	6880	8300	4196	800	0.50
H(14A)	5195	8679	3779	800	0.50
H(15A)	4233	7887	2888	800	0.50
H(17A)	7470	4313	2920	800	1.00
H(18A)	8872	5340	3239	800	1.00
H(19A)	9483	5715	4269	800	1.00
H(20A)	8707	5072	4988	800	1.00
H(21A)	7274	4065	4687	800	1.00
H(23A)	4700	4529	3882	800	1.00
H(24A)	3938	4578	4703	800	1.00
H(25A)	4240	3355	5430	800	1.00
H(26A)	5337	2123	5346	800	1.00
H(27A)	6173	2106	4552	800	1.00
H(29A)	5226	1523	3191	800	1.00
H(30A)	5845	18	3083	800	1.00
H(31A)	7601	-271	3308	800	1.00
H(32A)	8756	951	3653	800	1.00
H(33A)	8164	2477	3761	800	1.00

STRUCTURE DETERMINATION SUMMARY

Crystal Data

Empirical Formula	$C_{51}H_{42}P_2Cl_2Ru$
Color; Habit	Dark red cube
Crystal Size (mm)	0.20 x 0.23 x 0.33
Crystal System	Monoclinic
Space Group	C2/c
Unit Cell Dimensions	$\underline{a}$ = 13.466(5) Å
	$\underline{b}$ = 14.188(6) Å
	$\underline{c}$ = 22.62(2) Å
	$\beta = 104.50(6)^{\circ}$
Volume	4183(4) $Å^3$
Z	4
Formula weight	888.8
Density(calc.)	1.411 Mg/m^3
Absorption Coefficient	0.605 mm^{-1}
F(000)	1824

Data Collection

Diffractometer System	Siemens R3m/V
Radiation	MoKα (λ = 0.71073 Å)
Temperature (K)	178
Monochromator	Highly oriented graphite crystal
2θ Range	4.0 to 45.0°
Scan Type	θ–2θ
Scan Speed	Fixed; 4.00°/min. in ω
Scan Range (ω)	1.20° plus Kα-separation
Background Measurement	Estimated from 96 step profile
Standard Reflections	1 measured every 99 reflections
Index Ranges	$0 \leq h \leq 14$, $0 \leq k \leq 15$ $-24 \leq \ell \leq 23$
Reflections Collected	2769
Independent Reflections	2639 (R_{int} = 1.4%); ($\lvert F_o \rvert > 0$)
Observed Reflections	2482 ($\lvert F_o \rvert > 3.0\sigma(\lvert F_o \rvert)$)
Absorption Correction	Semi-empirical (ψ-scan method)
Min./Max. Transmission	0.4871 / 0.7596

Solution and Refinement

System Used	Siemens SHELXTL PLUS (PC Version)
Solution	Direct Methods
Refinement Method	Full-Matrix Least-Squares
Quantity Minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Hydrogen Atoms	Riding model, fixed isotropic U
Weighting Scheme	$w^{-1} = \sigma^2(\lvert F_o\rvert) + 0.0010(\lvert F_o\rvert)^2$
Final R Indices (obs. data)	$R_F = 4.5\%$, $R_{wF} = 5.9\%$
R Indicies (all data)	$R_F = 4.8\%$, $R_{wF} = 6.0\%$
Goodness-of-Fit	1.43
Number of Variables	246
Data-to-Parameter Ratio	10.1:1
Largest and Mean Δ/σ	0.001, < 0.001
Largest Difference Peak	0.85 eÅ^{-3}
Largest Difference Hole	-0.90 eÅ^{-3}

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* The ORTEP plot is shown at the 50% probability level.

Acknowledgement. Funds for the purchase of the Siemens R3m/V diffractometer system were made available to UCI from the National Science Foundation under Grant CHE-85-14495.

Appendix 3

Kinetic and Thermochemical Investigations of Phosphine Ligand Substitution Reactions in *trans* -$(PR_3)_2Cl_2Ru=C\text{-}C=CPh_2$ Complexes

Note: This appendix is a paper to be submitted to an American Chemical Society journal.
The format presented here is that required by the journal editors.

Kinetic and Thermochemical Investigations of Phosphine Ligand Substitution Reactions in *trans* -$(PR_3)_2Cl_2Ru{=}C{-}C{=}CPh_2$ Complexes

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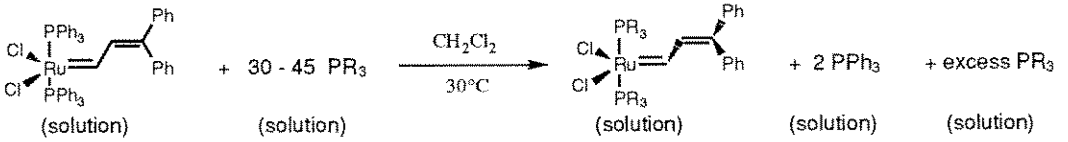
Abstract. The enthalpies of reaction of $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$, **1**, with a series of tertiary phosphine ligands, leading to the formation of $(PR_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ complexes (PR_3 = P^iPr_3, PPh_2Cy, $PPhCy_2$, PCy_3 and P^iBu_3) have been measured by solution calorimetry in CH_2Cl_2 at 30° C. The range of reaction enthalpies spans some 6.5 kcal/mol and help establish a relative order of complex stability for these six ruthenium carbene complexes. The relative enthalpy scale for tertiary phosphine complexes, *trans* -$(PR_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$, is as follows ($PR_3$, kcal/mol): PPh_3, 0; $PCyPh_2$, 1.8 (0.2); PCy_2Ph, 3.8 (0.2); P^iBu_3, 3.8 (0.2); P^iPr_3, 5.2 (0.1) and PCy_3, 6.5 (0.3). The thermodynamic investigation of the exchange of these sterically demanding tertiary phosphine ligands with the PPh_3 ligands of **1** provides an absolute measurement of the relative importance of phosphine stereoelectronic contribution to the enthalpy of reaction in this system. Correlations of various factors gauging the electron donating properties of the phosphine ligands clearly show the electronic factor to be the overwhelming contributor to the enthalpy of reaction.

Introduction

The field of organometallic thermochemistry has gained recognition as one of great relevance to catalysis.[1] Such valuable investigations have lead to a better understanding of bonding and reactivity patterns in a small number organometallic systems.[2,3] These studies have also proven powerful tools in predicting the thermodynamic feasibility of given reactions or individual steps comprising catalytic cycles.[3,4] In spite of the general view that such studies are fundamental to a better understanding of organometallic systems, this area remains one poorly explored for organogroup VIII metal centers.[5] This observation is particular surprising when one considers the predominance of group VIII metals in homogeneous catalysis and the important role that ligand association/dissociation steps play in these catalysis processes. For systems containing metal-ligand multiple bonds this lack of thermodynamic data is even more pronounced. Of the few publications devoted to the thermochemistry of group VIII metals, none involved a system with metal-ligand multiple bonds. This paper reports the first complete thermochemical studies of ligand exchanges on a metal carbene system that is active in a catalytic olefin metathesis system

Results and Discussion

Calorimetric Results. The $(PPh_3)_2Cl_2Ru(=C\text{-}C=CPh_2)$ complex was selected as the entryway into the thermochemistry of the ruthenium-carbene system in view of the labile nature of the PPh_3 ligand. In the present study, a series of sterically demanding tertiary phosphine ligands were investigated by batch solution calorimetry (eq 1). Excess phosphine is needed here to drive the reaction to completion.



(1)

All reactions investigated lead to a unique product under the calorimetric conditions as determined by NMR spectroscopy (*vide infra*). A list of all enthalpies of reaction involving phosphine ligands is provided in Table I.

Table I. Enthalpies of Ligand Substitution (kcal/mol) for Reaction (1).

PR_3	Tolman cone angle	Product	$-\Delta H_{rxn}$[a]
PPh_3	145	$(PPh_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$	0
PBz_3	165	$(PBz_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$	1.3 (0.2)
$PCyPh_2$	153	$(PCyPh_2)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$	1.8 (0.2)
PCy_2Ph	162	$(PCy_2Ph)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$	3.8 (0.2)
P^iBu_3	143	$(P^iBu_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$	3.8 (0.2)
P^iPr_3	150	$(P^iPr_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$	5.2 (0.1)
PCy_3	170	$(PCy_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$	6.5 (0.3)

[a] Enthalpy values are reported with 95 % confidence limits.

Correlation of Reaction Enthalpies with Tolman Electronic Parameter. One of us has recently[5, 10] interpreted enthalpies of phosphine ligand substitution in terms of contributions of steric and electronic phosphine effects by using a relationship first proposed by Tolman (eq 2).[11]

$$-\Delta H^\circ = A_0 + A_1\theta + A_2\nu \qquad (2)$$

where enthalpies of reaction are correlated to steric (θ, cone angle) and electronic (ν, carbonyl stretching frequency in $Ni(CO)_3L$ (L= tertiary phosphine)) factors. An excellent correlation is found to exist with the present ruthenium data (R = 0.995). The A_1/A_2 ratio can be taken as a measure of the relative importance of steric versus electronic factors. It would be expected that steric factors play only a minor role in this ruthenium system in view of the final trans arrangement of ligands. A value of 0.08 was calculated for the A_1/A_2 ratio and quantitatively denoted the important influence of the electronic factor. To further emphasize the importance of electronic effects, a plot correlating the reaction enthalpies in Table I with the corresponding Tolman ν factor was found to give an excellent fit (Figure 1).

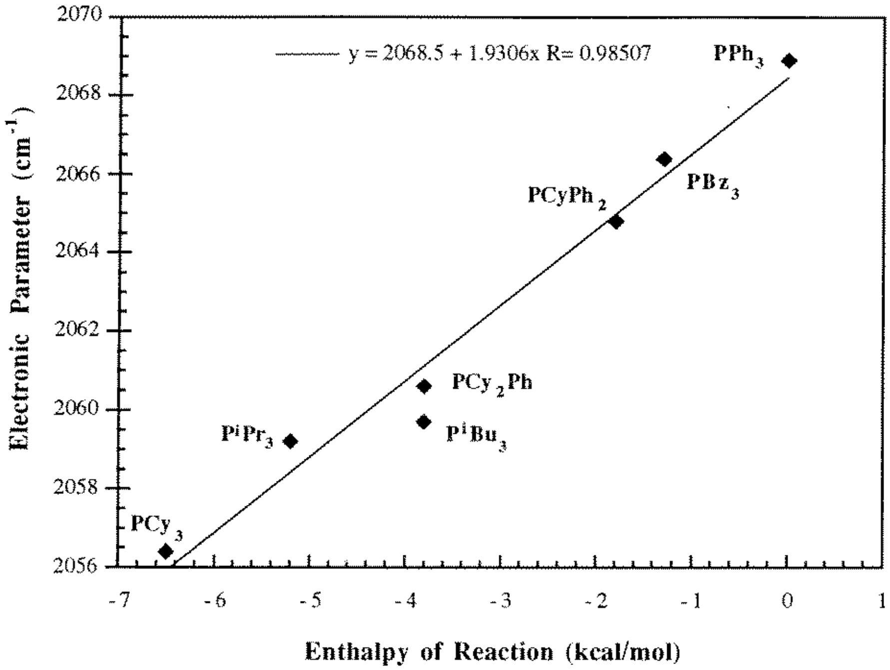


Figure 1. Enthalpy of Phosphine Exchange Reaction vs. Tolman Electronic Parameter (v, cm^{-1}) for *trans* -$(PR_3)_2Cl_2Ru$ (=C-C=CPh$_2$) Complexes. Slope = 1.93, R = 0.98.

Correlation of Reaction Enthalpies with Giering Electronic Factors. Recently, Giering and coworkers have developed a new model to extract information about the stereoelectronic factors that influence the thermodynamics and kinetics of chemical reactions.[12] This quantitative analysis of ligand effects (QALE).model attempts to separate steric and electronic ligand characteristics into independent parameters. Correlations obtained using this QALE parameters often are linear and can offer insights into structure and reactivity patterns. Such a treatment was performed for the present thermochemical data using only the QALE electronic parameter. Results of this correlations is illustrated in Figure 2.

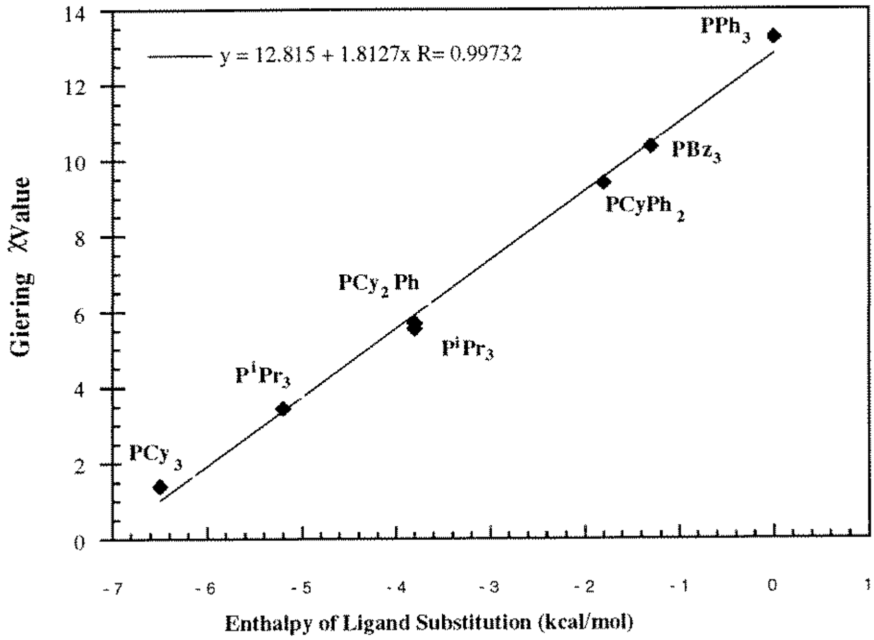


Figure 2. Enthalpy of Phosphine Exchange Reaction vs. Giering Electronic Parameter (χ) for *trans* -$(PR_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ Complexes. Slope = 1.813, R = 0.997.

From the excellent correlation between χ and ΔH, the electronic parameter can be taken as the origin of any variations in measured enthalpies of reaction. Enthalpies of reaction correlate in a linear fashion with the ligand electronic parameter (χ).[23]

Correlation of Reaction Enthalpies with pK_a of HPR_3^+. The pK_a value of the conjugated acid of trialkylphosphines , HPR_3^+ can be used as a rough estimate of the σ-donor ability of the phosphine. The reaction enthalpies from Table I also correlates well with these values (Figure 3), again suggesting that σ-donation is an important contribution to the reaction enthalpy.

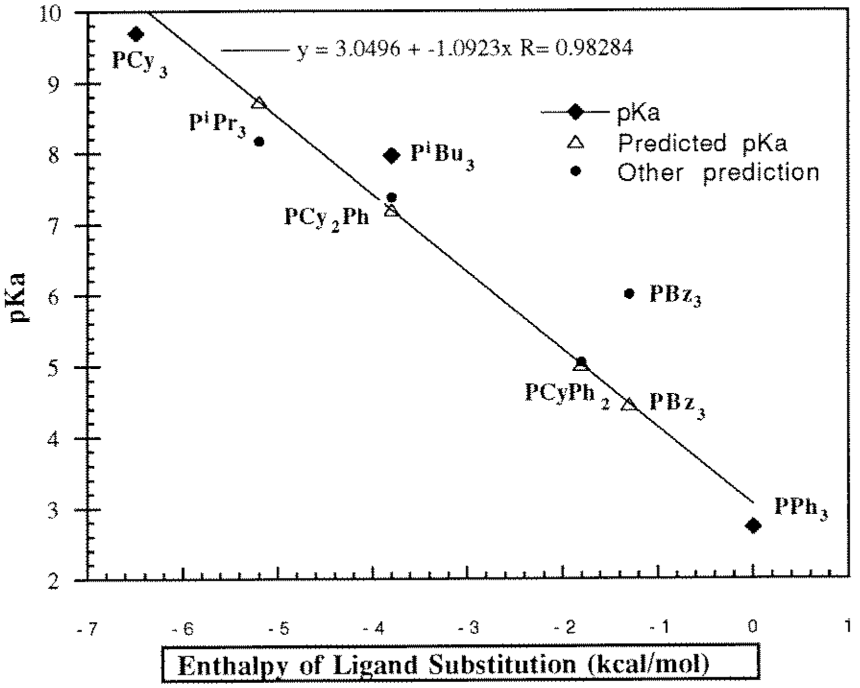
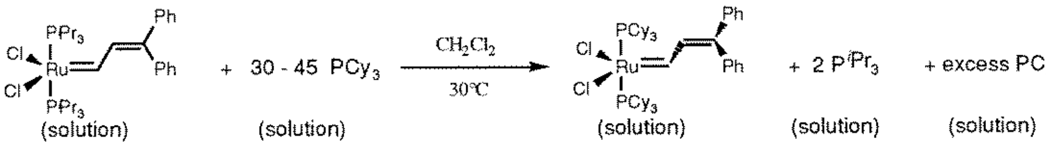


Figure 3. Enthalpy of Phosphine Exchange Reaction vs. pK_a of HPR_3^+ for *trans* $-(PR_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ Complexes. Slope = -1.092, R = 0.983.

Predicting Enthalpy of Other Ligand Exchange Processes. In the present system, the enthalpy associated with any ligand exchange process can be calculated by simply subtracting appropriate enthalpy values taken from Table I. For example, substitution of PCy_3 for P^iPr_3 can be calculated to be exothermic by some 1.3 kcal/mol (eq 3).

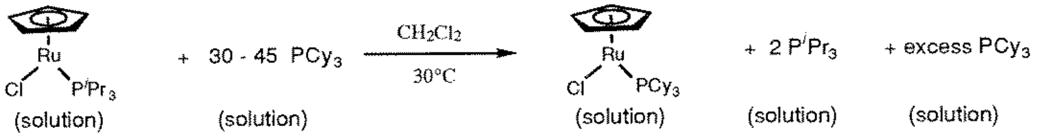


(3)

$$\Delta H(P^iPr_3\text{-}PCy_3) = \Delta H(PPh_3\text{-}PCy_3) - \Delta H(PPh_3\text{-}P^iPr_3) = -6.5 + 3.2 = -1.3 \pm 0.3 \text{ kcal/mol}$$

This enthalpy value is indicative of a stronger $Ru\text{-}PCy_3$ bond compared to $Ru\text{-}P^iPr_3$

interaction (by some 0.7 kcal/mol). Comparisons can be performed with a unique organoruthenium-sterically demanding phosphine system which had been investigated by solution calorimetry.[5e] In that system , only two ligands were investigated and exchange enthalpies can be calculated as illustrated in eq 4



(4)

$\Delta H(P^iPr_3\text{-}PCy_3) = -1.5 \pm 0.5$ kcal/mol

where the difference in Ru-PR$_3$ bond disruption enthalpies is 1.5 kcal/mol. We can see that within experimental error the two differences in Ru-PR$_3$ bond disruption enthalpies are similar. In both systems the Ru-PCy$_3$ interaction is stronger which is a trend in accord with the better donating properties of PCy$_3$.

Conclusion

The reported solution calorimetric investigation represents the first detailed thermochemical study of ligand substitution reaction involving a catalytically active transition metal carbene system. The data obtained can be used to quantitatively evaluate electronic effects of the ancillary phosphine ligands in the present ruthenium system. Simple relationships can be established between enthalpies of reaction and a variety of quantitative factors reflecting the overall electronic effect of phosphine binding. Excellent correlations are established with the phosphine electronic parameters as first proposed by Tolman and modified by Giering. Even a simple pK$_a$ model can describe this electronic influence fairly well. Our results clearly shows the importance of σ donation as a major contributor to enthalpy of ligand substitution reactions in this system

Acknowledgments. The National Science Foundation (CHE-9305492) is gratefully acknowledged for support of this research.

Experimental Section

General Considerations. All manipulations involving organoruthenium complexes were performed under inert atmospheres of argon or nitrogen using standard high vacuum or Schlenk tube techniques, or in a Vacuum/Atmospheres glovebox containing less than 1 ppm oxygen and water. Methylene chloride (CH_2Cl_2) was dried over CaH_2, vacuum-transferred into flame-dried glassware, and then degassed by three continuous freeze-pump-thaw cycles. Infrared spectra were recorded using a Perkin-Elmer FTIR model 2000 spectrometer in 0.1 mm NaCl cells. NMR spectra were recorded using a QE-300 Plus (300.10 MHz ^1H; 75.49 MHz ^{13}C) spectrometer . Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80) which was periodically calibrated using the TRIS reaction [6] or the enthalpy of solution of KCl in water.[7] The experimental enthalpies for these two standard reactions compared very closely to literature values. This calorimeter has been previously described[8] and typical procedures are described below. The organoruthenium complex $(PPh_3)_2(Cl)_2Ru(=C\text{-}C=CPh_2)$, **1**, was synthesized according to literature procedures[9]. Only materials of high purity as indicated by IR and NMR spectroscopies were used in the calorimetric experiments. All ligands were purchased from Strem Chemicals (Newburyport, MA) or Organometallics, Inc. (East Hampstead, NH) and purified by standard techniques prior to use.

Calorimetric Measurement for Reaction Involving $(PPh_3)_2Cl_2Ru=CH\text{-}CH=CPh_2$ and PCy_3. The following procedure describes a typical experiment. The mixing vessels of the Setaram C-80 were cleaned, dried in an oven maintained at 120° C, and then taken into the glovebox and allowed to cooled down to room temperature. Inside the glovebox, 20-30 mg sample of $(PPh_3)_2Cl_2Ru=CH\text{-}CH=CPh_2$, **1**, was transferred into a 2 mL volumetric flask and accurately weighed on a high-precision balance. Enough dry CH_2Cl_2 was added to make a 2 mL solution and the resulting green liquid was then syringed into the inner compartment of the calorimetric cell. Next, 1.5 g of the PCy_3 ligand was dissolved in enough CH_2Cl_2 to make a 10 mL stock solution. Two milliliters of this ligand solution was then syringed into the outer compartment of the cell. The vessel was closed, taken out of the glovebox, and loaded in the calorimeter. The reference vessel was charged in an identical manner except that the inner compartment only contain pure CH_2Cl_2 (2 mL). After the calorimeter had reached thermal equilibrium at 30.0° C (about 2 h) the reaction was initiated by inverting the calorimeter. At the end of the reaction (1-2 h) the vessels were removed from the calorimeter, taken into the glovebox. There the cell was opened, the solvent removed in vacuo and a ^1H NMR spectrum was recorded in CD_2Cl_2 solution. The conversion to the $(PCy_3)_2Cl_2Ru=CH-CH=CPh_2$ product was shown to be quantitative. The enthalpy of reaction, -6.5 ± 0.3 kcal/mol represents the average of five individual calorimetric determinations.

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Appendix 4

The X-Ray Diffraction Experiment for $(PCy_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$

X-Ray Diffraction Data for $C_{51}H_{78}P_2Cl_2Ru\cdot1.33(CH_2Cl_2)$: The crystals belong to the monoclinic system with unit cell parameters at 158 K: a = 24.877(4), b = 13.763(3), c = 47.612(8) Å, β = 92.356(12)°, and V = 16287(5) $Å^3$. The space group is C2/c with Z = 12 formula units/unit cell and D(calc.) = 1.27 Mg/m^3. Intensity data (8322 total) were collected on a Siemens R3m/V diffractometer system using monochromatized MoKα radiation ($\bar{\lambda}$ = 0.710730 Å) via an omega scan technique. Those 5505 reflections with $|F_o| > 6.0\sigma(|F_o|)$ were considered observed.

The structure was solved by direct methods and refined by full-matrix least-squares techniques. There are two independent molecules in the asymmetric unit. One molecule is in a general position while the second is located on a 2-fold rotation axis. There are 1.33 molecules of dichloromethane solvent present per one "Ru-complex". Hydrogen atoms were included using a riding model with d(C-H) = 0.96Å and U(iso) = 0.08$Å^2$. At convergence, R_F = 12.9%, R_{wF} = 15.7% and GOF = 4.17 for 428 variables.

Supplementary Material. Description of the X-ray diffraction experiment, thermal ellipsoid plots, tables of experimental data, atomic coordinates, thermal parameters, distances and angles (25 pages) and structure factor amplitudes (16 pages)and torsion angles (5 pages).

Collection of X-ray Diffraction Data. A dark red crystal of approximate dimensions 0.20 × 0.23 × 0.33 mm was oil-mounted[1] on a glass fiber and transferred to the Siemens P3 diffractometer which is equiped with a modified LT-2 low temperature system. Determination of Laue symmetry, crystal class, unit cell parameters and the crystal's orientation matrix were carried out by previously described techniques similar to those of Churchill[2]. Low temperature (158 K) intensity data were collected via an omega scan technique with MoKα radiation under the conditions given in Table 1. Although the crystal was not of high quality (broad peaks and weak diffraction pattern) it was decided to continue with data collection to establish the molecular connectivity.

All 8322 data were corrected for Lorentz and polarization effects and placed on an approximately absolute scale. An absorption correction (μ = 0.604 mm^{-1}) was deemed unnecessary. Any reflection with I(net) < 0 was assigned the value $|F_o| = 0$. The systematic extinctions observed were *hk*l for *h*+*k* = 2n+1 and *h*0l for l = 2n+1; the diffraction symmetry was 2/m. The two possible monoclinic space groups are Cc [C_s^4; No. 9] or C2/c [C_{2h}^6; No. 15]. The centrosymmetric space was chosen and later shown to be the correct choice.

Solution and Refinement of the Crystal Structure. All crystallographic calculations were carried out using either the UCI modified version of the UCLA Crystallographic Computing Package[3] or the SHELXTL PLUS program set[4]. The analytical scattering factors for neutral atoms were used throughout the analysis[5a]; both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[5b] were included. The quantity minimized during least-squares analysis was $\sum w(|F_o|-|F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0004(|F_o|)^2$.

The structure was solved by direct methods (SHELXTL PLUS); and refined by full-matrix least-squares techniques. There are two independent molecules in the asymmetric unit. One is located in a general position and the other is located about a two-fold rotation axis at 1/2, y, 3/4. There are also 1.33 molecules of dichloromethane solvent present per one "Ru-complex". The ruthenium atom of molecule (2) lies on the two-fold axis and was assigned a site-occupancy-factor of 1/2. The carbene portion of molecule (2) is disordered about the symmetry axis resulting in the observed partial orientations shown in the thermal ellipsoid diagrams (Figures 2-4). Carbon atoms labelled C(52) through C(66), and their associated hydrogen atoms, were included in the refinement with site-occupancy-factors of 1/2. All carbon atoms and the dichloromethane solvent molecules were refined using isotropic temperature factors. Hydrogen atoms were included using a riding model with d(C-H) = 0.96Å and U(iso) = 0.08Å^2. Refinement of positional and thermal parameters led to convergence with R_F = 12.9%, R_{wF} = 15.7% and GOF = 4.17 for 428 variables refined against those 5505 data with $|F_o| > 6.0\sigma(|F_o|)$. A final difference-Fourier map yielded $\rho(\max)$ = 2.02 $e\text{Å}^{-3}$.

While it is clear that there are problems with this structure, the main objective of the study, obtaining the molecular connectivity for the complex, has been accomplished.

Table 1. Experimental Data for the X-ray Diffraction Study

Formula: $C_{51}H_{78}P_2Cl_2Ru \cdot 1.33(CH_2Cl_2)$

Fw: 1038.3

Temperature (K): 158

Crystal System: Monoclinic

Space Group: C2/c

$\underline{a}$ = 24.877(4) Å

$\underline{b}$ = 13.763(3) Å

$\underline{c}$ = 47.612(8) Å

β = 92.356(12)°

$\underline{V}$ = 16287(5) $Å^3$

Z = 12

D_{calcd}, Mg/m^3 = 1.270

Diffractometer: Siemens P3 (R3m/V System)

Radiation: MoKα ($\bar{\lambda}$ = 0.710730 Å)

Monochromator: Highly oriented graphite

Data Collected: $+h,+k,\pm \ell$

Scan Type: Omega

Scan Range: 1.20°

Scan Speed: 3.0 deg min^{-1} (in ω)

2θ Range: 4.0 to 40.0°

μ(MoKα), mm^{-1} = 0.604

Reflections Collected: 8322

Reflections with $|F_o| > 6.0\sigma(|F_o|)$: 5505

No. of Variables: 428

R_F = 12.9%, R_{wF} = 15.7%

Goodness of Fit: 4.17

References.

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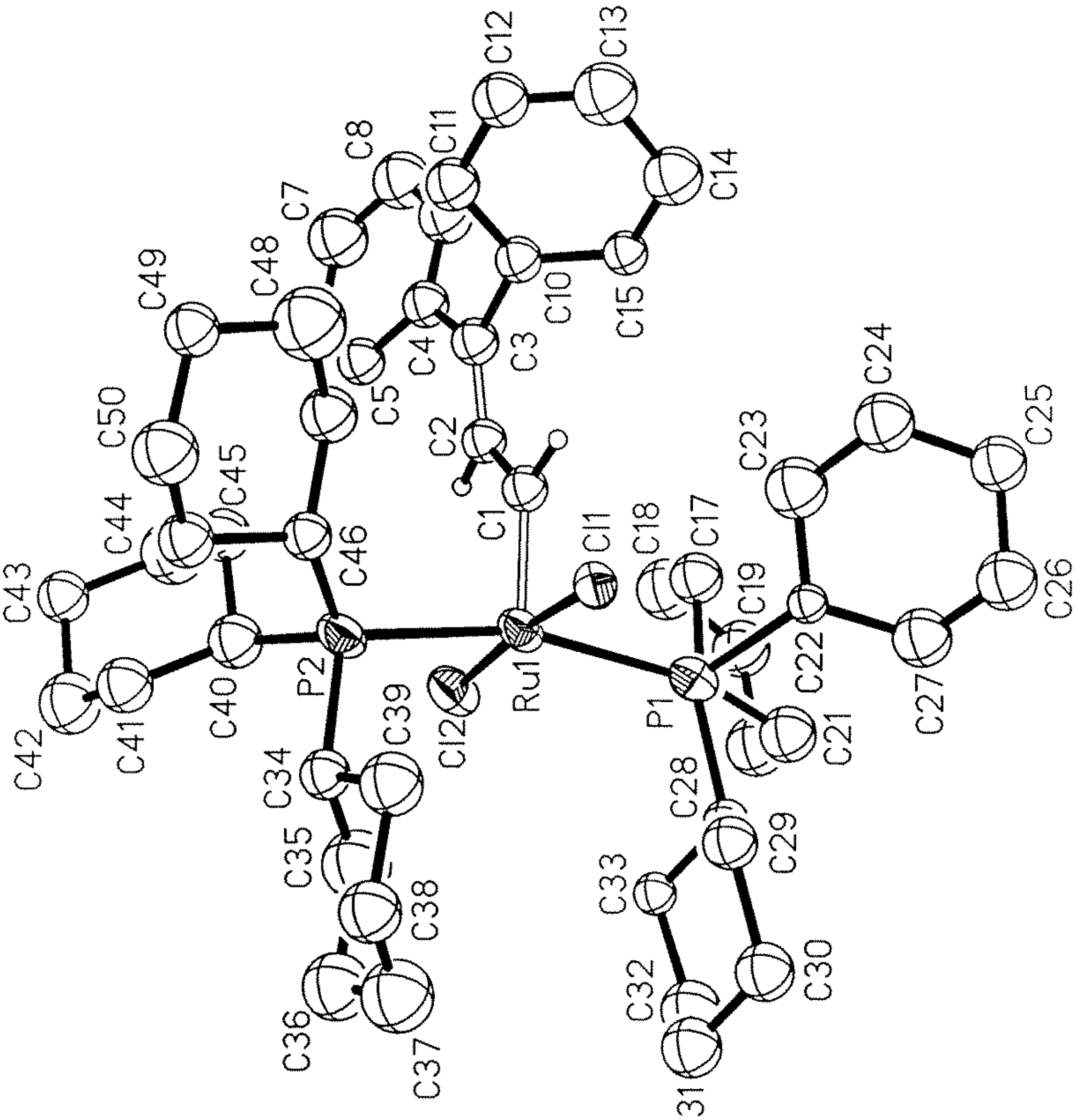
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C2
C23
C45
C44
C1
C46
C43
Cl1
C18
C17
C19
C22
C26
C40
P2
Ru1
C42
C41
Cl2
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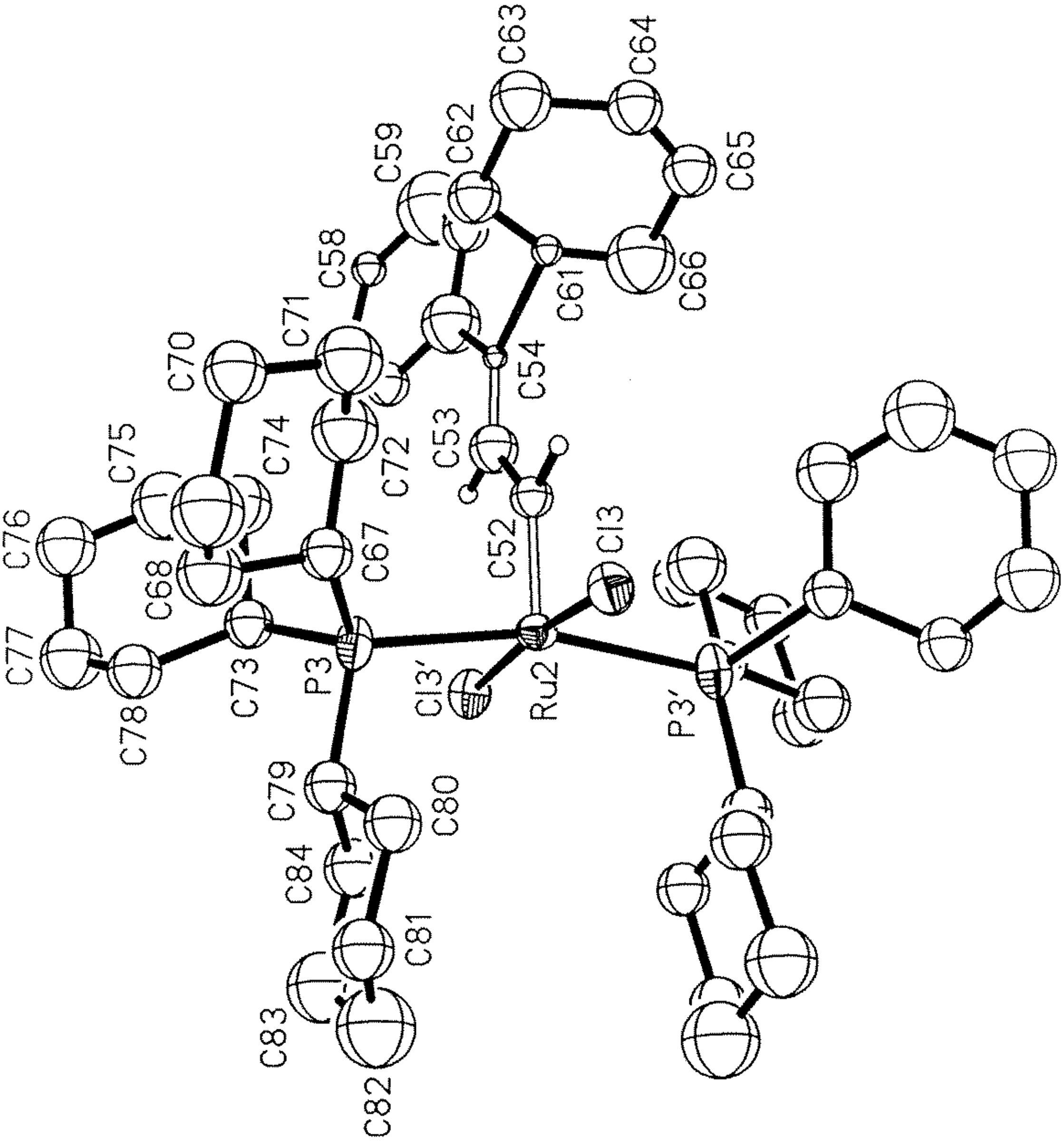
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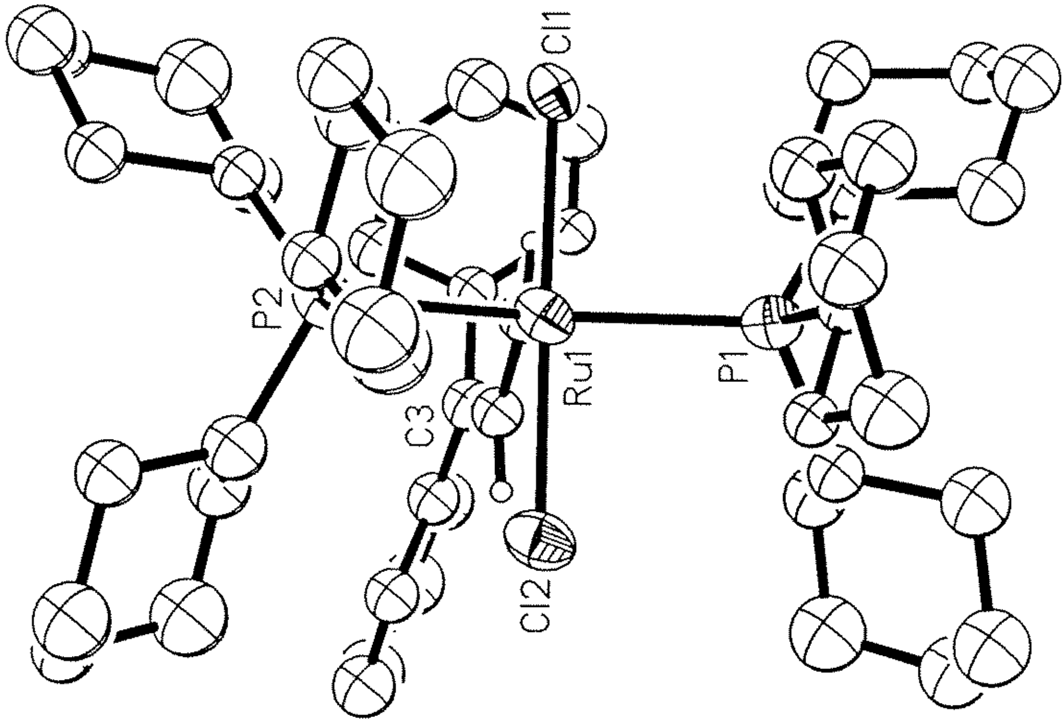
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P2
Ru1
P1
C3
Cl2

STRUCTURE DETERMINATION SUMMARY

Crystal Data

Empirical Formula	$C_{51}H_{78}P_2Cl_2Ru\cdot 1.33(CH_2Cl_2)$
Color; Habit	Red Prism
Crystal Size (mm)	0.10 x 0.33 x 0.43
Crystal System	Monoclinic
Space Group	C2/c
Unit Cell Dimensions	$\underline{a}$ = 24.877(4) Å $\underline{b}$ = 13.763(3) Å $\underline{c}$ = 47.612(8) Å β = 92.356(12)$^{\circ}$
Volume	16287(5) Å^3
Z	12
Formula weight	1038.3
Density(calc.)	1.270 Mg/m^3
Absorption Coefficient	0.604 mm^{-1}
F(000)	6576

Data Collection

Diffractometer System	Siemens R3m/V
Radiation	MoKα (λ = 0.71073 Å)
Temperature (K)	158
Monochromator	Highly oriented graphite crystal
2θ Range	4.0 to 35.0°
Scan Type	ω
Scan Speed	Fixed; 3.00°/min. in ω
Scan Range (ω)	1.20°
Background Measurement	Estimated from 96 step profile
Standard Reflections	2 measured every 98 reflections
Index Ranges	$-17 \le h \le 23$, $-3 \le k \le 13$ $-45 \le \ell \le 45$
Reflections Collected	8322
Independent Reflections	6876 (R_{int} = 2.4%); ($\lvert F_o \rvert > 0$)
Observed Reflections	5505 ($\lvert F_o \rvert > 6.0\sigma(\lvert F_o \rvert)$)
Absorption Correction	N/A

Solution and Refinement

System Used	Siemens SHELXTL (MicroVAX & PC Versions)
Solution	Direct Methods
Refinement Method	Full-Matrix Least-Squares
Quantity Minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Absolute Configuration	N/A
Extinction Correction	χ = 0.000066(15), where $F^* = F\ [\ 1 + 0.002\chi F^2/\sin(2\theta)\ ]^{-1/4}$
Hydrogen Atoms	Riding model, fixed isotropic U
Weighting Scheme	$w^{-1} = \sigma^2(\lvert F_o\rvert) + 0.0004(\lvert F_o\rvert)^2$
Final R Indices (obs. data)	R_F = 12.9%, R_{wF} = 15.7%
R Indicies (all data)	R_F = 15.4%, R_{wF} = 16.1%
Goodness-of-Fit	4.17
Number of Variables	428
Data-to-Parameter Ratio	12.9:1
Largest and Mean Δ/σ	0.005, 0.001
Largest Difference Peak	2.02 eÅ^{-3}
Largest Difference Hole	-1.22 eÅ^{-3}

Table 2. Atomic coordinates ($x10^4$) and equivalent isotropic displacement coefficients ($\AA^2 x10^3$)

	x	y	z	U(eq)	S.O.F.
Ru(1)	3193(1)	-4796(2)	5942(1)	35(1)	
Cl(1)	3533(2)	-5670(4)	6346(1)	35(2)	
Cl(2)	2949(2)	-3824(5)	5538(1)	48(2)	
P(1)	3026(2)	-3420(5)	6241(1)	36(2)	
P(2)	3638(2)	-5966(5)	5651(1)	38(2)	
C(1)	2542(8)	-5431(15)	5974(4)	36(6)	
C(2)	2078(8)	-5432(15)	5784(4)	35(6)	
C(3)	1651(9)	-6012(16)	5792(4)	40(6)	
C(4)	1224(9)	-6039(16)	5574(5)	41(6)	
C(5)	1310(9)	-5704(16)	5312(5)	42(6)	
C(6)	897(10)	-5679(18)	5104(5)	57(7)	
C(7)	395(11)	-6072(20)	5155(6)	73(8)	
C(8)	287(11)	-6387(19)	5416(5)	67(8)	
C(9)	716(10)	-6333(17)	5618(5)	56(7)	
C(10)	1592(8)	-6705(16)	6036(4)	37(6)	
C(11)	1569(9)	-7702(17)	5988(5)	47(7)	
C(12)	1494(9)	-8325(18)	6227(5)	49(7)	
C(13)	1474(10)	-8021(19)	6491(5)	62(8)	
C(14)	1498(9)	-6991(18)	6540(5)	56(7)	
C(15)	1550(8)	-6379(16)	6312(4)	33(6)	
C(16)	2540(8)	-2543(16)	6084(4)	39(6)	
C(17)	1964(9)	-2899(17)	6062(5)	50(7)	
C(18)	1627(11)	-2292(19)	5842(6)	76(9)	
C(19)	1637(10)	-1262(19)	5940(5)	66(8)	
C(20)	2204(10)	-865(20)	5989(6)	72(8)	
C(21)	2521(10)	-1523(17)	6212(5)	59(8)	
C(22)	2846(8)	-3736(14)	6604(4)	26(5)	
C(23)	2396(10)	-4413(18)	6623(5)	62(8)	
C(24)	2326(10)	-4813(17)	6922(5)	56(7)	
C(25)	2253(9)	-3898(17)	7121(5)	50(7)	
C(26)	2714(10)	-3246(18)	7095(5)	58(7)	
C(27)	2766(10)	-2859(17)	6810(5)	56(7)	
C(28)	3638(8)	-2644(15)	6289(4)	31(6)	
C(29)	4102(8)	-3253(16)	6434(5)	44(6)	
C(30)	4598(9)	-2515(17)	6476(5)	52(7)	

C(31)	4777(9)	-2054(18)	6220(5)	55(7)	
C(32)	4286(9)	-1489(18)	6084(5)	59(8)	
C(33)	3807(8)	-2186(15)	6027(4)	32(6)	
C(34)	4356(8)	-5596(16)	5648(4)	37(6)	
C(35)	4448(11)	-4584(20)	5579(6)	74(9)	
C(36)	5048(10)	-4266(20)	5554(5)	69(8)	
C(37)	5319(11)	-4568(20)	5829(5)	75(9)	
C(38)	5270(9)	-5555(17)	5913(5)	52(7)	
C(39)	4650(9)	-5840(18)	5931(5)	57(7)	
C(40)	3447(9)	-5896(18)	5274(5)	49(7)	
C(41)	3800(9)	-6254(17)	5049(4)	50(7)	
C(42)	3601(10)	-5877(19)	4752(5)	67(8)	
C(43)	3019(9)	-6278(17)	4695(5)	48(7)	
C(44)	2657(11)	-5934(20)	4934(5)	74(9)	
C(45)	2861(9)	-6283(17)	5207(5)	48(7)	
C(46)	3653(8)	-7204(15)	5769(4)	34(6)	
C(47)	3082(9)	-7616(16)	5817(5)	47(7)	
C(48)	3101(11)	-8629(19)	5942(6)	77(9)	
C(49)	3441(9)	-9342(16)	5787(5)	41(6)	
C(50)	3994(10)	-8946(17)	5732(5)	57(7)	
C(51)	3963(9)	-7957(15)	5598(4)	43(6)	
Ru(2)	5000	1857(2)	7500	25(1)	0.50
P(3)	4599(2)	2101(5)	7036(1)	35(2)	
Cl(3)	5874(2)	1970(4)	7309(1)	36(2)	
C(52)	5000	577(20)	7500	29(8)	0.50
C(53)	4580(18)	-170(33)	7582(8)	41(12)	0.50
C(54)	4642(13)	-1045(29)	7567(7)	10(9)	0.50
C(55)	4162(22)	-1720(43)	7643(11)	66(16)	0.50
C(56)	3641(17)	-1368(33)	7639(8)	37(12)	0.50
C(57)	3189(19)	-1959(34)	7701(9)	50(14)	0.50
C(58)	3272(16)	-2913(28)	7752(7)	24(10)	0.50
C(59)	3798(27)	-3293(57)	7770(14)	110(24)	0.50
C(60)	4207(24)	-2735(38)	7691(11)	39(14)	0.50
C(61)	5220(13)	-1705(28)	7478(8)	16(10)	0.50
C(62)	5147(18)	-2049(32)	7247(9)	45(13)	0.50
C(63)	5668(20)	-2576(39)	7158(12)	56(16)	0.50
C(64)	6090(23)	-2454(41)	7361(10)	46(15)	0.50
C(65)	6092(19)	-2051(33)	7565(10)	44(13)	0.50
C(66)	5527(22)	-1623(41)	7680(12)	79(18)	0.50

C(67)	5021(9)	1673(16)	6747(4)	40(6)
C(68)	4831(10)	1966(19)	6448(5)	59(7)
C(69)	5290(10)	1796(19)	6247(5)	69(8)
C(70)	5477(10)	696(16)	6254(5)	50(7)
C(71)	5618(10)	411(19)	6553(5)	63(8)
C(72)	5167(10)	626(18)	6749(5)	63(8)
C(73)	3890(8)	1640(15)	6989(4)	38(6)
C(74)	3860(10)	495(18)	6980(5)	60(8)
C(75)	3275(11)	236(21)	6962(6)	80(9)
C(76)	2946(10)	648(18)	6749(5)	62(8)
C(77)	2983(10)	1743(18)	6754(5)	65(8)
C(78)	3538(9)	2101(17)	6745(4)	47(7)
C(79)	4541(9)	3411(15)	6969(4)	40(6)
C(80)	5060(9)	3932(16)	6935(5)	47(7)
C(81)	4973(10)	5005(17)	6868(5)	52(7)
C(82)	4633(12)	5485(22)	7068(6)	91(10)
C(83)	4111(11)	4968(19)	7129(6)	75(9)
C(84)	4201(10)	3900(17)	7203(5)	53(7)
C(85)	6588(15)	3990(27)	7084(7)	127(13)
C(86)	3432(20)	-2275(38)	4978(11)	230(26)
Cl(6)	6496(4)	4257(7)	6760(2)	109(3)
Cl(7)	7055(6)	4466(10)	7330(3)	178(5)
Cl(8)	3345(8)	-1358(15)	5244(4)	282(9)
Cl(9)	4061(9)	-2634(15)	4930(4)	275(9)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 3. Interatomic Distances (Å) with Esd's

Molecule 1.

Ru(1)-Cl(1)	2.391(5)	Ru(1)-Cl(2)	2.401(6)
Ru(1)-P(1)	2.413(6)	Ru(1)-P(2)	2.423(7)
Ru(1)-C(1)	1.851(21)	P(1)-C(16)	1.844(22)
P(1)-C(22)	1.856(20)	P(1)-C(28)	1.866(20)
P(2)-C(34)	1.857(22)	P(2)-C(40)	1.842(22)
P(2)-C(46)	1.795(21)		

C(1)-C(2)	1.436(28)	C(2)-C(3)	1.332(30)
C(3)-C(4)	1.452(30)	C(3)-C(10)	1.516(30)
C(4)-C(5)	1.358(30)	C(4)-C(9)	1.350(33)
C(5)-C(6)	1.396(32)	C(6)-C(7)	1.392(38)
C(7)-C(8)	1.354(38)	C(8)-C(9)	1.408(35)
C(10)-C(11)	1.392(32)	C(10)-C(15)	1.399(28)
C(11)-C(12)	1.444(33)	C(12)-C(13)	1.329(34)
C(13)-C(14)	1.438(36)	C(14)-C(15)	1.382(32)
C(16)-C(17)	1.515(30)	C(16)-C(21)	1.531(32)
C(17)-C(18)	1.557(35)	C(18)-C(19)	1.492(37)
C(19)-C(20)	1.522(36)	C(20)-C(21)	1.581(35)
C(22)-C(23)	1.465(32)	C(22)-C(27)	1.575(30)
C(23)-C(24)	1.542(33)	C(24)-C(25)	1.591(32)
C(25)-C(26)	1.465(33)	C(26)-C(27)	1.467(32)
C(28)-C(29)	1.565(29)	C(28)-C(33)	1.474(28)
C(29)-C(30)	1.604(31)	C(30)-C(31)	1.459(32)
C(31)-C(32)	1.566(33)	C(32)-C(33)	1.545(31)
C(34)-C(35)	1.452(34)	C(34)-C(39)	1.545(30)
C(35)-C(36)	1.563(37)	C(36)-C(37)	1.505(36)
C(37)-C(38)	1.422(36)	C(38)-C(39)	1.598(32)
C(40)-C(41)	1.496(32)	C(40)-C(45)	1.571(31)
C(41)-C(42)	1.565(32)	C(42)-C(43)	1.562(33)
C(43)-C(44)	1.553(34)	C(44)-C(45)	1.457(33)
C(46)-C(47)	1.555(30)	C(46)-C(51)	1.543(30)
C(47)-C(48)	1.516(35)	C(48)-C(49)	1.509(35)
C(49)-C(50)	1.511(32)	C(50)-C(51)	1.505(32)

Molecule 2.

Ru(2)-P(3)	2.409(5)	Ru(2)-Cl(3)	2.398(5)
Ru(2)-C(52)	1.761(28)	P(3)-C(67)	1.863(22)
P(3)-C(73)	1.878(22)	P(3)-C(79)	1.835(22)

C(52)-C(53)	1.528(48)	C(53)-C(54)	1.217(60)
C(54)-C(55)	1.569(68)	C(54)-C(61)	1.767(50)
C(55)-C(56)	1.382(70)	C(55)-C(60)	1.418(78)
C(56)-C(57)	1.430(64)	C(57)-C(58)	1.350(61)
C(58)-C(59)	1.409(80)	C(59)-C(60)	1.342(92)
C(61)-C(62)	1.207(59)	C(61)-C(66)	1.206(66)
C(62)-C(63)	1.559(70)	C(63)-C(64)	1.406(74)
C(64)-C(65)	1.117(69)	C(65)-C(66)	1.640(73)
C(67)-C(68)	1.532(30)	C(67)-C(72)	1.485(33)
C(68)-C(69)	1.539(35)	C(69)-C(70)	1.584(34)
C(70)-C(71)	1.506(32)	C(71)-C(72)	1.519(35)
C(73)-C(74)	1.578(32)	C(73)-C(78)	1.561(29)
C(74)-C(75)	1.496(36)	C(75)-C(76)	1.397(37)
C(76)-C(77)	1.509(35)	C(77)-C(78)	1.469(33)
C(79)-C(80)	1.492(31)	C(79)-C(84)	1.575(32)
C(80)-C(81)	1.523(32)	C(81)-C(82)	1.456(38)
C(82)-C(83)	1.520(40)	C(83)-C(84)	1.526(35)

C(85)-Cl(6)	1.596(34)	C(85)-Cl(7)	1.740(37)
C(86)-Cl(8)	1.808(56)	C(86)-Cl(9)	1.664(55)

Table 4. Interatomic Angles (Deg.) with Esd's

Molecule 1.

Cl(1)-Ru(1)-Cl(2)	173.4(2)	Cl(1)-Ru(1)-P(1)	89.2(2)
Cl(2)-Ru(1)-P(1)	89.5(2)	Cl(1)-Ru(1)-P(2)	88.3(2)
Cl(2)-Ru(1)-P(2)	91.0(2)	P(1)-Ru(1)-P(2)	162.2(2)
Cl(1)-Ru(1)-C(1)	88.8(6)	Cl(2)-Ru(1)-C(1)	97.8(6)
P(1)-Ru(1)-C(1)	98.7(7)	P(2)-Ru(1)-C(1)	98.9(7)

Ru(1)-P(1)-C(16)	113.7(7)	Ru(1)-P(1)-C(22)	114.7(7)
C(16)-P(1)-C(22)	110.6(9)	Ru(1)-P(1)-C(28)	111.2(7)
C(16)-P(1)-C(28)	101.1(9)	C(22)-P(1)-C(28)	104.2(9)
Ru(1)-P(2)-C(34)	106.6(7)	Ru(1)-P(2)-C(40)	114.7(8)
C(34)-P(2)-C(40)	100.8(10)	Ru(1)-P(2)-C(46)	117.1(7)
C(34)-P(2)-C(46)	104.7(10)	C(40)-P(2)-C(46)	110.9(10)

Ru(1)-C(1)-C(2)	129.2(16)	C(1)-C(2)-C(3)	127.3(20)
C(2)-C(3)-C(4)	123.9(20)	C(2)-C(3)-C(10)	120.0(19)
C(4)-C(3)-C(10)	116.1(19)	C(3)-C(4)-C(5)	120.6(20)
C(3)-C(4)-C(9)	124.1(21)	C(5)-C(4)-C(9)	115.2(21)
C(4)-C(5)-C(6)	121.4(22)	C(5)-C(6)-C(7)	120.4(23)
C(6)-C(7)-C(8)	119.9(25)	C(7)-C(8)-C(9)	115.8(25)
C(4)-C(9)-C(8)	126.9(23)	C(3)-C(10)-C(11)	119.9(19)
C(3)-C(10)-C(15)	122.2(19)	C(11)-C(10)-C(15)	117.9(20)
C(10)-C(11)-C(12)	117.4(20)	C(11)-C(12)-C(13)	124.8(23)
C(12)-C(13)-C(14)	117.4(23)	C(13)-C(14)-C(15)	118.7(22)
C(10)-C(15)-C(14)	123.7(21)	P(1)-C(16)-C(17)	114.7(15)
P(1)-C(16)-C(21)	118.0(15)	C(17)-C(16)-C(21)	106.2(18)
C(16)-C(17)-C(18)	110.7(19)	C(17)-C(18)-C(19)	107.4(20)
C(18)-C(19)-C(20)	113.0(22)	C(19)-C(20)-C(21)	109.4(21)
C(16)-C(21)-C(20)	106.3(19)	P(1)-C(22)-C(23)	115.0(14)
P(1)-C(22)-C(27)	116.3(14)	C(23)-C(22)-C(27)	109.4(18)
C(22)-C(23)-C(24)	113.7(19)	C(23)-C(24)-C(25)	106.7(19)
C(24)-C(25)-C(26)	109.0(19)	C(25)-C(26)-C(27)	113.7(19)
C(22)-C(27)-C(26)	108.4(19)	P(1)-C(28)-C(29)	109.4(14)
P(1)-C(28)-C(33)	113.6(13)	C(29)-C(28)-C(33)	111.8(16)

C(28)-C(29)-C(30)	105.4(17)	C(29)-C(30)-C(31)	115.6(18)
C(30)-C(31)-C(32)	107.5(19)	C(31)-C(32)-C(33)	110.4(19)
C(28)-C(33)-C(32)	111.1(17)	P(2)-C(34)-C(35)	115.2(16)
P(2)-C(34)-C(39)	110.8(15)	C(35)-C(34)-C(39)	109.4(19)
C(34)-C(35)-C(36)	116.5(21)	C(35)-C(36)-C(37)	104.6(21)
C(36)-C(37)-C(38)	117.9(23)	C(37)-C(38)-C(39)	110.2(20)
C(34)-C(39)-C(38)	108.8(18)	P(2)-C(40)-C(41)	123.1(16)
P(2)-C(40)-C(45)	112.3(15)	C(41)-C(40)-C(45)	108.1(18)
C(40)-C(41)-C(42)	111.3(19)	C(41)-C(42)-C(43)	107.3(19)
C(42)-C(43)-C(44)	108.9(19)	C(43)-C(44)-C(45)	111.2(21)
C(40)-C(45)-C(44)	110.7(20)	P(2)-C(46)-C(47)	112.6(14)
P(2)-C(46)-C(51)	118.5(15)	C(47)-C(46)-C(51)	108.1(17)
C(46)-C(47)-C(48)	112.3(19)	C(47)-C(48)-C(49)	114.5(21)
C(48)-C(49)-C(50)	112.4(19)	C(49)-C(50)-C(51)	111.6(19)
C(46)-C(51)-C(50)	113.6(18)		

Molecule 2.

P(3)-Ru(2)-Cl(3)	89.5(2)	P(3)-Ru(2)-C(52)	98.0(2)
Cl(3)-Ru(2)-C(52)	93.7(1)	P(3)-Ru(2)-P(3A)	164.0(3)
Cl(3)-Ru(2)-Cl(3A)	172.6(3)	Ru(2)-P(3)-C(67)	114.1(7)
Ru(2)-P(3)-C(73)	114.5(7)	C(67)-P(3)-C(73)	111.1(10)
Ru(2)-P(3)-C(79)	108.8(7)	C(67)-P(3)-C(79)	103.0(10)
C(73)-P(3)-C(79)	104.1(10)		

Ru(2)-C(52)-C(53)	132.3(18)	C(52)-C(53)-C(54)	124.2(37)
C(53)-C(54)-C(55)	118.3(38)	C(53)-C(54)-C(61)	129.0(35)
C(55)-C(54)-C(61)	112.7(33)	C(54)-C(55)-C(56)	120.7(45)
C(54)-C(55)-C(60)	124.3(47)	C(56)-C(55)-C(60)	114.6(50)
C(55)-C(56)-C(57)	122.8(44)	C(56)-C(57)-C(58)	118.4(41)
C(57)-C(58)-C(59)	120.4(46)	C(58)-C(59)-C(60)	119.0(60)
C(55)-C(60)-C(59)	123.5(57)	C(54)-C(61)-C(62)	109.0(32)
C(54)-C(61)-C(66)	104.8(39)	C(62)-C(61)-C(66)	146.2(47)
C(61)-C(62)-C(63)	109.4(40)	C(62)-C(63)-C(64)	111.5(46)
C(63)-C(64)-C(65)	129.1(58)	C(64)-C(65)-C(66)	119.8(49)
C(61)-C(66)-C(65)	102.9(45)	P(3)-C(67)-C(68)	116.1(16)
P(3)-C(67)-C(72)	116.5(16)	C(68)-C(67)-C(72)	109.2(18)
C(67)-C(68)-C(69)	109.2(19)	C(68)-C(69)-C(70)	110.9(20)

C(69)-C(70)-C(71)	109.0(19)	C(70)-C(71)-C(72)	112.4(20)
C(67)-C(72)-C(71)	111.7(20)	P(3)-C(73)-C(74)	112.6(15)
P(3)-C(73)-C(78)	116.6(15)	C(74)-C(73)-C(78)	111.1(17)
C(73)-C(74)-C(75)	106.6(20)	C(74)-C(75)-C(76)	118.9(24)
C(75)-C(76)-C(77)	111.2(22)	C(76)-C(77)-C(78)	113.0(21)
C(73)-C(78)-C(77)	110.0(19)	P(3)-C(79)-C(80)	115.4(15)
P(3)-C(79)-C(84)	109.7(15)	C(80)-C(79)-C(84)	111.3(18)
C(79)-C(80)-C(81)	111.9(18)	C(80)-C(81)-C(82)	112.7(21)
C(81)-C(82)-C(83)	115.8(24)	C(82)-C(83)-C(84)	112.2(22)
C(79)-C(84)-C(83)	109.0(19)		

Solvent Molecules.

Cl(6)-C(85)-Cl(7)	129.0(24)	Cl(8)-C(86)-Cl(9)	116.4(30)

Table 5. Anisotropic displacement coefficients ($\mathrm{\AA}^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru(1)	25(1)	51(1)	31(1)	-5(1)	4(1)	1(1)
Cl(1)	33(3)	42(4)	29(3)	-4(3)	5(3)	-6(3)
Cl(2)	42(4)	64(5)	37(3)	-2(4)	6(3)	8(3)
P(1)	31(4)	42(4)	37(4)	1(3)	5(3)	5(3)
P(2)	26(3)	53(5)	36(4)	-5(3)	7(3)	0(3)
Ru(2)	25(2)	21(2)	29(2)	0	2(1)	0
P(3)	27(3)	51(4)	25(3)	1(3)	-4(3)	-6(3)
Cl(3)	32(3)	43(4)	34(3)	3(3)	0(3)	0(3)

The anisotropic displacement exponent takes the form:
$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$

Table 6. H-Atom coordinates ($\times 10^4$) and isotropic displacement coefficients ($\mathrm{\AA}^2 \times 10^3$)

	x	y	z	U	S.O.F.
H(1A)	2501	-5835	6136	80	
H(2A)	2081	-4964	5635	80	
H(5A)	1661	-5483	5264	80	
H(6A)	965	-5430	4921	80	
H(7A)	114	-6042	5011	80	
H(8A)	-51	-6687	5455	80	
H(9A)	637	-6511	5807	80	
H(11A)	1598	-7973	5803	80	
H(12A)	1467	-9013	6195	80	
H(13A)	1441	-8470	6644	80	
H(14A)	1472	-6717	6724	80	
H(15A)	1556	-5690	6344	80	
H(16A)	2636	-2461	5892	80	
H(17A)	1813	-2847	6244	80	
H(17B)	1959	-3569	6006	80	
H(18A)	1265	-2527	5816	80	
H(18B)	1797	-2318	5665	80	
H(19A)	1476	-1246	6119	80	
H(19B)	1423	-866	5812	80	
H(20A)	2196	-205	6054	80	
H(20B)	2374	-883	5811	80	
H(21A)	2879	-1283	6249	80	
H(21B)	2338	-1541	6385	80	
H(22A)	3153	-4078	6683	80	
H(23A)	2455	-4949	6499	80	
H(23B)	2070	-4092	6560	80	
H(24A)	2639	-5178	6982	80	
H(24B)	2018	-5232	6928	80	
H(25A)	2230	-4117	7312	80	
H(25B)	1926	-3560	7069	80	
H(26A)	3039	-3592	7146	80	
H(26B)	2680	-2719	7225	80	
H(27A)	2442	-2521	6755	80	
H(27B)	3062	-2412	6804	80	
H(28A)	3549	-2126	6413	80	

H(29A)	4201	-3791	6319	80
H(29B)	3993	-3497	6612	80
H(30A)	4897	-2850	6566	80
H(30B)	4493	-2005	6599	80
H(31A)	4890	-2550	6093	80
H(31B)	5074	-1623	6259	80
H(32A)	4386	-1192	5911	80
H(32B)	4181	-985	6210	80
H(33A)	3512	-1838	5937	80
H(33B)	3914	-2688	5901	80
H(34A)	4519	-5973	5505	80
H(35A)	4302	-4207	5727	80
H(35B)	4248	-4426	5408	80
H(36A)	5077	-3581	5520	80
H(36B)	5204	-4613	5403	80
H(37A)	5168	-4175	5972	80
H(37B)	5694	-4410	5824	80
H(38A)	5457	-5663	6090	80
H(38B)	5430	-5959	5775	80
H(39A)	4614	-6520	5972	80
H(39B)	4493	-5475	6078	80
H(40A)	3415	-5213	5236	80
H(41A)	3813	-6951	5052	80
H(41B)	4156	-6009	5090	80
H(42A)	3841	-6082	4611	80
H(42B)	3583	-5180	4750	80
H(43A)	3034	-6974	4702	80
H(43B)	2884	-6085	4512	80
H(44A)	2294	-6150	4897	80
H(44B)	2660	-5236	4935	80
H(45A)	2633	-6079	5353	80
H(45B)	2868	-6981	5204	80
H(46A)	3833	-7200	5951	80
H(47A)	2890	-7647	5638	80
H(47B)	2899	-7168	5934	80
H(48A)	2741	-8875	5949	80
H(48B)	3249	-8583	6131	80
H(49A)	3255	-9477	5610	80
H(49B)	3481	-9945	5887	80

H(50A)	4175	-9381	5610	80	
H(50B)	4201	-8909	5906	80	
H(51A)	4320	-7714	5575	80	
H(51B)	3787	-8002	5415	80	
H(52A)	5325	292	7436	80	0.50
H(53A)	4244	62	7648	80	0.50
H(56A)	3594	-687	7601	80	0.50
H(57A)	2830	-1705	7709	80	0.50
H(58A)	2979	-3349	7784	80	0.50
H(59A)	3858	-3952	7830	80	0.50
H(60A)	4557	-3024	7680	80	0.50
H(62A)	4822	-2017	7131	80	0.50
H(63A)	5702	-2923	6985	80	0.50
H(64A)	6423	-2761	7316	80	0.50
H(65A)	6421	-1998	7676	80	0.50
H(66A)	5465	-1339	7860	80	0.50
H(67A)	5358	2005	6776	80	
H(68A)	4728	2638	6449	80	
H(68B)	4524	1584	6390	80	
H(69A)	5590	2199	6304	80	
H(69B)	5175	1981	6059	80	
H(70A)	5784	618	6140	80	
H(70B)	5191	299	6175	80	
H(71A)	5945	727	6617	80	
H(71B)	5683	-277	6554	80	
H(72A)	4852	249	6701	80	
H(72B)	5288	454	6937	80	
H(73A)	3714	1820	7157	80	
H(74A)	4054	221	7139	80	
H(74B)	4019	269	6812	80	
H(75A)	3134	422	7139	80	
H(75B)	3256	-460	6950	80	
H(76A)	2580	451	6772	80	
H(76B)	3056	412	6570	80	
H(77A)	2831	1978	6923	80	
H(77B)	2777	2009	6597	80	
H(78A)	3684	1906	6570	80	
H(78B)	3549	2797	6755	80	
H(79A)	4332	3477	6796	80	

H(80A)	5241	3646	6781	80
H(80B)	5284	3852	7102	80
H(81A)	4815	5082	6682	80
H(81B)	5316	5328	6874	80
H(82A)	4546	6122	6997	80
H(82B)	4837	5567	7242	80
H(83A)	3884	5005	6961	80
H(83B)	3934	5300	7276	80
H(84A)	4397	3851	7381	80
H(84B)	3861	3580	7218	80
H(85A)	6666	3307	7085	80
H(85B)	6245	4066	7167	80
H(86A)	3278	-2037	4803	80
H(86B)	3225	-2824	5035	80