Olefin Metathesis with Group VIII Transition Metal Complexes: Mechanism, Reactivity, and Catalyst Development

Thesis by

Marcia Beth France

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To my mother and father

and

in loving memory of my grandfather,

Jack France

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Abstract

Group VIII olefin metathesis catalysts are unusually functional group tolerant but are limited by their low reactivity and ill-defined nature. In order to address these concerns, mechanistic investigations of the $Ru(H_2O)_6(tos)_2$-catalyzed ring-opening metathesis polymerization of norbornene and 7-oxanorbornene derivatives in aqueous media have been undertaken. Primarily through chain transfer studies and end group analysis, evidence supporting the intermediacy of ruthenium carbene species has been obtained. Furthermore, acyclic olefins have been shown to provide efficient molecular weight regulation during these polymerizations, allowing control of the polymer molecular weight and the identification of ring-opened units with well-defined functionalized end groups. The molecular weight regulation appears to occur by a standard chain-transfer mechanism.

Methods of expanding the reactivity of group VIII metathesis catalysts to a wider variety of substrates have been developed. The polymerization of low-strain cyclic olefins such as cyclooctene was achieved with $Ru(H_2O)_6(tos)_2$ in the presence of ethyl diazoacetate as an initiator. Such a finding indicates that the difficulties in polymerizing such monomers in the original system lies in the initiation and not in the propagation step. This result is an important indication that the development of more reactive group VIII systems is possible if the barrier to initiation can be overcome.

In addition, several iridium based systems for the polymerization of low-stain olefins are presented. Furthermore, $[(COE)_2IrCl]/AgO_2CCF_3$ was found to be an active catalyst for the simultaneous isomerization/olefin metathesis of acyclic olefins, including methyl oleate. This transformation is essentially a single-step analogue of the two-step Shell Higher Olefins Process. The reaction conditions can also be varied to favor more selective metathesis without accompanying isomerization.

Finally, a number of new, isolable ruthenium carbene complexes have been prepared by alkylidene transfer from diazo compounds. Several of these species are active catalysts for the ring-opening metathesis polymerization of norbornene, and one such system appears to be living. This route offers a facile entry into complexes with catalytic activity identical to that observed with ruthenium carbenes prepared from the less accessible 3,3-diphenylcyclopropene. This method appears to be a general route into ruthenium carbene complexes.

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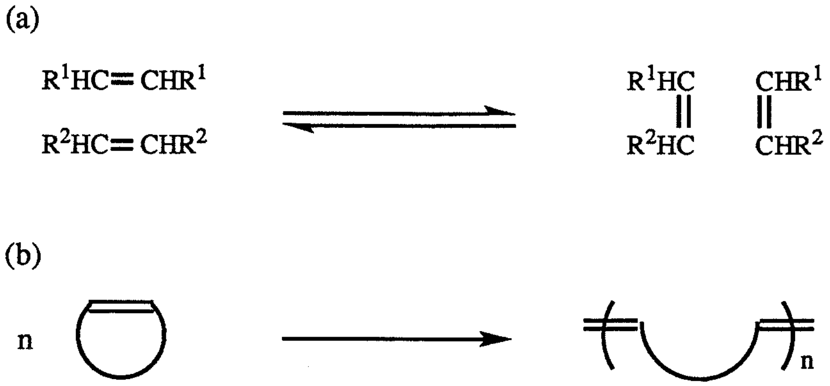
Chapter 1

Introduction

Background

Since the first open publications appeared in the early 1960s,[1, 2] the related reactions of acyclic olefin metathesis (Scheme 1a) and ring-opening metathesis polymerization (ROMP) (Scheme 1b) have received a great deal of attention.[3-7] By allowing the interchange of carbon atoms between a pair of double bonds, the metathesis reaction provides a route into alkenes and polymers that are difficult to prepare by other methods; consequently, this reaction has many important potential commercial applications.[7-15] Furthermore, in contrast to other olefin polymerization methods, ROMP is of interest because it preserves all the double bonds found in the monomeric units, resulting in the formation of polymers with a high degree of unsaturation in the backbone.

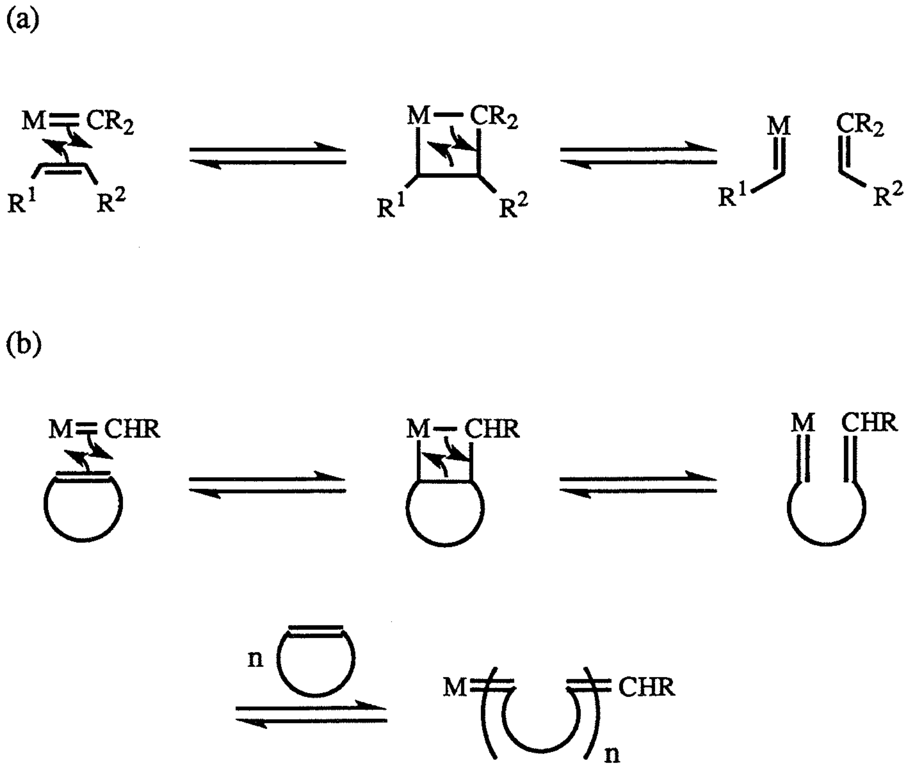
Scheme 1. (a) Acyclic olefin metathesis and (b) ring-opening metathesis polymerization (ROMP).



Metathesis forms the basis for several important industrial processes, such as the Shell Higher Olefins Process and the Phillips Triolefin Process,[16-20] and several ROMP polymers are available commercially, including Metton (polydicyclopentadiene), Vestenamer (polyoctenamer), and Norsorex (polynorbornene).[7, 21] In addition, the utility of the metathesis reaction for the preparation of new materials, including conducting polymers,[22-26] star polymers,[27] and side-chain liquid crystal polymers,[28-33] has also been explored.

The active species in metathesis is generally accepted to be a metal alkylidene complex. The mechanism (Scheme 2) involves a [2+2] cycloaddition of the metal carbene to the olefin to form a metallacyclobutane. This intermediate can either revert back to starting material or open in a productive manner to regenerate a metal alkylidene and produce a new olefin. In the case of a cyclic alkene, cleavage of the metallacyclobutane leads to formation of an olefin which is still tethered to the metal alkylidene. Reaction with additional cyclic monomers in this manner results in the formation of a polymer (Scheme 2b).[5] Technically, all the steps in these mechanisms are reversible; the metathesis of acyclic olefins results in an equilibration of all olefinic species (Scheme 1a) and can be driven towards completion by removal of a volatile component, such as ethylene in the case of terminal olefins, or by use of a large excess of

Scheme 2. Mechanism of (a) acyclic olefin metathesis and (b) ring-opening metathesis polymerization (ROMP).



one alkene. The ROMP of cyclic olefins results in an equilibrium distribution of high polymer, cyclic oligomers (formed by a "backbiting" reaction of the metal alkylidene with an acyclic double bond on the polymer backbone), and monomer. The relative amounts of these species are determined by the identity and initial concentration of the monomer.[5, 34-36]

A wide variety of metal complexes catalyze olefin metathesis and ROMP.[3-5, 37, 38] Traditionally, these could be divided into three general types of catalysts (Figure 1). More recently, a fourth type, well-defined group VIII metal carbene complexes, has been prepared; discussion of this new class of catalysts is reserved for Chapter 5 and such species will not be considered here. The first category of metathesis catalysts, classical co-catalyst systems, generally involve a metal halide complex and a non-transition metal co-catalyst; examples include $WCl_6/SnMe_4$ and $MoCl_5/EtAlCl_2$. The transition metal utilized is typically tungsten, molybdenum, or rhenium, although other early transition metals such as titanium and tantalum have also been used.[4, 5] Although these metal complexes do not contain metal carbene or metallacyclobutane ligands, it is believed that the active species is generated in some manner from the alkyl substituents on the co-catalyst. In fact, the formation of $[W]{=}CH_2$ as the initiating species has been detected by ^1H and ^{13}C NMR spectroscopy in the $WCl_6/SnMe_4$ metathesis system.[39]

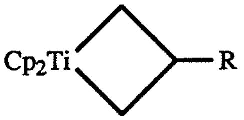
Well-defined metallacyclobutane and metal alkylidene complexes make up the second class of metathesis catalysts. Once again, these are based on early transition metals such as molybdenum, tungsten, titanium, and rhenium. Examples include the titanium metallacycle **1** studied extensively in our laboratories[3, 40-44] and the molybdenum and tungsten alkylidenes **2** developed by Schrock and coworkers.[37, 38] Many of these complexes have even been found to be catalysts for the living polymerization of norbornene (i.e., polymerization systems in which the rates of chain termination and chain transfer are slow on the time scale of the polymerization and the rate of initiation is approximately equal to or greater than the rate of propagation).[37, 38, 40]

1. Co-Catalyst Systems (Mo, W, Re)

Examples: $WCl_6/SnMe_4$ Re_2O_7/Al_2O_3-$SnMe_4$

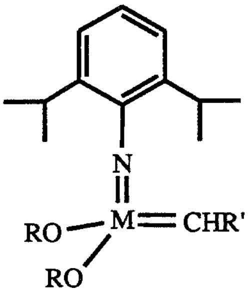
2. Metal Alkylidene or Metallacyclobutane Complexes (Mo, W, Ti, Re)

Examples:



Cp = cyclopentadienyl

1



M = Mo, W

2

3. Group VIII Complexes (Ru, Ir, Os)

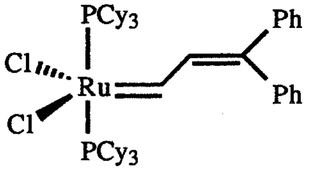
Examples: $Ru(H_2O)_6(tos)_2$
tos = *p*-toluenesulfonate
3

$MCl_3 \cdot xH_2O$
M = Ru, Ir, Os

$[(COE)_2IrCl]_2$
COE = cyclooctene

4. Group VIII Carbene Complexes (Ru, Ir)

Examples:



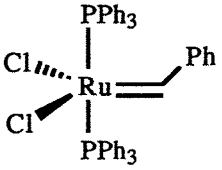


Figure 1. Types of metathesis catalysts.

The third group of metathesis catalysts are based on group VIII transition metals, mainly ruthenium, iridium, and osmium. These include the highly active $Ru(H_2O)_6(tos)_2$ (tos = *p*-toluenesulfonate) **3**[45-47] as well as $[(COE)_2IrCl]_2$ (COE = cyclooctene)[48, 49] and the hydrated trichlorides of ruthenium, iridium, and osmium.[50-54] Unlike the first two classes of catalysts, this last group does not possess well-defined metal carbene or metallacyclobutane ligands nor do these species require alkyl-containing co-catalysts from which such functionality could be derived. The mechanism for the generation of the active species in these group VIII systems remains a mystery, and it has never been clearly demonstrated that the active species is, in fact, a metal carbene.

The group VIII metathesis catalysts are of great interest for several reasons:

First, they are generally much more tolerant of functional groups than their early transition metal counterparts (Table 1).[55] The most systematic study of the functional group tolerance of different metathesis catalysts was carried out in our laboratories. Among the catalysts examined for the ROMP of 7-oxanorbornene derivatives, the most successful were the group VIII complexes. While the highly Lewis acidic transition metal complexes employed in the classical systems were found to coordinate to the bridging oxygen and ultimately decompose the monomer, metathesis was observed with well-defined tungsten alkylidene complexes. However, these compounds were also subject to deactivating side reactions.[46, 47]

Table 1. Relative reactivities of metathesis catalysts toward various functional groups.[51]

higher reactivity ↑

Titanium	Tungsten	Molybdenum	Ruthenium
aldehydes	aldehydes	aldehydes	olefins
ketones	ketones	olefins	aldehydes
esters, amides	olefins	ketones	ketones
olefins	esters, amides	esters, amides	esters, amides

lower reactivity

More recently, better functional group tolerance has been observed for well-defined molybdenum[56-61] and rhenium[62] complexes, and some progress has been made with classical systems as well.[9,-12, 14, 63, 64] However, these systems are all less reactive in the presence of functional groups than in the absence.[9-12, 62] Slow catalyst decomposition appears to be a factor in several systems,[56, 60, 65] and it has also been proposed in some cases that rates are limited by coordination of the functional groups in competition with the olefinic double bond.[62] The choice of solvent is important in the well-defined systems; in some cases, coordinating solvents such as THF or DME have been observed to attenuate the rate, but these solvents are often required for functionalized olefin metathesis reactions, possibly by stabilizing the alkylidene intermediates[61] or by competing successfully with the substrate functionality for coordination to the metal.[38, 60] Despite the advances made in the early transition metal systems, the functional group tolerance is still greater for the group VIII catalysts. Hydroxyl groups are incompatible with early transition metal complexes,[60] and aldehydes are frequently used as chain terminators in these systems because they react with the metal carbene in a Wittig-type fashion.[37, 66, 67] Both these functionalities are tolerated by group VIII catalysts, and some reactions have even been performed in protic solvents.[45, 47, 50-53]

Second, in many cases, metathesis reactions involving group VIII complexes are co-catalyzed by water, and some of these species, in particular **3**, will rapidly polymerize functionalized monomers in aqueous solution.[45, 47] The use of water as a solvent is quite desirable, due to its low-cost, non-toxicity, and relative ease of disposal.

Finally, many of these group VIII catalysts are moderately air stable, and polymerization can be carried out under an atmosphere of air.[45, 47] The unusual air and water tolerance of these systems makes them much easier to handle than early transition metal catalysts, an attractive feature for industrial applications.

Unfortunately, the group VIII catalysts tend to be much less reactive than the early transition metal catalysts of the first two types. Most of these late transition metal complexes are only active for the polymerization of highly strained monomers, particularly bicyclic olefins such as norbornene and 7-oxanorbornene derivatives. They are inactive for the polymerization of low strain monocyclic olefins such as cyclooctene and for the metathesis of acyclic olefins.[5]

Due to the unusual functional group tolerance as well as the air and water stability of these group VIII systems, it is of great interest to extend their reactivity to a wider variety of substrates. In order to fully exploit the potential of these catalysts, it is essential to gain a better understanding of the mechanisms of initiation and propagation occurring in these systems. Not only would such insight aid in expanding reactivity, but it would also help promote the development of well-defined ruthenium carbene complexes that might catalyze living polymerizations. Clearly, the development of functional group tolerant, living late transition metal catalysts of broader substrate activity would potentially be of great commercial importance. Much progress in all these directions has been made and is the focus of the current work.

Thesis Research

The goal of the research presented herein was to address some of the limitations of the group VIII metathesis catalysts. Chapter 2 deals with mechanistic investigations of the **3** catalyzed ring-opening metathesis polymerization of norbornene and 7-oxanorbornene derivatives in aqueous media. Molecular weight regulation studies with acyclic olefins in conjunction with analysis of the resulting oligomeric mixtures were utilized to probe the mechanisms of initiation, propagation, and chain transfer. Equipped with better evidence for the involvement of ruthenium carbene species in this chemistry, attention was turned to expanding the reactivity of the group VIII catalysts to a wider range of substrates, including low-strain cyclic olefins (Chapters 3 and 4) and acyclic olefins (Chapter 4). Finally, a method of generating ruthenium carbenes *in situ* developed in Chapter 3 was applied towards the preparation of isolable ruthenium carbene complexes that are active metathesis catalysts. This work is described in Chapter 5 and includes one example of a novel, well-defined, living system.

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Chapter 2

Mechanistic Investigations of Ru(H_2O)$_6$(tos)$_2$ Catalyzed Ring-Opening Metathesis Polymerization -- Chain Transfer and End Group Analysis[1]

Introduction

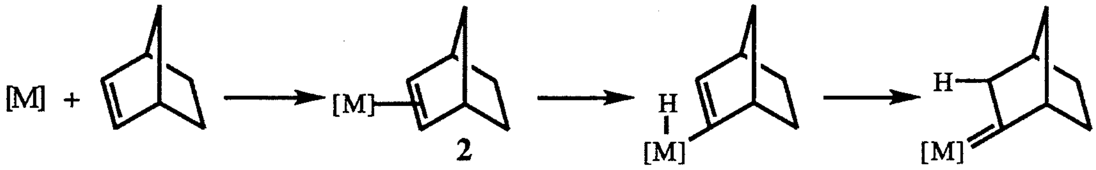
Since the mid-1960s, group VIII coordination complexes such as the hydrated trichlorides of ruthenium, iridium, and osmium have been recognized to be active catalysts for the ring-opening metathesis polymerization (ROMP) of norbornene and functionalized norbornene derivatives in alcoholic solvents.[2-6] More recently, certain group VIII complexes, including $Ru(H_2O)_6(tos)_2$ (tos = *p*-toluenesulfonate) (**1**), were demonstrated to show increased activity for the polymerization of highly functionalized 7-oxanorbornene derivatives when the reactions were run in *aqueous* media.[7, 8] The remarkable functional group tolerance and the unusual air and water stability of these group VIII metathesis catalysts make them of considerable interest in organometallic chemistry. Unfortunately, such complexes are less reactive than their early transition metal counterparts, and their chemistry is limited to the use of highly strained bicyclic monomers; they are inactive for the polymerization of less strained monocyclic olefins and for acyclic olefin metathesis.[9-12]

Clearly, these late transition metal complexes do not contain well-defined metal alkylidene or metallacyclobutane ligands, nor do they contain alkyl substituents from which this active functionality could be generated during the course of the reaction. In light of the growing literature on both metathesis and ROMP,[9-12] a metal alkylidene complex is postulated to be the propagating species during these polymerizations. However, there is no experimental evidence supporting the existence of such an active species, and little is known about its structure and reactivity patterns or about the initiation mechanism leading to its formation. A better understanding of the mechanisms of initiation and propagation in these group VIII systems is necessary in order to overcome their limitations. Ultimately, the future of these metathesis systems will rely on such improvements as the extension of their reactivity to a wider variety of substrates, the preparation of well-defined group VIII alkylidenes, and the development of living late transition metal ROMP systems.[13-20]

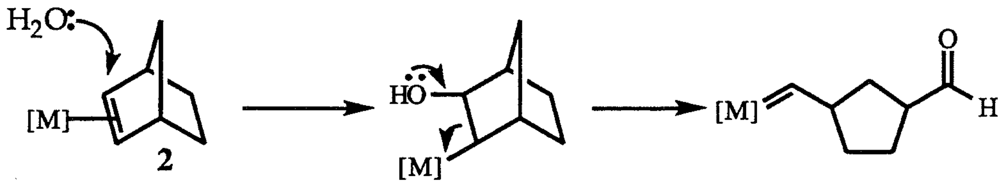
A number of different routes for generating a metal carbene in group VIII systems can be envisioned; several are depicted in Scheme 1. Quite a few conflicting observations that might support or contradict the various proposed mechanisms have been reported. In all cases, the initial step is believed to be formation of the metal-olefin complex **2**. Olefin complexes of this type have been isolated from reaction mixtures of **1**

Scheme 1. Proposed Initiation Mechanisms for Group VIII Catalysts.

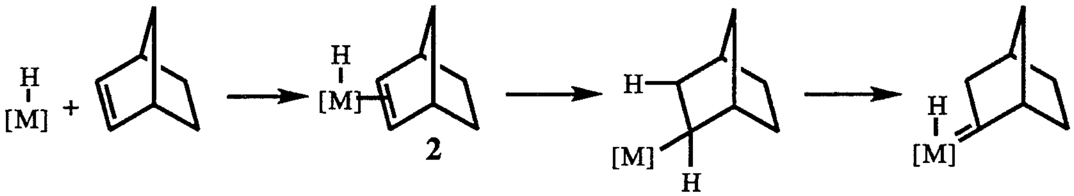
1. Alkene activation mechanism



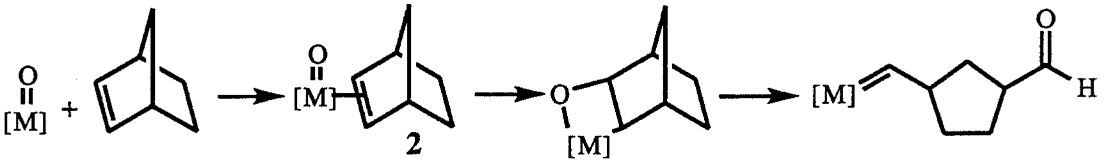
2. Water assisted mechanism



3. Metal hydride mechanism

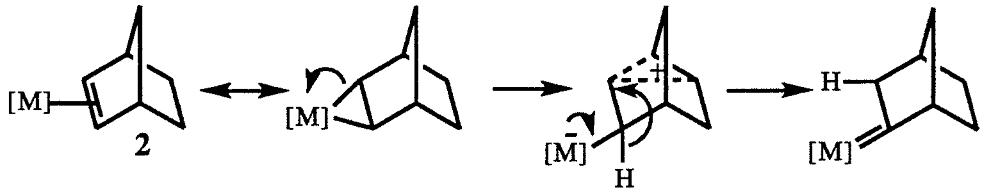


4. Metal oxo mechanism

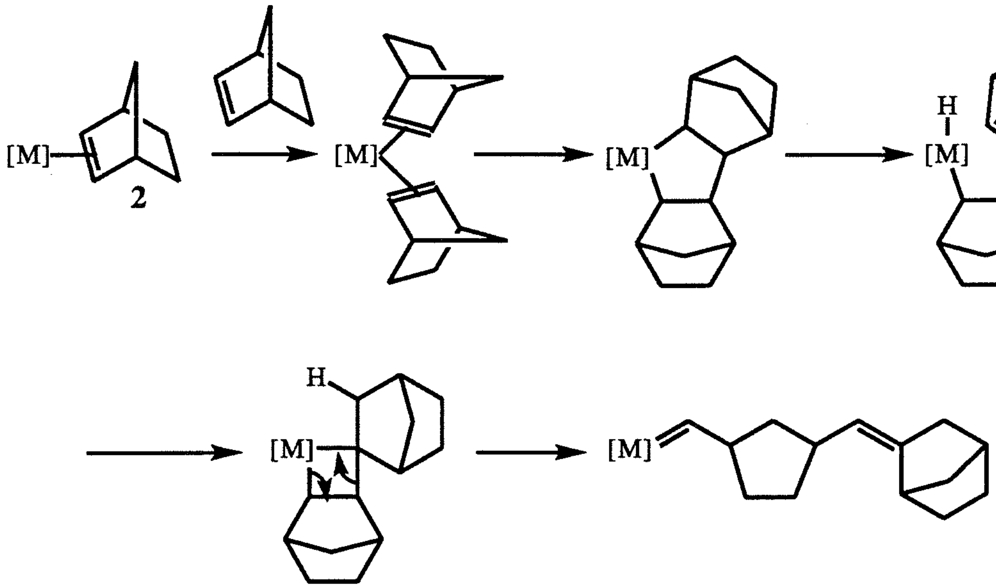


Scheme 1. Continued.

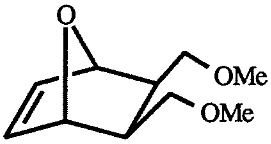
5. Norbornyl cation mechanism



6. Dimerization mechanism



with *exo,exo*-5,6-bis(methoxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene (**3**), and solutions of this complex (**4**) have been demonstrated to be more active catalysts than **1** itself.[21]



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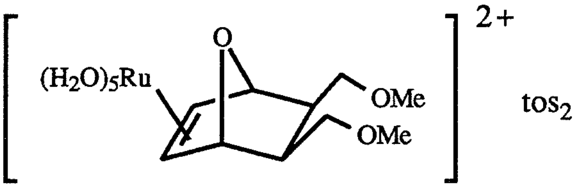

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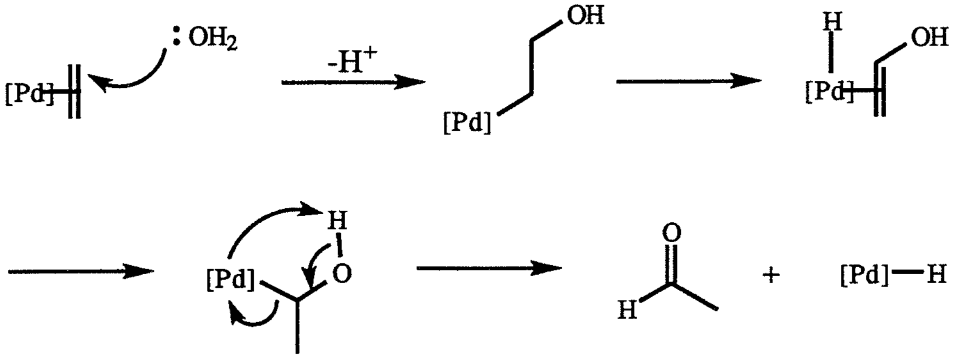
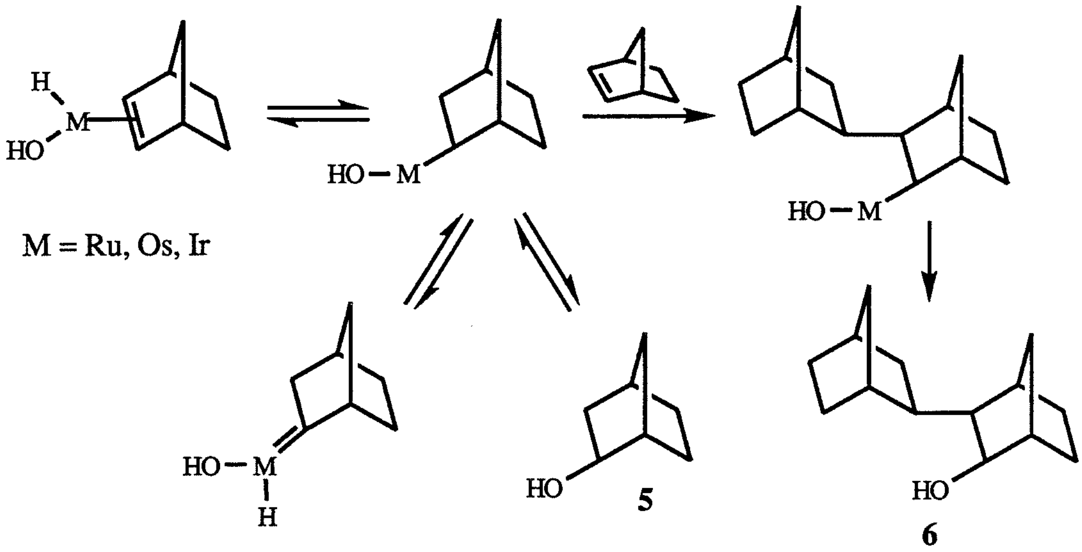
The first mechanism in Scheme 1 involves insertion of the metal into a carbon-hydrogen bond followed by a 1,3-hydride shift to generate a metal alkylidene. The second involves attack of a water molecule on the intermediate metal-olefin complex, followed by rearrangement to a metal alkylidene. Such an attack by water on a coordinated olefin finds a parallel in the currently accepted mechanism for the Wacker process (Scheme 2).[22] A water-assisted mechanism of this type is supported by the observation that ruthenium(III) catalysts undergo a dramatic initiation rate acceleration as the amount of water present in the system is increased, leveling off at about 7-8% water. However, the initiation rates in the more active ruthenium(II) systems are independent of water concentration. These systems instead show behavior similar to the ruthenium(III) catalysts in the regime above the water-saturation limit.[21]

Scheme 2. Mechanism of the Wacker Process.



The third and fourth mechanisms invoke the possibility that some type of impurity, either a metal hydride (mechanism 3)[23, 24] or a metal oxo (mechanism 4)[25] species, is actually responsible for the chemistry observed. This is not unreasonable, since it is believed that less than one percent of the catalyst precursor is actually initiated.[21] Laverty and coworkers have detected the formation of secondary alcohols **5** and **6** during polymerizations using hydrates of MCl_3 (M = Ru, Os, Ir) as catalysts. They have proposed that these products could arise from a metal hydride mechanism as

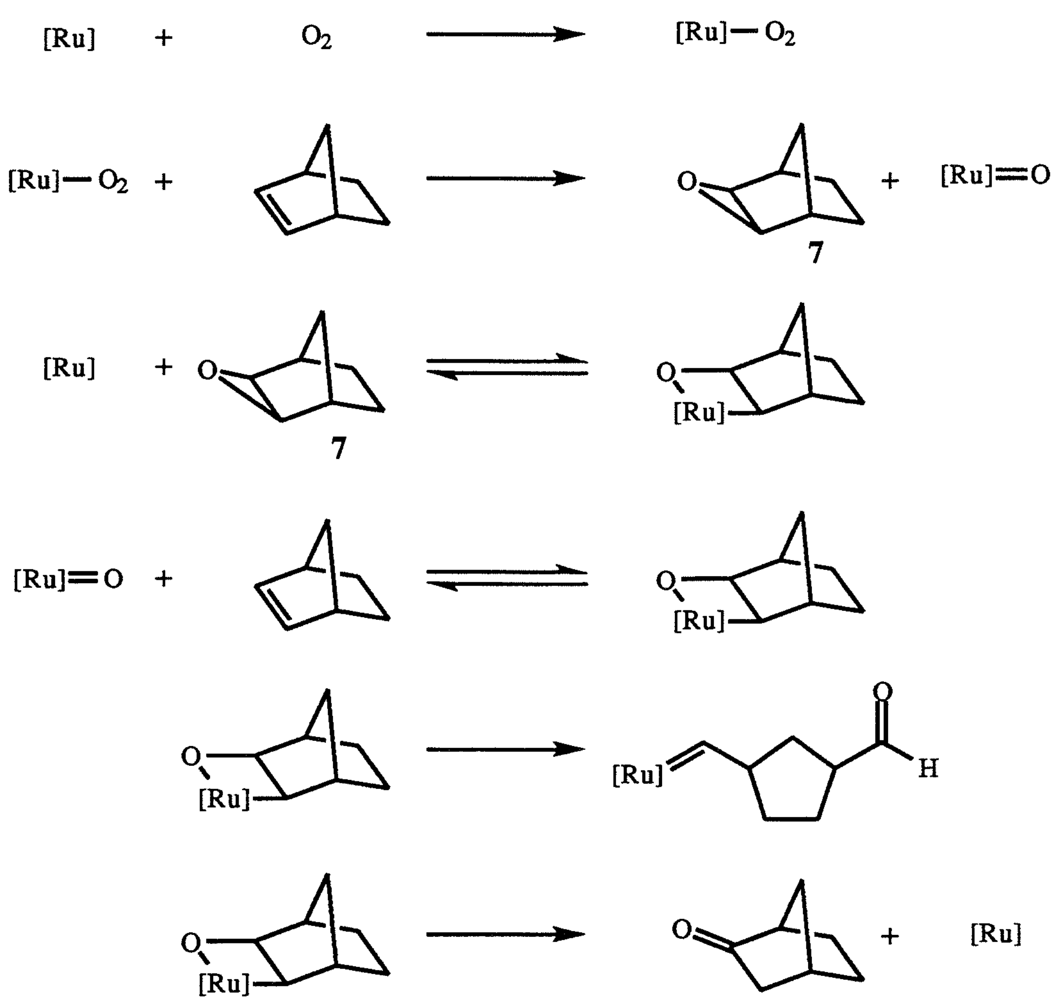
Scheme 3. Proposed mechanism for formation of alcohols **5** and **6**.[23,24]



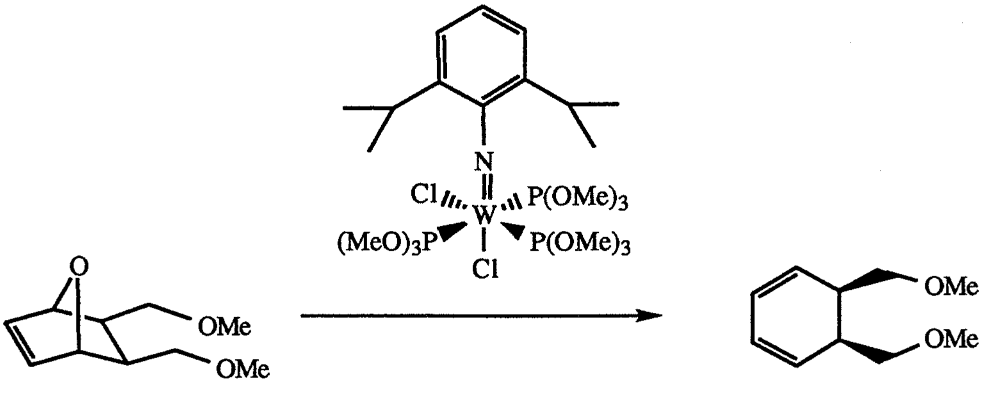
depicted in Scheme 3.[23, 24] Furthermore, IR and NMR spectroscopy have provided evidence for hydride ligands in metathesis systems with highly active cyclooctadiene complexes of iridium, ruthenium, and osmium; the reactivities of these complexes are proportional to the concentrations of hydride ligand observed.[23, 24] Additional evidence obtained in our laboratories (*vide infra*) indicates that metal hydrides are also likely to be present in the $Ru(H_2O)_6(tos)_2$ systems.[26-28] However, other studies have failed to show improved reactivity for a ruthenium-hydride complex ($RuHCl(PPh_3)_3$) over an analogous non-hydride-containing complex ($RuCl_2(PPh_3)_3$).[21]

The literature also contains evidence in support of the metal oxo mechanism. For example, the hydride in $RuHCl(PPh_3)_3$ can be displaced by oxygen to yield a catalyst that is even more active than the original. In addition, bubbling oxygen through solutions of $(PPh_3)_3RuCl_2$ and several other catalysts prior to use has been observed to increase the rate of reaction up to one hundred-fold. Both the epoxide **7** and norbornanone have been isolated from reaction mixtures of these oxidized ruthenium species (Scheme 4), and the epoxide **7** can be used to activate these catalysts in the absence of oxygen.[25] In a

Scheme 4. Proposed Mechanism for Formation of **7** and Norbornanone.[25]



comparison of $K_2RuO_3(OH)_2$/18-Crown-6 with K_2RuCl_5 carried out in our laboratories, the ruthenium oxo species demonstrated higher activity towards **3** than the complex containing no preformed metal oxo. However, under different conditions, K_2RuCl_5 became a far more active catalyst.[21] It is interesting to note that $WCl_2[N\text{-}2,6\text{-}C_6H_3\text{-}(i\text{-}Pr)_2][P(OMe)_3]_3$ has been observed to abstract the oxygen from 7-oxanorbornene **3** to yield the cyclohexadiene **8** and an uncharacterized organometallic product. This indicates that **3** is a potential source of oxo ligands, and epoxide **7** might act in a similar manner.[29]



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8

On the other hand, it should also be mentioned that, while traces of oxygen accelerate the metathesis of vinyl silanes by certain rhodium and ruthenium complexes, bubbling oxygen through these reaction mixtures results in deactivation of the catalysts.[30]

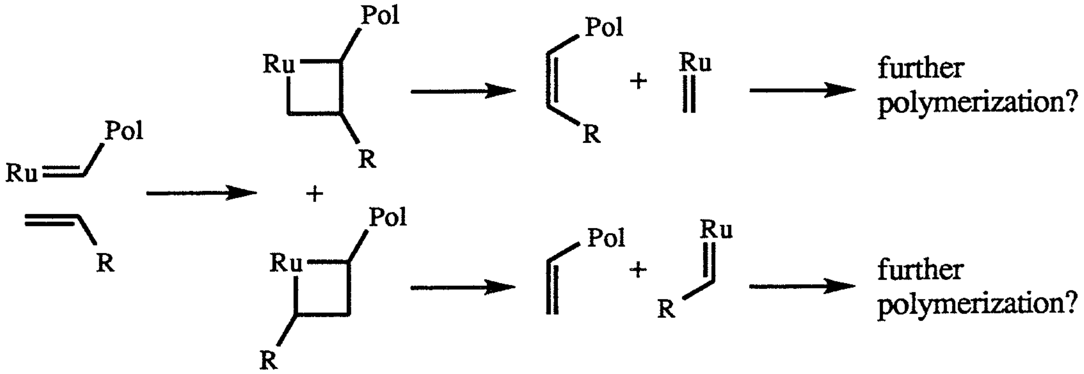
The norbornyl cation mechanism (mechanism 5) is also interesting to consider.[31] Since only strained bicyclic monomers of this type can initiate polymerization with the group VIII catalyst precursors, perhaps there is some special feature of these monomers that is responsible for initiation. That special feature might be the unusual stability of the norbornyl cation.

The last mechanism invokes formation of a bis-olefin complex prior to rearrangement to an alkylidene. Although bis-olefin complexes formed from **1** to date have only been observed for chelating olefins,[28, 32] it is not possible to rule out the intermediacy of such a species.

Upon an examination of the pathways depicted in Scheme 1, it can be seen that, depending upon the method of carbene generation, the initiating alkylidene can have different structures. This moiety will be incorporated into the final polymeric product at the starting end of the polymer chain. If this end group can be identified, it may be possible to rule out some of the mechanistic possibilities discussed above. Unfortunately, due to the small percentage of the catalyst that is actually activated, the high molecular weight of the polymer product precludes direct observation of the tiny amount of end group by ^{1}H NMR, ^{13}C NMR, or IR spectroscopy.[21] If the molecular weight of the polymers can be reduced, however, the ratio of end groups to repeating units of the polymer backbone will be increased, and it might become possible to identify these end groups and gain insight into the mechanism of initiation.

Rinehart and Smith have shown that acyclic olefins can act as molecular weight regulators when added to aqueous ring-opening emulsion polymerization systems of norbornene with iridium and ruthenium halide catalysts.[5] In addition, it has recently been reported that ROMP of 7-oxanorbornene derivatives by hydrated MCl_3 (M = Ru, Os, Ir) in the presence of functionalized acyclic olefins such as *cis*-2-butene-1,4-diol produces low yields of low molecular weight oligomers.[33, 34] The acyclic olefin may be acting as a chain transfer agent by end-capping the growing polymer chain and forming a new ruthenium carbene (Scheme 5) or, alternatively, by binding the active site of the catalyst and thus inhibiting polymerization. In the case of a chain transfer mechanism, the question of whether the new ruthenium carbenes generated during the course of the reaction are capable of initiating a new polymer chain must also be considered.

Scheme 5. Molecular Weight Regulation with Acyclic Olefins



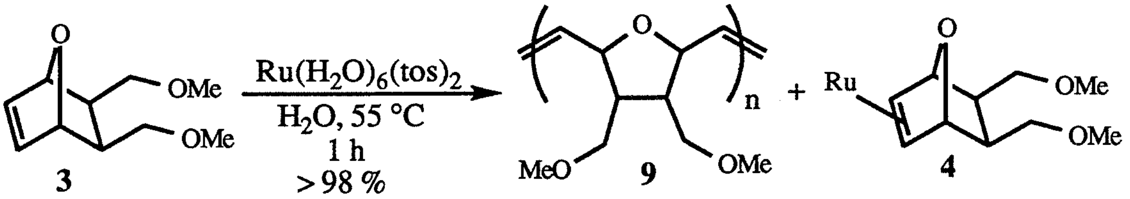
Molecular weight regulation studies with acyclic olefins are potentially of great interest for several reasons. First, by analyzing the end groups of the oligomeric species obtained, it might be possible to gain insight into the method of initiation of the group VIII catalyst precursors. Second, by studying how different acyclic olefins interact with the propagating species, it may be possible to learn about the behavior of this intermediate. Furthermore, the tolerance of functionality exhibited by the group VIII catalysts should allow chain transfer with functionalized acyclic olefins to produce oligomers with specific functionalized end groups.[35-39] Such materials are useful in their own right for the production of larger polymeric materials and block copolymers.[9, 37, 40] In addition, cross-metathesis of functionalized olefins with cyclic olefins provides an important route into functionalized α,ω-diolefins.[38, 41-44]

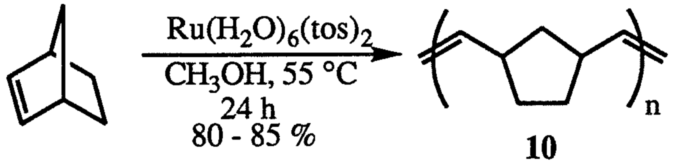
This chapter focuses on investigations of one of the most active group VIII ROMP systems reported to date, the $Ru(H_2O)_6(tos)_2$ catalyzed ROMP of 7-oxanorbornene **3** and norbornene, in order to gather information on the mechanisms of initiation and propagation. The nature of the reactive species has been probed by analyzing the ability of a series of acyclic functionalized olefins to regulate molecular weight and by identifying the end groups of the resulting oligomers. Evidence is presented that indicates that molecular weight regulation occurs by a true chain transfer mechanism and that the active ruthenium propagating species shows behavior consistent with that of known, well-defined metal-alkylidene complexes. The implications of these observations with regards to the mechanism of initiation are also discussed.

Results and Discussion

Molecular Weight Regulation with Acyclic Olefins

In the absence of added acyclic olefin, the polymerization of **3** by $Ru(H_2O)_6(tos)_2$ (**1**) in water at 55 °C proceeded rapidly after an induction period of less than one minute. Work-up after one hour led to quantitative yield of the high molecular weight polymer **9**.[8, 21] Polymerization of the parent norbornene proceeded better in methanol, due to the insolubility of this monomer in water. In this case, initiation occurred in about ten minutes, and after 24 hours high molecular weight polynorbornene **10** was isolated in good yield.





In contrast, when the polymerization of **3** was carried out in the presence of acyclic olefins such as methyl acrylate or 3-buten-1-ol, a drastic reduction in the molecular weight of the product polymer was observed. The yields varied, ranging from 65 to 95%, depending upon the reaction time and the nature and amount of chain transfer agent. Acyclic olefins were chosen for this study that were known not to undergo isomerization under the conditions of the reaction.[27, 32] The number average molecular weight M_n of an oligomeric mixture obtained with 200 equiv methyl acrylate and 56 equiv **3** per ruthenium was 3.5×10^3 compared to 125×10^3 for polymer prepared under identical conditions, but in the absence of methyl acrylate.[45]

At low concentrations of methyl acrylate, a lower molecular weight polymer was observed when the acyclic olefin was heated with precatalyst **1** for 15 minutes prior to addition of monomer **3**. If methyl acrylate (10 equiv per ruthenium) and the monomer (56 equiv per ruthenium) were added to the reaction mixture simultaneously, the oligomeric mixtures obtained were of higher molecular weight ($M_w = 46 \times 10^3$) and polydispersity (PDI = 7.1) than when **3** was added after 15 minutes incubation time ($M_w = 29 \times 10^3$, PDI = 5.3).[45] As the concentration of methyl acrylate was increased, a saturation effect was observed and the difference in molecular weight values decreased; for a methyl acrylate concentration of 50 equiv to ruthenium, the difference in the values obtained under the two separate reaction conditions was negligible. No significant effect due to incubation time was observed with 3-buten-1-ol, which binds to the ruthenium more strongly than methyl acrylate and has been found to be a more effective chain transfer agent. For consistency, all experiments were carried out using the 15 minute incubation time.

A typical gel permeation chromatograph of one of these oligomeric mixtures is depicted in Figure 1b, contrasted with the results obtained in the absence of added acyclic olefin (Figure 1a). The multimodal GPC trace of the product prepared in the presence of methyl acrylate shows that this material consists of a mixture of oligomeric species and lower molecular weight polymer. The lowest molecular weight signal at 470 is known to correspond to the monomer. Presumably, the other peaks represent discrete oligomers, the signals for which grow closer together until the GPC can no longer resolve them. This interpretation is supported by the high resolution GPC trace depicted in Figure 2.[46]

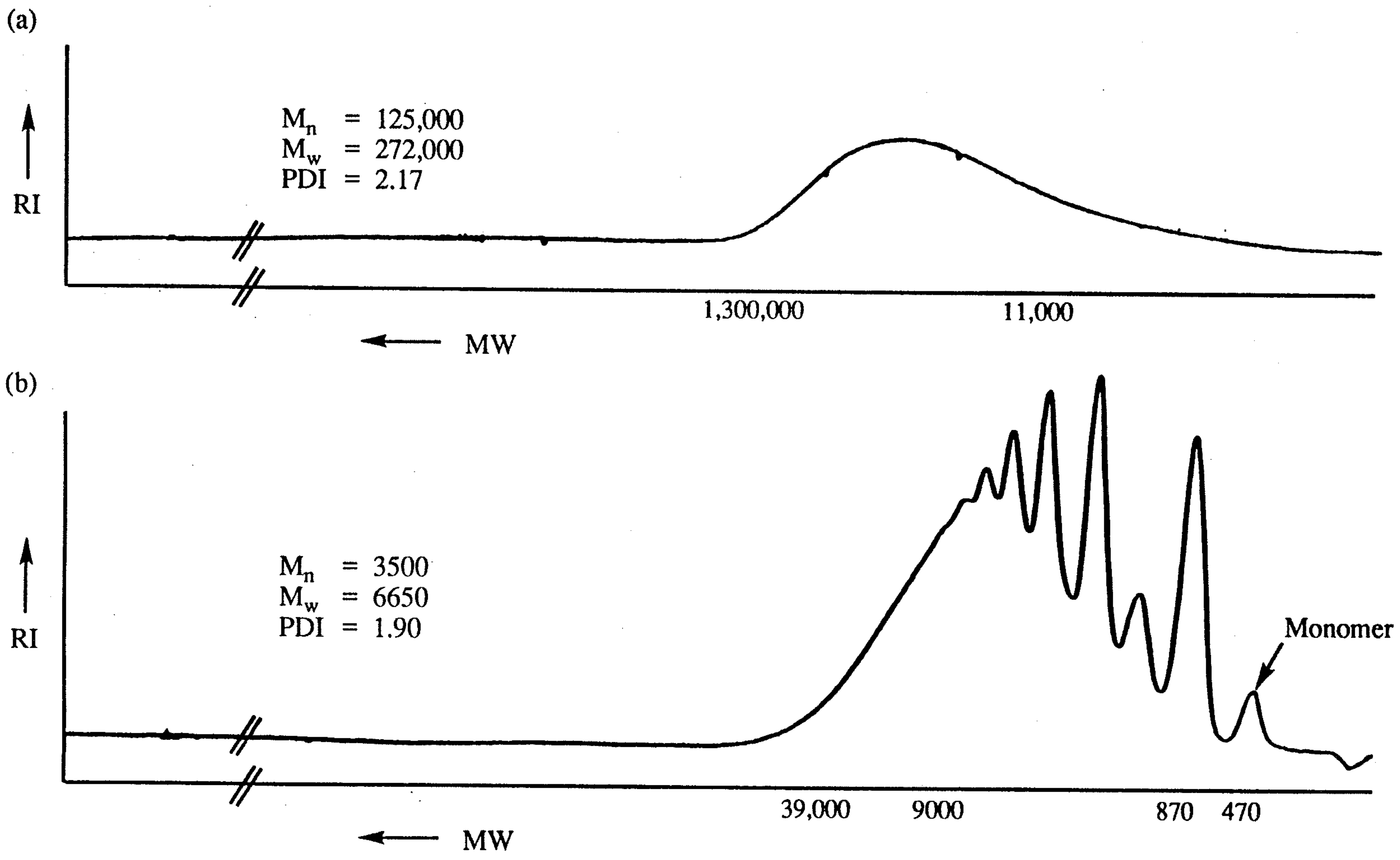


Figure 1. Gel Permeation Chromatograph of **9** prepared with **1** (a) in the absence of added acyclic olefin and (b) in the presence of 200 µL of methyl acrylate.[45] (The two traces are not on the same scale.)

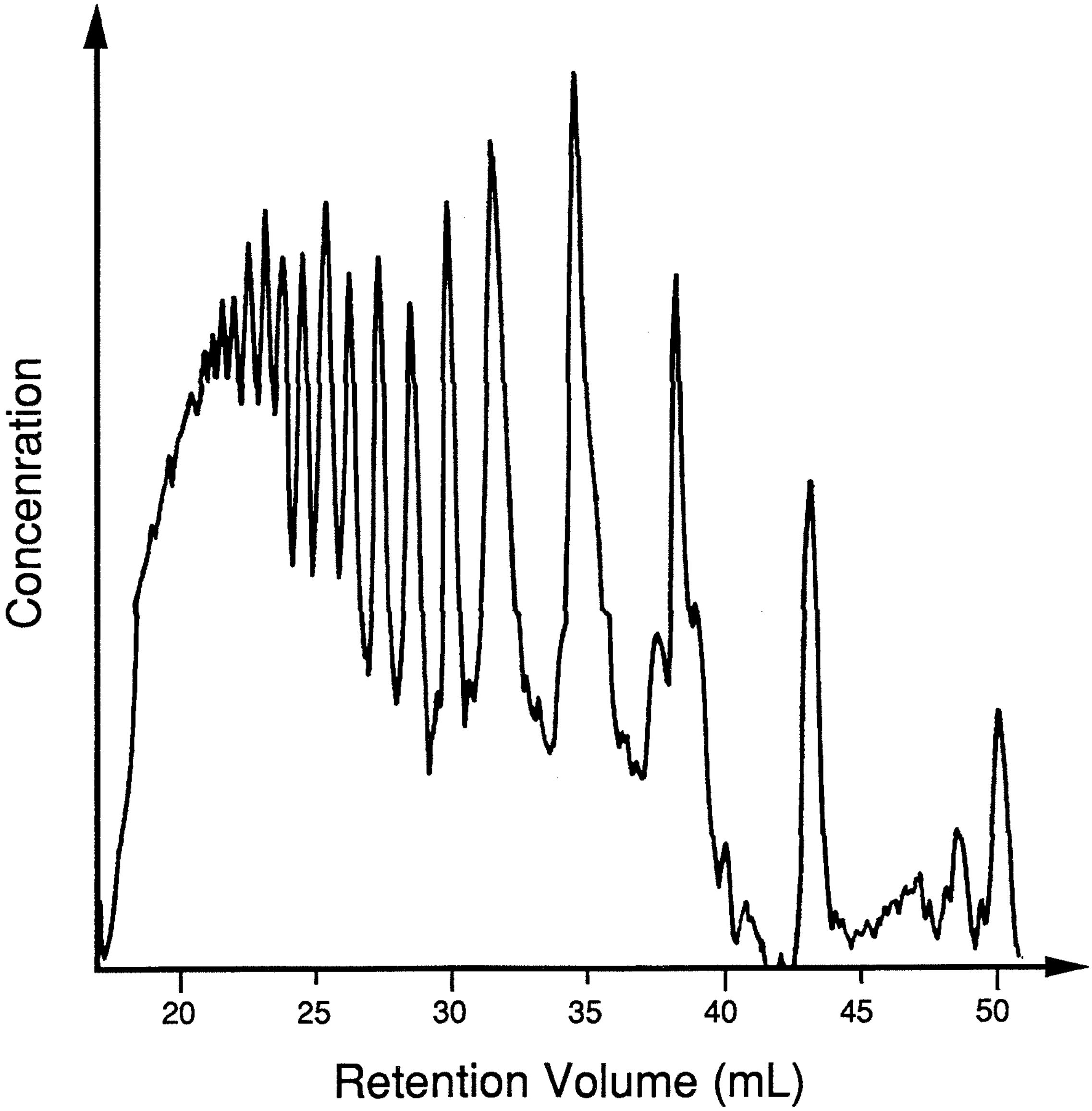
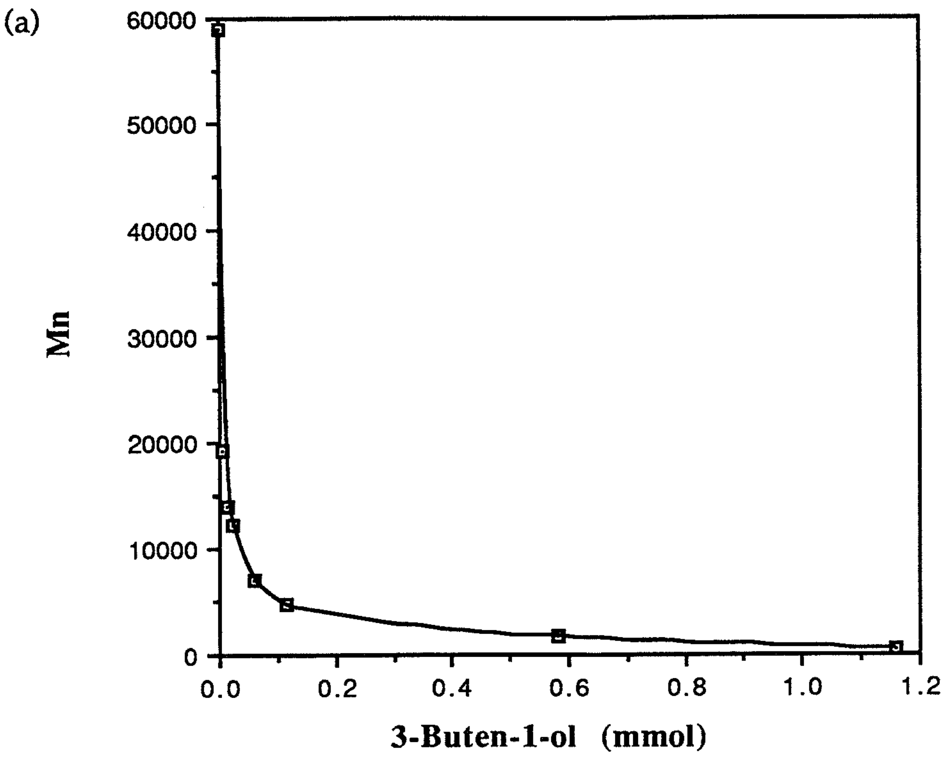


Figure 2. High Resolution GPC trace of poly(**3**) regulated with 3-buten-1-ol ([3-buten-1-ol]:[**3**] = 0.89).

Examination of a range of different concentrations of chain transfer agent leads to plots of molecular weight (M_n) versus acyclic olefin concentration (Figure 3).[47] Initially, the molecular weight drops off rapidly with increasing acyclic olefin concentration and then levels off to a constant, low value. Such behavior would be predicted by the chain transfer mechanism depicted in Scheme 5, but not by a mechanism involving competitive



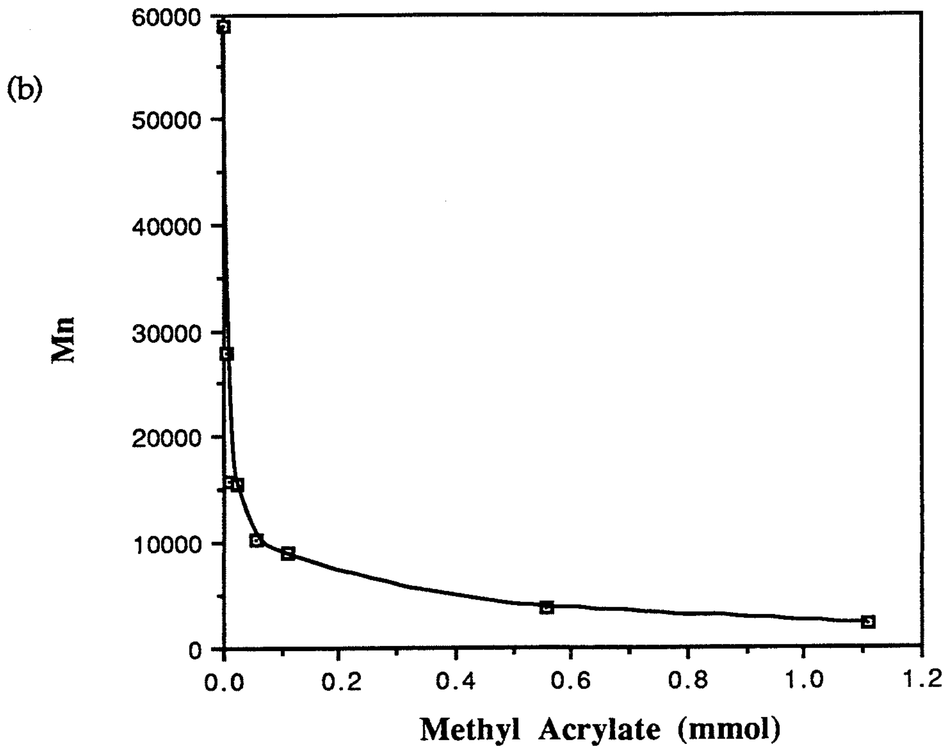


Figure 3. Plots of molecular weight (M_n) versus concentration of acyclic olefin for **3** polymerized by **1** in the presence of (a) 3-buten-1-ol and (b) methyl acrylate.[47]

inhibition by the acyclic olefin. This type of inhibition mechanism was, in fact, observed for a series of unsaturated nitriles (2-pentenenitrile, 3-pentenenitrile, and 4-pentenenitrile). In these cases, yields and polymer molecular weights decreased steadily and eventually dropped to zero when the nitrile was present in high enough concentration (>~10 equiv to ruthenium) to completely deactivate the catalyst. A similar effect of nitrile-containing olefins has also been observed with tungsten co-catalyst systems.[39]

Chain transfer constants, defined as the ratio of the chain transfer rate constant to the propagation rate constant, are available from slopes of plots of the reciprocal of the number-average degree of polymerization versus the ratio [acyclic olefin]/[monomer].[11] The data depicted in Figure 3 leads to chain transfer plots (Figure 4) with slopes of 4.0 x

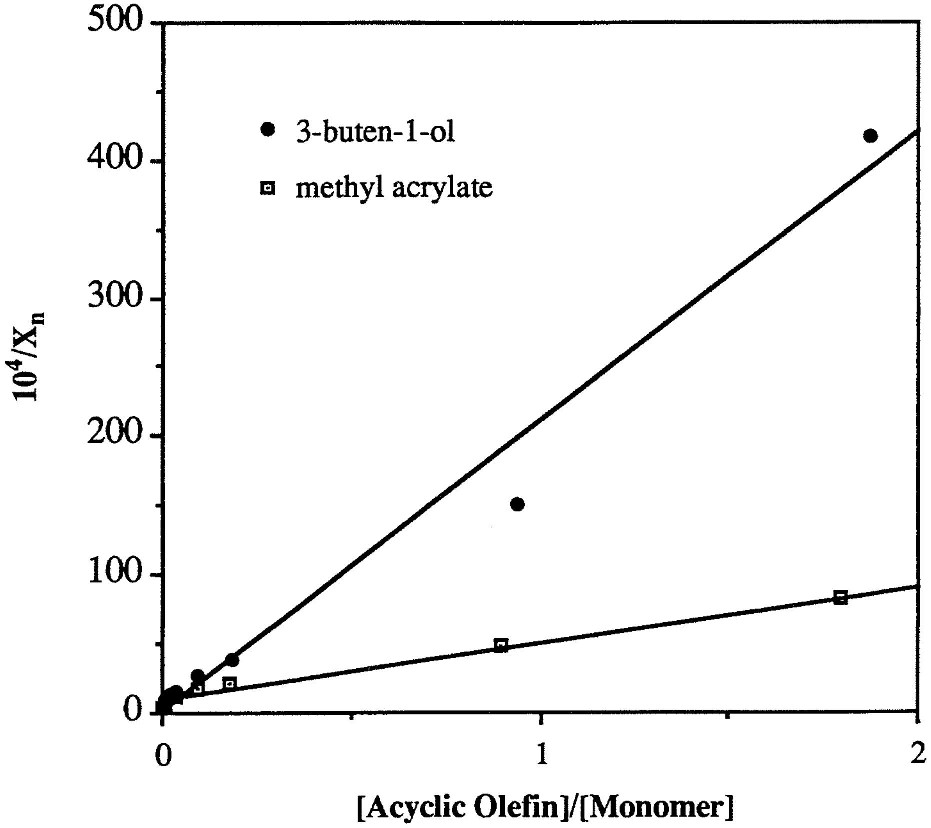


Figure 4. Chain Transfer plots for 3-buten-1-ol and methyl acrylate regulated ROMP of **3** by **1**.

10^{-2} for methyl acrylate and 2.1×10^{-1} for 3-buten-1-ol; these values indicate that 3-buten-1-ol is a more effective molecular weight regulator than methyl acrylate. Although the absolute values of chain transfer constants are unreliable, particularly in cases such as those presented here that involve multimodal molecular weight distributions, comparison of relative values is possible provided that the polymerizations are run under similar conditions.[11] A comparison of the two plots from Figure 3 can be found in Figure 5 and clearly demonstrates the difference in the efficiency of chain transfer for these two acyclic olefins.

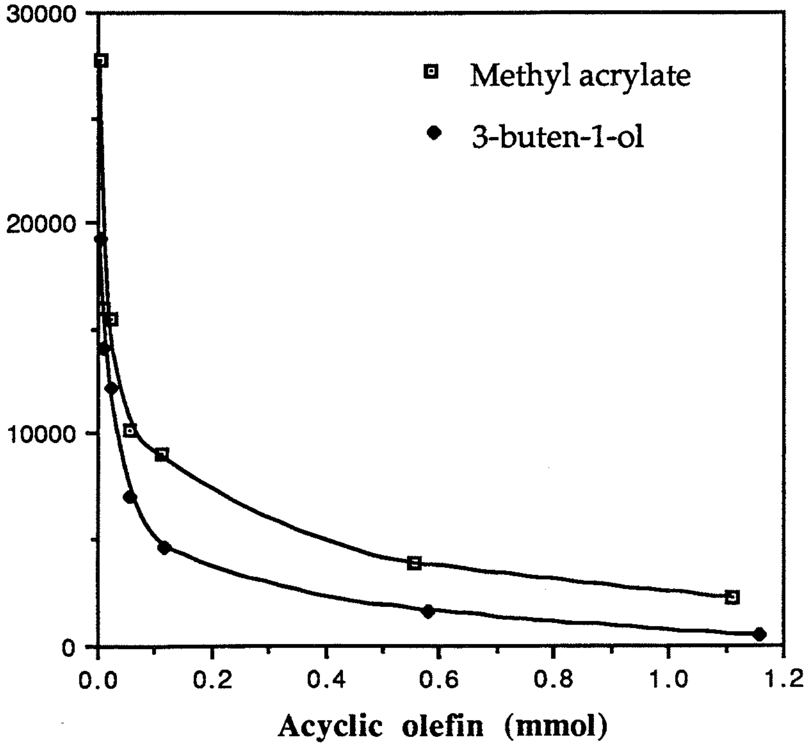
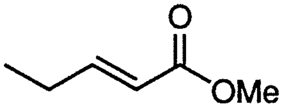
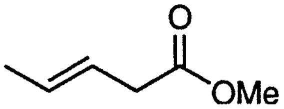
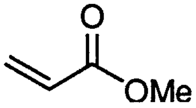
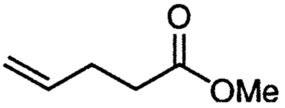


Figure 5. Comparison of the plots of molecular weight (M_n) versus concentration of acyclic olefin for **3** polymerized by **1** in the presence of 3-buten-1-ol and methyl acrylate. The values for no added olefin have not been included in this plot for clarity.[47]

An examination of molecular weight data obtained with a series of acyclic esters as chain transfer agents at constant concentration proves enlightening (Table 1).[45, 47] Interestingly, the reactivity patterns observed with these acyclic olefins parallel that

Table 1. Molecular Weight Regulation by Acyclic Ester Chain Transfer Agents

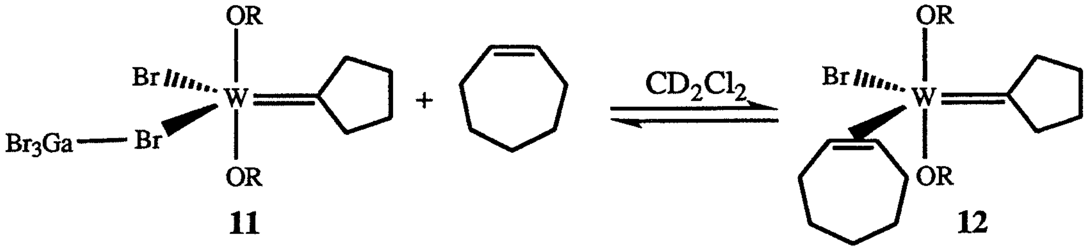
Ester[a]	**M_n**	**M_w**
	37,700	350,000
	12,000	64,000
	3890	13,900
	1100	6610

[a] Polymerizations were performed under the conditions indicated in the Experimental with [Ester]/[**1**] = 50.

which would be predicted from the reactivity of known, well-characterized metal alkylidene complexes with olefins. For example, the debilitating effect of an electron withdrawing group on the ability of an olefin to undergo metathetical cleavage has been observed before in both chain transfer reactions[39, 48, 49] and acyclic self- and cross-metathesis.[41, 43, 50-52] Chain transfer reactivity increases with increasing distance between the olefin and ester functionalities, both in classical systems[39, 50] and in this study (entries 3 and 4). In addition, the greater steric requirements of internal (entry 1) versus terminal (entry 3) olefins impede their reactivity with well-characterized transition-metal-alkylidene complexes such as W(=CH-*t*-Bu)(NAr)$(OR)_2$.[53, 54]

A consideration of both the electronic and steric factors involved in chain transfer efficiency provides a satisfying method for rationalizing the data in Table 1. The ordering of relative reactivities is predicted to be terminal olefins > deactivated terminal olefins > internal olefins > deactivated internal olefins. While the factors influencing the molecular weight data are admittedly complex, the trends observed with the ruthenium catalyst follow this prediction and parallel that of known, well-defined metathesis catalysts.

It is possible that such trends might reflect the ability of the olefin to bind to the metal center (i.e., more electron-rich, less hindered olefins might be expected to coordinate to the catalyst more strongly). This correlation is important to consider since there is strong evidence that prior coordination of the olefin occurs during metathesis. The tungsten-carbene-olefin complex **12**, detected in the reaction of cycloheptene with **11** at 200 K, has been shown to be an intermediate in the ROMP of cycloheptene.[55] Similarly, the higher activity of ruthenium-olefin complexes **4** over **1** indicates that formation of such a species is en route to the active catalyst in the $Ru(H_2O)_6(tos)_2$ system as well.[21]



11

$R = -CH_2CMe_3$

12

This interpretation involving the importance of prior olefin complex formation allows explanations for other trends that have also been observed. First, 3-buten-1-ol might be a more effective chain transfer agent than methyl acrylate, not only because it lacks the electron withdrawing ester functionality adjacent to the double bond, but also because it contains an alcohol funtionality that can chelate to the metal center of the active catalyst. Such chelation is known to occur in complexes of this substrate with the catalyst precursor **1**.[27, 32] Second, styrene is observed to be a relatively ineffective chain transfer agent with the 7-oxanorbornene monomer **2**. This lower activity might be explained by conjugation of the olefin with the aromatic ring; as a result, the electrons in the double bond are expected to be less readily shared and thus styrene's ability to bind to the metal center would be diminished.

This logic can be further extended to explain the results obtained for chain transfer studies with norbornene. When the polymerization of norbornene with $Ru(H_2O)_6(tos)_2$ was run in the presence of 3-buten-1-ol or methyl acrylate as chain transfer agent, very little ring-opened product was formed, and this amount decreased with increasing acyclic olefin concentration. This result may be due to the lower tendency of norbornene to bind to the ruthenium than is displayed by **3**.[56] Norbornene is thus incapable of competing effectively with the stronger binding acyclic olefins, and as a result, the acyclic olefins act instead as inhibitors in much the same way that the unsaturated nitriles did in the 7-oxanorbornene system (*vide supra*). However, when styrene was used as the chain transfer agent with norbornene, efficient molecular weight regulation took place because the monomer could effectively compete with this weaker binding acyclic olefin.

While the ability of the acyclic olefins to bind with **1** itself does not necessarily parallel their ability to bind with the active species, the same patterns appear to be followed and allow an explanation of the incubation time effect discussed above. The 15 min incubation period required for efficient chain transfer at low concentrations of methyl acrylate allows for complete formation of the **1**-methyl acrylate olefin complex prior to polymerization. When this waiting period is decreased, formation of the olefin complex is incomplete, and the polymer formed is of higher molecular weight. As the amount of methyl acrylate is increased, this incubation time becomes less important because the system is swamped with excess acyclic olefin and all the ruthenium becomes complexed more quickly. By the same reasoning, the incubation time is unnecessary for the stronger binding 3-buten-1-ol at all concentrations. While no direct evidence has yet been obtained addressing whether prior coordination of the acyclic olefin is required for chain transfer or whether the acyclic olefin even remains coordinated throughout carbene generation and initiation of polymerization, the results presented here support that either prior coordination of the acyclic olefin or a proximity effect of the dissociated olefin might be important factors in governing efficiency of chain transfer.

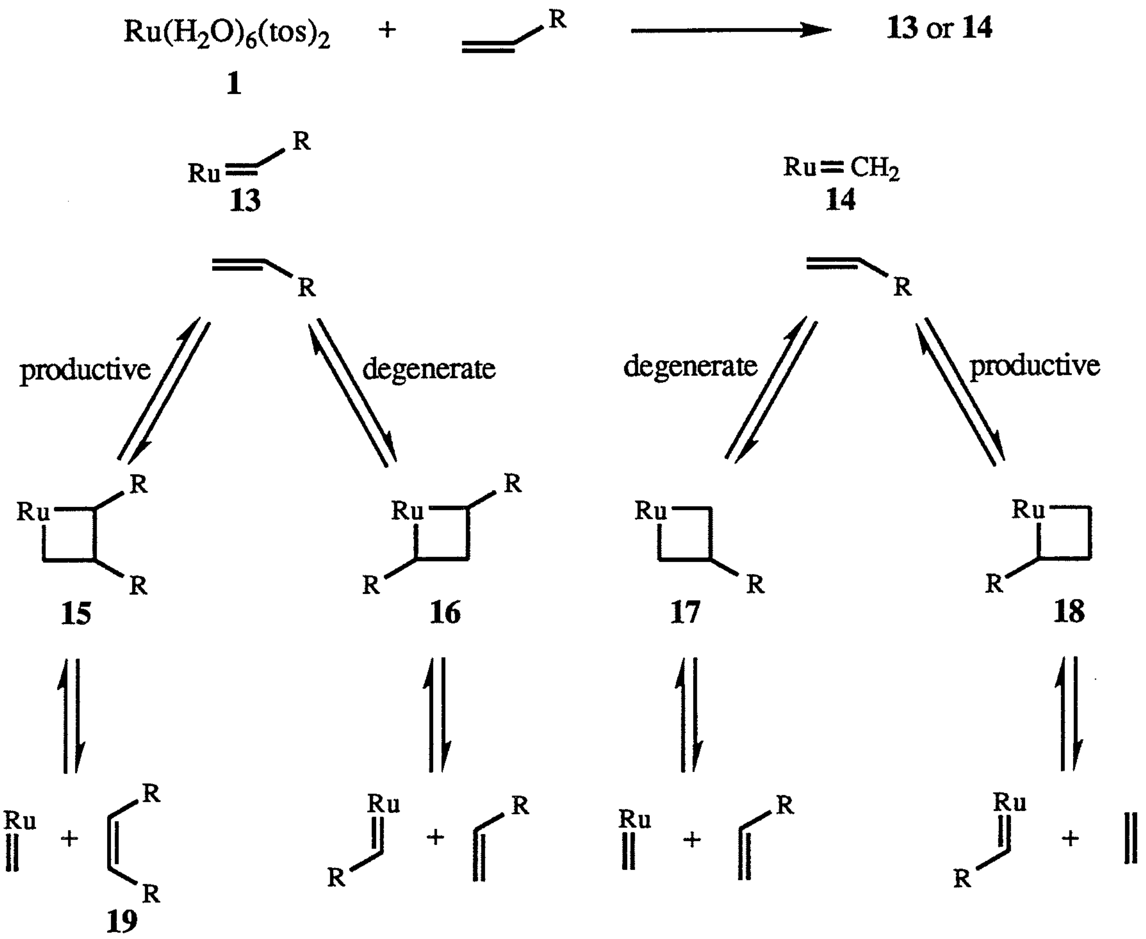
Interaction of $Ru(H_2O)_6(tos)_2$ with Acyclic Olefins

The proposed chain transfer mechanism requires that the acyclic olefin must undergo metathesis by the active chain carrier once initiation has occurred. However, productive metathesis of an acyclic olefin by $Ru(H_2O)_6(tos)_2$ has never been observed. To our knowledge, the only example of the metathesis of an acyclic olefin using a traditional ruthenium catalyst[57] is work by Marciniec and co-workers, who observed the self-metathesis of tris(alkoxy)vinylsilanes and their cross-metathesis with various terminal olefins catalyzed by $RuCl_3 \cdot nH_2O$ and $(PPh_3)_3RuCl_2$.[30, 58-62]

The self-metathesis of a terminal acyclic olefin is depicted in Scheme 6. Either of the two carbenes **13** or **14** may be produced, leading to the metallacyclobutanes **15** and **16** or **17** and **18** respectively. The symmetric internal olefin **19**, the only new species besides ethylene, has never been observed during either the chain transfer studies[26] or during investigations of olefin complexes of $Ru(H_2O)_6(tos)_2$.[63] Although there have been examples of cases in which a less active olefin undergoes metathesis in the presence of a more active olefin (such as norbornene),[49, 64-66] examination of numerous acyclic olefins with $Ru(H_2O)_6(tos)_2$ in the presence of **3** showed no evidence of the productive metathesis product **19**.

These results are not surprising; terminal acyclic olefins are known to undergo degenerate metathesis at a much greater rate than productive metathesis, and the products of productive metathesis are often not observed at all.[11, 12, 54, 67-70] These findings are

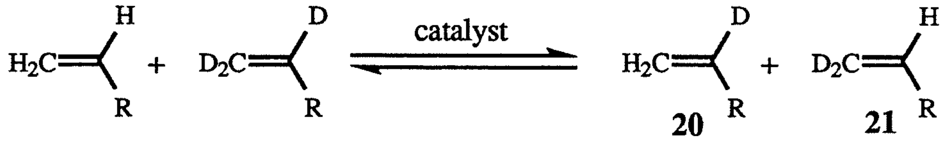
Scheme 6. Self-Metathesis of Terminal Acyclic Olefins



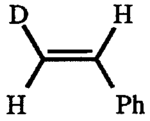
probably due to a combination of steric and electronic effects that favor metallacyclobutane **16** over **15** and **17** over **18**.[50, 53, 54, 67-70] Therefore, the possibility that degenerate metathesis of the acyclic olefin might be occurring in the $Ru(H_2O)_6(tos)_2$ system must be considered.

Degenerate metathesis in other systems has been detected by means of cross-over experiments such as the one depicted in Scheme 7.[68-70] If products **20** and **21** are observed in either the presence or absence of a small amount of **3** as initiator, then degenerate metathesis is occurring. Such a study has been carried out using **1** and

Scheme 7. Crossover Experiment.



styrene-vinyl-1,2,2-d_3 in the presence and in the absence of **3** and investigated by ^{1}H and ^{13}C NMR spectroscopy (Figure 6).[71, 72] In addition to the detection of **20** after 72 hours, the existence of products **22-25** was also confirmed . Although all possible combinations cannot be positively identified, it appears that complete scrambling of the vinylic protons has occurred, leading to products that cannot be explained by metathesis alone. Control tests ruled out the possibility of scrambling occurring in the absence of **1**, as well as from the aromatic ring protons or from the solvent, and lead to the conclusion that alkene activation is likely occurring and that this chemistry may be due to trace amounts of a ruthenium hydride species present in the reaction mixture. Although this scrambling takes place quite slowly (only small amounts of scrambling products were visible after 72 hours), the possibility that degenerate metathesis might still be taking place cannot be ruled out; it can only be stated that if such a process is occurring, it is slower than the scrambling of the isotopic labels. Since styrene is known to be a poor chain transfer agent for **3** with Ru(H_2O)$_6$(tos)$_2$, it is possible that a more active molecular weight regulator such as 3-buten-1-ol or methyl acrylate might undergo degenerate metathesis when initiated with **3** at a rate that is faster than the scrambling.[73]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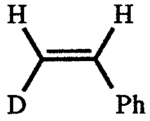
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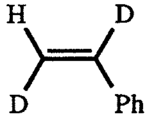
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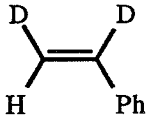
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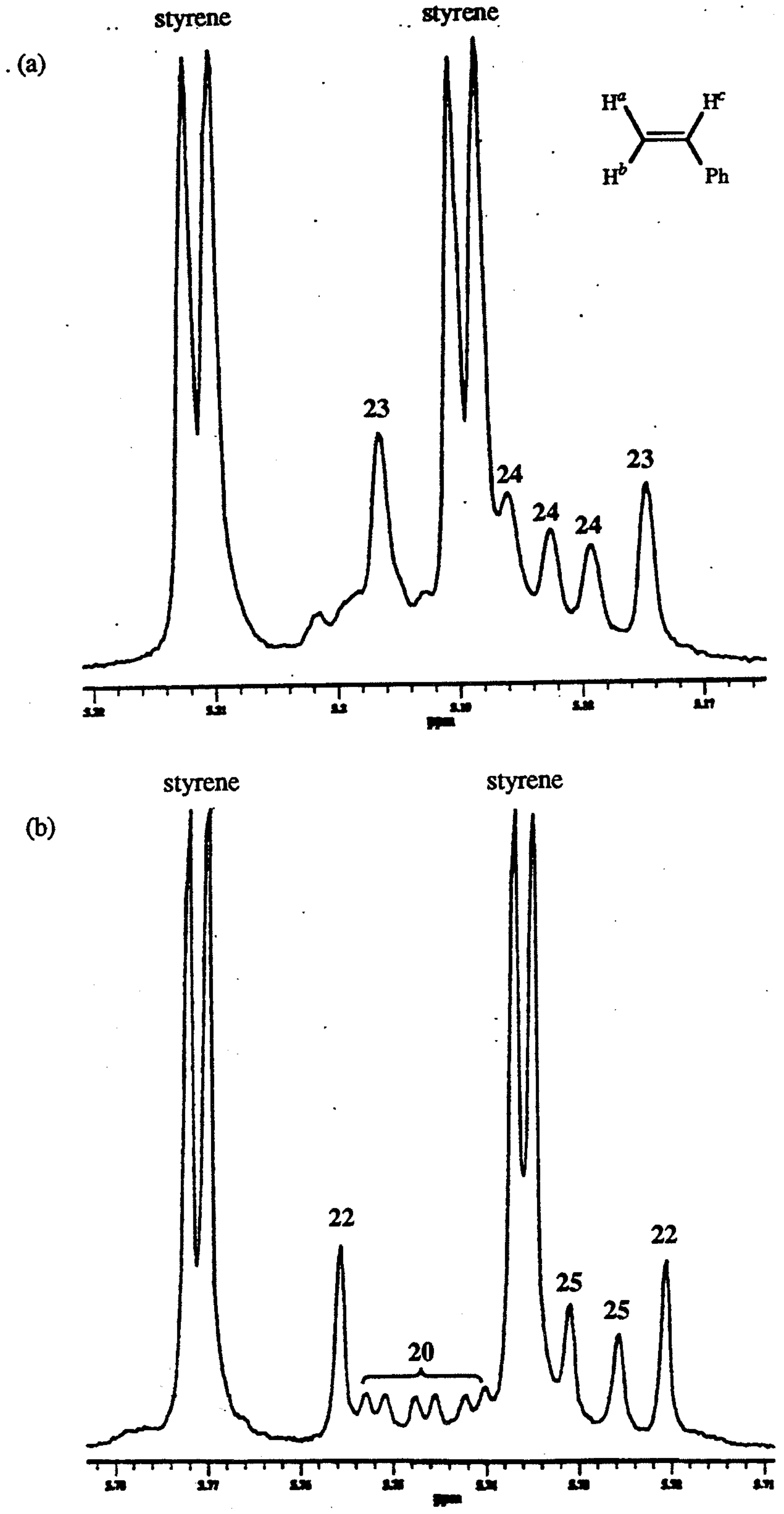
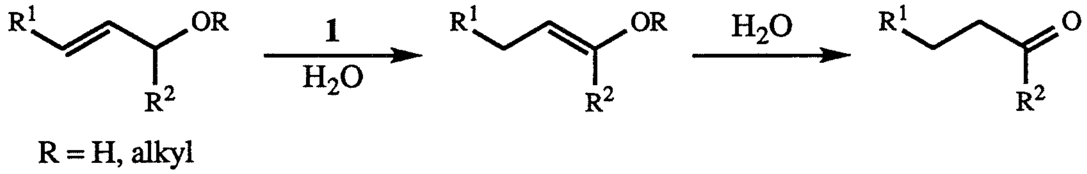


Figure 6. Portions of the ^{1}H NMR spectrum of the reaction mixture produced during the crossover experiment. (a) Resonances for proton *a*. (b) Resonances for proton *b*.[71, 72]

The conclusion that ruthenium hydride species are likely generated during the course of the reaction is quite interesting in light of some recent work in our group. Labeling studies of the isomerization of allylic alcohols and ethers by $Ru(H_2O)_6(tos)_2$ (Scheme 8) indicate that the reaction appears to take place by a modified metal hydride addition-elimination mechanism.[27, 28] While we have no evidence that ruthenium hydride species are actually involved in the metathesis chemistry, we do have two independent pieces of evidence supporting that such ruthenium hydride complexes are quite likely to at least be present in the reaction mixture. Such a conclusion provides some support for the metal hydride mechanism in Scheme 1 above.

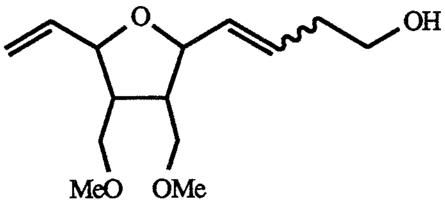
Scheme 8. Isomerization of allylic alcohols and ethers by **1**.



End Group Analysis

In order to further consider the mechanism of ROMP initiation in the group VIII systems, it is important to identify the end groups found on the polymer chains. Although the polymer formed in the absence of added acyclic olefin was of too high a molecular weight to allow direct observation of the end groups, the lower molecular weight oligomers produced during the chain transfer studies did allow detection of end groups due to the added acyclic olefins. ^1H and ^{13}C NMR of the oligomeric samples of **9** obtained by $Ru(H_2O)_6(tos)_2$ in the presence of 3-buten-1-ol and methyl acrylate indicated the presence of both alkylidene moieties ($=CH_2$ and $=CHR$) derived from each of these olefins. Fully assigned two-dimensional ^1H-^1H shift correlation (COSY) NMR spectroscopy has helped establish connectivity between the end groups and the polymer chain.[1, 27, 74]

Further evidence of the connectivity of these groups to the oligomers was obtained by gas chromatography-high resolution mass spectrometry. Analysis by electron ionization (EI) of samples of oligomer prepared in the presence of 3-buten-1-ol failed to reveal parent ion peaks (high-mass peak of only *m/e* = 211);[1, 27] however, chemical ionization (CI) techniques allowed observation of a parent ion peak at *m/e* 257.1753 (MH^+) (calculated 257.1753). This mass has been assigned to the *cis* and *trans* isomers of structure **26**. The mass of *m/e* = 211 observed with EI presumably arises from loss of a $-CH_2CH_2OH$ fragment or loss of a methoxymethyl group.[75] In addition, GC-HRMS has allowed identification of the symmetric dimethylene structure **27** among the reaction products in this system (*m/e* 213.1470 (MH^+)) (calculated 213.1490). The asymmetric structure **28**, from the methyl acrylate regulated polymerization of **3**, was also identified by GC-HRMS (CI) (*m/e* = 271.1545 (MH^+)) (calculated 271.1545) as well as the doubly-ester-capped structure **29** (GC-HRMS (CI) at *m/e* = 329.1593 (MH^+)) (calculated 329.1600). Once again, there is a parallel in known alkylidene catalyzed



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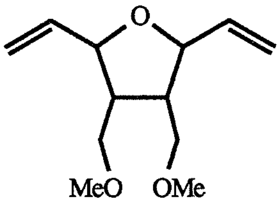

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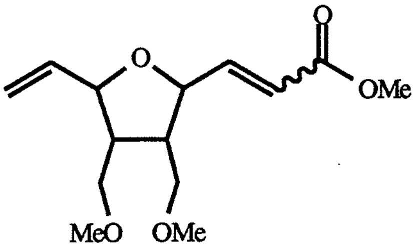
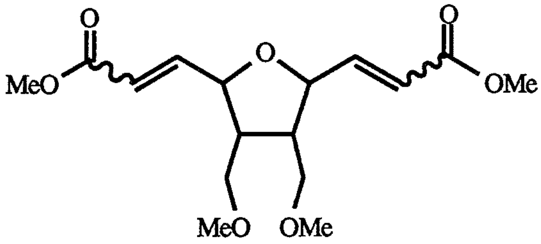


28



29

chemistry. The doubly-ester-capped monomer unit analogous to **29** was also characterized by GC-MS in the $WCl_6/SnMe_4$ catalyzed cross-metathesis of norbornene with dimethyl dihydromuconate.[35] Products **26** - **29** can only be formed by the cross metathesis of the acyclic olefin with the cyclic monomer. This is the first example of metathesis of an acyclic olefin by $Ru(H_2O)_6(tos)_2$. Marciniec's work[30, 58-62] (*vide supra*) represents the only previous example, to our knowledge, of the metathesis of an acyclic olefin using a ruthenium catalyst.[57]

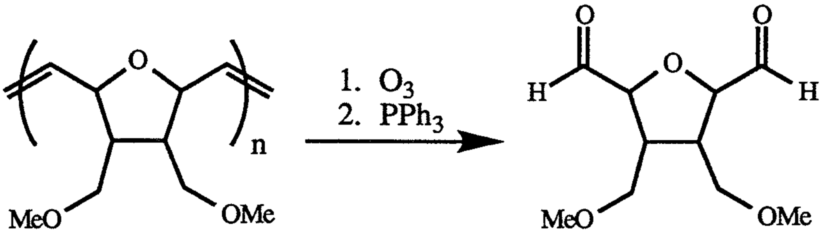
The identification of these cross-metathesis species is also significant, because these products can only be formed if the alkylidenes produced during chain transfer ($Ru{=}CH_2$ and $Ru{=}CHR$, Scheme 5) are themselves active catalysts. This finding, thus, is very good evidence supporting that molecular weight regulation is, in fact, occurring by a true chain transfer mechanism.

Degradation of Oligomeric Mixtures

Unfortunately, studies of the oligomeric mixtures produced in the chain transfer studies have still provided no evidence of end groups that might be formed during initiation. Due to the small percentage of catalyst precursor that is actually initiated,[21] such groups are expected to be present in very small quantities. Only a tiny fraction of the oligomers in a given reaction mixture are actually initiated by the starting carbene compared to the relatively large number produced by a chain-carrying carbene derived from the added acyclic olefin. Detection of such a small amount is not easy and is further complicated by the relatively broad NMR spectra of the polymeric samples, even the lower molecular weight oligomers. In order to help clarify the NMR spectra and better observe the end groups, methods of degrading the oligomeric samples into even smaller pieces were investigated.

Due to the high degree of unsaturation found in the backbone of ROMP polymers, they are particularly good substrates for degradation by ozonolysis.[76] Unfortunately, in the case of **9**, clean degradation of the oligomeric mixture was unsuccessful. Reductive ozonolysis of this compound led to a product (**30**) that appeared to be unstable (Scheme 9). The protons α to the carbonyl in **30** are relatively acidic due to the oxygen in the tetrahydrofuran ring. It is possible that **30** undergoes decomposition before it can be isolated or trapped as an acetal derivative. In fact, very few examples of the ozonolysis of 7-oxanorbornene derivatives have been reported.[77] Oxidative ozonolysis and the Lemieux-Johnson reaction also failed to provide clean product.[78]

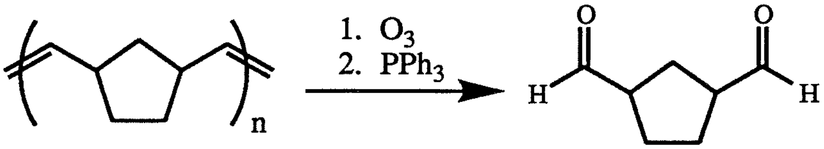
Scheme 9. Ozonolysis of Polymer **9**.



9 **30**

In the case of the **10**, however, clean degradation could be accomplished by ozonolysis followed by a reductive workup with triphenylphosphine (Scheme 10).[79] The product obtained was identical whether starting from the high molecular weight polymer

Scheme 10. Ozonolysis of Polymer **10**.

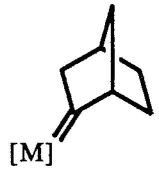
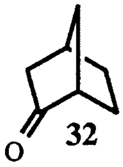
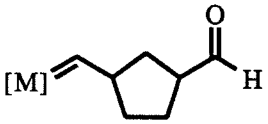
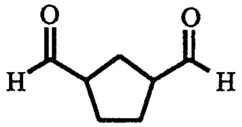
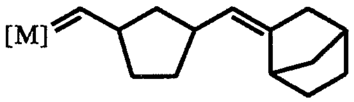
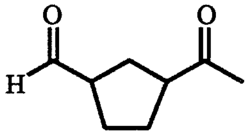
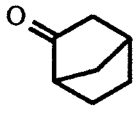


10 **31**

10, the oligomeric samples obtained by chain transfer with styrene, or norbornene itself. Following ozonation of oligomeric samples of **10**, the reaction mixtures were investigated in crude form to avoid losing during purification the small "impurities" due to the initiating end group. These crude reaction mixtures have been examined by ^{1}H NMR and GC/MS, but, to date, the end group that would result from the favored metal hydride mechanism has never been detected.

Table 2 depicts the products that would be expected from reductive ozonolysis of the initiating end groups for each mechanism. The alkene activation, the metal hydride, the norbornyl cation, and the dimerization mechanisms all would require the formation of norcamphor (**32**) as one of the degradation products. The initiating end groups in the water assisted and the metal oxo mechanisms, on the other hand, would give ozonolysis product **31**, identical with that formed by the bulk of the polymer chain. The results presented here, therefore, indicate that if one of the former group of mechanisms is occurring (the alkene activation, the metal hydride, the norbornyl cation or the dimerization mechanism), the amount of initiating end group formed is below the detection limits of the instrumentation utilized. The estimate of less than 1% activation is, in fact, an upper limit, and it is possible that the amount initiated is even less than previously thought. Alternatively, the water-assisted or the metal oxo mechanism might be responsible for the metathesis chemistry.

Table 2. Polymer End Group Ozonolysis Products

Mechanism	Initiating Carbene	Reductive Ozonolysis Product
Alkene activation Metal hydride Norbornyl cation		 **32**
Water assisted Metal oxo		 **31**
Dimerization		 **31** +  **32**

Conclusions

It has been demonstrated that a variety of acyclic olefins are efficient chain transfer agents for the ring-opening metathesis polymerization of **3** by **1** and that the relative chain transfer efficiencies of these olefins parallel trends predicted by a knowledge of established metathesis systems. Chain transfer plots and the observation of individual telechelomers by mass spectrometry provide evidence that molecular weight regulation with acyclic olefins in the aqueous ruthenium(II) system proceeds by a true chain transfer mechanism. Oligomers endcapped with both alkylidene moieties derived from the unsymmetric acyclic olefins (=CH_2 and =CHR) have been identified. Not only do these products represent the first examples of cross metathesis of an acyclic olefin with a cyclic olefin by $Ru(H_2O)_6(tos)_2$, but they also demonstrate that the carbenes resulting from both halves of the olefin (Ru=CH_2 and Ru=CHR) are active.

Although some evidence supporting the presence of ruthenium hydride species in solutions of $Ru(H_2O)_6(tos)_2$ containing acyclic olefins has been obtained, degradation of olgimeric samples has failed to identify the end groups expected from such a mechanism. It must be concluded that either such end groups are formed in a quantity too small to be detected or that initiation occurs by a different mechanism, such as the metal oxo or the water-assisted mechanism.

While the active species in group VIII catalyzed ROMP systems have not yet been directly observed, mounting evidence suggests that they are surprisingly similar to known, well-characterized metal alkylidene species and supports the intermediacy of a ruthenium-alkylidene which is capable of reacting with acyclic as well as cyclic olefins. Such an understanding of these systems is essential for rationally considering methods of extending the activity of such catalysts to low strain cyclic olefins and acyclic olefins. The observation of cross-metathesis products derived from less reactive olefins in a system that has previously been initiated by a strained bicyclic olefin provides an encouraging indication that the development of group VIII catalysts possessing broader activity is possible. Results obtained in this area are presented in the next two chapters.

Experimental

General. All manipulations involving air- and/or moisture-sensitive compounds were carried out using standard high vacuum or Schlenk techniques. Argon was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4Å molecular sieves. Solids were transferred and stored in a nitrogen-filled Vacuum Atmospheres glove box equipped with a MO-40-1 purification train, a DK-3E Dri-Kool conditioner, and a Dri-Cold Freezer.

Instrumentation. NMR spectra were recorded on a JEOL GX-400 (399.65 MHz ^1H, 61.25 MHz ^2H, 100.40 MHz ^{13}C) spectrometer or a GE QE-300 (300.19985 MHz ^1H, 75.49283 MHz ^{13}C) spectrometer. Proton chemical shifts are referenced to internal residual solvent protons. Carbon chemical shifts are referenced to the carbon signal of the deuterated solvents. Gel permeation chromatography (GPC) was performed on either (a) a homemade HPLC instrument employing an Altex model 110A pump, a Rheodyne model 7125 injector with a 100 µL injection loop, three Shodex Styragel size exclusion columns (KF 803, KF 804, and KF 805), and a Knauer differential refractometer with methylene chloride as the eluent (0.5 wt% solution) at a flow rate of 1.0 mL/min. or (b) a Waters Association instrument employing a Waters syphen pump, a 400 µL injection loop, 4 microstygel columns (10^5, 10^4, 500 and 100 in series), and a Waters model 401 differential refractometer with toluene as the eluent (0.25% solution) at a flow rate of 2.04 mL/min.[80] GPC samples were filtered through a 0.5 µm filter prior to injection. The molecular weights are referenced to narrow dispersity polystyrene samples (Polysciences). High resolution GPC was graciously performed by Prof. W. Risse of the Phillips Universitat, Marburg, Germany. Low-resolution mass spectrometry analyses were performed on a Hewlett-Packard model 5970 mass selective detector in conjunction with a Series 5890 GC equipped with a 15 m SE-30 capillary column. High-resolution mass spectrometry was performed by Dr. F. Kitson and Dr. R. Zubyk at the mass spectrometry facilities at E. I. DuPont de Nemours and Co, Inc., Wilmington DE. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FT-IR. Elemental analysis was performed at the analytical facilities of the California Institute of Technology. Ozone was generated using a Welsbach ozonator.

Materials. Water was purchased from Aldrich (HPLC grade) and degassed prior to use. Methanol used in polymerizations was also degassed prior to use. Methylene chloride used in ozonolysis and reagent grade ether were used without any purification. Chloroform-*d* and benzene-d_6 were purchased from Cambridge Isotope Laboratories and used as received. Deuterium oxide and methanol-d_4 were purchased from Aldrich or Cambridge Isotope Laboratories and degassed prior to use. Styrene-vinyl-1,2,2-d_3 was purchased from Cambridge Isotope Laboratories and used as received. 3-Buten-1-ol was purchased from Aldrich and purified by passage through reagent grade alumina before use. Methyl acrylate was purchased from Aldrich and stored degassed in the dark at 0 °C in a dry glass vessel equipped with a Teflon valve closure after being vacuum transferred from calcium hydride. Styrene (MCB) was stirred over alumina overnight, vacuum transferred, degassed, and stored under argon in the dark at 0 °C. Methyl 2-pentenoate, methyl 3-pentenoate, and methyl 4-pentenoate were prepared from the corresponding carboxylic acids (Aldrich) by standard procedures. Monomer **3**, 5,6-*exo*-bis(methoxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene, was prepared by literature procedures.[21] Norbornene was purchased from Aldrich and refluxed over sodium and distilled or vacuum transferred prior to use.[81] Rocco Paciello, Alto Benedicto, and Dominic McGrath are gratefully acknowledged for initial samples of $Ru(H_2O)_6(tos)_2$ (**1**). All samples of $Ru^{II}(H_2O)_6(tos)_2$ prepared in these laboratories and at DuPont were according to the literature procedure.[82, 83]

Polymerization of 3. In a Schlenk flask equipped with a magnetic stir bar, $Ru(H_2O)_6(tos)_2$ **1** (6 mg, 0.011 mmol) was dissolved in H_2O (1.1 mL) and degassed. Monomer **3** (100 mL, 0.62 mmol, 56 equiv) was added and the reaction was left to proceed at 55 °C for one hour. The reaction mixture turned cloudy in less than one minute, became increasingly viscous, and eventually stopped stirring. The supernatant yellow liquid was drawn off the precipitated white polymer and concentrated to a yellow-brown solid (olefin complex **4**). The polymer was dissolved in a minimum of ethanol (~10 mL, degassed), stirred until completely dissolved (12 h), and precipitated in degassed H_2O (75 mL). Polymer **9** was collected and dried under vacuum. (Quantitative yield). ^1H NMR ($CDCl_3$): δ 5.78 (b), 5.50 (b), 4.55 (b), 4.18 (b), 3.38 (b), 3.25 (b), 2.20 (b). GPC (CH_2Cl_2): $M_n = 125{,}000$; $M_w = 272{,}000$; PDI = 2.17.

Polymerization of Norbornene. $Ru(H_2O)_6(tos)_2$ **1** (6 mg, 0.011 mmol) was dissolved in degassed methanol (2 mL) in a teflon-stoppered reaction vessel. Norbornene (60 mg, 0.64 mmol, 58 equiv) was added and the reaction was left to proceed in the sealed vessel under argon at 55 °C for 24 hours. The reaction mixture turned cloudy in about ten minutes, became increasingly viscous, and eventually stopped stirring. The supernatant yellow liquid was drawn off the precipitated white polymer. Polymer **10** was washed six times with H_2O (2 mL), six times with ethanol (2 mL), dried under vacuum, and stored under inert atmosphere (yield 80-85%). ^1H NMR ($CDCl_3$): δ 5.32 (b), 5.18 (b), 2.78 (b), 2.40 (b), 1.82 (b), 1.72 (b), 1.33 (b), 1.02 (b). GPC (CH_2Cl_2): $M_n = 285{,}000$; $M_w = 650{,}000$; PDI = 2.28.

Polymerization of 3 in the Presence of Chain Transfer Agent. A Schlenk flask charged with **1** (6 mg, 0.011 mmol), acyclic olefin (0.5 - 200 equiv), and H_2O (1.1 mL) was heated under argon at 55 °C for 15 minutes during which time the solution turned bright yellow, indicating formation of the olefin complex **4**. 7-oxanorbornene monomer

3 (100 mL, 0.62 mmol, 56 equiv) was added to the solution all at once via syringe, and the reaction was left at 55 °C for 1-2 hours. At very low concentrations of chain transfer agent, polymer precipitated out of the reaction mixture and was washed with water and dried under vacuum. At higher concentrations, the cloudy solution was allowed to cool to room temperature, extracted three times with Et_2O (1 mL), dried over $MgSO_4$, filtered, and concentrated to a clear viscous oil (yield 65-95%). (Longer reaction times may be allowed in order to increase yields when large excesses of regulator are used.) ^1H NMR ($CDCl_3$): δ 5.78 (b), 5.50 (b), 4.55 (b), 4.18 (b), 3.38 (b), 3.25 (b), 2.20 (b).

Polymerization of Norbornene in the Presence of Acyclic Olefin. A Kontes reaction vessel charged with $Ru(H_2O)_6(tos)_2$ **1** (6 mg, 0.011 mmol), acyclic olefin (10 - 100 eq), and methanol (2 mL) was heated at 55 °C for 15 minutes. Norbornene (60 mg, 0.64 mmol, 58 equiv) was added all at once to the resulting yellow solution, and the reaction was heated for 24 hours in the sealed vessel under argon. Methanol was removed under vacuum, and the brown residue was partitioned between H_2O (1 mL) and Et_2O (1 mL). The aqueous layer was washed 3 times with Et_2O (2 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated to a yellow-brown film (yield 5-25% impure product). ^1H NMR ($CDCl_3$): δ 5.32 (b), 5.18 (b), 2.78 (b), 2.40 (b), 1.82 (b), 1.72 (b), 1.33 (b), 1.02 (b).

Polymerization of Norbornene in the Presence of Styrene for Degradation Studies. A Schlenk flask was charged with **1** (6 mg, 0.011 mmol) and methanol (0.5 mL). In a separate vial, norbornene (75 mg, 0.80 mmol, 72.4 equiv) and styrene (100 µL, 1.06 mmol, 96.0 equiv) were dissolved in 0.5 mL methanol. The olefin solution was added all at once to the Schlenk flask containing the ruthenium solution, and the reaction mixture was left to stir at 55 °C for 48 h. Methanol was removed under vacuum and the resulting oil was partitioned between CH_2Cl_2 (1 mL) and H_2O (1 mL). The aqueous layer was washed 4 times with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, filtered, concentrated, and dried under vacuum. The entire sample was carried through to the ozonolysis step.

Ozonolysis of Oligomers of 10. The entire product mixture from the preceding reaction was dissolved in CH_2Cl_2 (7 mL) in a 3-neck round-bottom flask equipped with a stir bar, gas inlet and a drying tube. The reaction mixture was cooled to -78 °C in a dry ice/acetone bath; a trace of Sudan III indicator (Aldrich) was added and the reaction mixture was ozonylized until disappearance of the red color. Nitrogen was bubbled through the reaction mixture for 15 min. Triphenylphosphine (200 mg, 0.76 mmol, 0.95 equiv to norbornene) was added and the reaction mixture was allowed to warm to room temperature slowly overnight. The solution was concentrated to a mixture of ozonylized product, triphenylphosphine oxide, and unreacted triphenylphosphine. The crude reaction mixture was analyzed to avoid losing the trace amounts of end group during purification. **31:** ^1H NMR ($CDCl_3$): δ 9.61 (d, 2H), 2.72 (m, 2H), 2.15 (m, 1H), 1.87 (m, 1H), 1.75 (m, 4H). GC/MS: *m/e* 126 (M^+), 108, 79, 65, 57.

Crossover Experiment with Styrene and Styrene-vinyl-1,2,2-d_3. An NMR tube charged with **1** (3 mg, 0.0054 mmol), styrene (3.5 μL, 0.030 mmol, 5.6 eq), styrene-vinyl-1,2,2-d_3 (3.5 μL, 0.030 mmol, 5.6 equiv), and CD_3OD (0.5 mL) was heated to 55 °C and followed by ^1H and ^{13}C NMR spectroscopy over a period of 72 h. A second NMR tube that also contained **3** (1 μL, 0.0062 mmol, 1.1 equiv) was prepared and monitored simultaneously. Control tests included running similar reactions in the absence of **1**, **3**, styrene, and styrene-vinyl-1,2,2-d_3.

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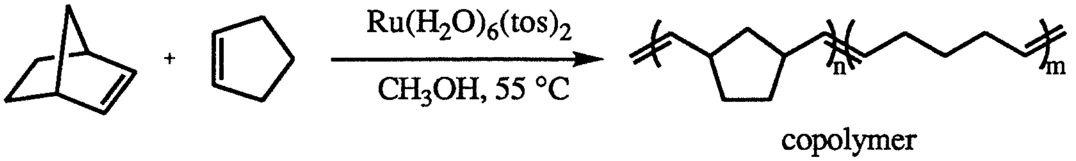
Chapter 3

Initiation of Ring-Opening Metathesis Polymerization in Protic Media. Extension of $[Ru(H_2O)_6]^{2+}$ Catalyzed Polymerizations to Less-Strained Cyclic Monomers

Introduction

The preceding chapter described mechanistic studies of the $Ru(H_2O)_6(tos)_2$ (**1**) catalyzed ring-opening metathesis polymerization of strained bicyclic olefins. The results demonstrate that molecular weight regulation with acyclic olefins in this system appears to proceed by a true chain transfer mechanism. The reaction products indicate that chain-carrying species derived from the acyclic olefin are produced and that the chemistry of these propagating species closely parallels that known for well-characterized metal alkylidene/metallacyclobutane metathesis systems.

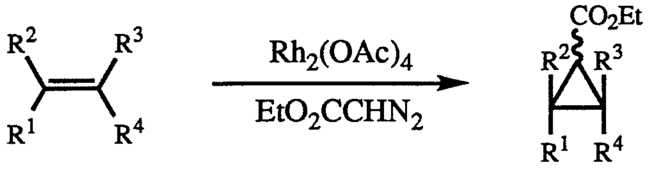
In the course of the mechanistic studies, products were identified whose formation could only be explained by invoking cross-metathesis of less reactive acyclic olefins with highly active cyclic olefins, indicating that once the active species has been generated, it can react with less-strained double bonds. These results suggested that if it were possible to directly generate reactive alkylidene ligands on low-valent ruthenium complexes such as **1**, metathesis catalysts of broader activity could be prepared. In fact, this approach has been explored to some extent previously. Encouraging results in our laboratories have shown that **1** is capable of ring-opening cyclopentene in the presence of norbornene to generate a random copolymer of the two monomers (Equation 1).[1]



(1)

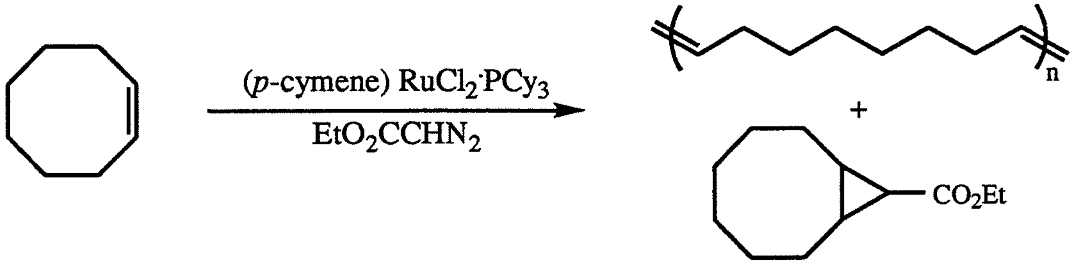
Porri and coworkers have reported similar results copolymerizing cyclooctene and cyclopentene with norbornene using $[(COE)_2IrCl]_2$ (COE = cyclooctene) and several related iridium catalysts. The copolymers are obtained in moderate to low yields, the amount decreasing as the ratio [cycloolefin]/[norbornene] is increased. The presence of ring-opened cyclooctene and cyclopentene units was established by IR and NMR spectroscopy and confirmed by degradation of the polymers by ozonolysis. Although $[(COE)_2IrCl]_2$ is incapable of metathesizing acyclic olefins on its own, in the presence of norbornene, self-metathesis of 1- and 2-pentene is observed, in addition to cross-metathesis with the bicyclic olefin.[2-4]

Although these results are very encouraging, it would be desirable to find routes to prepare homopolymers of monocyclic olefins. Only limited success has been achieved in this area. $[(COE)_2IrO_2CCF_3]_2$ has been found to be an inefficient catalyst for the ROMP of cyclooctene and cyclopentene at 50 - 60°C, polymerizing these monomers in ~1% yield.[2] The concept of using initiators to generate metal carbenes *in situ* has been investigated to some extent. This is a common practice in cyclopropanation chemistry; diazo compounds, in particular ethyl diazoacetate, are frequently used as the stoichiometric carbene source in metal catalyzed cyclopropanation reactions (Equation 2). These reactions are believed to proceed by metal catalyzed decomposition of the diazo compound to generate a metal carbenoid intermediate that is the active catalytic species.[5-8]



(2)

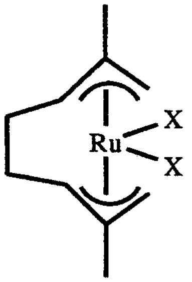
A similar approach has been investigated with ROMP chemistry as well. Several ruthenium complexes, including $[(p\text{-cymene})RuCl_2]_2$ and $(PPh_3)_3RuCl_2$, have been reported to give low yields (<8% conversion for all complexes except $(p\text{-cymene})RuCl_2 \cdot PCy_3$, which gave 25%) of polyoctenamer in neat olefin in the presence of ethyl diazoacetate (Equation 3). In most cases, continuous addition of the diazo compound is necessary to sustain polymerization, and large amounts of cyclopropanated product (up to 99%) are obtained. Only in the case of $(p\text{-cymene})RuCl_2 \cdot PCy_3$ are



(3)

cyclopropanation products not observed; this system therefore only requires a catalytic amount of the diazo initiator.[9, 10]

Other initiators have also been used with some success. Allylic ruthenium catalysts **2** are reported to be inactive with low-strain cyclic monomers until treated with



X = Cl, O_2CCF_3

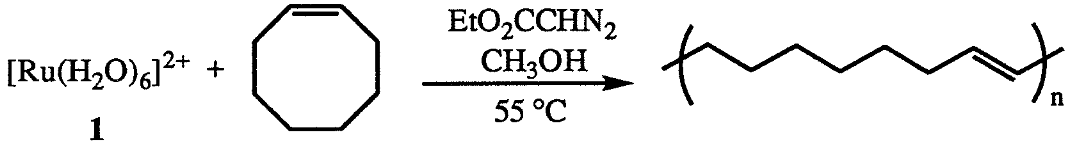
2

H_2, after which polypentenamer (20-25% yield) can be obtained. Surprisingly, this system is not active for the polymerization of other cycloolefins, such as cyclooctene.[2, 4] In a related study, iridium and ruthenium catalysts prepared by activation of a variety of precursors with trifluoroacetic acid could be used to prepare polypentenamer and polyoctenamer.[11] Although the exact role of the hydrogen and the trifluoroacetic acid is unknown, these molecules are clearly involved in initiation in some manner.

In this chapter, we report the successful generation of an active ruthenium catalyst system based on **1** using carbene precursors in protic media and the polymerization of less reactive monomers, such as cyclooctene and cyclopentene, which are not normally polymerized by group VIII ROMP catalysts. The results obtained suggest that the bicyclic structure of the norbornene derivatives is only important for catalyst generation and is not essential for propagation.

Results and Discussion

Our strategy involved the reaction of $Ru^{II}(H_2O)_6(tos)_2$ **1** with small molecules that could serve as precursors to alkylidene or vinylidene ligands in the presence of cycloolefins in protic media. Small molecules such as diiodomethane, propylene oxide, *tert*-butylacetylene, and ethyl diazoacetate (EDA), were screened using cyclooctene as the substrate. In methanol using **1** and EDA, the ROMP of both cyclooctene (Equation 4) and cyclopentene was observed. A ring-opened structure was confirmed by both ^1H and ^{13}C NMR spectroscopy. ^{13}C NMR spectroscopy indicated a *cis*/*trans* ratio of approximately 1:2.3 for polyoctenamer and 1:3.2 for polypentenamer.[12]



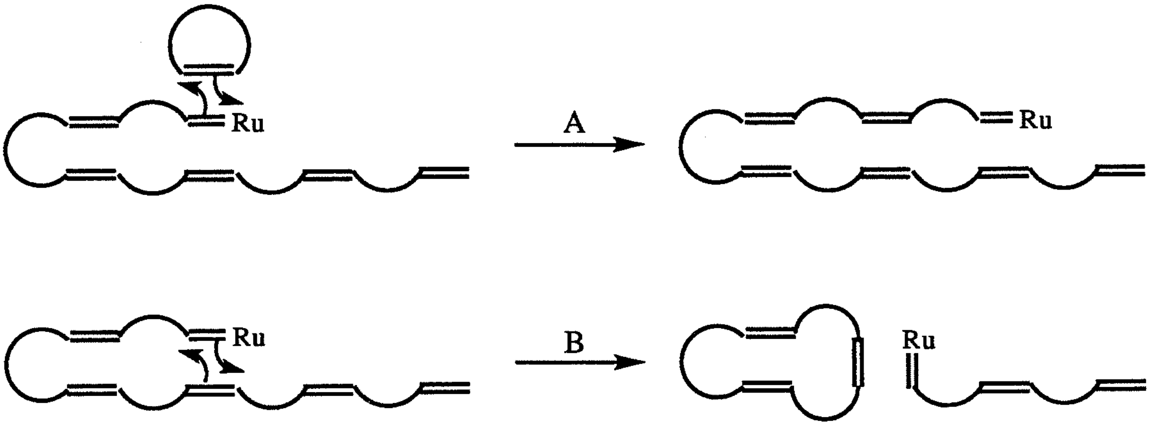
(4)

The choice of solvent appeared to be important in these reactions. Initial investigations in 5 % (v/v) H_2O/THF failed to produce any polymeric product. Attempts at running the reaction in longer chain alcoholic solvents (ethanol, *n*-butanol, *t*-butanol, and hexyl alcohol) to increase solubility of the organic substrates were accompanied by a decrease in the solubility of **1** and proved to be less satisfactory.

Control experiments have shown that both **1** and EDA are necessary for polymerization activity with unstrained cycloolefins in methanol. In contrast to the [(*p*-cymene)$RuCl_2$]$_2$ system,[10] cyclopropanation products have not been observed by either capillary GC or ^1H NMR under typical polymerization conditions.[13] Little cyclopropanation would be expected under the conditions employed because metal-catalyzed carbene coupling normally predominates when the diazo compound is added quickly (i.e., is present in relatively high concentration).[5, 14, 15] In fact, traces of diethyl maleate and diethyl fumarate, the coupling products of EDA, have been detected by ^1H NMR in the polymerization mixtures. Reaction of cyclooctene with EDA in the presence of complexes such as $[Pd(CH_3CN)_4](BF_4)_2$, $[(COD)RhCl]_2$ or $Rh_2(OAc)_4$, which would be expected to act as carbene coupling and/or cyclopropanation catalysts,[16] yielded no polymer.

During the course of the polymerization using the system **1**/EDA/MeOH, a small amount of polymer, which was clean by ^{13}C and ^1H NMR spectroscopy, precipitated from the solution. The yield of polymer isolated in this manner was quite low (5-15%). This is partially due to the polymer/ring equilibrium for this system.[17, 18] As the reaction proceeds, the propagating carbene has the option of reacting with a new molecule of monomer to add another ring-opened unit onto the growing polymer chain (pathway A) or bending back on itself and reacting with an acyclic olefin on the polymer backbone to generate a cyclic oligomer (pathway B) (Scheme 1). Above a certain minimum starting monomer concentration (the critical concentration), the absolute concentrations of the individual cyclic oligomers at equilibrium are constant; therefore, the amount of high polymer produced increases as the initial monomer concentration is increased. Below this critical dilution, no linear polymer is formed.[17-19] Our polymerization system is limited by the solubilities of the components involved. While **1** is only soluble in water and methanol, cyclooctene is clearly most soluble in organic solvents; thus a homogeneous system in methanol with concentrations of cyclooctene high enough to give

Scheme 1. Formation of Cyclic Oligomers During ROMP Chemistry.



good polymer yields has proved difficult to achieve. At attainable concentrations, ~0.6 M, the theoretical yield of high polymer at equilibrium is estimated to be ~60%.[18]

When the solvent was removed from the remainder of the reaction mixture, which was generally a heterogeneous mixture of precipitated, swollen polymer in a viscous liquid, an additional 5-15% yield of product was obtained. Any remaining unreacted cycloolefin was removed under vacuum along with the solvent. It has been demonstrated for metathesis systems at low initial monomer concentrations that only cyclic oligomers are formed early in the reaction, and polymer is not observed to form until the equilibrium concentration of each cyclic species is exceeded.[17, 18] The low yields and disproportionately small quantity of high polymer in the **1**/EDA/MeOH system indicate that equilibrium is not reached before the catalytic species becomes inactive. Similar to the (*p*-cymene)$RuCl_2$•PCy_3 system in which no cyclopropanation products were formed (and in contrast to the [(*p*-cymene)$RuCl_2$]$_2$ system),[10] addition of more EDA during the course of the polymerization did not result in significantly increased yields of polymer.

In all cases, the product isolated from the methanol solution has proved difficult to redissolve. All polymer purification techniques attempted to date, including removal of ruthenium by passage through silica or alumina, centrifugation, or complexation with

EDTA-containing Amberlite resin IRD-718, have failed to isolate this portion of the product cleanly. Poorer solubility due to enhanced crystallinity of polyoctenamer upon drying has been noted previously; however, the extremely poor solubility observed implies crosslinking. Sonication of the reaction mixture at 55 °C overnight resulted in formation of precipitated polymer that was insoluble in all common solvents. Crosslinking of the material likely occurred in this case as well.

As expected for polymerizations of cyclooctene below the critical concentration, a representative GPC trace of the residue after polymerization was distinctly bimodal, consisting of a mixture of cyclic oligomers and higher molecular weight polymer (polyoctenamer, total sample, M_n ~2750, M_w ~12,500, PDI ~4.5) (Figure 1). In some cases, better resolution of the lower molecular weight peak indicated the existence of several different oligomeric species. Similar GPC traces were obtained when the polymerization was carried out using a traditional co-catalyst system ($WCl_6/SnMe_4$) or a well-defined metal alkylidene ($Mo(NAr)(OC(CF_3)_2CH_3)(=CH\text{-}t\text{-}Bu)$) as the catalyst.

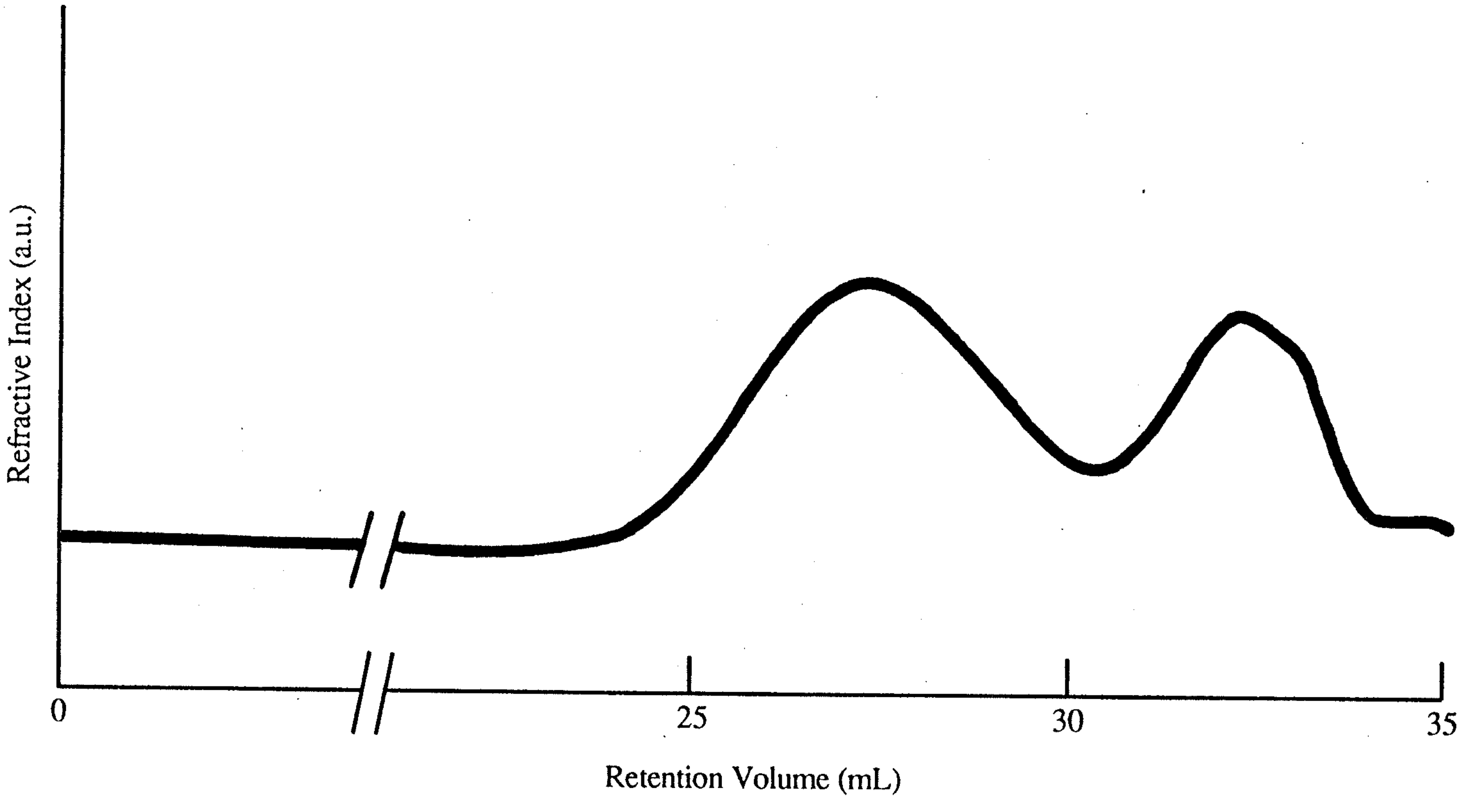
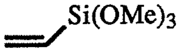


Figure 1. Gel permeation chromatograph of crude polymerization product. ([COE] = 0.6 M, [**1**] = 0.011 M) Total sample, Mn ~2750, Mw ~ 12,500, PDI ~4.5.

Ruthenium(III) complexes $Ru(H_2O)_6(tos)_3$ and $RuCl_3{\cdot}nH_2O$ have not proved to be effective polymerization catalysts in the presence of EDA under the same reaction conditions. The tetramer $[Cp^*RuCl]_4$ also failed to produce polymer when treated with EDA in neat cyclooctene; however when the reaction was run in the presence of P-*i*-Pr_3, a trace of ring-opened product was formed.[20] These results are summarized in Table 1.

Table 1. Polymerization of Low-Strain Cyclic Monomers Using Various Catalysts and Initiators.[a]

	none	EDA	TMS-CHN_2	CH_2N_2	
1/MeOH	–	‡	–	–	‡
$Ru(H_2O)_6(tos)_3$/MeOH	–	–			+
$RuCl_3{\cdot}nH_2O$/MeOH	–	–			
$[Cp^*RuCl]_4$	–	–	–		
$[Cp^*RuCl]_4$/P-*i*-Pr_3	–	+	–		
$[Cp^*RuCl]_4$/PCy_3	–	–	+	–	

[a] - indicates that no ring-opened product was formed.
+ indicates that a trace of ring-opened product was observed by ^1H NMR.
‡ indicates that ring-opened product was isolated.

In addition to EDA, a number of other potential initiators were also investigated. Other diazo compounds studied to date, diazomethane and trimethylsilyl diazomethane, have not yielded effective catalyst systems in the presence of **1** (Table 1). Although metal hydride[21, 22] and metal oxo[23] species have been proposed as intermediates in group VIII ROMP systems, potential hydride (*p*-toluenesulfonic acid and $NaBH_4$[24]) and oxo sources (iodosobenzene, 4-methylmorpholine *N*-oxide, H_2O_2, and NaOCl) were ineffective at promoting the reaction. A trace of impure ring-opened product was detected when trifluoroacetic acid, which has been employed successfully in certain iridium systems,[11] was added to reaction mixtures of **1** and cyclooctene.

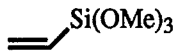
Other potential initiators investigated included molecules such as diiodomethane,[25, 26] propylene oxide,[26, 27] *tert*-butylacetylene,[28] diphenylcyclopropene,[29] and vinyltrimethoxysilane[30] that might serve as carbene sources or rearrange to an alkylidene or vinylidene ligand in the presence of **1**. Although diphenylcyclopropene has been used to successfully generate an isolable ruthenium carbene upon reaction with $(PPh_3)_3RuCl_2$,[29] it failed to initiate polymerization of low-strain cycloolefins with **1**. This is not surprising, since the isolated carbene is itself only active for the polymerization of strained bicyclic olefins.[31, 32] However, in the presence of PPh_3, trace amounts of ring-opened product were detected when diphenylcyclopropene was used as the initiator. Of the other systems examined, only the vinyltrimethoxysilane initiator produced a small amount of ring-opened product. This finding is of interest in light of the fact that vinyltriethoxysilane can be cross-metathesized with olefins by ruthenium complexes, such as $RuCl_3 \cdot nH_2O$ and $(PPh_3)_3RuCl_2$; this is an unusual example of an acyclic olefin metathesized by a traditional ruthenium system in the absence of any added initiator.[30]

Polymerization reactions have also been screened in the presence of coordinating molecules that might react with **1** to create a ligand environment better able to stabilize a metal carbene. Polyoctenamer could be isolated using **1** and EDA in methanol in the presence of one equivalent of $PPh_2(C_6H_4SO_3Na \bullet H_2O)$ (**3**) (*cis*/*trans* ≈ 1.7) or $PPh(C_6H_4SO_3Na \bullet H_2O)_2$ (**4**) (*cis*/*trans* ≈ 1). Complex **1** is known to bind aromatic compounds to form π-bonded complexes,[33] thus these sulfonated phosphine systems may bear similarities to the $[(p\text{-cymene})RuCl_2]_2$ system.[9, 10] For example, contrary to the observation for the $Ru(H_2O)_6(tos)_2$-catalyzed polymerization, traces of cyclopropanation product were observed when the sulfonated phosphines were present. Unlike the parent system, when **3** or **4** was added to the **1**/EDA reaction mixture run in 5% (v/v) H_2O/THF instead of methanol, a trace of ring-opened product was observed. Neither the sulfonated triphenylphosphines nor other bases, such as pyridine, tricyclohexylphosphine, trimethylphosphine, or triethylamine, promoted polymerization in conjunction with the remaining potential initiators. Table 2 summarizes these results.

The active system **1**/EDA/MeOH was investigated to some extent with other substrates. Functionalized acyclic olefins (methyl acrylate, methyl-3-butenoate, methyl-2-pentenoate, methyl-3-pentenoate, and methyl-4-pentenoate) were not observed to undergo productive metathesis. Likewise, functionalized cyclic alkenes, 5-cyclooctenol and *trans*-cycloocten-5,6-diol also failed to polymerize under the reaction conditions.

Presumably **1** catalyzes the decomposition of EDA to yield a ruthenium carbene of the type $[Ru]=CHCO_2Et$, although attempts to observe this active species by ^1H NMR have failed, even at low temperatures. This result is not unexpected since **1** does not have a ligand environment that would be predicted to stabilize the metal carbene. However, a ruthenium carbene generated by the reaction of EDA with $(PPh_3)_3RuCl_2$ has been observed. This species showed a ^1H NMR resonance (triplet) at 17.92 ppm compared with a resonance of 17.94 ppm for the structurally characterized carbene prepared from $(PPh_3)_3RuCl_2$ and diphenylcyclopropene.[29] There was a second alkylidene resonance (doublet) at 13.95 ppm, which was presumably due to a monophosphine complex. These carbenes were unstable in solution at room temperature and decomposed within about 30 minutes of preparation; however, the downfield carbene has been isolated, and it appeared to be stable in the solid form at -20 °C. Although both of these isolated ruthenium systems generated from $(PPh_3)_3RuCl_2$ polymerized norbornene, neither was active for the polymerization of unstrained cyclic olefins. Apparently, the ligands present in the isolated systems stabilize the carbene enough such that only strained rings react. Further details of this isolated carbene and of several related systems also prepared from diazo compounds are the subject of Chapter 5.

Table 2. Polymerization of Low-Strain Cyclic Monomers Using **1** under Various Conditions.[a]

	none	CH_2I_2		*t*-Bu—≡	EDA		
1/THF/H_2O	—	—	—	—	—		
1/MeOH	—	—	—	—	‡	—	‡
1/PPh_3/MeOH or CH_2Cl_2					+		
1/**3**/THF/H_2O		—	—	—	+		
1/**3**/MeOH					‡		
1/**4**/THF/H_2O		—	—	—	+		
1/**4**/MeOH					‡		
1/pyridine/THF/H_2O		—	—	—	—		
1/PCy_3/THF/H_2O		—	—	—	—		
1/PMe_3/THF/H_2O		—	—	—	—		
1/Et_3N/THF/H_2O		—	—	—	—		

[a] - indicates that no ring-opened product was formed. + indicates that a trace of ring-opened product was observed by ^{1}H NMR. ‡ indicates that ring-opened product was isolated.

Conclusions

Activation of $Ru(H_2O)_6(tos)_2$ using ethyl diazoacetate as a carbene transfer reagent in protic media has enabled the polymerization of monomers previously inaccessible with this catalyst. Although the yield of polymer is low, this system is important in that it represents the first example of the polymerization of low-strain monocyclic olefins by a group VIII complex in protic media. Furthermore, these results demonstrate that while the strained ring monomers are essential for initiation in the original $Ru(H_2O)_6(tos)_2$ system, they are not necessary for propagation.

The isolation of a ruthenium carbene generated by the reaction of ethyl diazoacetate with $(PPh_3)_3RuCl_2$ provides strong support that the mechanism of action of EDA in this system involves decomposition of the diazo compound to generate a ruthenium carbene ($[Ru]=CHCO_2Et$) *in situ.* Results obtained for the reactions of EDA and other diazo compounds with several ruthenium complexes will be presented in Chapter 5.

Experimental

General. All manipulations involving air- and/or moisture-sensitive compounds were carried out using standard high vacuum or Schlenk techniques. Argon was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4Å molecular sieves. Solids were transferred and stored in a nitrogen-filled Vacuum Atmospheres glove box equipped with a MO-40-1 purification train, a DK-3E Dri-Kool conditioner, and a Dri-Cold Freezer.

Instrumentation. NMR spectra were recorded on a GE QE-300 NMR spectrometer (300.19985 MHz ^{1}H, 75.49283 MHz ^{13}C). Proton chemical shifts are referenced to internal residual solvent protons. Carbon chemical shifts are referenced to the carbon signal of the deuterated solvents. Gel permeation chromatography (GPC) was performed on a homemade HPLC instrument employing an Altex model 110A pump, a Rheodyne model 7125 injector with a 100 µL injection loop, an American Polymer Standards Mixed Bed Linear 10 µm column, and a Knauer differential refractometer with methylene chloride as the eluent (0.5 wt % solution) at a flow rate of 1.0 mL/min. GPC samples were filtered through a 0.5 µm filter prior to injection. The molecular weights are referenced to narrow dispersity polystyrene samples (Polysciences).

Materials. Methanol used in polymerizations was degassed prior to use. Chloroform-*d* and benzene-d_6 were purchased from Cambridge Isotope Laboratories and used as received. Rocco Paciello, Alto Benedicto, and Dominic McGrath are gratefully acknowledged for initial samples of $Ru(H_2O)_6(tos)_2$ (**1**). All samples of $Ru^{II}(H_2O)_6(tos)_2$ prepared in these laboratories and at DuPont were according to the literature procedure.[34, 35] Cyclooctene and cyclopentene (Aldrich) were vacuum transferred from CaH_2 and degassed prior to use. Alternatively, high purity cyclooctene (99.9%) was purchased from Wiley, degassed by repeated freeze-pump-thaw cycles, and used without any further purification. Ethyl diazoacetate was purchased from Aldrich and used as received. Its purity was checked by ^1H NMR frequently. Authentic samples of polyoctenamer were prepared by standard procedures; $Mo(NAr)(OC(CF_3)_2CH_3)(=CH\text{-}t\text{-}Bu)$ was provided by Greg Fu. *trans*-Cyclohexene-5,6-diol was a gift from Marc Hillmyer.

Polymerization of Cycloolefins using 1/EDA/MeOH. To a solution of **1** (6 mg, 0.011 mmol) in methanol (1 mL) under argon was added cycloolefin (0.61 mmol, 55 equiv). The reaction mixture was stirred at 55 °C for 15 minutes to allow formation of the yellow olefin complex and then cooled to room temperature. Ethyl diazoacetate (10 µL, 0.095 mmol, 8.6 equiv) was added all at once via syringe. After evolution of N_2 had ceased, the reaction was stirred at 55 °C overnight. The cloudy yellow solution was decanted off of the polymer film coating the reaction vessel. This film, consisting of clean polymer and oligomer, was dried in vacuo (yield 5-15%). The remaining liquid also contained some ring-opened product, as shown by precipitation into water. Isolation was difficult (see text), but small amounts (5-15%) have been purified by removal of ruthenium by passage through silica or alumina, centrifugation, or complexation with EDTA-containing Amberlite resin IRD-718. Polyoctenamer: ^1H NMR ($CDCl_3$): δ 5.38 (b), 1.97 (b), 1.29 (b); ^{13}C NMR ($CDCl_3$):[12]: δ 130.32, 129.84, 32.60, 29.73, 29.62, 29.18, 29.03, 27.20; *cis*/*trans* = 1: 2.3. Polypentenamer: ^1H NMR ($CDCl_3$): δ 5.38 (b), 1.98 (b), 1.39 (b); ^{13}C NMR:[12] δ 130.28, 129.78, 32.19, 32.05, 29.68, 29.52, 26.73; *cis*/*trans* = 1:3.2.

Screening of Catalyst Systems. The reactions were run as described for the polymerization of cycloolefins with **1**/EDA/MeOH, using 0.011 mmol metal complex, 4-5 equiv initiator, 1 equiv coordinating ligand, and 55 equiv cycloolefin. All reactions were run in 1 mL CH_3OH or 1 mL 5% (v/v) H_2O/THF unless otherwise stated. After stirring at 55 °C overnight, the solution was decanted off the precipitated polymer (if any) and concentrated in vacuo. The products were analyzed by ^{1}H NMR. Resonances for the ring-opened olefinic protons (5.38 ppm for cyclooctene, 5.38 ppm for cyclopentene) were considered diagnostic for the desired catalytic activity.

Cyclooctadiene Monoepoxide.[36] A 500 mL three-neck round bottom flask equipped with a magnetic stir bar, condenser, addition funnel, and Ar inlet was charged with cyclooctadiene (11.07 g. 0.102 mmol). A solution of *m*CPBA (50-60 %) (32 g, ~0.102 mmol, ~1 equiv) in $CHCl_3$ (250 mL) was placed in the addition funnel and added dropwise over 3.5 h. After the addition was complete, the reaction was refluxed for 3 h. While heating, the milky white precipitate dissolved to form a clear, colorless reaction mixture. The reaction mixture was then cooled to 0°C to precipitate *m*-chloro benzoic acid and filtered. The liquid was concentrated to a clear, yellow oil that was purified by distillation (9 mm Hg, 75-85 °C, 42% yield) or flash chromatography (10% ethyl acetate/hexanes, 33% yield). ^{1}H NMR ($CDCl_3$): δ 5.55 (b, 1 H), 2.99-3.06 (b, 1 H), 2.33-2.48 (m, 1 H), 1.95-2.18 (m, 3 H).

5-Cyclooctenol. LAH (1 M in THF; 2.01 mL, 2.01 mmol, 0.5 equiv) was added dropwise to a solution of cyclooctadiene monoepoxide (500 mg, 4.04 mmol) in THF (4 mL). The resulting reaction mixture was stirred at room temperature overnight. H_2O was added dropwise by syringe and the reaction mixture was extracted into ether. The aqueous layer was washed 3 times with ether. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated to an oil that was purified by flash chromatography (20% ethyl acetate/hexanes, ≥98% yield). ^{1}H NMR ($CDCl_3$): δ 5.58-5.78 (m, 2 H), 3.80-3.9 (m, 1 H), 1.5-2.4 (m, 10 H).

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(19) The equilibrium distribution is independent of temperature in the range 0 - 80°C. See references 17 and 18.

(20) This finding is consistent with the observation that an isolated ruthenium carbene prepared from $[Cp^*RuCl]_4$ and EDA is also inactive for the polymerization of cyclooctene. Studies of this ruthenium precursor are discussed in more detail in Chapter 5.

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(24) $NaBH_4$ causes decomposition of **1** before any monomer is added to the reaction mixture.

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Chapter 4

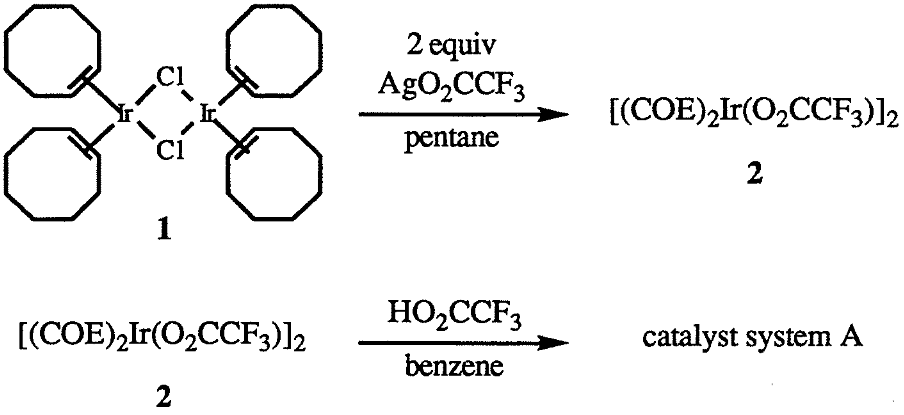
Iridium Based Catalyst Systems for Olefin Metathesis and Isomerization/Metathesis of Acyclic Olefins[1]

Introduction

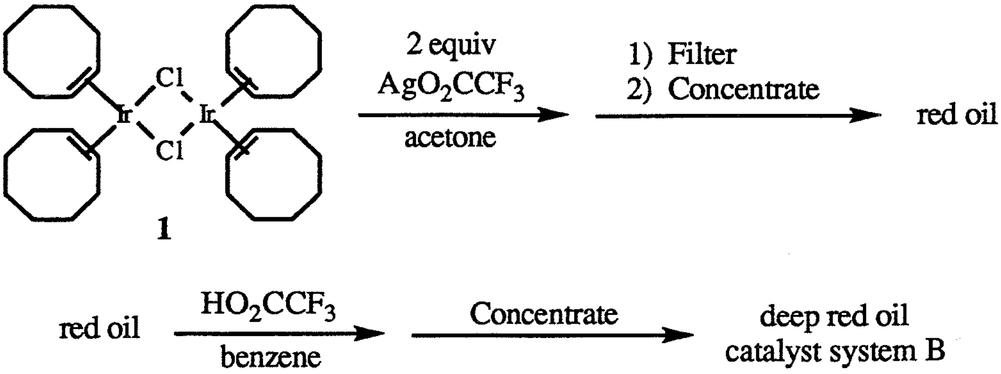
The preceding chapter presented a ruthenium based system for the ring-opening metathesis polymerization of low-strain cyclic olefins. Although this system is one of the rare examples of the metathesis of less strained double bonds by a group VIII transition metal complex, it is limited by its low yields and its inability to metathesize acyclic or functionalized olefins. Due to the unusual functional group tolerance of the late transition metal metathesis catalysts, it remains of great interest to further pursue systems that might extend the reactivity of these complexes to a wider variety of substrates.

An early advance in this area was reported by Porri and coworkers in the mid 1970s.[2-5] During molecular weight regulation studies with 1- and 2-pentene in $[(COE)_2IrCl]_2$ (COE = cyclooctene) (**1**) catalyzed polymerizations of norbornene, self-metathesis products of the acyclic olefins were observed.[3, 4, 6] In addition, a related complex, $[(COE)_2Ir(O_2CCF_3)]_2$ (**2**) (prepared from **1** and silver trifluoroacetate) has been found to exhibit very slight activity for the polymerization of cyclooctene and cyclopentene at 50-60°C (~1% yield).[2, 4] Further examination of these systems showed that when trifluoroacetic acid (TFAA) is added to a benzene solution of **2**, the system shows greatly increased activity for the ring-opening metathesis polymerization of cycloolefins (20-30% yield) at 60°C (Porri's "catalyst system A," Scheme 1). Surprisingly, an ill-defined system made from the same components but without the isolation and purification of **2** is even more active. This "catalyst system B" is prepared by treatment of **2** with 2 equiv AgO_2CCF_3, followed by filtration to remove precipitated AgCl. The crude product is then reacted with TFAA. The resulting reaction mixture is concentrated to an ill-defined deep red oil and employed as a metathesis catalyst without any further purification (Scheme 2). Utilizing these systems, polymers are obtained in moderate to high yields, the amount depending greatly upon the reaction conditions. Furthermore, catalyst system B has been found to be active for the metathesis of acyclic olefins, although concurrent isomerization of the double bond position is also observed.[5]

Scheme 1. Preparation of Porri's Catalyst System A.



Scheme 2. Preparation of Porri's Catalyst System B.



The exact role of the TFAA in these reactions is unknown, although it is clearly involved in initiation in some manner.

These iridium systems show great promise and merit further investigation for a number of reasons:

(1) While these complexes represent a rare example of late transition metal catalysts capable of metathesizing less reactive substrates, they were never explored to their full potential.

(2) The metathesis of functionalized olefins was not studied at all with these iridium systems. To date, ROMP of functionalized low-strained cyclic olefins has proved difficult due to the lower tolerance of functionality typically displayed by early transition metal catalysts. A group VIII system that can metathesize these types of olefins could potentially provide a route into polymers that are difficult to prepare by other means.

(3) Acyclic olefins were not investigated beyond the chain transfer studies and the self-metathesis of 1-pentene. A group VIII system (such as these iridium systems) that is active for the metathesis of acyclic olefins could provide a valuable route into functionalized olefins that are difficult to synthesize by other methods. Limited success in this area has already been obtained with selected early transition metal catalysts.[7-10] The homogeneous system $WCl_6/SnMe_4$[11] and the heterogeneous system $Re_2O_7/Al_2O_3/SnMe_4$.[12] are among the most successful systems that have been described to date. Although encouraging results have been obtained for the metathesis of unsaturated esters, such as methyl oleate,[10-15] the homogeneous catalysts are several of orders magnitude less reactive towards functionalized than unsubstituted olefins, and thus they require relatively long reaction times and large amounts of catalyst. The heterogeneous catalysts display greater reactivity and more functional group tolerance, but the reaction rates are still too low to be industrially useful,[7-9] and the development of new systems for this type of transformation remains important.

(4) The isomerization of the double bond position that Porri observed accompanying the metathesis chemistry in the case of acyclic olefins is potentially interesting. Such a combination is industrially useful and, in fact, is currently utilized commercially in the Shell Higher Olefins Process (SHOP) (Figure 1).[16] The key steps in this process consist of an isomerization followed by a metathesis reaction. This represents the largest commercial application of olefin metathesis. The olefins produced in the SHOP process are hydroformylated to produce long chain alcohols that are utilized

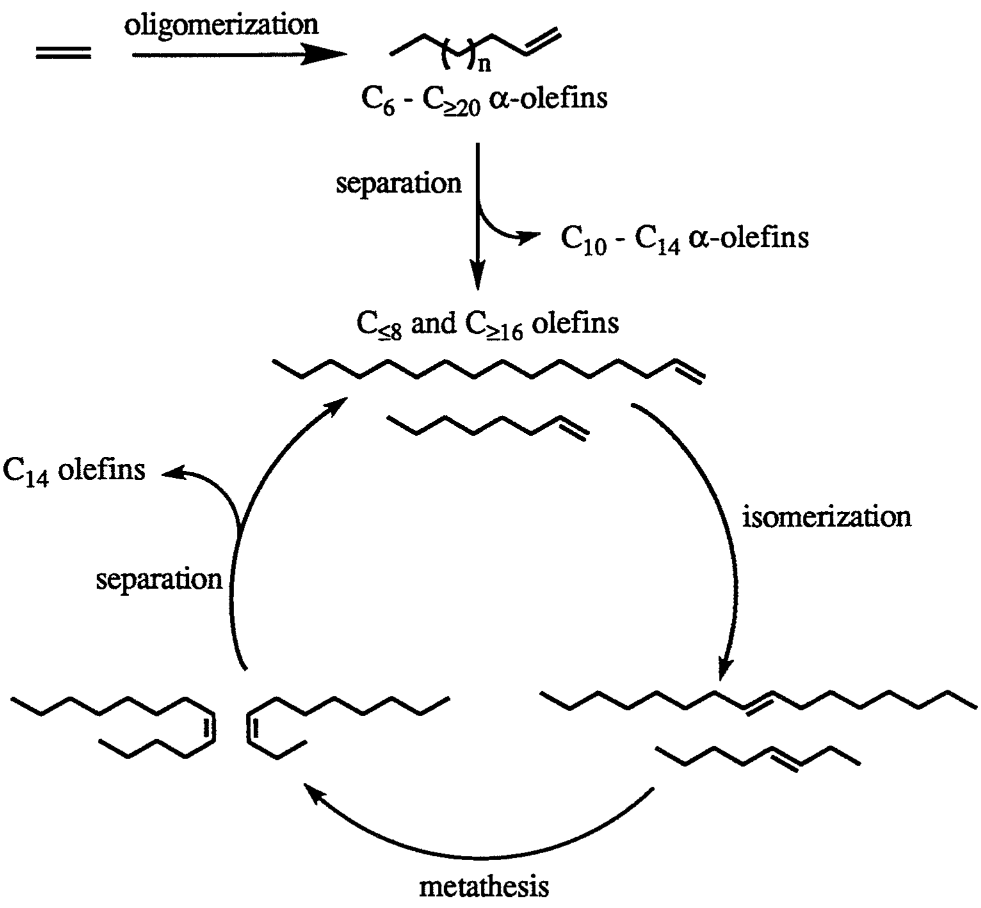


Figure 1. Shell Higher Olefins Process.

in the manufacturing of plasticizers and surfactants.[16, 17] Further investigations of Porri's iridium systems might allow for the development of a one-step variation of this process or for its extension to functionalized olefins. Ideally, a method could be found that would allow control of the reactivity of these iridium systems to favor more selective metathesis or isomerization/metathesis as needed.

(5) The lack of information about the mechanism of initiation and the nature of the active species leads to questions concerning the conditions Porri utilized for these reactions. For example, why is the ill-defined system B better than A? Is it possible that some impurity formed during the preparation of the system is actually responsible for the chemistry observed? Is it necessary to remove AgCl or would an even simpler, less clean

in situ version consisting of **1** and AgO_2CCF_3 work as well? What is the role of TFAA and would more direct carbene sources work just as well as initiators?

This chapter presents results obtained upon further investigation of Porri's iridium catalysts, as well as a number of related systems using several different initiators in order to determine the optimal polymerization conditions. This knowledge has been utilized for the preparation of extremely high molecular weight materials. Observations during the course of this work, as well as a consideration of the higher activity of ill-defined system B over A, have led to the development of a system that allows the simultaneous isomerization/metathesis of olefins, including functionalized olefins, without the need for added initiators besides AgO_2CCF_3. By controlling the reaction conditions, the system can be altered to favor isomerization of the double bond position, isomerization/metathesis, or metathesis. This system is significantly more active than that described in the preceding chapter.

Results and Discussion

Ring-Opening Metathesis Polymerization with Cyclic Olefins

Complexes **1** and **2** were investigated for their reactivity with norbornene, cyclooctene, and cyclopentene. In addition to these isolated complexes, the reactivity of **2** prepared *in situ* by reaction of **1** with 2 equiv AgO_2CCF_3 (i.e., without removal of precipitated AgCl by filtration) was also investigated. Such an *in situ* procedure would save time and make the reactions easier to run. Several different initiators were also examined, including TFAA, ethyl diazoacetate (EDA),[18] and diphenylcyclopropene.[19] Although Porri does not report any problems during his studies, polymerizations with **1** where found to be somewhat inconsistent and appeared to be quite dependent on the particular batch of catalyst, olefin, and AgO_2CCF_3 used. Although specific numbers were not always reproducible, the general trends were clear. No such difficulties were observed with **2**.

Complexes **1** and **2** both polymerized norbornene readily in organic solvents (toluene or THF) without the need for added initiators. Within minutes, the reaction mixtures completely solidified into swollen masses that had absorbed all the solvent originally present in the system and were molded into the shape of the reaction vessels in which they were prepared. Upon removal of the solvent under vacuum, the polymers shrank to a smaller, more brittle material but often retained their shape. Based on yields and relative rates, the catalysts exhibited the following relative reactivities: **2** > **1**/AgO_2CCF_3 > **1**. (Table 1) All of these polymers were clearly of extremely high molecular weight, but no gel permeation chromatography data is available because they were all essentially insoluble in common organic solvents. This insolubility might be due to crosslinking occurring during the course of the polymerization. That the polymers were in fact ROMP polymers, however, was established by ^1H NMR of the lower molecular weight material that did dissolve.

Table 1. Polymerization of Norbornene with Iridium Complexes.

Catalyst	**Yield (%)**	**Approximate time for Visible Polymer Formation**
1	33	2-5 minutes
1/AgO_2CCF_3	83	1-2 minutes
2	95	seconds

Our investigations have shown that the system **1**/AgO_2CCF_3 also readily polymerizes neat cyclooctene and cyclopentene in the presence of TFAA or EDA to form low to moderate yields of high molecular weight polymer. TFAA was clearly a more effective initiator, and only a trace of polymer (detected by ^1H NMR, but not isolable) was formed when neither AgO_2CCF_3 nor EDA was present. The reaction mixtures became viscous much more quickly when either of the initiators were utilized. When **2**

Table 2. Polymer Yields Under Various Conditions.[a]

Olefin	**Catalyst**[b]	**No Initiator**	**TFAA**	**EDA**
Cyclopentene	**1**/2 equiv Ag	trace	10	4
Cyclopentene	**1**/>4 equiv Ag	trace	24	3
Cyclopentene	**2**	9	90	5
Cyclooctene	**1**/2 equiv Ag	trace	3	3
Cyclooctene	**1**/>4 equiv Ag	trace	2	5
Cyclooctene	**2**	8	98	40

[a] Relative reaction rates: Catalysts: **2** > **1**/AgO_2CCF_3; Initiators: TFAA > EDA > none.
[b] Ag = AgO_2CCF_3

was employed as catalyst, very high yields of high molecular weight materials were formed at noticeably faster rates. These results are summarized in Table 2.

As with the polynorbornene prepared using these catalysts, the polymers were often molded to the shape of the containers in which they were made and ranged in consistency from rubbery materials to extremely hard plastics that could not be cut or broken. Once again, the high molecular weight of the polymers rendered them insoluble and precluded analysis by gel permeation chromatography. This insolubility is due to crosslinking, as evidenced by the observation that polymer yields (although not solubility) improved when the reactions were run in the presence of BHT (butylated hydroxytoluene), a free radical inhibitor that is often employed during ROMP polymerizations to reduce crosslinking.[20] For example, **1**/AgO_2CCF_3/TFAA polymerized neat cyclopentene in 44% yield in the presence of BHT versus 24% in the absence. By reducing crosslinking, BHT might allow the polymer to stay in solution longer, thus allowing time for more of the monomer to react, thereby improving yields.

EDA appeared to be less effective when AgO_2CCF_3 was present in the system. For example, yields of polyoctenamer formed by **2** decreased rapidly as the amount of silver was increased. However, in the absence of any initiator, increased silver actually promoted the reaction (Table 3). This observation is more readily understood in light of our findings with acyclic olefins (*vide infra*).

Table 3. Polymerization of Cyclooctene with **2**.[a]

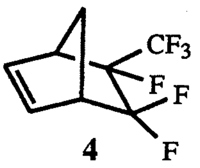
Equivalents AgO_2CCF_3	No Initiator	TFAA	EDA
0	8	98	40
2	18	83	7
>4	26	84	6

[a] Relative reaction rates essentially parallel yields.

Another potential initiator, diphenylcyclopropene,[19] failed to initiate polymerization in the $1/AgO_2CCF_3$ system. In this case, it is possible that the initiator instead reacted with AgO_2CCF_3 to form a silver alkylidene, because the ^1H NMR spectrum exhibited resonances at 12.7 ppm (b, Ag=C*H*-CH=CPh_2) and 9.5 ppm (d, Ag=CH-C*H*=CPh_2). This alkylidene was not active for the polymerization of norbornene. In contrast, when isolated **2** was used as the catalyst, diphenylcyclopropene initiated fast polymerization of cycloolefins. A number of attempts at observing the active species by ^1H NMR have failed. However, isolation of an iridium complex prepared from the analogous cyclooctadiene complex $[(COD)Ir(O_2CCF_3)]_2$ (COD = 1,5-cyclooctadiene) (**3**) and diphenylcyclopropene has recently been reported.[21]

A number of other iridium and rhodium complexes have also been screened for activity as ROMP catalysts with norbornene (Table 4). None studied to date have proved as active as the systems based on $1/AgO_2CCF_3$ and **2**, although the analogous complexes $[(COE)_2IrI]_2$ and $[(COD)_2IrCl]_2$ also appeared to be promising candidates.

The catalyst system $1/AgO_2CCF_3$/TFAA was also active for the polymerization of the fluorinated monomer **4** in toluene. Such fluorinated monomers are very difficult to ROMP, and no early transition metal catalyst is reliable for the efficient, reproducible polymerization of this monomer.[22] Our system appeared to be very active, converting this starting material to high molecular weight polymer in less than thirty minutes. The polymeric product has not been fully characterized. The 7-oxa analogues **5** and **6** did not polymerize, but this was expected since the non-fluorinated monomer **7** also failed to polymerize with these iridium catalysts. Two cyclooctene derivatives with oxygen



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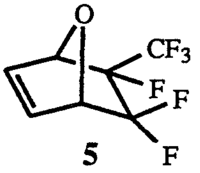

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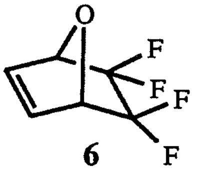

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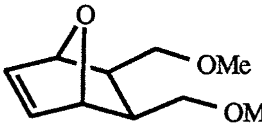

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Table 4. Activity of Group VIII Transition Metal Complexes for ROMP of Norbornene.

Complex	**Solvent**	**Temperature (°C)**	**Activity without Ag**[a,b]	**Activity with Ag**[a,b]
$[(COE)_2IrCl]_2$	toluene	25	VF	VF
$[(COE)_2IrI]_2$	toluene	25	F	
$[(COE)_2Ir(O_2CCF_3)]_2$	toluene	25	VF	VF
$[(COD)IrCl]_2$	toluene	25	S	S
$[Cp^*IrCl]_4$	toluene	25	N	N
$IrCl_3 \cdot nH_2O$	ethanol	25	S	--
$IrCl_3 \cdot nH_2O$	ethanol	55	F	
$IrCl(PPh_3)_2CO$	ethanol	25	N	S
$IrCl(PPh_3)_2CO$	ethanol	55	S	
$[Cp^*RuCl]_4$	ethanol	25	N	
$[(COE)_2RhCl]_2$	toluene	25	N	N
$[(COD)_2RhCl]_2$	toluene	25	N	N
(COE)Rh(acac)	toluene	25	N	--
$(COD)Rh(BPH_4)$	toluene	25	N	--
$[(COD)Rh(DPPB)]BF_4$	toluene	25	N	--
$[RhCl(DIPPE)]_2$	toluene	25	N	N

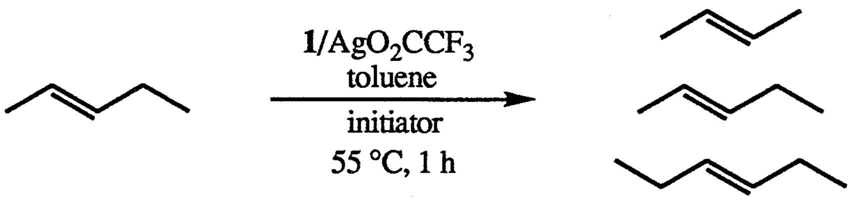
[a] N = not active (no polymer detected after >24 h); S = slow polymerization (polymer detected after 12-24 h); F = fast polymerization (polymer detected within several hours); VF = very fast polymerization (polymer detected within several minutes).

[b] Ag = AgO_2CCF_3

functionality, 5-hydroxycyclooctene and cyclooctadiene monoepoxide, proved to be unsatisfactory substrates for the most active system (**2**/TFAA) as well.

Reactions with Acyclic Olefins

Isomerization/Metathesis. During the course of investigating the ROMP systems with **1** or **2** in the presence of AgO_2CCF_3, it was noted that a small amount of silver metal consistently plated out onto the walls of the reaction flask, indicating that some type of oxidation/reduction chemistry was taking place in addition to the chloride abstraction. This observation seemed particularly important when considered in conjunction with the findings that the polymerization of cyclooctene in the absence of initiators proceeded better as the amount of silver was increased (Table 3). Similar results were obtained with acyclic olefins. The system **1**/≥4 equiv AgO_2CCF_3 was found to be active for the metathesis of 2-pentene in toluene; the reaction required the presence of the silver salt, but it actually proceeded better in the absence of TFAA or EDA (Table 5)



These observations hinted that AgO_2CCF_3 actually plays two roles in these reactions. Not only does it serve to precipitate silver chloride, but it also oxidizes the resulting iridium(I) trifluoroacetate complex. In fact, X-ray powder diffraction of the insoluble products formed during the reaction of **1** with 4 equiv AgO_2CCF_3 in toluene for

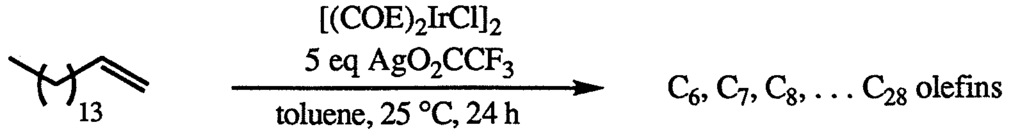
Table 5. Acyclic Metathesis of 2-pentene.

Catalyst	Initiator	Hexene[a,b] / Pentene
1	none	--
1/AgO_2CCF_3	none	0.295
1/AgO_2CCF_3	TFAA	0.047
1/AgO_2CCF_3	EDA	0.042

[a] Ratio determined by GC integration.
[b] Butene gas not detected under these conditions.

several hours at 25°C has shown that these products consist of a ~1:1 mixture of AgCl and Ag metal.[23] The increased activity observed in systems that lack initiators other than excess silver indicates that the oxidized iridium species might play a crucial role in the metathesis chemistry. This appears to be the case, as evidenced by the discovery that a highly active catalyst for the metathesis of acyclic olefins, accompanied by isomerization of the double bond position, could be prepared *in situ* with the system **1**/≥4 equiv AgO_2CCF_3 without the need for any additional initiators. At least 4 equiv AgO_2CCF_3 must be used or the isomerization chemistry takes over as the predominant reaction, and minimal or no metathesis products are formed.[24, 25] Presumably the reaction of isolated **2** with 2 equiv AgO_2CCF_3 leads to the same oxidized species.

The system formed by **1**/≥4 equiv AgO_2CCF_3 reacted with unsaturated hydrocarbons over several hours to yield a mixture of olefins formed by isomerization of the double bond position of the starting material accompanied by metathesis of the resulting olefinic mixture. A representative gas chromatograph of the product obtained



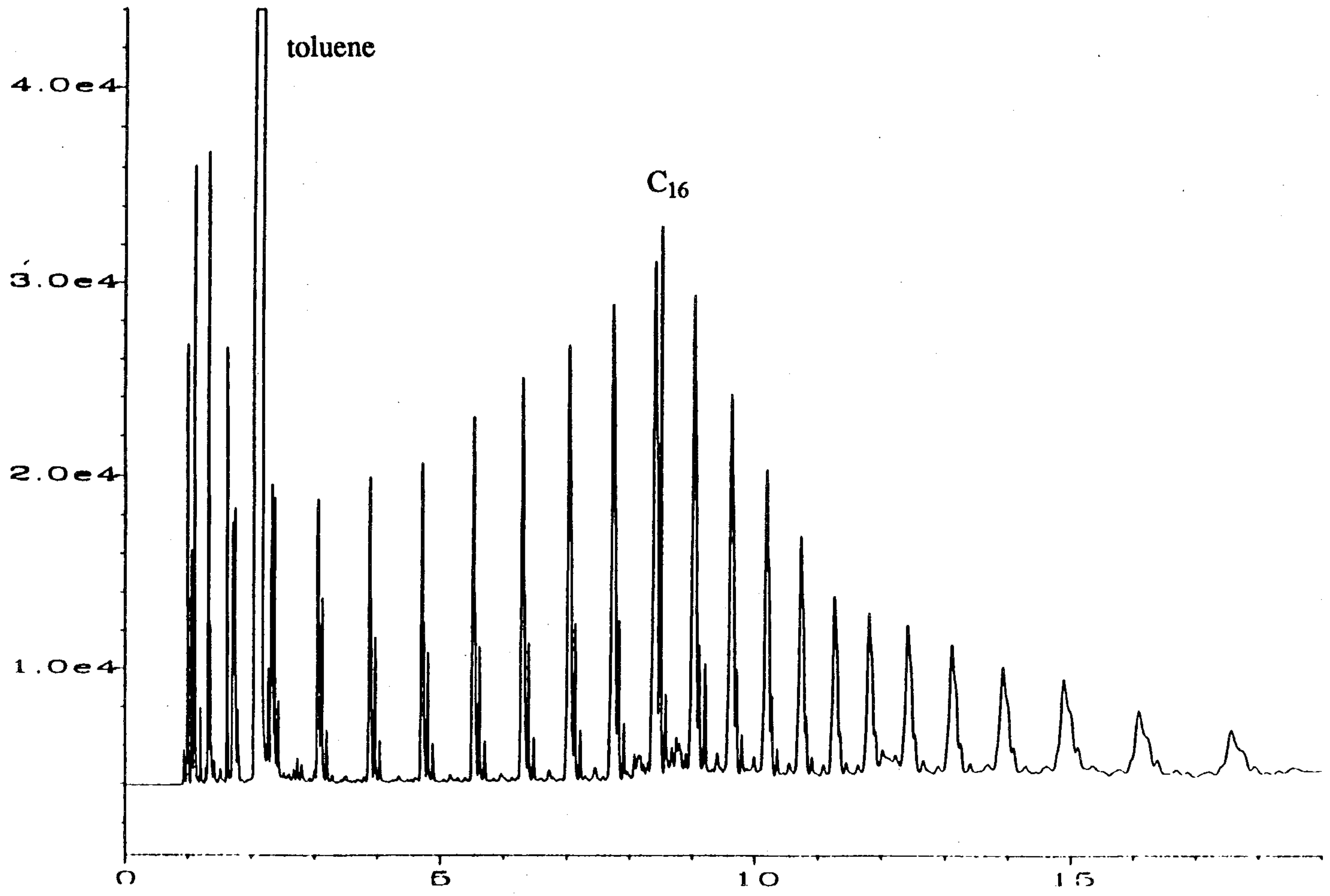


Figure 2. Gas chromatogram of the product mixture formed by the isomerization/metathesis of 1-hexadecene by **1**/≥ 4 equiv AgO_2CCF_3. (Abundance versus retention time.)

by the isomerization/metathesis of 1-hexadecene is depicted in Figure 2. New olefins ranging from 6 to at least 28 carbon atoms can be detected. Each discrete signal shows some fine structure due to double bond position and cis/trans isomers of the olefins with a given molecular weight, since these have similar GC retention times.[25, 26] The same product mixtures were obtained starting from **2** and 2 equiv AgO_2CCF_3. These results represent a rare example of the metathesis of acyclic olefins by an iridium catalyst. In addition, by combining isomerization and metathesis, this reaction is essentially a single-step analogue of the two-step Shell Higher Olefins Process (SHOP) (Figure 3). However, while the SHOP process is limited to hydrocarbons, this iridium system is also capable of metathesizing functionalized olefins, such as methyl oleate.[27]

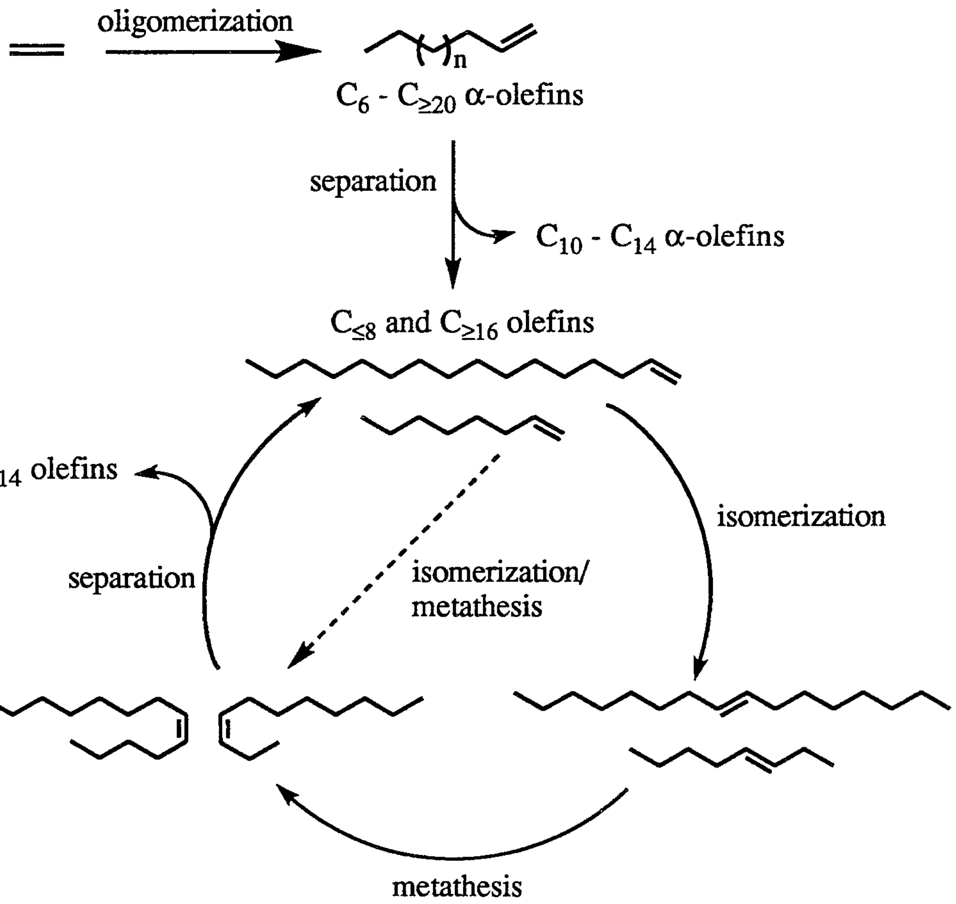


Figure 3. The Application of Isomerization/Metathesis to the Shell Higher Olefins Process.

When methyl oleate (**8**) was treated with 1/≥4 equiv AgO_2CCF_3, the resulting product mixture was extremely complex, consisting of a mixture of olefins, unsaturated esters, and unsaturated diesters distributed over a wide range of molecular weights (Figure 4).

$$\underset{\mathbf{8}}{H_3C(CH_2)_7CH{=}CH(CH_2)_7CO_2Me} \xrightarrow[\text{toluene, 85 °C, 24 h}]{\begin{array}{c}[(COE)_2IrCl]_2\\ 6\text{ eq } AgO_2CCF_3\end{array}} \begin{array}{l} CH_3(CH_2)_aCH{=}CH(CH_2)_bCH_3\ + \\ CH_3(CH_2)_cCH{=}CH(CH_2)_dCO_2Me\ + \\ MeO_2C(CH_2)_eCH{=}CH(CH_2)_fCO_2Me \end{array}$$

Although the conversion was lower than in the hydrocarbon case, this is an unusual example of such a transformation on a functionalized substrate. Once again, the gas chromatograph was complicated by the presence of double bond position and cis/trans isomers. The product mixture can be greatly simplified by hydrogenation to yield a mixture of alkanes, saturated esters, and saturated diesters.[28] The gas chromatogram of

$$\begin{array}{l} CH_3(CH_2)_aCH{=}CH(CH_2)_bCH_3\ + \\ CH_3(CH_2)_cCH{=}CH(CH_2)_dCO_2Me\ + \\ MeO_2C(CH_2)_eCH{=}CH(CH_2)_fCO_2Me \end{array} \xrightarrow{\begin{array}{c}H_2\\ Pd/C\end{array}} \begin{array}{l} C_9 - C_{26}\text{ alkanes } + \\ C_8 - C_{28}\text{ saturated esters } + \\ C_{11} - C_{26}\text{ saturated diesters} \end{array}$$

the hydrogenated mixture (Figure 5) actually indicated the presence of three distinct series, 9 - 26 carbon linear alkanes, 8 - 28 carbon saturated methyl esters, and 11 - 26 carbon saturated dimethyl esters. Careful examination of the signals in the gas chromatogram revealed that each consisted of two or three closely spaced peaks representing one compound of similar molecular weight from each of these groups. For example, the peak with a retention time of 21 minutes corresponds to octadecane, methyl pentadecanoate, and dimethyl dodecandioate (Figure 6). The isomerization/cross-metathesis of methyl oleate with 3-hexene has also been achieved with this system.

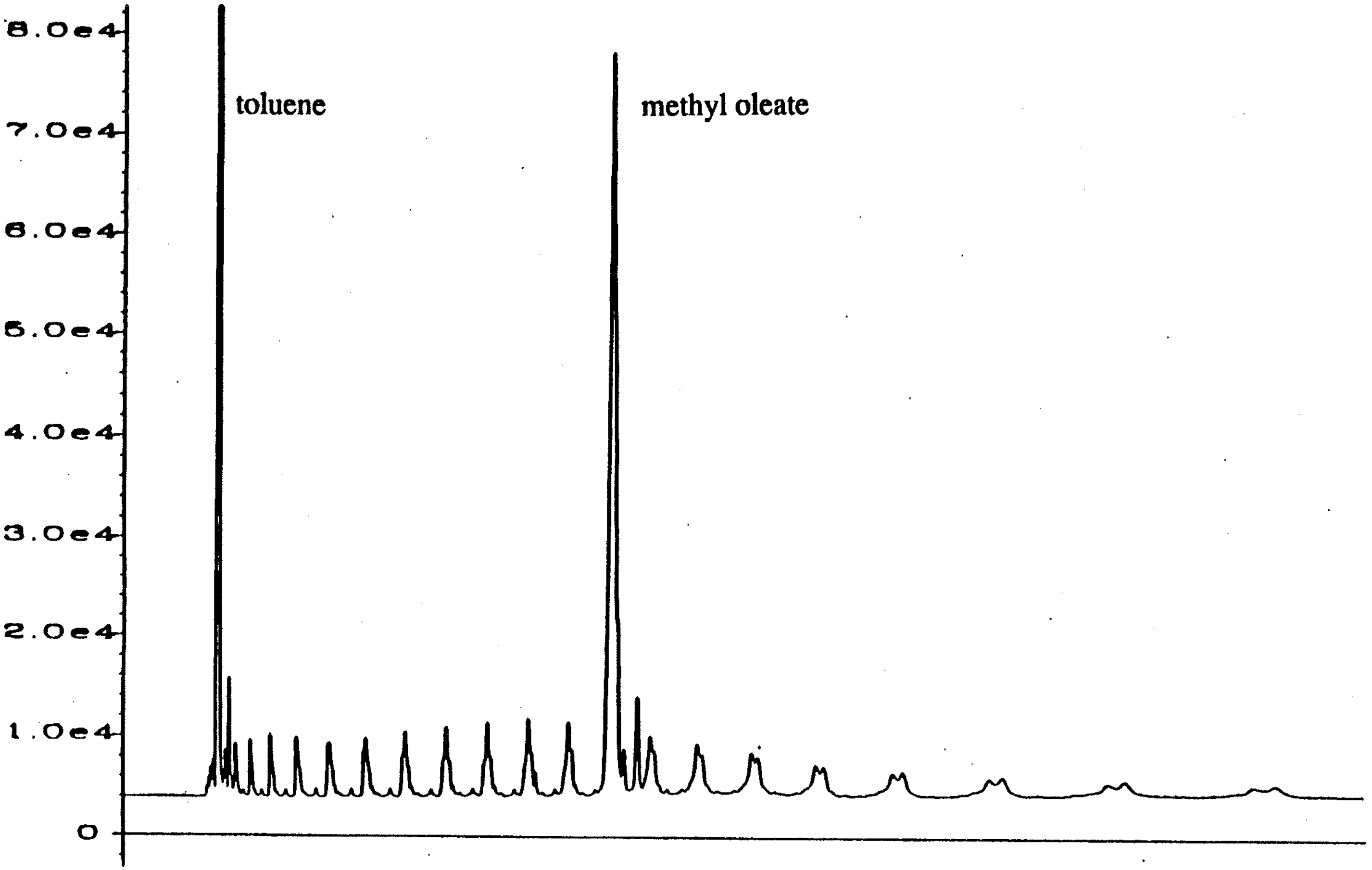


Figure 4. Gas chromatogram of the product mixture formed by the isomerization/metathesis of methyl oleate by **1**/≥ 4 equiv AgO_2CCF_3. (Abundance versus retention time.)

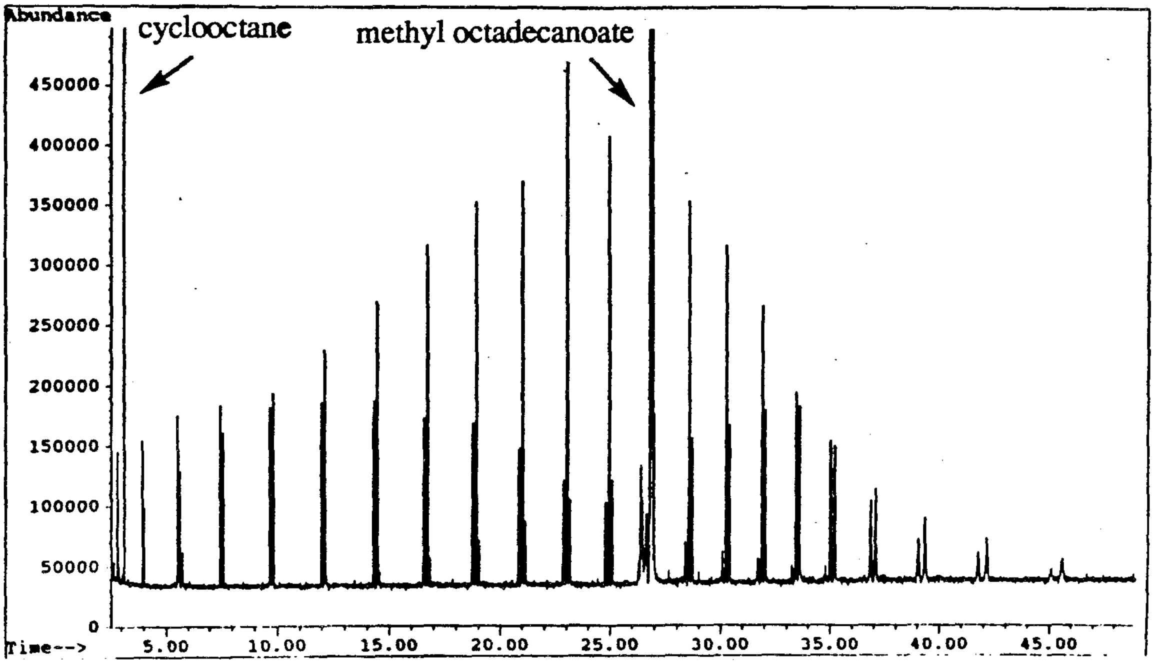


Figure 5. Gas Chromatogram of the product mixture formed by hydrogenation of the methyl oleate isomerization/metathesis product. (Abundance versus retention time.) Peaks corresponding to cyclooctane (derived from hydrogenation of COE ligand) and methyl octadecanaote (derived from hydrogenation of methyl oleate, ~ 50% of reaction mixture) are off scale.

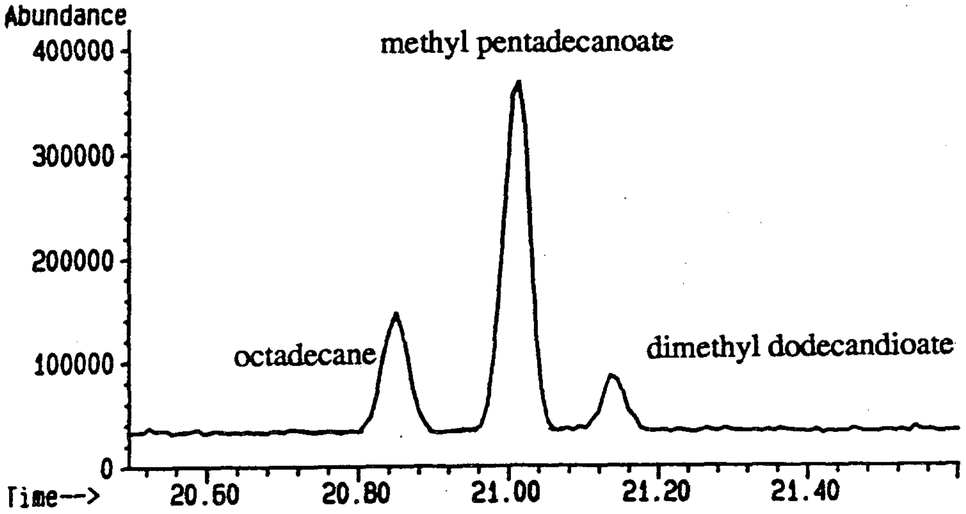


Figure 6. Expanded plot of the group of peaks with retention time ~ 21 min. (Abundance versus retention time.)

Selective Olefin Metathesis. Although the novel isomerization/metathesis reaction has potential industrial applications, it also remains of interest to metathesize acyclic olefins, particularly functionalized ones, more selectively. Ideally, it would be desirable to be able to control conditions to favor isomerization, isomerization/metathesis, or metathesis as needed.

During his molecular weight regulation studies using these iridium catalysts, Porri observed that in the presence of norbornene, complexes **1** and **2** are transformed into species active for the metathesis of acyclic olefins.[3, 4] It thus seemed possible that norbornene, which is active enough to rapidly generate an iridium alkylidene in these systems, might be capable of serving as an initiator of the metathesis reaction before appreciable isomerization can occur. In fact, when ≥4 equiv AgO_2CCF_3 was added to a toluene solution of **1** containing 20 equiv norbornene and 35-50 equiv methyl oleate, a

$$\underset{\mathbf{8}}{CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2Me} \xrightarrow[\substack{\text{norbornene} \\ \text{toluene, } 55^\circ\text{C}}]{\substack{[(COE)_2IrCl]_2 \\ \geq 4 \text{ eq } AgO_2CCF_3}} \begin{array}{c} CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3 + \\ CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2Me + \\ MeO_2C(CH_2)_7CH{=}CH(CH_2)_7CO_2Me \end{array}$$

more selective system was obtained. The major products, 9-octadecene and $MeO_2C(CH_2)_7CH{=}CH(CH_2)_7CO_2Me$, were identified by comparison of their GC retention times with that of authentic samples.[29] Although some isomerization still took place, the extent was drastically reduced. Under the conditions of the reaction, no high molecular weight polynorbornene was obtained. This was most likely due to either chain transfer or competitive inhibition by the acyclic olefin.

Further investigations have revealed that the use of norbornene can be avoided by allowing **2** and excess AgO_2CCF_3 to react for several hours at room temperature prior to addition of the acyclic olefin. In this case, presumably the oxidation/reduction chemistry has come to completion and all of the starting iridium complex has been oxidized. Under

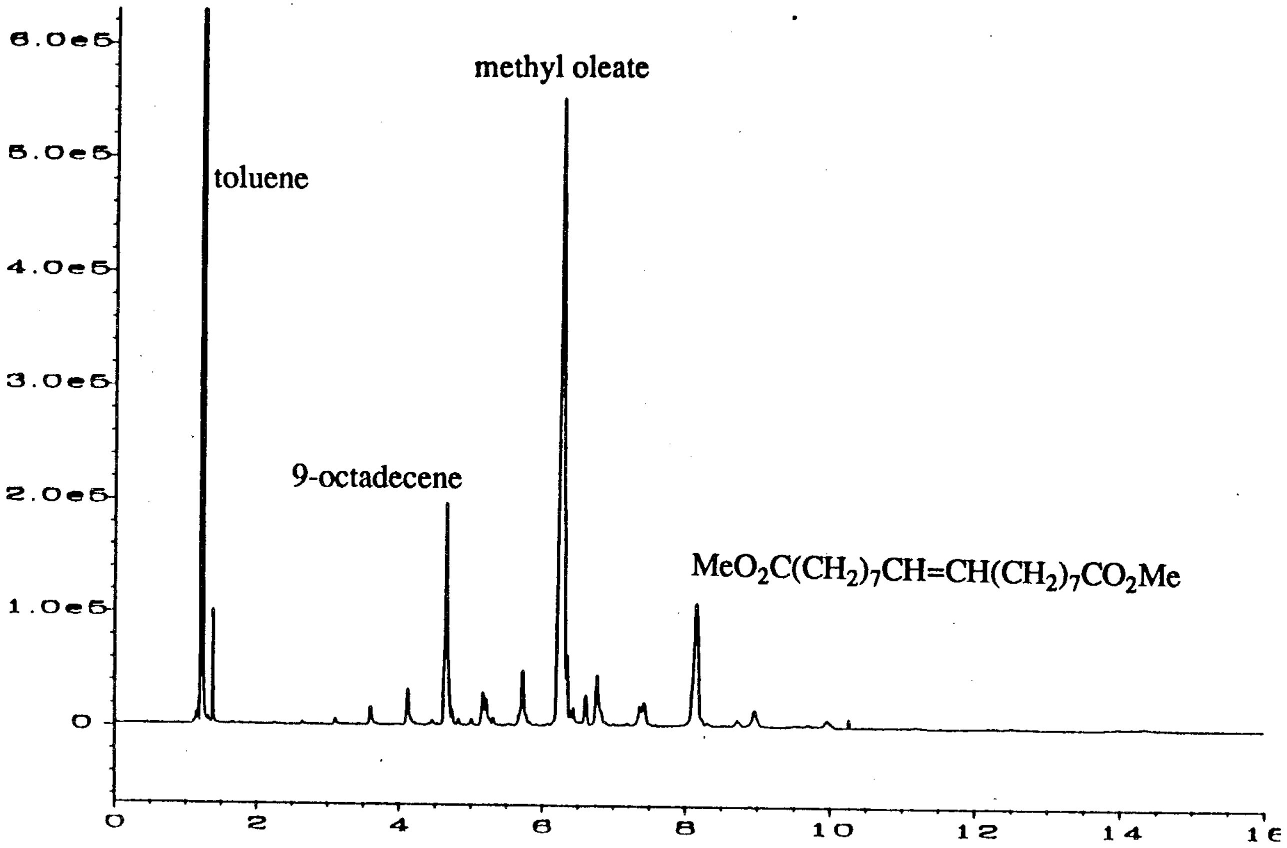
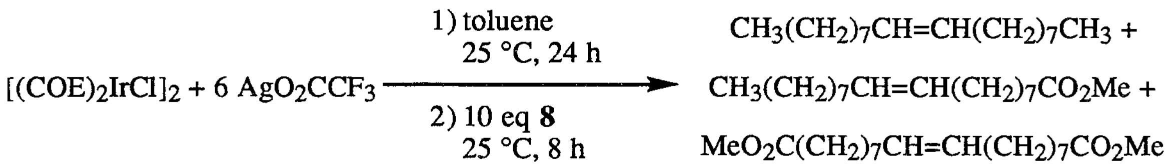


Figure 7. Gas chromatogram of the product mixture formed by the selective metathesis of methyl oleate by **1**/≥ 4 equiv AgO_2CCF_3. (Abundance versus retention time.) Unlabeled peaks correspond to olefins formed by isomerization/cross-metathesis of the reaction mixture.

these conditions, the reaction became selective for metathesis, with the complications due to isomerization once again greatly diminished (Figure 7).[25, 26]



$$\mathrm{[(COE)_2IrCl]_2 + 6\ AgO_2CCF_3} \xrightarrow[\text{2) 10 eq }\mathbf{8}\text{, 25 °C, 8 h}]{\text{1) toluene, 25 °C, 24 h}} \begin{array}{c} \mathrm{CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3\ +} \\ \mathrm{CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2Me\ +} \\ \mathrm{MeO_2C(CH_2)_7CH{=}CH(CH_2)_7CO_2Me} \end{array}$$

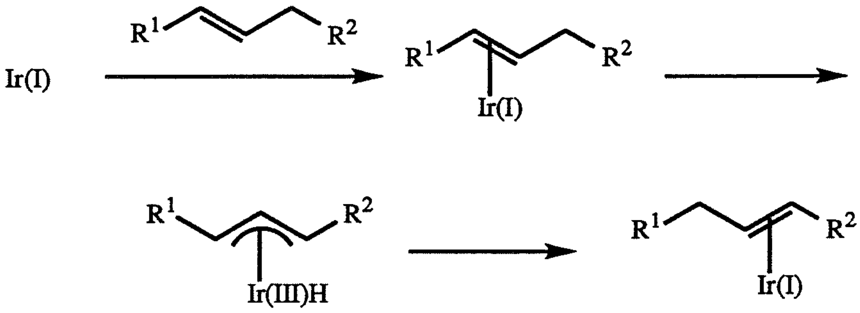
Mechanistic Considerations

Porri's investigations into the mechanism of initiation in these catalyst systems have shown that **1** reacts with AgO_2CCF_3 in methylene chloride to form a mixture of **2**, the cyclooctadiene complex **3**, and cyclooctane. In pentane, only complex **2** is formed. When complexes **2** and **3** are treated with TFAA in the presence of arenes, they are converted into $[(COE)_2Ir(arene)]^+$ and $[(COD)Ir(arene)]^+$. However, salts of these cations have not been found to be active catalysts for the polymerization of cycloolefins, and thus they do not appear to be relevant to the mechanism of catalyst activation.[30] Furthermore, our results in this area indicate that the formation of **3** is unimportant since it is a less active catalyst than **2** and that the metathesis reactions can be carried out neat; thus, the presence of aromatic or chlorinated solvents is unnecessary (*vide supra*). During the course of his investigations, Porri makes no mention of the oxidizing properties of AgO_2CCF_3 and appears to be unaware of its dual role in this system.[30]

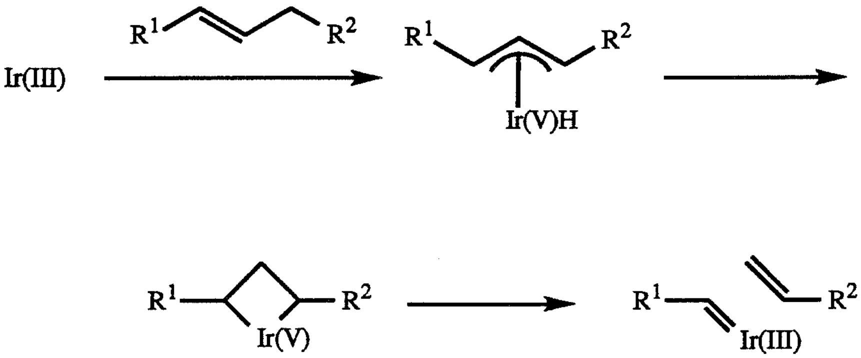
Our results obtained with acyclic olefins indicate that the most likely candidate for the active metathesis catalyst is the oxidized iridium species obtained when **1** is reacted with ≥4 equiv AgO_2CCF_3 or when **2** is reacted with 2 equiv AgO_2CCF_3. It seems reasonable that allowing **2** to react with AgO_2CCF_3 for a longer time prior to addition of the olefin might permit this oxidation process to go to completion. In this case, most of the iridium is found in the oxidized form and the metathesis chemistry predominates. The iridium(I) species **2** appears to be responsible for the isomerization observed with acyclic olefins. While this complex is active enough to ROMP more strained double bonds, such as norbornene, it can not metathesize the less reactive olefins, and only isomerization is observed. Presumably, at intermediate reaction times both iridium species are present and simultaneous isomerization/metathesis is observed. Proposed mechanisms for the action of the iridium(I) and the oxidized complexes are presented in Scheme 2.[31, 32] Some evidence for this type of isomerization via an allyl iridium hydride has been reported,[31] and a mechanism similar to that suggested for the metathesis initiation has been proposed to explain metallacyclobutane formation from η^3-allyl molybdenum and tungsten complexes in the presence of hydrides.[33] In addition,

Scheme 3. Proposed Mechanisms for Isomerization and Metathesis.

Isomerization: Ir(I)



Metathesis: Ir(III)



metallacyclobutane complexes have also been isolated from the reaction of η^3-allyl iridium complexes with a variety of nucleophiles, including hydride.[34,35]

Since some silver metal is formed even in polymerizations with **1** and only 2 equiv AgO_2CCF_3, it is clear that at least a portion of the starting material is oxidized in these cases. This might help explain why Porri's ill-defined catalyst system B is more reactive than catalyst system A; during the course of isolating and purifying **2**, the oxidized species might be lost. This hypothesis is supported by the observation that **2** prepared from **1** and KO_2CCF_3 is noticeably less reactive than the same compound prepared with the silver salt.

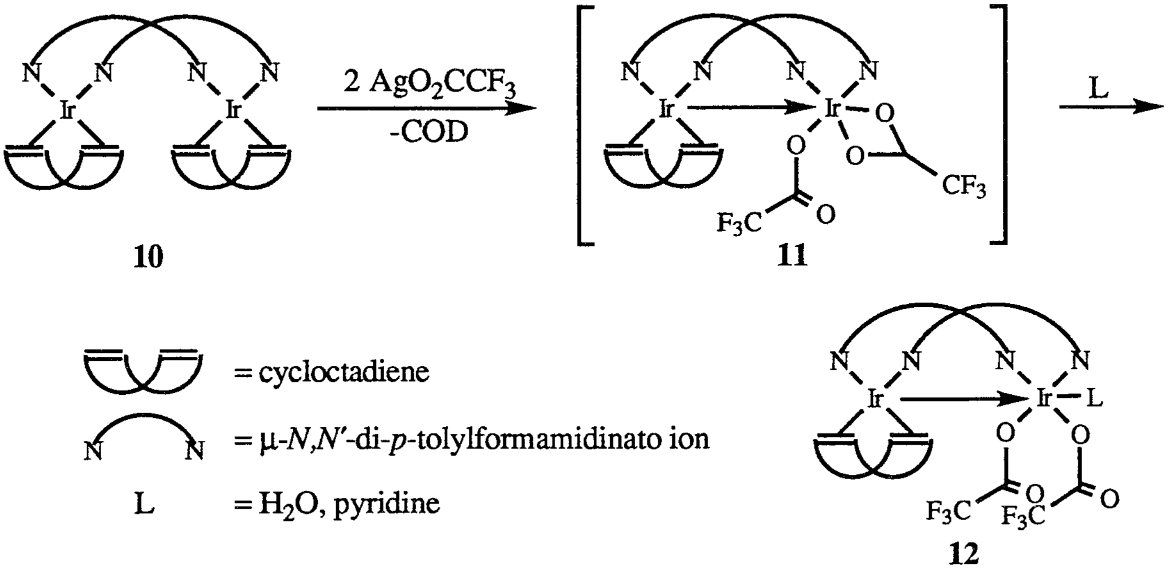
Although the mechanism of action of AgO_2CCF_3 on **1** is unknown, it has recently been reported that the analogous cyclooctadiene complex $[(COD)IrCl]_2$ reacts with 4 equiv AgO_2CCF_3 to yield the polymeric complex $[(COD)IrAg(\mu\text{-}O_2CCF_3)_2]_n$. The same complex is formed from **3** and 2 equiv AgO_2CCF_3.[36] The cyclooctene system most likely proceeds via an analogous Ir(I)·Ag(I) complex, which breaks down to form silver metal and oxidized iridium species (Scheme 3).

Scheme 4. Proposed Oxidation of **1**.

$$\begin{tikzcd}
{[(COE)_2IrCl]_2 + 2\ AgO_2CCF_3} \arrow[r] & {[(COE)_2Ir(O_2CCF_3)]_2 + 2\ AgCl} \arrow[d, "2\ AgO_2CCF_3"] \\
{Ag + Ir(III)(O_2CCF_3)\ \text{complexes}} & {2\ \text{"}[(COE)_2IrAg(O_2CCF_3)]_2\text{"}} \arrow[l]
\end{tikzcd}$$

The exact nature of the oxidized iridium species is unclear. By ^{1}H NMR, the oxidized product appears to be a complex mixture of diamagnetic iridium complexes. The silver salt AgO_2CCF_3 is known to oxidize iridium(I) to iridium(III) (Scheme 4). The mixed valence Ir(I)→Ir(III) complex **11** is formed by oxidation of the iridium(I) dimer **9**. Presumably the reaction proceeds via the intermediate **10**, which readily reacts with

Scheme 5. Oxidation of Ir(I) to Ir(III) by AgO_2CCF_3.



donor ligands to yield the final product.[37] The active metathesis catalyst in the systems presented here is likely iridium(III), but iridium(II) cannot be ruled out.

Conclusions

Several late transition metal metathesis catalysts were investigated and found to be very active for the preparation of extremely high molecular weight polymers of norbornene, cyclooctene, and cyclopentene. Carbene sources such as ethyl diazoacetate can be used to initiate polymerization, but the most active system for the formation of high polymer is **2**/TFAA.

The catalyst systems **1**/2 equiv AgO_2CCF_3 and **2** are active olefin isomerization catalysts with acyclic alkenes. In the presence of 2 additional equivalents AgO_2CCF_3, these systems are transformed into species active for the simultaneous isomerization/metathesis of acyclic olefins, including functionalized compounds such as methyl oleate. This unusual isomerization/metathesis reaction is a single-step analogue of the two-step SHOP process.

The reaction conditions can be further varied to favor selective olefin metathesis with limited isomerization. Thus, the relative rates of the isomerization and the metathesis processes can be controlled. Surprisingly, the most active systems for the metathesis of acyclic olefins require only AgO_2CCF_3, but not TFAA or any other additional initiator. This work thus represents a rare example of the use of an iridium complex to metathesize acyclic olefins in the absence of TFAA or norbornene as well as the first instance of the metathesis of a functionalized acyclic olefin by an iridium complex. The importance of excess silver in these reactions indicates that the active catalyst might in fact be an iridium(III) species and not an iridium(I) species.

Experimental

General. All manipulations involving air- and/or moisture-sensitive compounds were carried out using standard high vacuum or Schlenk techniques. Argon was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4Å molecular sieves. Solids were transferred and stored in a nitrogen-filled Vacuum Atmospheres glove box equipped with a MO-40-1 purification train, a DK-3E Dri-Kool conditioner, and a Dri-Cold Freezer.

Instrumentation. NMR spectra were recorded on a GE QE-300 NMR spectrometer (300.19985 MHz ^{1}H, 75.49283 MHz ^{13}C). Proton chemical shifts are referenced to internal residual solvent protons. Carbon chemical shifts are referenced to the carbon signal of the deuterated solvents. Gas chromatography (GC) was performed on an HP model 5890 Series II gas chromatograph equipped with a crosslinked methyl silicone capillary column (25 m x 0.32 mm x 0.52 μm film thickness) and a flame ionization detector. GC/MS was performed by Ms. Beth Fenner, E. I. DuPont de Nemours and Co., Inc., Wilmington, DE.

Materials. Solvents used in polymerizations were degassed prior to use. Chloroform-*d* and benzene-*d*$_6$ were purchased from Cambridge Isotope Laboratories and used as received. R. T. Baker is gratefully acknowledged for initial sample of $[(COE)_2IrCl]_2$ (**1**). All samples of $[(COE)_2IrCl]_2$ prepared in these laboratories and at DuPont were according to the literature procedure.[38] **2** was prepared as described by Porri.[5] AgO_2CCF_3 was dried under vacuum at 60 °C for 48 hours prior to use. Norbornene was purchased from Aldrich and refluxed over sodium and distilled or vacuum transferred prior to use.[39] Cyclooctene and cyclopentene (Aldrich) were passed through alumina or vacuum transferred from CaH_2 and degassed prior to use. Alternatively, high purity cyclooctene (99.9%) was purchased from Wiley, degassed by repeated freeze-pump-thaw cycles, and used without any further purification. Trifluoroacetic acid, ethyl diazoacetate, and 2,6-di-*tert*-butyl-4-methylphenol (BHT) were purchased from Aldrich and used as received. The purity of EDA was checked by ^{1}H NMR frequently. Fluorinated monomers were provided by Steve McLain. Acyclic olefins and methyl oleate were purchased from Aldrich and used as received or passed through alumina prior to use.

Polymerization of Norbornene. Method 1: Under inert atmosphere, a small vial was charged with catalyst **1** or **2** (0.0056 mmol), AgO_2CCF_3 (0 - ≥4 equiv), and norbornene (100 equiv). Toluene (1 mL) was added via syringe and the reaction mixture was shaken. The sample completely solidified within several minutes. The reaction was allowed to sit for several hours after which the solvent was removed under vacuum. Method 2: Catalyst **1** or **2** (0.0056 mmol) and AgO_2CCF_3 (0 - ≥4 equiv) were weighed into a small vial under inert atmosphere. A solution of norbornene (100 equiv) in toluene (1 mL) was added and the reaction was shaken. The sample completely solidified within several minutes. The reaction was allowed to sit for several hours after which the solvent was removed under vacuum. Method 3: Catalyst **1** or **2** (0.0056 mmol) and AgO_2CCF_3 (0 - ≥4 equiv) were weighed into a small vial under inert atmosphere and dissolved in toluene (0.5 mL). A solution of norbornene (100 equiv) in toluene (0.5 mL) was added and the reaction was shaken. The sample completely solidified within several minutes. The reaction was allowed to sit for several hours after which the solvent was removed under vacuum. ^{1}H NMR ($CDCl_3$): δ 5.32 (b), 5.18 (b), 2.78 (b), 2.40 (b), 1.82 (b), 1.72 (b), 1.33 (b), 1.02 (b).

Polymerization of Cycloolefins using 1 or 2/AgO_2CCF_3/initiator. Catalyst **1** or **2** (0.0056 mmol) and AgO_2CCF_3 (0 - ≥4 equiv) were weighed into a small vial under inert atmosphere. The cycloolefin (0.5 mL) was added via syringe followed by TFAA

(15 µL, 0.195 mmol, 35 equiv) or EDA (15 µL, 0.143 mmol, 26 equiv). The reaction was left to stir at room temperature or at 55 °C overnight. If the reaction mixture was completely solidified, the polymer was washed in methanol and dried under vacuum. Other reaction mixtures were generally extremely viscous; these were precipitated into degassed methanol and the resulting polymer was dried under vacuum. In some cases, reactions were run with a trace of BHT present. The insolubility of the products has made gel permeation chromatography and ^{13}C NMR difficult. Polyoctenamer: ^{1}H NMR ($CDCl_3$): δ 5.38 (b), 1.97 (b), 1.29 (b); Polypentenamer: ^{1}H NMR ($CDCl_3$): δ 5.38 (b), 1.98 (b), 1.39 (b).

Screening of Catalyst Systems. The metal complex (0.011 mmol metal) and AgO_2CCF_3 (0 - ≥4 equiv) were weighed into a small vial under inert atmosphere. Norbornene (50 equiv per metal center) was added followed by solvent (1 mL). Reaction mixtures were stirred at room temperature until (a) the reaction mixture became noticeably viscous or (b) several days had passed. Activity for polymerizing norbornene was assessed visually, or, in some cases, reactions were precipitated into degassed methanol or water or were concentrated under vacuum and analyzed by ^{1}H NMR spectroscopy.

Cyclooctadiene Monoepoxide.[40] A 500 mL three-neck round bottom flask equipped with a magnetic stir bar, condenser, addition funnel, and Ar inlet was charged with cyclooctadiene (11.07 g. 0.102 mmol). A solution of *m*CPBA (50-60 %) (32 g, ~0.102 mmol, ~1 equiv) in $CHCl_3$ (250 mL) was placed in the addition funnel and added dropwise over 3.5 h. After the addition was complete, the reaction was refluxed for 3 h. While heating, the milky white precipitate dissolved to form a clear, colorless reaction mixture. The reaction mixture was then cooled in ice to precipitate *m*-chloro benzoic acid and filtered. The liquid was concentrated to a clear, yellow oil that was purified by distillation (9 mm Hg, 75-85 °C, 42% yield) or flash chromatography (10% ethyl acetate/hexanes, 33% yield). ^{1}H NMR ($CDCl_3$): δ 5.55 (b, 1 H), 2.99-3.06 (b, 1 H), 2.33-2.48 (m, 1 H), 1.95-2.18 (m, 3 H).

5-Cyclooctenol. LAH (1 M in THF; 2.01 mL, 2.01 mmol, 0.5 equiv) was added dropwise to a solution of cyclooctadiene monoepoxide (500 mg, 4.04 mmol) in THF (4 mL). The resulting reaction mixture was stirred at room temperature overnight. H_2O was added dropwise by syringe and the reaction mixture was extracted into ether. The aqueous layer was washed 3 times with ether. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated to an oil that was purified by flash chromatography (20% ethyl acetate/hexanes, ≥98% yield). ^{1}H NMR ($CDCl_3$): δ 5.58-5.78 (m, 2 H), 3.80-3.9 (m, 1 H), 1.5-2.4 (m, 10 H).

Isomerization of Acyclic Olefins.[41] A reaction vessel was charged with AgO_2CCF_3 (0.056 mmol, 2 equiv to **1**) and the acyclic olefin (0.700 mmol, 25 equiv). Toluene (1 mL) was added followed by catalyst **1** (0.028 mmol) and the reaction mixture was stirred at room temperature for 15 h and analyzed by GC. Similar results were obtained when the reaction was run in the presence of TFAA (0.14 mmol, 5 equiv).

Isomerization/Metathesis of Acyclic Olefins.[41] Under inert atmosphere, AgO_2CCF_3 (≥4 equiv per **1**) and the acyclic olefin (2.18 mmol, 25 equiv) were dissolved in toluene (4 mL) Catalyst **1** (0.087 mmol) was added and the reaction mixture was stirred at room temperature for 24 h and analyzed by GC and GC/MS. Similar results were obtained using **2** and ≥2 equiv AgO_2CCF_3.

Selective Metathesis of Methyl Oleate. Method 1: Catalyst **1** (0.0056 mmol) was weighed into a reaction vessel under inert atmosphere. In a separate vial, norbornene

(20 equiv) and methyl oleate (35 equiv) were dissolved in toluene (1 mL). This solution was added to the vessel containing the catalyst followed by AgO_2CCF_3 (≥4 equiv). The reaction was stirred at 55 °C for several hours and analyzed by GC. Method 2[41]: A reaction vessel was charged with catalyst **1** (0.028 mmol) and AgO_2CCF_3 (≥4 equiv). Toluene (2 mL) was added and the reaction mixture was allowed to stir at room temperature for 45 h. Methyl oleate (0.28 mmol, 10 equiv) was added, and the reaction was stirred at room temperature for an additional 8 h and analyzed by GC and GC/MS. Similar results were obtained using **2** and ≥2 equiv AgO_2CCF_3.

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(1) This research was carried out in collaboration with Dr. Jerald Feldman, E. I. DuPont de Nemours and Co., Inc. Experiments that he carried out are acknowledged in the references.

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(26) This particular gas chromatogram is courtesy of Dr. J. Feldman, E. I. DuPont de Nemours and Co., Inc.

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Chapter 5

Synthesis of Ruthenium Carbene Complexes via Alkylidene Transfer from Diazo Compounds

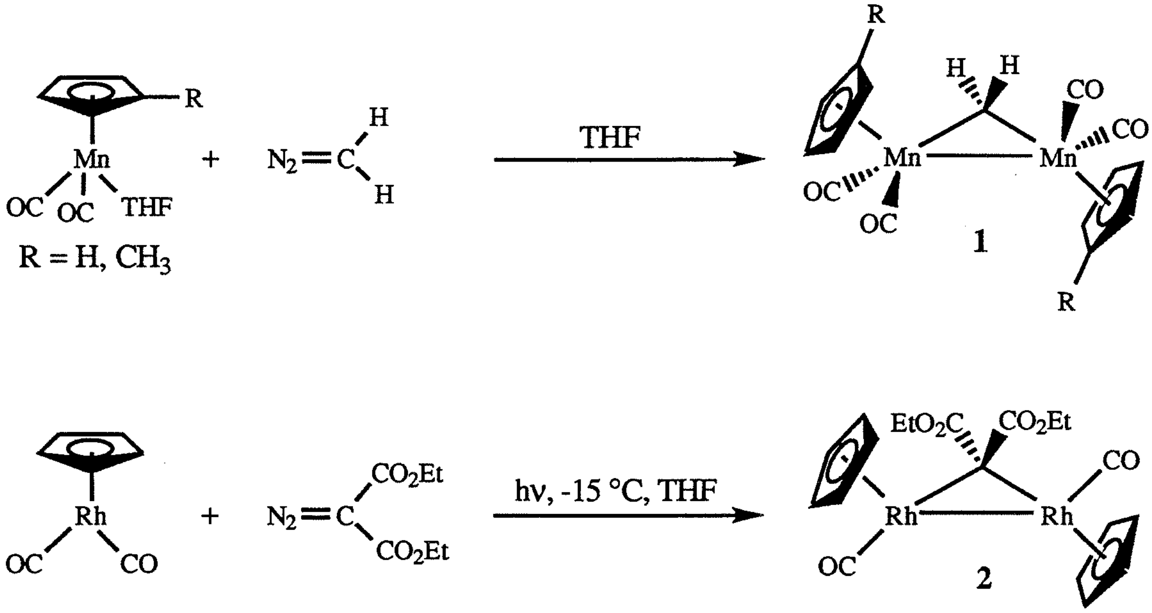
Introduction

Chapter 3 presented a system in which ethyl diazoacetate (EDA) was used to initiate the Ring-Opening Metathesis Polymerization (ROMP) of low strain cyclic olefins with $Ru(H_2O)_6(tos)_2$ (tos = *p*-toluenesulfonate). Presumably the active catalyst in that system is a ruthenium carbene of the type $[Ru]{=}CHCO_2Me$, but this species has never been isolated or even observed. It is quite likely that the failure to detect the carbene species during these reactions is at least partially due to the ligand environment about the metal center; a coordination sphere consisting of six water molecules would not be expected to stabilize such a carbene ligand. It should, however, be possible to find a ligand system that would allow isolation of this type of complex. In addition, it would be of interest to investigate other diazo compounds that are not substituted with an electron-withdrawing ester functionality.

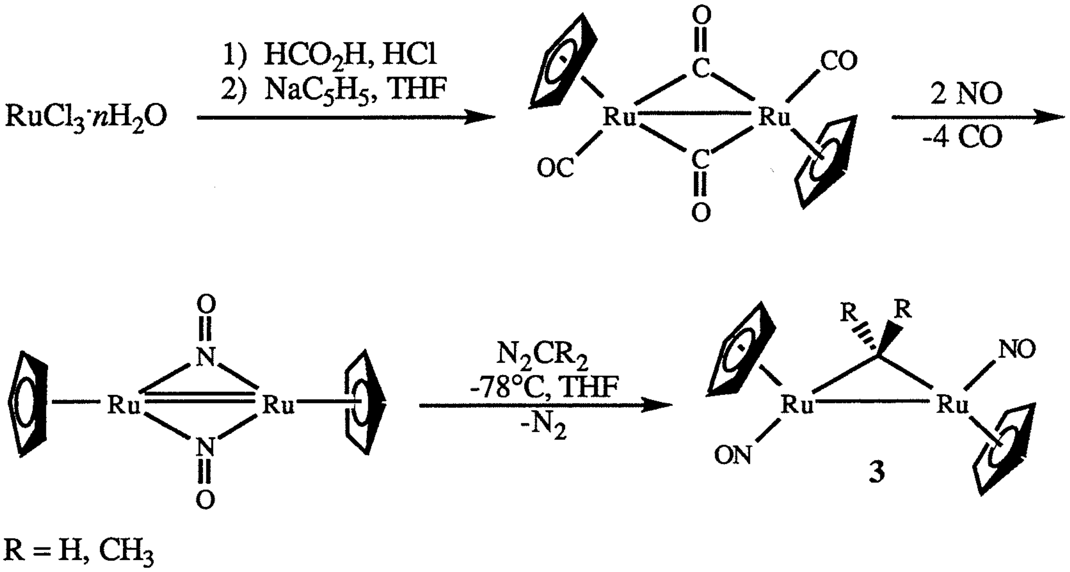
The interaction of diazo species with transition metal complexes has been studied in a number of systems.[1-4] Quite a few metal complexes with coordinated intact diazo ligands have been reported. In addition, a number of isolable transition metal carbene and μ-alkylidene complexes generated from diazo compounds have appeared in the literature, although none have been demonstrated to show activity as metathesis catalysts.

The best documented reactions of diazo compounds with transition metal complexes involve the preparation of metal carbene systems that contain bridging alkylidene ligands.[5-7] Complexes of this type have been reported for a wide range of different metallic starting materials, including chromium,[8] manganese,[8] iron,[5, 7] cobalt,[9] rhodium,[10] and osmium.[5] Either mononuclear or dinuclear metal precursors can be utilized as starting materials. Examples of μ-alkylidene complexes prepared by the former method include the manganese alkylidene **1** and the related rhodium compound **2** (Scheme 1).[2, 11-13] The latter route is illustrated by one of the relatively few reported systems involving the reaction of ruthenium precursors with diazo compounds, leading to the formation of the dinuclear product **3** (Scheme 2).[14]

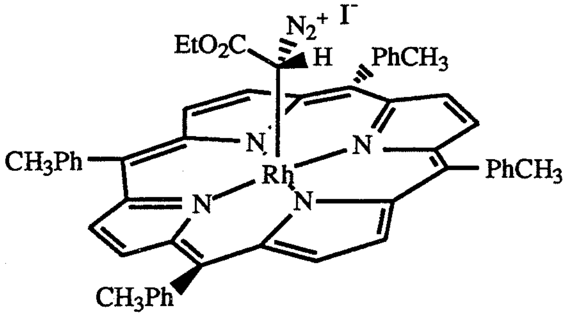
Scheme 1. Preparation of bridging alkylidene complexes by reaction of diazo species with mononuclear metal compounds.



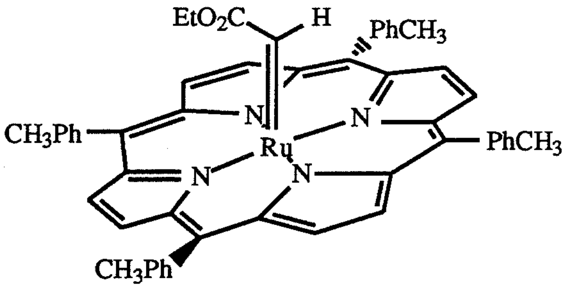
Scheme 2. Preparation of bridging alkylidene complexes by reaction of diazo species with dinuclear metal compounds.



Examples of terminal metal carbene complexes formed from diazo compounds are rarer. Much interest in this area has been prompted by cyclopropanation systems, which have long employed diazo compounds as stoichiometric carbene sources with metal catalysts.[15-18] In one such system involving RhTTPI (TTP = tetra(*p*-tolyl) porphyrin),[19] spectroscopic evidence for the formation of rhodium porphyrin-EDA adduct **4** has been obtained.[20] Presumably this species is an intermediate along the reaction pathway to the metal carbene complex believed to be the active catalytic species.[15-18, 21] The corresponding ruthenium carbene **5** has been isolated from the reaction of $[Ru(TTP)]_2$ with EDA, although no catalytic activity has been reported for this compound.[22]

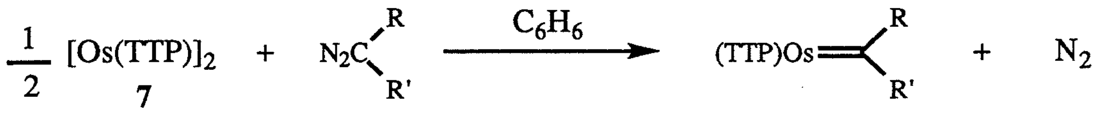


4



5

The analogous osmium porphyrin carbene complexes **6a-c** have been prepared in high yield by the reaction of the osmium porphyrin dimer **7** with the appropriate diazo compound.[23] Carbene **6c** is the first example of an isolated carbene complex that is catalytically active towards cyclopropanation in the presence of additional EDA.[21]



$$\frac{1}{2}\,\underset{7}{[Os(TTP)]_2} + N_2C\begin{smallmatrix}R\\R'\end{smallmatrix} \xrightarrow{C_6H_6} (TTP)Os{=}C\begin{smallmatrix}R\\R'\end{smallmatrix} + N_2$$

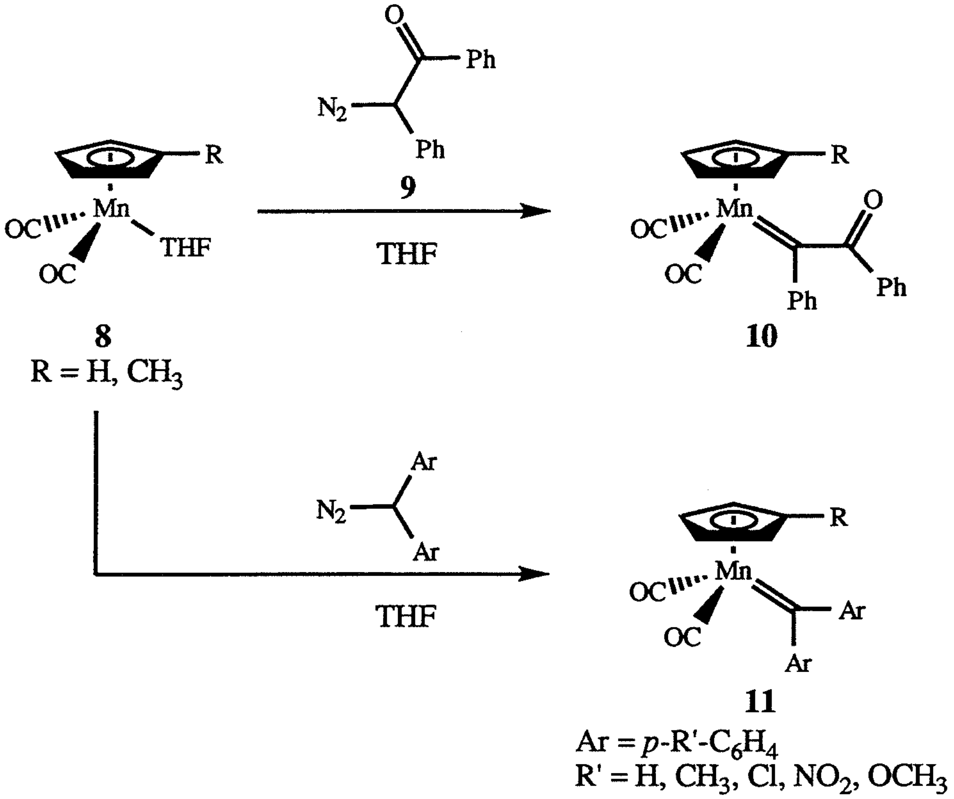
TTP = *meso*-tetra(*p*-tolyl) porphyrin

6a R = R' = p-C_6H_4-CH_3
b R = H, R = $SiMe_3$
c R = H, R' = CO_2Et

Although osmium is a metal that is known to catalyze ROMP,[24] no metathesis activity has been reported for this carbene.

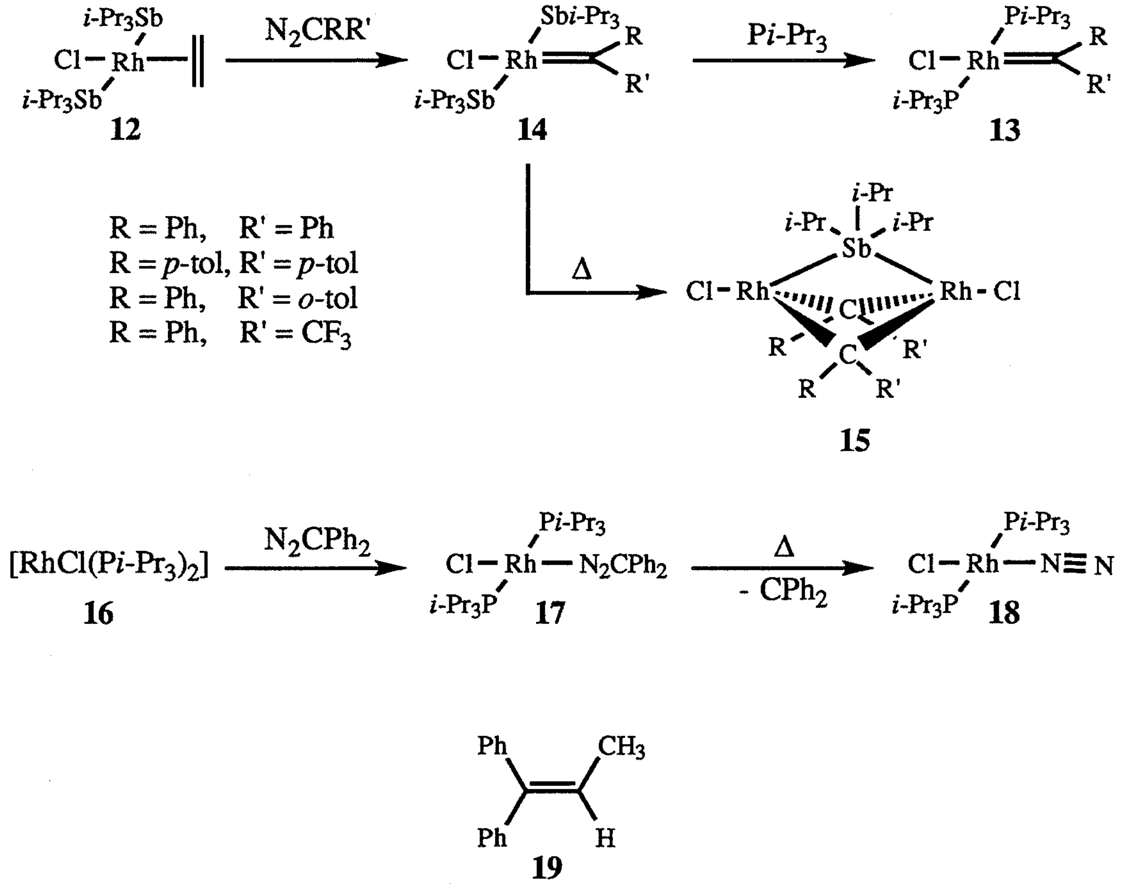
Metal carbene complexes prepared from diazo compounds have also been studied in other contexts. For example, the manganese complex **8** has been used to trap the intermediate keto carbene formed during the Wolff rearrangement of **9** to yield the metal carbene complex **10** (Scheme 3).[2,25] Analogous complexes (e.g., **11**) have been prepared from *para*-substituted derivatives of diphenyl diazomethane.[2] as well as from other diazo compounds.[26,27]

Scheme 3. Formation of Manganese Carbene Complexes from Diazo Compounds.



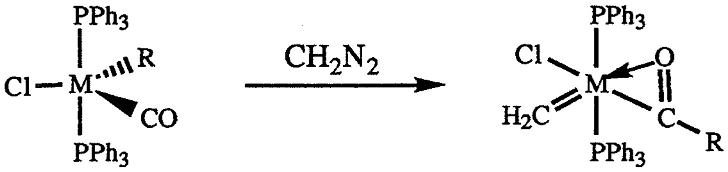
Recently, diphenyl diazomethane has been investigated for reactivity with a number of rhodium complexes. Reaction of the stibane complex **12** with diphenyl diazomethane followed by P*i*-Pr3 produces carbene **13** (Scheme 4).[28] The intermediate

Scheme 4. Reactions of Rhodium Complexes with Diazo Compounds.



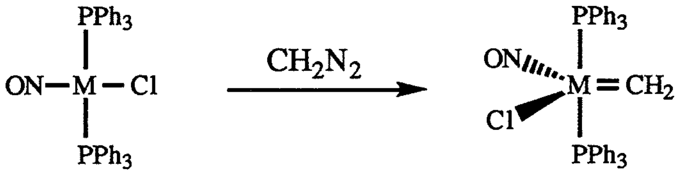
stibane carbene complex **14** dimerizes upon heating to form **15**, a complex containing two bridging alkylidene ligands.[29] Attempts to prepare **13** directly from [RhCl(P*i*-Pr$_3$)$_2$] (**16**) result instead in formation of the diazoalkane complex **17**. Upon warming it eliminates :CPh$_2$ instead of N$_2$ to yield the dinitrogen complex **18**. A number of iridium diazoalkane complexes similar to **17** (CH$_3$(P*i*-Pr$_3$)$_2$Ir(N$_2$CRR')) have also been prepared.[30] Neither cyclopropanation nor metathesis activity has been reported for any of these complexes; in fact, **17** catalyzes the unexpected formation of **19** from excess diphenyl diazomethane and ethylene.[31]

Among the rare examples of group VIII terminal carbene complexes prepared from diazo compounds are the methylene complexes **20** and **21**.[32, 33] Although the



M = Ru, Os
R = Ph, *o*-tolyl, *p*-tolyl

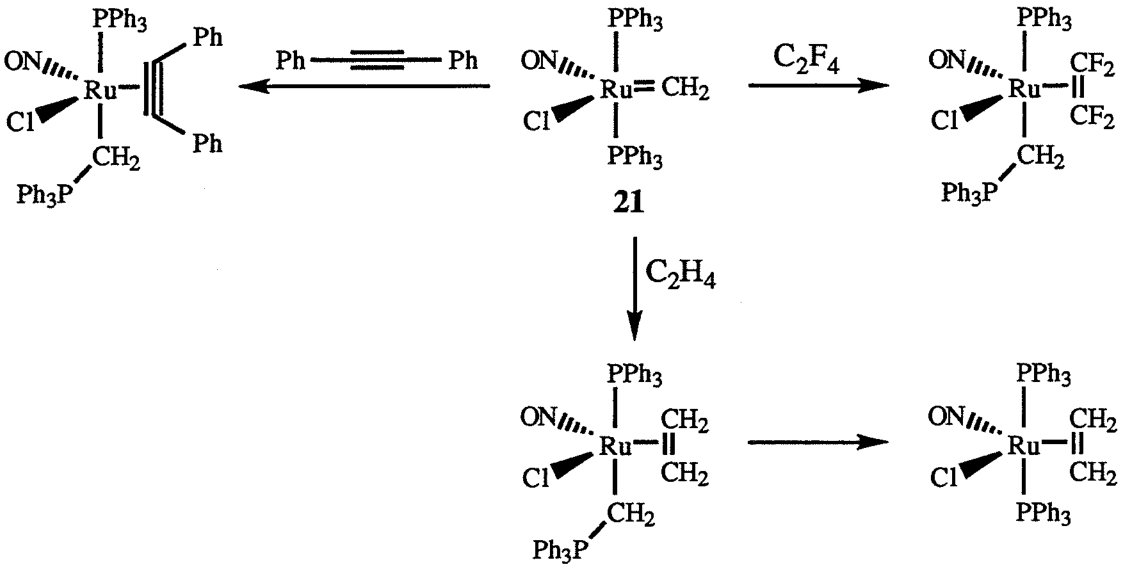
20



M = Ru, Os

21

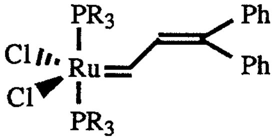
Scheme 5. Reactions of **21** with olefins and acetylenes.



osmium analogue of **21** fails to react with simple acetylenes and alkenes, the ruthenium complex reacts with these molecules to yield olefin and acetylene complexes, but not metathesis products (Scheme 5).[33]

Although alkylidene transfer from diazo compounds is not among the more thoroughly studied entries into terminal transition metal carbene complexes and no compounds prepared in this manner have demonstrated metathesis activity, it is clear that this method of synthesis shows great potential. Due to the large number of readily available diazo compounds,[34] the preparation of a wide variety of substituted alkylidenes should be possible, since the reaction involves the straightforward transfer of an intact carbene from the diazo compound. The incorporation of different alkylidene substituents is important because the nature of all ligands, including the carbene, can have a profound effect on catalyst initiation and activity.[35-37] In addition, variation of the alkylidene ligand allows control of the polymer end-group during ROMP.[38-40]

In order to prepare well-defined metathesis catalysts by this novel route, it is important to identify metal complexes that might be good candidates for carbene transfer from diazo compounds. Although only a limited number of well-defined ruthenium carbene complexes have appeared in the literature,[4] they provide a good starting point for studies with diazo compounds by indicating ligand environments that are suitable for stabilizing a metal carbon double bond. Of particular interest are complexes **22a-c**,



22a R = Ph
b R = Cy
c R = *i*-Pr

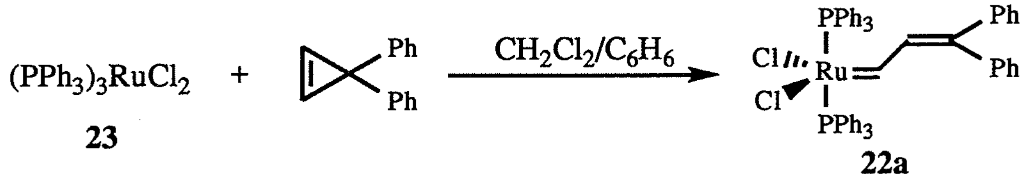
which have been shown to possess highly promising metathesis activity.[41, 42] The reactivity of diazo species with several ruthenium starting materials has been investigated, and the results are presented in this chapter. While detailed studies have mainly focused on ruthenium carbene species that show metathesis activity analogous to

22a and **c**, additional carbene complexes, both terminal and bridging, are also presented in order to demonstrate the generality of this synthetic method.

I. Preparation of Ruthenium Carbenes from $(PPh_3)_3RuCl_2$

Background

Our laboratory has recently reported the preparation of an isolable ruthenium carbene complex (**22a**) from the reaction of $(PPh_3)_3RuCl_2$ (**23**) with 3,3-diphenylcyclopropene. This carbene displays catalytic activity for the living ring-opening metathesis polymerization of norbornene, although, like most other late transition metal catalysts, it is inactive for the metathesis of less strained olefins. As would be predicted from our knowledge of the ill-defined group VIII catalysts, complex **22a** is moderately air stable and tolerates water, alcohols, ethers, and other functionalized organic molecules. This complex represents the first example of an isolated ruthenium carbene that exhibits both stability to protic media and metathesis activity.[41] Carbene complexes analogous to **22a** but with better σ-donating alkylphosphines, such as PCy_3 (**22b**) or $P\textit{i}\text{-}Pr_3$ (**22c**), have also been prepared and show broader metathesis activity, including ROMP of low strain monocyclic olefins and acyclic olefin metathesis.[42, 43]



23

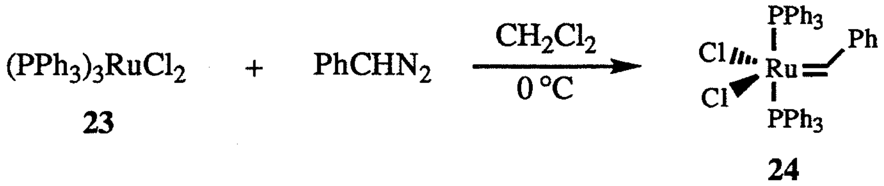
22a

Although complexes **22a-c** are highly promising metathesis catalysts, the need for 3,3-diphenylcyclopropene for their synthesis is a serious drawback, since this reagent is difficult to prepare.[44] The development of a new route into these species that does not require this reagent would be desirable, and diazo complexes could provide a suitable alternative. Ruthenium carbene complexes generated from **23** and diazo precursors would differ from **22a-c** only by the substituent on the carbene ligand and would be expected to generate the identical active species upon initiation.

Results and Discussion

Preparation of $(PPh_3)_2Cl_2Ru{=}CHPh$ from Phenyl Diazomethane - A Facile Entry into Metathesis Catalysts Analogous to 22a and 22b

Ruthenium carbene complex **24** was prepared in 60% isolated yield by the slow addition of two equivalents phenyl diazomethane to a methylene chloride solution of **23**



23 **24**

at 0 °C. This carbene, formed as a grayish green solid, was moderately air stable and soluble in common organic solvents such as benzene and methylene chloride. ^1H NMR spectroscopy revealed a triplet for the carbene proton resonance at 19.56 ppm in C_6D_6 (J_{PH} = 10.2 Hz). Downfield chemical shifts of this magnitude are characteristic of mononuclear metal carbene complexes of this type. For example, the analogous complex **22a** exhibited a carbene proton resonance at 17.94 ppm (pseudo-quartet, J_{HP} = 9.7 Hz) (C_6D_6).[41]

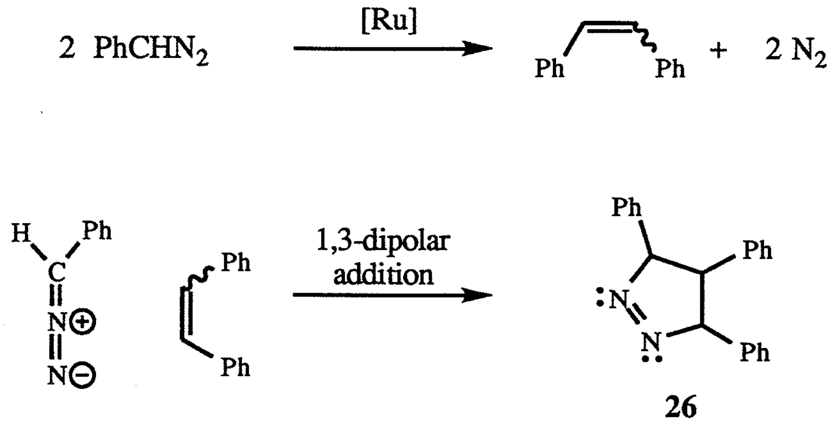
The ^{13}C NMR spectrum showed a resonance for the carbene carbon at 310.2 ppm (CD_2Cl_2). It has not been possible to clearly resolve the carbon-phosphorus coupling, even at 500 mHz using long delay times and a large number of scans, but J_{CP} appeared to be on the order of 10 to 11 Hz. The chemical shift of this carbon was similar to that observed for **22a** (288.9 ppm (J_{CP} = 10.4 Hz) (CD_2Cl_2)).[41] The ^{31}P NMR resonance appeared at 30.68 ppm (s) (CD_2Cl_2), compared to 28.2 (s) (C_6D_6) for the analogous **22a**.[41] Although X-ray quality crystals have not yet been obtained for **24**, the indicated structure has been confirmed by comparison of its spectroscopic data with that of **22a**, which has been characterized crystallographically,[41] and by elemental analysis and exact mass determination.

Depending upon the reaction conditions, varying amounts (*vide infra*) of another ruthenium complex (**25**) were sometimes formed as well. The presence of compound **25** was detected by the appearance of a small doublet at 19.80 ppm (J_{PH} = 14.7 Hz) in the ^1H NMR spectrum (C_6D_6), indicating that the ruthenium in this species is likely bonded to a terminal carbene ligand and only one phosphine. There appeared to be an equilibrium between the two ruthenium complexes; **25** was observed by ^1H NMR to form gradually in a solution (CD_2Cl_2 or C_6D_6) of essentially pure **24**. Furthermore, when excess triphenylphosphine was added to a solution containing mostly **25**, complete conversion to the bisphosphine complex **24** was observed, indicating that **25** differs from **24** only by substitution of a phosphine ligand.

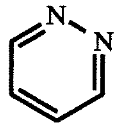
The exact structure of **25** has not been conclusively demonstrated. In order to form a monophosphine complex, some type of coordinating group that is capable of displacing a phosphine must be present in this system. Mass spectrometry of a sample containing mostly **25** detected higher molecular weight species (up to *m/e* 1097 and 1394). While these fragments might not correspond to the molecular ion peak, clearly **25** is some type of multinuclear complex. It is unlikely, however, that the structure contains a bridging alkylidene ligand, since ^1H and ^{13}C NMR resonances for μ-alkylidenes usually appear significantly upfield of the chemical shifts observed.[7]

Although several potentially coordinating species such as stilbene and the heterocycle **26** might result from decomposition of $PhCHN_2$ and be present in the

Scheme 6. Some possible decomposition pathways of phenyl diazomethane.



reaction mixture (Scheme 6),[45] none of these appears to be responsible for the formation of **25**. While *cis*- and *trans*-stilbene were detected by ^{1}H NMR during the reaction of **23** with phenyl diazomethane and trace amounts were also observed forming in solutions of **24** that had been left to sit overnight, addition of these olefins to solutions of **24** in C_6D_6 or CD_2Cl_2 did not appear to promote formation of **25**. Although not strictly analogous to **26**, pyridazine (**27**) reacted with **24** in C_6D_6 to form a monophosphine carbene complex



27

that showed a doublet at 19.46 ppm (J_{HH} = 17.0 Hz) in the ^{1}H NMR spectrum. However, elemental analysis of an impure sample of **25** showed no nitrogen; therefore, **26**, N_2, and any other nitrogen-containing ligands can be ruled out. Furthermore, mass spectrometry of this species failed to reveal the presence of **26**.

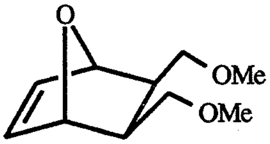
When the reaction of **23** with phenyl diazomethane was run directly in an NMR tube in C_6D_6, **24** and **25** were both formed in approximately a 2:1 ratio. In contrast, **24** was isolated cleanly from a preparative scale reaction using 2 equiv of phenyl diazomethane. However, when only 1 equiv of the diazo compound was used, the major carbene-containing product was **25**, isolated as very small amount of a tan solid. It is possible that this observation was purely coincidental and that the difference in product distribution was instead due to another factor such as the rate of addition of the diazo compound or the concentration of the reaction mixture. However, these observations were reproducible, even when attempts were made to keep all other reaction conditions constant. Some variation of the product distribution was also noted upon changing the reaction scale or the length of time the diphenyl diazomethane was stored prior to use. In all cases when large amounts of **25** were formed, product yields were significantly lower. In general, optimal results were obtained when 2 equiv fresh phenyl diazomethane was employed. In any case, while the exact factors governing the product distribution, as well as the identity of **25**, remain to be investigated further, the reaction conditions can be controlled to minimize production of this side product.

Polymerization of Norbornene Using $(PPh_3)_2Cl_2Ru{=}CHPh$. Isolated carbene **24** was found to be active for the ring-opening metathesis polymerization of norbornene. Upon addition of norbornene to a solution of **24** in C_6D_6, the propagating carbene was observed in the ^1H NMR as a pseudo-quartet (two overlapping triplets) at 17.79 ppm. Once initiation has occurred, the propagating species should be identical to that formed in reactions of **22a** with norbornene; that propagating carbene also displayed a ^1H chemical shift as a pseudo-quartet at 17.79 ppm.[41] By analogy, it is assumed that the polymerization is living in the case of **24** as well.

The polymerization of norbornene was more rapid in methylene chloride than in benzene. The reaction required approximately 30 min to reach 90% conversion in the former solvent and 3.5 h in the latter. Catalyst **22b** has been observed to metathesize *cis*-2-pentene approximately four times faster in CD_2Cl_2 than in C_6D_6;[42] thus, the observed rate difference upon changing solvents in the present system is expected. The rate in the chlorinated solvent was on the same order of magnitude as that found for norbornene polymerization with **22a** under similar conditions (essentially complete after 2 h with **24** (CD_2Cl_2) versus complete in 3 h for **22a** (1:8 CD_2Cl_2/C_6D_6)).[41, 46] In both solvents, the propagating carbene remained visible in the ^1H NMR throughout the reaction, even after polymerization was complete.

The polymer prepared in methylene chloride, isolated in 82% yield,[47] was 92% trans and had $M_n = 42{,}600$, $M_w = 44{,}600$, and PDI = 1.05. This extremely narrow molecular weight distribution supports the assumption that the polymerization is in fact living and that this system provides a pathway to the same catalytic species as was formed from **22a**.

Analogous to the findings with **22a**, complex **24** was found to be inactive for the polymerization of the functionalized norbornene derivative **28** and low-strain cyclic olefins such as cyclooctene. It was also inactive for the metathesis of acyclic olefins.



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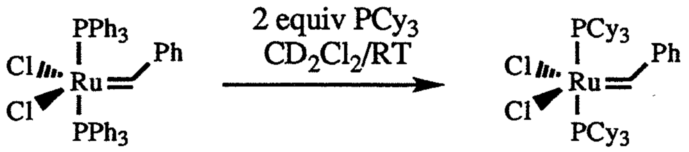
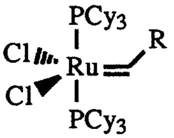
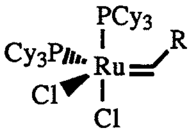
Preparation of $(PCy_3)_2Cl_2Ru{=}CHPh$. Upon treatment of **24** with 2 equiv PCy_3 in CD_2Cl_2, an immediate color change from dark brown to red was observed and rapid exchange of the phosphine ligands occurred to yield the tricyclohexyl phosphine derivative **29** (Scheme 7). This complex is analogous to the highly active metathesis catalyst **22b**.[42] However, while **22b** and **c** were both formed as mixtures of cis and trans isomers (predominantly trans) (Table 1), **29** showed only one alkylidene resonance in the ^1H NMR spectrum, appearing at 20.02 ppm (s) in CD_2Cl_2. Since the trans isomers of **22b** and **c** did not exhibit phosphorus-hydrogen coupling while the cis isomers did,[42]

Scheme 7. Preparation of tricyclohexyl phosphine ruthenium carbene complexes.



24 **29**

Table 1. Production of *cis*- and *trans*- cyclohexyl phosphine derivatives.

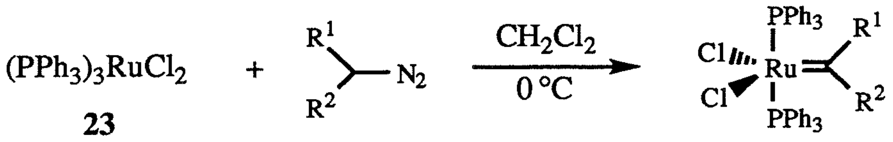
Ruthenium Precursor	**% starting material unreacted**		
22a[42] R = CH=CPh$_2$	5%	**22b-*trans*** 78%	**22b-*cis*** 16%
24 R = Ph	---	**29-*trans*** 100%	**29-*cis*** ---

carbene **29**, which appeared as a singlet, is assumed by analogy to be the trans isomer (**29-*trans***). Furthermore, although preparative scale formation of **22b** and **c** left behind unreacted **22a** (5 and 13% respectively),[42] no unreacted **24** was detected by ^{1}H NMR in the present system (run directly in an NMR tube), and the reaction appeared to be quite clean.[48] Complex **29** showed a resonance at 36.63 ppm (s) in the ^{31}P NMR spectrum and one at 294.62 ppm in the ^{13}C NMR.[49] Since **25** is known to form **24** in the presence of excess PPh$_3$, it is assumed that it also reacted with PCy$_3$ to form **29-*trans***. Thus, samples containing small amounts of **25** are not expected to limit the utility of this system.

Preliminary observations indicated that, as expected, **29** possessed broader metathesis activity than **24**. Addition of 58 equiv *cis*-cyclooctene to the complex prepared *in situ* from **24** and PCy$_3$ in CD$_2$Cl$_2$ resulted in the formation of a propagating carbene species with a proton resonance at 19.26 ppm (t, J_{HP} = 5.3 Hz). For comparison, the propagating carbene resonance for the polymerization of this monomer using **22b** appeared as a triplet at 19.47 ppm in 5:4 CH_2Cl_2/C_6D_6.[42] This slight difference in chemical shift is presumably due to the different solvents used for the two reactions.[50] The polymerization appeared to be extremely slow, reaching only approximately 50% conversion after 2 days, but the presence of the 2 equiv free PPh_3 generated during the preparation of **29** is expected to affect the rate. Excess phosphine is known to inhibit reactions of **22c**.[51] At low conversion, only a portion of the catalyst was activated under these conditions, and the starting and propagating alkylidenes were both detected by ^1H NMR spectroscopy. After two days, essentially the only remaining carbene visible in the NMR spectrum was that due to the propagating species. It should be noted that while this system did not appear to be living, catalyst **22b** was not found to be living either.[42]

Reaction of $(PPh_3)_3RuCl_2$ with Other Diazo Compounds

The reaction of **23** with other diazo species was also explored. A comparison of all the analogous ruthenium carbene complexes in this series can be found in Table 2. Formation of carbenes **30** and **31** was observed upon reaction of **23** with EDA and $TMSCHN_2$, respectively, but **32** did not appear to be formed. The spectral data for complexes **30** and **31** were similar to that obtained for **24** and **22a**, and their structures were inferred by analogy. During the preparation of the ester and silyl carbene compounds, generation of the diazo coupling products was detected by ^1H NMR



30 $R^1 = CO_2Et$ $R^2 = H$
31 $R^1 = TMS$ $R^2 = H$
32 $R^1 = Ph$ $R^2 = Ph$

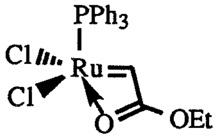
Table 2. Selected NMR data for complexes $(PR^3_3)_2Cl_2Ru{=}CR^1R^2$

Complex	**R^1**	**R^2**	**R^3**	**Carbene Chemical Shift**	
				^1H (ppm)	**^{13}C (ppm)**
24	Ph	H	Ph	19.56^{a}	310.2^{b}
30	CO_2Et	H	Ph	$17.92^{a,c}$	$280.3^{b,c}$
31	TMS	H	Ph	17.65^{b}	
32	Ph	Ph	Ph	---	---
22a[41]	$CH{=}CPh_2$	H	Ph	17.94^{a}	288.9^{b}
22b[42]	$CH{=}CPh_2$	H	Cy	$19.09^{b,d}$	$289.3^{b,d}$
29	Ph	H	Cy	$20.02^{b,d}$	$294.6^{b,d}$
22c[42]	$CH{=}CPh_2$	H	*i*-Pr	$19.24^{b,d}$	$290.6^{b,d}$

[a] in C_6D_6
[b] in CD_2Cl_2
[c] at -40°C
[d] trans isomer

spectroscopy. Tetraphenylethylene, the coupling product of Ph_2CN_2, proved difficult to detect due to the extremely complicated aromatic region in the ^1H and ^{13}C NMR spectra of this system.

Reaction with Ethyl Diazoacetate. The isolation of carbene **30** is of particular importance because it demonstrates that EDA can, in fact, react with a ruthenium precursor to generate a ruthenium carbene complex, as proposed in Chapter 3. Although **30** was the only carbene isolated, when the reaction was monitored in an NMR tube, formation of what is believed to be a monophosphine carbene complex (**33**) was also observed (**30**:**33** ~ 3:1). This complex showed a ^1H NMR resonance (C_6D_6) at 13.95 ppm (d, J_{HP} = 12.1 Hz). Carbene **33** is not necessarily analogous to the monophosphine complex **25** observed in the phenyl carbene system, and the large chemical shift difference between these two species implies that they are not the same. A dinuclear structure with a bridging alkylidene is more likely for **33** than for **25**, since the proton chemical shift is in the range expected for a μ-alkylidene ligand. Several coordinating species such as diethyl maleate, diethyl fumarate, and a heterocycle analogous to **26** might be present, resulting from decomposition of EDA. Although these were ruled out for **25**, they may play a role in the formation of **33**. In addition, a new structure is also possible in this case that was not available to **25**; since the carbonyl of the ester functionality is capable of coordinating to the metal center, structure **A** or some type of dinuclear structure with a chelating carbene ligand must also be considered.



A

Although in the solid form isolated **30** was stable indefinitely when stored at -25 °C under inert atmosphere, it was found to be unstable in solution at room temperature, decomposing to form diethyl maleate and diethyl fumarate, the coupling products of EDA. The monophosphine complex **33** was not observed to be formed among the decomposition products. When **30** was prepared *in situ* by mixing the reagents directly in an NMR tube, the sample decomposed extremely rapidly, and the triplet carbene resonance completely disappeared in about 20 min. Decomposition of **33** was more gradual. The degradation of **30** was slowed somewhat in the case of the isolated complex, prepared at 0°C. Since similar difficulties were not encountered with the analogous carbenes **22a** and **24**, it was originally postulated that **30** was destabilized by the electron withdrawing nature of the ester functionality. However, the results obtained for **31** (*vide infra*) indicate that the explanation might be more complicated. It should be noted that, despite the rapid decomposition in solution, in the solid form carbene **30** was moderately stable upon exposure to air.

Carbene **30** was found to be an active catalyst for the ring-opening metathesis polymerization of norbornene. Approximately 27% conversion was observed after 1 h in C_6D_6 at room temperature, and complete reaction after 36 h led to a polymer that was 80% trans. In contrast to systems employing **22a** or **24**, the propagating species was not observed and the resonance corresponding to the starting carbene disappeared in approximately 20 min. The polymerization continued after this time, indicating that only a small amount of the propagating species had been generated. This finding might be related to the instability of the carbene in solution. It has been reported for **22a** that initiation is slower than propagation;[41] it is postulated for this system that initiation might also be slower than decomposition.

Reaction with Trimethylsilyl Diazomethane. Since it was thought that the electron-withdrawing nature of the ester substituent might contribute to the instability of carbene **30** relative to carbenes **22a** and **24**, trimethylsilyl diazomethane was investigated as a source of a more electron-donating carbene. Surprisingly, although formation of complex **31** was observed, it did not exhibit greater stability than **30**. It is possible that the conjugation with the vinyl group and with the aromatic rings in **22a** and **24** is a crucial contributing factor in their stability.

Reaction with Diphenyl Diazomethane. Reaction of **23** with diphenyl diazomethane has also been attempted. The expected product, **32**, is reminiscent of the diphenyl vinyl carbene **22a**. Characterization of products obtained in reactions with this diazo compound are rendered more difficult due to the lack of protons on the carbene carbon. As a result, ^{13}C NMR spectroscopy is required to positively identify any carbene species that are formed in the reaction. The carbene carbons in the analogous complexes

24 and **30** were extremely difficult to observe clearly, and the quaternary diphenyl carbene of **32** was predicted to be even harder to detect. To date, this carbene carbon resonance has not been observed in the ^{13}C NMR spectrum, even for a concentrated (~0.12 M) sample scanned at 500 mHz for 7 hours.[52] However, if only a small amount of **32** was formed in the reaction, it might have eluded detection.

During the course of this reaction, no bubbling due to loss of nitrogen from the diazo compound was observed. In order to ensure that the diazo species was in fact decomposed under the conditions utilized, the reaction was also attempted at elevated temperatures and in the presence of CuCl,[53] which is known to decompose diphenyl diazomethane.[45, 54] Once again, no carbene carbon resonance was observed in the ^{13}C NMR, and both ^{13}C and ^{1}H NMR spectroscopy indicated that the product mixture was significantly more complicated than in the absence of CuCl. Under most of the conditions examined, the reaction seemed reasonably clean, consisting of what appeared to be a mixture of two main ruthenium products. This interpretation was supported by variations in the relative intensities of signals observed in the ^{1}H NMR spectra for samples carried out under different reaction conditions. Furthermore, ^{31}P NMR spectroscopy indicated a mixture of two phosphorus-containing products, one in which the phosphines were equivalent (39.87 ppm (s)) and one in which they were not (49.08 ppm (d, J_{PP} = 38.0 Hz), 47.75 ppm (d, J_{PP} = 38.0 Hz)). In addition, free PPh_3 was detected when the reaction was run directly in an NMR tube, indicating that displacement of a phosphine had indeed occurred.

This ruthenium precursor may behave in a similar manner to the rhodium complex **16**, which reacted with diphenyl diazomethane to generate a diazo complex (**17**) or a dinitrogen complex (**18**), but not a carbene (Scheme 4).[28] Several other metal precursors have also failed to react with diphenyl diazomethane to yield metal carbene complexes.[30, 31, 55, 56] A small ^{13}C NMR resonance at 88.19 ppm was observed under some of the reaction conditions. This might correspond to a diazoalkane complex similar to **17**; that compound showed a resonance of 78.7 ppm for the diazo carbon.[31]

If carbene **32** was produced in this reaction, it would be expected to be active for the ROMP of norbornene, as was observed for other carbenes formed from **23**. It seemed reasonable that the propagating carbene might be observable by ^{1}H NMR as was the case for **24** and **22a**; however, upon addition of 16 equiv norbornene to a solution of the reaction product in CD_2Cl_2, neither a propagating carbene species nor the formation of polynorbornene was detected. Although it is possible that **32** might be too hindered to initiate, all observations made in this system to date collectively indicate that it is unlikely that 32 has actually been produced by the reaction of **23** with diphenyl diazomethane.

II. Preparation of Ruthenium Carbenes from $CpRu(PPh_3)_2Cl$

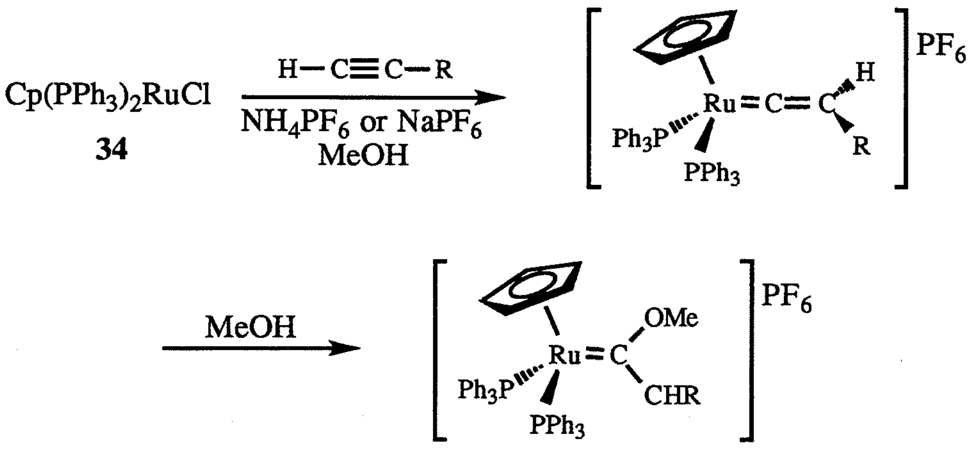
Background

A wide range of terminal carbene and vinylidene complexes have been prepared from terminal acetylenes and $CpRu(PPh_3)_2Cl$ (Cp = η^5-C_5H_5) (**34**), following removal of the chloride (Scheme 8).[57-59] The relatively large number of compounds of this type suggests that these starting materials might be good candidates for alkylidene transfer from diazo species. The known ruthenium carbenes in this series are Fischer-type; however, diazo compounds would allow the preparation of analogous species with non-π-donor substituents on the carbene. To our knowledge, such complexes have not been prepared previously from **34**.

Results and Discussion

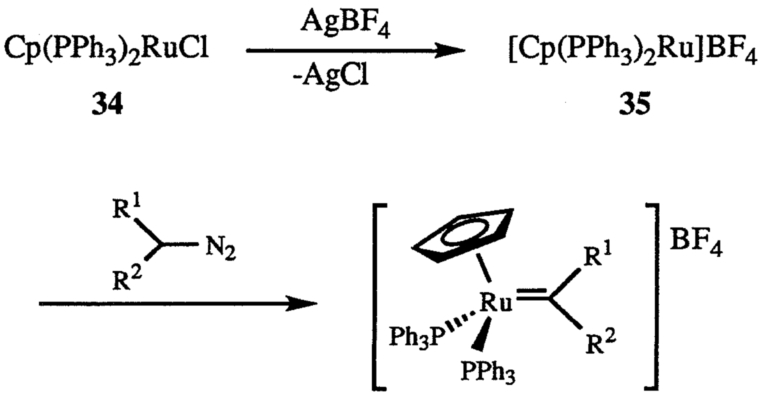
Addition of EDA to a solution of **34** in CD_2Cl_2 only led to the formation of

Scheme 8. Preparation of ruthenium carbenes from **34** via terminal acetylenes.



diethyl maleate and diethyl fumarate; however, following removal of the chloride with $AgBF_4$, the resulting cationic ruthenium intermediate $[CpRu(PPh_3)_2](BF_4)$ (**35**) reacted readily with a number of diazo compounds to form metal carbene species **36-38** (Scheme

Scheme 9. Preparation of ruthenium carbene complexes from **34** via diazo compounds.



36 $R^1 = Ph$ $R^2 = H$
37 $R^1 = CO_2Et$ $R^2 = H$
38 $R^1 = TMS$ $R^2 = H$
39 $R^1 = Ph$ $R^2 = Ph$

Table 3. Selected NMR data for complexes $[Cp(PPh_3)_2Ru{=}CR^1R^2]BF_4$

Complex	**R^1**	**R^2**	**Carbene Chemical Shift** **^1H (ppm)**	 **^{13}C (ppm)**
36	Ph	H	16.08^b	
37	CO_2Et	H	15.54^a	312.9^a
38	TMS	H	20.55^b	381.7^b
39	Ph	Ph	---	---

^{a}in C_6D_6
^{b}in CD_2Cl_2

9). Once again, reaction with Ph_2CN_2 failed to produce a carbene complex (**39**). Selected NMR data for these ruthenium carbene species is presented in Table 3.

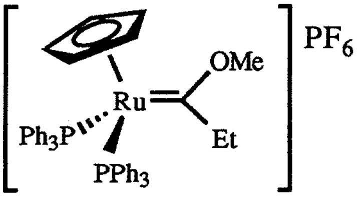
The choice of counter ion was crucial for effective carbene generation. Addition of EDA following treatment of **34** with NH_4PF_6 or AgO_2CCF_3 proved less satisfactory. No carbene was detected by ^1H NMR spectroscopy with the former and only a tiny broad resonance at 15.20 ppm was observed for the latter.

Compounds **36-38** appeared to be soluble in methylene chloride and much less so in benzene. Like other known ruthenium carbene complexes, they also exhibited moderate air stability. Diazo coupling products were observed forming during the preparation of **36** and **37** but not **38**. These cationic complexes were not found to be active catalysts for the ring-opening metathesis polymerization of norbornene. Upon treatment of either **37** or **38** with norbornene in CD_2Cl_2, no polymer was detected after >24 h. The starting carbene resonance remained unchanged for **38** but disappeared for **37**. This finding was not unexpected, because, unlike the ruthenium carbenes derived from **23**, these complexes are 18 electron species and lack the open coordination site required for metathesis.

Reaction with Ethyl Diazoacetate. Treatment of **34** with $AgBF_4$ followed by reaction with EDA resulted in the formation of **37** as a purple solid. The carbene proton appeared as a triplet at 15.45 ppm (J_{HP} = 8.3 ppm) in the ^1H NMR spectrum in CD_2Cl_2, indicative of a species with two equivalent phosphine ligands, and the carbene carbon appeared at 312.9 ppm in the ^{13}C NMR spectrum.[60] The ^{31}P NMR spectrum showed only one signal, appearing as a singlet at 44.39 ppm, and mass spectrometry was also consistent with the structure **37**. In addition, ^{19}F NMR spectroscopy showed a strong resonance for the BF_4^- counter ion. X-ray crystallography confirmed this structure (Figure 1).

Crystal Structure of 37. X-ray quality crystals of **37** were grown in benzene. An X-ray diffraction study of these crystals revealed a cationic carbene complex with a regular three-legged piano stool geometry (Figure 1). Selected bond distances and angles can be found in Table 4.[61] The plane of the carbene ligand does not bisect the P(1) - Ru(1) - P(2) angle, but is skewed towards the Ru(1) - P(2) vector by approximately 12-13°.

The structure clearly shows the presence of the carbene ligand; the Ru - C(6) bond length of 1.907 Å is within the range typically reported for ruthenium alkylidene complexes (1.83 - 1.91 Å).[62] Ruthenium carbon double bond distances of 1.959 Å and 1.92 Å have been reported for the analogous Fischer carbene complexes **40**[59] and **41**,[63]



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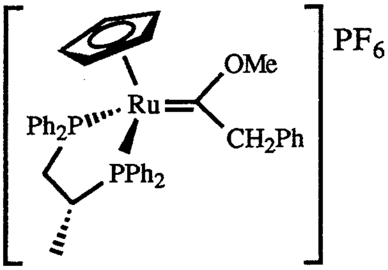

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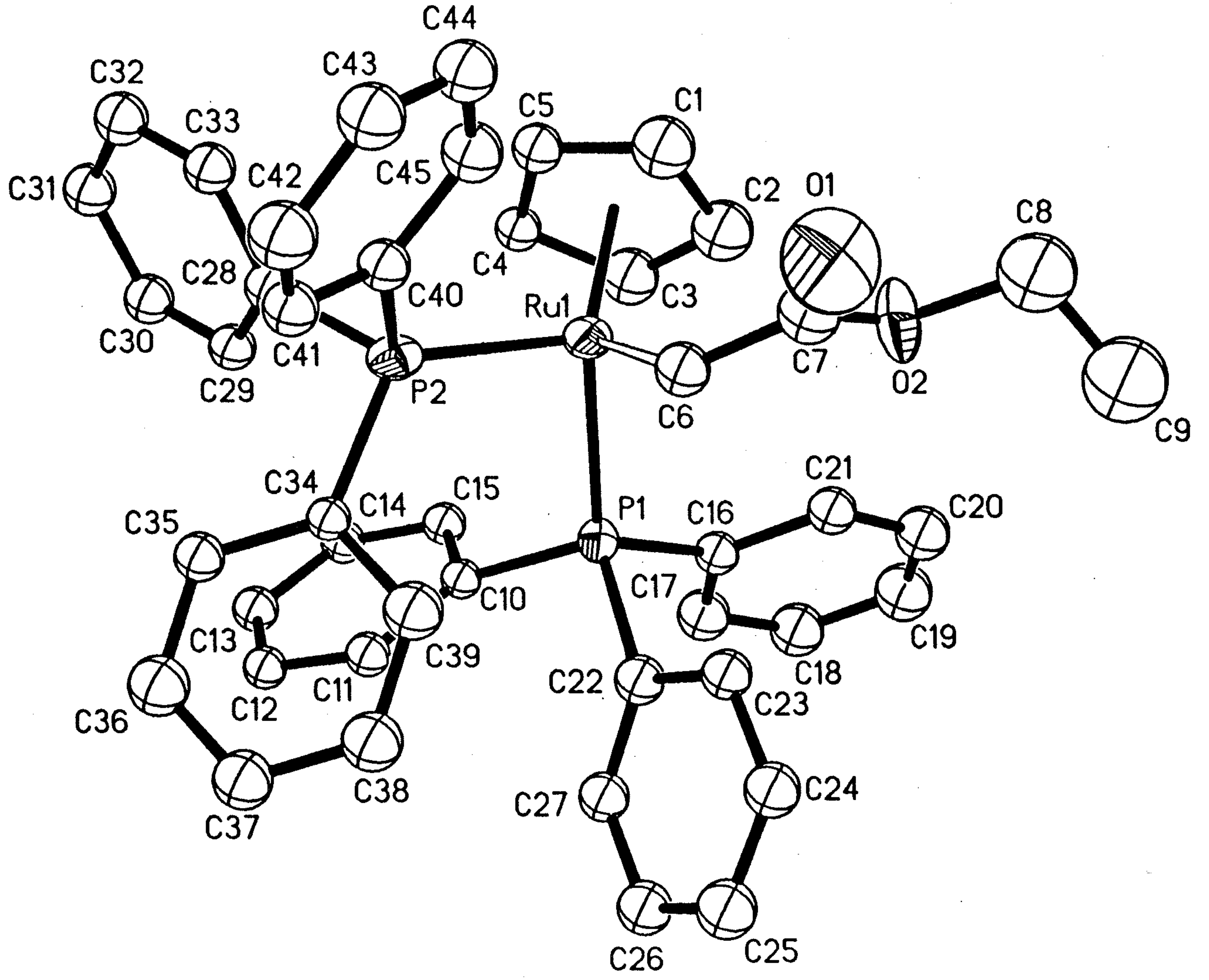


Figure 1. ORTEP plot of **37**. (BF_4^- counter ion not shown.)

Table 4. Selected bond lengths and angles for **37**.

Bond Lengths (Å)

Ru(1) - P(1)	2.378 (3)	P(1) - C(16)	1.815 (17)
Ru(1) - P(2)	2.318 (5)	P(1) - C(22)	1.833 (15)
Ru(1) - C(1)	2.230 (16)	P(2) - C(28)	1.825 (12)
Ru(1) - C(2)	2.299 (20)	P(2) - C(34)	1.837 (15)
Ru(1) - C(3)	2.267 (19)	P(2) - C(40)	1.867 (16)
Ru(1) - C(4)	2.287 (14)	C(6) - C(7)	1.456 (21)
Ru(1) - C(5)	2.225 (13)	O(1) - C(7)	1.199 (21)
Ru(1) - Cnt[a]	1.920	O(2) - C(7)	1.332 (28)
Ru(1) - C(6)	1.907 (13)	O(2) - C(8)	1.501 (20)
P(1) - C(10)	1.834 (12)	C(8) - C(9)	1.481 (23)

Bond Angles (°)

P(1) - Ru(1) - P(2)	97.7 (2)	Ru(1) - P(1) - C(10)	111.9 (4)
P(1) - Ru(1) - C(6)	96.5 (4)	Ru(1) - P(1) - C(16)	112.1 (4)
P(2) - Ru(1) - C(6)	89.1 (5)	Ru(1) - P(1) - C(22)	122.1 (4)
P(1) - Ru(1) - Cnt[a]	118.1	C(10) - P(1) - C(16)	106.1 (7)
P(2) - Ru(1) - Cnt[a]	121.8	C(10) - P(1) - C(22)	105.9 (7)
C(6) - Ru(1) - Cnt[a]	126.4	C(16) - P(1) - C(22)	96.9 (7)
Ru(1) - C(6) - C(7)	130.0 (15)	Ru(1) - P(2) - C(28)	110.1 (6)
C(6) - C(7) - O(1)	123.3 (21)	Ru(1) - P(2) - C(34)	121.6 (4)
C(6) - C(7) - O(2)	113.2 (14)	Ru(1) - P(2) - C(40)	113.8 (6)
O(1) - C(7) - O(2)	123.5 (16)	C(28) - P(2) - C(34)	104.1 (6)
O(2) - C(8) - C(9)	107.4 (12)	C(28) - P(2) - C(40)	104.5 (6)
C(7) - O(2) - C(8)	119.5 (12)	C(34) - P(2) - C(40)	101.1 (8)

[a] Cnt is the centroid of the C(1) - C(5) ring.

respectively. The Ru - C(6) - C(7) bond angle of 130.0° is reasonable for a planar sp^2 carbon.

There is no interaction between the metal and the ester functionality on the carbene ligand, which is reasonable, particularly since the complex is an 18 electron species. The BF_4^- counter ion is non-coordinating and there is a benzene molecule in the unit cell.

Reaction with Trimethylsilyl Diazomethane. Complex **38** was isolated in 67% yield by the reaction of $TMSCHN_2$ with **35**. The spectroscopic data of compound **38** was very similar to that obtained for **37**. Carbene **38** exhibited a resonance at 20.55 ppm (t, J_{HP} = 9.6 Hz) (CD_2Cl_2) in the ^1H NMR, indicative of a mononuclear complex with two phosphine ligands. The carbene carbon appeared as a triplet at 381.67 ppm (J_{HP} = 7.5 Hz), supporting this structural assignment. The two phosphines were equivalent, as demonstrated by the ^{31}P NMR spectrum, which showed only one signal at 46.07 ppm (s). Exact mass determination and elemental analysis confirmed this structure.

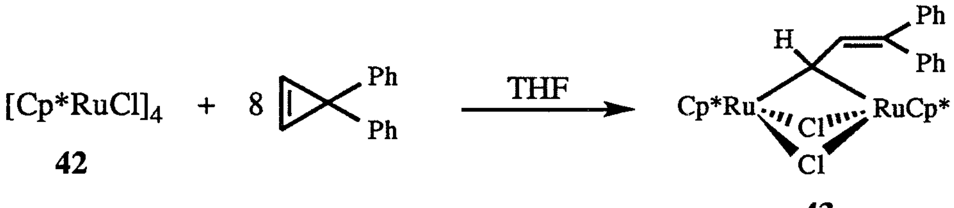
Reaction with Phenyl Diazomethane. The observed spectroscopic data for **36** is similar to that found for **37** and **38**. By analogy, it is assumed to have the same structure as these compounds.

Reaction with Diphenyl Diazomethane. Following treatment of **35** with diphenyl diazomethane, no downfield alkylidene resonances were observed in the ^{13}C NMR spectrum of the reaction mixture, even for a concentrated solution scanned at 500 MHz overnight. Therefore, it seems unlikely that a monomeric carbene such as **36** - **38** was produced. Unlike during the attempted preparations of **32**, nitrogen evolution was observed upon addition of the diazo compound. Two resonances were observed at 184.38 ppm (t, J_{CP} = 3.8 Hz) and 160.26 ppm in the ^{13}C NMR spectrum, so the formation of a dinuclear species with a bridging alkylidene ligand cannot be ruled out. The reaction appeared to be reasonably clean, only contaminated by a small amount of starting material. ^{1}H NMR spectroscopy revealed a Cp resonance at 4.72 ppm, and ^{31}P NMR revealed only one signal at 39.81 ppm. The exact identity of the product of this reaction is still under investigation, but it cannot be a terminal alkylidene complex analogous to **36** - **38**.

III. Preparation of Ruthenium Carbenes from [Cp*RuCl]$_4$

Background

The tetrameric starting material [Cp*RuCl]$_4$ (Cp* = η^5-C_5Me_5) (**42**) has been utilized to prepare an isolable ruthenium carbene complex upon reaction with 3,3-diphenylcyclopropene (8 equiv). The resulting triply bridged dinuclear complex **43** is reminiscent of the μ-alkylidene complexes, such as **15**, discussed above. This carbene complex is active for the ROMP of norbornene, although the polymerization does not appear to be living in this case.^{64}



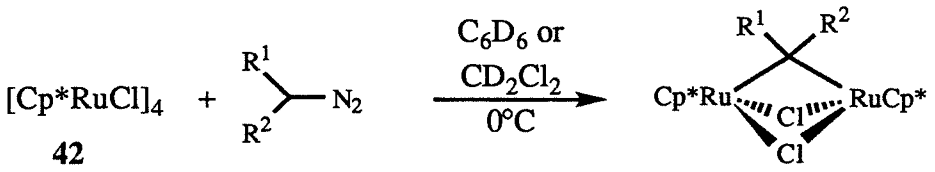
42

43

When **42** is reacted with only 2 equiv diphenylcyclopropene, two other alkylidene species are formed in addition to **43**, all three present in roughly equimolar amounts. These species are at equilibrium with one another and react with additional diphenylcyclopropene to increase the percentage of **43** at the expense of the other two. It has therefore been postulated that the other two alkylidene species result from incomplete breakdown of the tetrameric starting material.[64]

Results and Discussion

Bridging alkylidene species **44**-**47** were observed upon reaction of **42** with the corresponding diazo reagents, and their structures were assigned based on comparisons with the known compound **43**. The results are summarized in Table 5. The ^{1}H and ^{13}C



44 $R^1 = Ph$ $R^2 = H$
45 $R^1 = CO_2Et$ $R^2 = H$
46 $R^1 = TMS$ $R^2 = H$
47 $R^1 = Ph$ $R^2 = Ph$

Table 5. Selected NMR data for complexes $[Cp^*Ru]_2(\mu\text{-}Cl)_2(\mu\text{-}CR^1R^2)$

Complex	**R^1**	**R^2**	**Carbene Chemical Shift**	
			^{1}H (ppm)	**^{13}C (ppm)**
43[64]	$CH=CPh_2$	H	13.32[b]	194.9[b]
44	Ph	H	13.57[a]	
45	CO_2Et	H	11.89[a]	186.3[a]
46	TMS	H	13.96[a]	210.7[a]
47	Ph	Ph	---	227.2[a]

[a] in C_6D_6
[b] in THF-d_8

NMR chemical shifts were indicative of dinuclear species with bridging alkylidene ligands, analogous to **43**.[64] As noted previously for this method of metal carbene generation (*vide supra*), diazo coupling products were observed forming during the course of the reactions.

In many of these reactions, small amounts of several additional alkylidene species were also detected by ^1H NMR spectroscopy, similar to the findings for **43**.[64] Once again, most of these species are postulated to result from incomplete breakdown of the tetrameric starting material.[64]

The bridging carbene complexes **44-47** generally appeared to be more stable than the corresponding products derived from **23**. They were soluble in common organic solvents, including pentane, making crystallization difficult. In addition, they also exhibited moderate air stability. These catalysts were considerably less active for the polymerization of norbornene than the carbenes derived from **23**, but more reactive than those derived from **35**. Propagating species were not observed in any of these systems, and the reactions did not appear to be living. These findings parallel those observed for **43**.[64] Polymerization with μ-alkylidenes of this type is expected to be slow, because the dimer must break up in order to generate an active catalyst.

Reaction with Trimethylsilyl Diazomethane. Only one carbene was observed upon reaction of **42** with $TMSCHN_2$. This carbene (**46**), which was formed more cleanly than the analogous carbenes in this series (**45** and **44-47**), showed a singlet at 13.96 ppm in the ^1H NMR for the carbene proton and a singlet at 1.33 ppm for the Cp^* protons (C_6D_6). These chemical shifts were similar to those found for **43** (13.32 and 1.49, respectively (THF-d_8)).[64] Integration of these two peaks showed a ratio of 30 Cp^* resonances per carbene, supporting the dinuclear structure. This interpretation was confirmed by ^{13}C NMR spectroscopy, which showed a resonance at 210.70 ppm (CD_2Cl_2), compared to 194.9 ppm (THF-d_8) for **43**.[64] Upon addition of norbornene to a solution of **46** in C_6D_6, only a trace of polynorbornene was observed after 2 days at room temperature.

Reaction with Ethyl Diazoacetate. Although carbene **45** was isolated in >90% yield, the product was somewhat impure, showing several different Cp* methyl resonances in addition to the major one at 1.52 ppm (C_6D_6). Attempts at purifying the product met with only limited success. As in the case of **43**, several other carbene products were identified when **45** was formed *in situ* by mixing the reagents directly in an NMR tube. These appeared at 18.32 ppm (b) (**48**) and 9.1 ppm (b) (**49**) in a ratio of approximately 1:1:0.1 for **45**:**48**:**49**. The downfield chemical shift of **48** indicated that this was likely to be a mononuclear species. Although such a structure has not been detected for other carbenes derived from **42**, breakup of the dimer may be facilitated by the possible chelation of the ester functionality, analogous to that discussed above for **33**.

Isolated carbene **45** was found to catalyze the polymerization of norbornene, although the reaction was relatively slow. The reaction was approximately 23% complete after 24 h in C_6D_6, and the reaction mixture had completely solidified after 48 h. The polymer obtained was 80% trans, while the polymer obtained using **43** was reported to be high cis;[64] the reason for this difference is unclear.

Reaction with Diphenyl Diazomethane. Unlike the case for ruthenium precursors **23** and **35**, addition of diphenyl diazomethane to a solution of **42** was accompanied by vigorous N_2 evolution leading to the formation of **47** in 50% yield. No other carbenes were observed in this system. However, since carbene carbons generated by Ph_2CN_2 are both conjugated and quaternary, they can be difficult to detect, and the possibility that small amounts of other ruthenium carbene-containing species were formed in this reaction, as they were in other reactions of carbene precursors with **42**, cannot be ruled out.

Although the ^{1}H and ^{13}C NMR spectra were reasonably clean, small signals in the methyl region indicated the presence of trace amounts of starting material (1.67 ppm (s), C_5Me_5) and another compound (1.38 ppm (s), C_5Me_5) (C_6D_6). In solution, there appeared to be an equilibrium between the three species corresponding to these Cp* resonances. After a solution of isolated product consisting almost exclusively of **47** was allowed to sit overnight at room temperature, the two downfield Cp* resonances increased at the expense of **47**. A similar equilibration was observed for a sample of **47** prepared *in situ* by combining the reagents in an NMR tube. In addition, following attempts at purifying the reaction product by washing with various solvent combinations or by passing through a short plug of silica or deactivated alumina, similar product redistributions were once again observed.

Reaction with Phenyl Diazomethane. The reaction of **42** with phenyl diazomethane to form **44** was extremely vigorous; as soon as the diazo compound made contact with trace amounts of ruthenium at the top of the NMR tube in which the reaction was run, a cloud of fumes was emitted. However, the reaction to produce **44** did occur upon immediate shaking of the NMR tube. The reaction was clearly not quantitative, and only a relatively small amount of the metal carbene product was detected. When the reaction was run more concentrated, polymeric material was obtained.

As was the case for reactions of **42** with other carbene sources, this system resulted in the formation of several different metal alkylidene species. A ^{1}H NMR spectrum (C_6D_6) taken immediately after mixing the two reagents showed small signals at δ 13.57 (s), 11.51 (b), 9.63 (s), and 8.69 (s). Although the exact identity of most of these species was unclear and it is unknown whether they all in fact represent ruthenium carbenes, it was evident that a dynamic process was occurring. After 20 min at room temperature, the signals redistributed slightly, and an additional broad resonance appeared at 12.90 ppm. However, after sitting at room temperature overnight, only the singlet at 13.57 remained. The presence of three large singlets in the methyl region indicated that the solution also contained additional, non-carbene ruthenium species.

Future Work

The results presented here indicate that diazo compounds provide a very effective carbene source for the generation of alkylidene ligands on ruthenium templates. Although several of these compounds have not been studied in detail, preliminary laboratory observations indicate that these can be purified and more fully characterized. It should be possible to prepare X-ray quality crystals for some of these molecules. In addition, their catalytic activity remains to be more thoroughly probed. In particular, the scope of the reactivity of carbene **29** should be further explored. Furthermore, studies are currently underway to investigate the applicability of diazo compounds to a one-step *in situ* process recently developed in our laboratories for the preparation of **22b**.[65]

Other ruthenium complexes should be investigated for reactivity with diazo compounds, and the resulting carbenes should be tested for metathesis activity. In addition, the large number of readily available diazo compounds[34] allows for systematic variation of the substituents on the carbene ligand. Thus, the influence of the steric and electronic properties of the carbene on factors such as metathesis initiation rates, carbene stability, and the physical properties of the metal alkylidene complexes can be probed. In particular, a number of substituted phenyl diazomethanes are known[34, 66, 67] and would allow the facile synthesis of ruthenium carbenes with diverse electronic properties.

It is possible that the complexes in the series **36** - **38** might be transformed into active metathesis catalysts in the presence of CuCl as a phosphine sponge to open a coordination site.[68, 69] In addition, the indenyl analogue of these species might be catalytically active, since this ligand can slip from η^5 to η^3 to allow olefin complexation.[70, 71] Such a modification might be particularly interesting since these complexes have two phosphine ligands in a cis orientation. Exchange with chiral, chelating phosphines might allow for the development of a chiral, well-defined group VIII metathesis catalysts.[72]

Conclusions

A number of ruthenium carbene complexes have been prepared by alkylidene transfer from diazo species, demonstrating that this appears to be a general route into compounds with this functionality. These ruthenium species represent the first examples of isolable metal carbene complexes generated in this manner that are active catalysts for the ring-opening metathesis polymerization of norbornene. One such complex (**24**), has been clearly demonstrated to provide an entry into the well-documented ruthenium carbene catalyst system **22a** and the cyclohexyl phosphine substituted system **22b**. The propagating carbene derived from **24** and norbornene has been observed, and the system appears to be living, producing polymers with extremely narrow molecular weight distributions. The more active cyclohexyl phosphine derivative **29** has also been generated and appears to be formed almost exclusively as the trans isomer. In addition, one of these novel carbene complexes (**37**) has been characterized by X-ray crystallography.

One limitation of the complexes **22** and **43** is that they are prepared from 3,3-diphenylcyclopropene, a starting material that requires a difficult, multi-step synthesis.[44] The diazo route presented here avoids the need for this reagent, providing an entry into these catalysts in one step from readily available starting materials. In addition, the cyclopropene method only allows the preparation of vinylcarbene species and is further limited by the inaccessibility of a variety of substituted analogues. On the other hand, diazo compounds with a wide range of substituents are commercially available or can be readily prepared in one step. Since the exact nature of the carbene can influence metathesis initiation rates, the ability to systematically vary the carbene substitution is of great importance. Three series of analogous complexes have been prepared, allowing preliminary investigations of these effects as well as demonstrating the profound influence that the remainder of the metal ligand coordination sphere has on reactivity. The ease of preparing a wide variety of different substituted diazo compounds will allow these effects to be studied more thoroughly.

The preparation of such a large number of ruthenium carbene complexes from diazo compounds supports the conclusion that the role of EDA in the polymerization system presented in Chapter 3 is, in fact, to react with the metal starting material to generate a ruthenium carbene derived from the diazo precursor. Overall, this facile route appears to provide a promising entry into metal carbene complexes of this type and into metathesis chemistry with well-defined group VIII catalysts.

Experimental

General. All manipulations involving air- and/or moisture-sensitive compounds were carried out using standard high vacuum or Schlenk techniques. Argon was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4Å molecular sieves. Solids were transferred and stored in a nitrogen-filled Vacuum Atmospheres glove box equipped with a MO-40-1 purification train, a DK-3E Dri-Kool conditioner, and a Dri-Cold Freezer.

Instrumentation. NMR spectra were recorded on a JEOL FX-90Q spectrometer (89.60 MHz ^{1}H, 22.53 ^{13}C), a GE QE-300 spectrometer (300.19985 MHz ^{1}H, 75.49283 MHz ^{13}C) or a Bruker AM-500 spectrometer (500.136 MHz ^{1}H, 125.759 mHz ^{13}C.) Proton chemical shifts are referenced to internal residual solvent protons. Carbon chemical shifts are referenced to the carbon signal of the deuterated solvents. Phosphorous chemical shifts are reported relative to an external phosphoric acid reference. Gel permeation chromatography (GPC) was performed at 65 °C on a Waters 150-C ALC/GPC equipped with four Waters Ultrastyragel columns (105, 104, 103, and 500A) and a Waters refractometer with toluene as the eluent. The molecular weights are referenced to narrow dispersity polystyrene samples (Polysciences). Elemental analysis was performed by Oneida Research Service or Midwest Microlab. Mass sprectrometry was performed at the Mass Spectrometry Facility of the University of California at Riverside. X-Ray crystallography was performed by Dr. J. W. Ziller at the University of California at Irvine.

Materials. $(PPh_3)RuCl_2$ and $Cp(PPh_3)_2RuCl$ were purchased from Aldrich and used as received. $[Cp^*RuCl]_4$ was a gift from Dr. J. Feldman.[73] Ethyl diazoacetate was purchased from Aldrich and used as received. Trimethylsilyl diazomethane was purchased from Aldrich (2.0 M in hexanes) or Petrarch (Hüls) (10% in hexanes or 10% in

CH_2Cl_2) and degassed by repeated freeze-pump-thaw cycles or used as received. Phenyl diazomethane[66, 67] and diphenyl diazomethane[74] were prepared according to literature procedures and degassed under vacuum at low temperature (-78°C or 0°C, respectively) prior to use. The purity of all diazo compounds was checked by ^1H NMR frequently. Best results were obtained when freshly prepared diazo compounds were employed. AgO_2CCF_3 was dried under vacuum at 60°C for 48 hours prior to use. $AgBF_4$ was purchased from Lancaster and used as received.[75] Methylene chloride and methylene chloride-d_2 (Cambridge Isotope Laboratories) were vacuum transferred from calcium hydride and degassed by repeated freeze-pump-thaw cycles. Benzene and benzene-d_6 (Cambridge Isotope Laboratories) were vacuum transferred from sodium-benzophenone ketyl and degassed by repeated freeze-pump-thaw cycles. Pentane was stirred over concentrated H_2SO_4, dried over $MgSO_4$ and CaH_2, and transferred onto sodium-benzophenone ketyl solubilized with tetraglyme. It was then vacuum transferred and degassed by repeated freeze-pump-thaw cycles. Norbornene was purchased from Aldrich and refluxed over sodium and distilled or vacuum transferred prior to use.[76] Cyclooctene (Aldrich) was passed through alumina or vacuum transferred from CaH_2 and degassed prior to use. Alternatively, high purity cyclooctene (99.9%) was purchased from Wiley, degassed by repeated freeze-pump-thaw cycles, and used without any further purification. Pyridazine, PPh_3, PCy_3, 2,6-di-*tert*-butyl-4-methylphenol (BHT), ethyl vinyl ether, and *cis*- and *trans*-stilbene were purchased from Aldrich and used as received.

Caution! *Diazo compounds are highly toxic and potentially explosive. Although no problems have been encountered during the course of this study, these compounds should always be handled and stored with extreme care.*

$(PPh_3)_2Cl_2Ru{=}CHPh$ (24). A solution of $(PPh_3)RuCl_2$ (200 mg, 0.209 mmol) in CH_2Cl_2 (10 mL) was cooled to 0°C in an ice/water bath. A solution of phenyl diazomethane (50 mg, 0.423 mmol, 2.02 equiv) in CH_2Cl_2 (5 mL) kept at -78°C in a dry ice/acetone bath was added slowly to the ruthenium solution via a polyethylene cannula, during which time the reaction changed from orange-brown to dark brown The reaction mixture bubbled vigorously upon addition of the diazo compound; bubbling was allowed to cease between additions. The reaction was left to stir at 0°C for 30 min, after which the solvent was removed *in vacuo*. The black residue was dissolved in minimal CH_2Cl_2 (1-2 mL) and precipitated by the addition of pentane (5 mL). The suspension was stirred for 5 min, allowed to settle, and filtered via cannula filtration. This washing procedure was repeated three times, keeping the solution at 0°C. The resulting gray-green solid was allowed to warm to room temperature while drying under vacuum overnight (yield 57%). ^1H NMR (C_6D_6): δ 19.56 (t, Ru=C*H*Ph, J_{HP} = 10.2 Hz), 6.63-7.79 (m, Ru=CH(C_6H_5), P(C_6H_5)$_3$); ^{13}C NMR (CD_2Cl_2): δ 310.21 (t, Ru=*C*HPh, J_{CP} ~ 10-11 Hz), 154.91, 127.04-135.20, 118.48, 117.35 (Ru=CH(C_6H_5), P(C_6H_5)$_3$); ^{31}P NMR (CD_2Cl_2): δ 30.68 (s). Elemental analysis: calculated for $C_{43}H_{36}Cl_2P_2Ru$: C, 65.65%; H, 4.61%; P, 7.87 %; found: C, 65.83%; H, 4.59%; P 7.93%. FAB MS: calculated *m/e* 786.07062; found 786.06930.

Preparation of 25. The procedure was carried out as described for **24**, but using only 25-28 mg $PhCHN_2$ (1-1.1 equiv). ^1H NMR (C_6D_6): δ 19.77 (d, 1H, Ru=C*H*Ph, J_{HP} = 14.6 Hz), 8.83 (d, 2H, J = 7.9), 8.60 (dd, 1H, J = 7.9, 15.0), 6.65-8.08 (m, Ru=CH(C_6H_5), P(C_6H_5)$_3$). Elemental analysis (crude product): C, 66.01%; H, 4.40%, N, 0.00%. FAB MS: 1394, 1097, 833, 751, 696, 625, 547. Upon addition of excess PPh_3, **25** was converted to **24**.

Observation of $(PCy_3)_2Cl_2Ru$=CHPh (29). To a solution of **24** (5.2 mg, 0.0066 mmol) in CD_2Cl_2 (0.5 mL) in an NMR tube was added PCy_3 (3.7 mg, 0.013 mg, 2 equiv). The reaction mixture immediately turned red upon shaking the NMR tube. ^1H

NMR (CD_2Cl_2): δ 20.02 (s, Ru=C*H*Ph), 6.98-8.46 (m, Ru=CH(C_6H_5), free P(C_6H_5)$_3$), 1.21-2.65 (m, P(C_6H_{11})$_3$); ^{13}C NMR (CD_2Cl_2): δ 294.6 (b, Ru=*C*HPh), 153.1, 127.9-140.5, 118.7, 118.1 (Ru=CH(C_6H_5), free P(C_6H_5)$_3$), 35.9, 35.8, 26.0-32.8 (P(C_6H_{11})$_3$); ^{31}P NMR (CD_2Cl_2): δ 36.63 (s, *P*Cy$_3$).

Polymerization of Norbornene with 24.[77] Norbornene (20 mg, 0.21 mmol, 84 equiv) was added to a solution of **24** (2 mg, 0.0025 mmol) in CH_2Cl_2 (0.5 mL), and the reaction was left to stir at room temperature for 24 h. The reaction was opened to air and to it was added 75 µL of a solution consisting of CH_2Cl_2 (2 mL), ethyl vinyl ether (400 µL), and BHT (100 mg). This reaction mixture was stirred for 2 h during which time it turned a dark grayish yellow. This solution was then passed through a plug of silica gel, washing with CH_2Cl_2 containing a trace of BHT. The combined eluants were concentrated, redissolved in CCl_4 containing a trace of BHT, and precipitated into methanol containing a trace of BHT. The resulting white polymer was washed with methanol and dried under vacuum overnight (yield 82%, 92% trans). ^{1}H NMR ($CDCl_3$): δ 5.32 (b), 5.18 (b), 2.78 (b), 2.40 (b), 1.82 (b), 1.72 (b), 1.33 (b), 1.02 (b). GPC (toluene): $M_n = 42{,}600$, $M_w = 44{,}600$, PDI = 1.05.

Observation of the Propagating Alkylidene in the Polymerization of Norbornene with 24. The reaction was set up in an NMR tube in CD_2Cl_2 or C_6D_6 as described for the polymerization of norbornene above. Propagating species: ^{1}H NMR (C_6D_6): δ 17.79 (pseudo-quartet, Ru=C*H*, J_{HH} = 11.8 Hz, J_{HP} = 7.9 Hz) or ^{1}H NMR (CD_2Cl_2): δ 17.66 (pseudo-quartet, Ru=C*H*). Work-up of the CD_2Cl_2 reaction mixture as described previously resulted in the isolation of a white polymer (yield 42%, 90% trans). GPC (toluene): $M_n = 34{,}313$, $M_w = 36{,}140$, PDI = 1.05.

Observation of the Propagating Alkylidene in the Polymerization of Cyclooctene with 29. To a CD_2Cl_2 (0.5 mL) solution of **29** (0.0066 mmol), prepared *in situ* in an NMR tube as described for the observation of **29** above, was added cyclooctene (50 μL, 0.384 mmol, 58 equiv). Propagating species: ^1H NMR (CD_2Cl_2): δ 19.26 ppm (t, Ru=C*H*, J_{HP} = 5.3 Hz).

Preparation of $(PPh_3)_2Cl_2Ru{=}CHCO_2Et$ (30). A solution of $(PPh_3)RuCl_2$ (120 mg, 0.125 mmol) in CH_2Cl_2 (20 mL) was cooled to 0°C in an ice/water bath. EDA (15 μL, 0.143 mmol, 1.1 equiv) was added via syringe. The reaction mixture bubbled vigorously upon addition of the diazo compound. After stirring at 0°C for 30 min, the solvent was removed *in vacuo*. The residue was dissolved in minimal CH_2Cl_2 (1 mL) and precipitated by the addition of pentane (5 mL). The suspension was allowed to settle and then filtered via cannula. This washing procedure was repeated three times. The resulting brown solid was allowed to warm to room temperature while drying under vacuum overnight (yield 60%). Note: Due to the rapid decomposition of this compound in solution, it is important to keep the reaction mixture at 0°C and perform all manipulations as promptly as possible. ^1H NMR (CD_2Cl_2, -40°C): δ 17.45 (t, 1H, Ru=C*H*, J_{HP} = 11.7 Hz), 6.81-7.85 (m, $P(C_6H_5)_3$), 3.21 (q, 2H, CH_2CH_3, J_{HH} = 7.1 Hz), 0.92 (t, 3H, CH_2CH_3, J_{HH} = 7.1 Hz); ^{13}C NMR (CD_2Cl_2, -40°C): δ 280.32 (b, Ru=*C*H), 170.10 (s, CO_2Et), 134.84-127.34 ($P(C_6H_5)_3$), 60.91 (s, CH_2CH_3), 13.63 (s, CH_2CH_3); ^{31}P NMR (CD_2Cl_2, -40°C): δ 30.42 (s).

Polymerization of Norbornene with 30. A solution of norbornene (34.4 mg, 0.365 mmol, 57 equiv) in CH_2Cl_2 (0.5 mL) was added to a reaction vessel charged with **30** (5 mg, 0.0064 mmol). The reaction mixture was left to stir at 0°C overnight and then precipitated into rapidly stirring degassed H_2O to yield 14.6 mg of a white polymer (yield

42%, 90% trans). ^{1}H NMR ($CDCl_3$): δ 5.32 (b), 5.18 (b), 2.78 (b), 2.40 (b), 1.82 (b), 1.72 (b), 1.33 (b), 1.02 (b).

Observation of $(PPh_3)_2Cl_2Ru{=}CHTMS$ (31). An NMR tube was charged with $(PPh_3)RuCl_2$ (50 mg, 0.052 mmol) in CD_2Cl_2 (0.5 mL). $TMSCHN_2$ (10% in hexanes, 60 mg, 0.052 equiv) was added via syringe and the NMR tube was shaken. Vigorous nitrogen evolution was observed. Selected spectroscopic data for the product, which decomposed within several minutes: ^{1}H NMR (CD_2Cl_2): δ 17.65 (t, Ru=C*H*TMS, J_{HP} = 20.5 Hz).

Observation of $[Cp(PPh_3)_2Ru{=}CHPh]BF_4$ (36). Method 1: A solution of $Cp(PPh_3)_2RuCl$ (23 mg, 0.032 mmol) in C_6D_6 or CD_2Cl_2 (0.5 mL) was treated with 1 equiv $AgBF_4$ at room temperature overnight. The reaction mixture was filtered through a 5 μm filter in the drybox, transferred into an NMR tube and removed from the box. Under a purge of argon, one drop $PhCHN_2$ was added and the NMR tube was capped and shaken. Vigorous bubbling was observed. Method 2: A solution of $Cp(PPh_3)_2RuCl$ (250 mg, 0.344 mmol) in C_6H_6 (5 mL) was treated with $AgBF_4$ (67 mg, 0.344 mmol, 1.0 equiv) 1.5 h at room temperature. The reaction mixture was filtered through a 5 μm filter in the drybox to yield a clear orange solution, and transferred to a Schlenk flask. A solution of phenyl diazomethane (41 mg, 0.356 mmol, 1.03 equiv) in C_6D_6 (1 mL) was added slowly to the ruthenium solution via a polyethylene cannula, during which time the reaction changed from orange to dark red. The reaction was left to stir 1.5 h, during which time a small amount of purple solid precipitated from the reaction mixture. The reaction mixture was filtered via cannula filtration, and the solid was dried under vacuum. (The solution contained product as well.) Selected spectroscopic data: ^{1}H NMR (CD_2Cl_2): δ 16.07 (t, 1H, Ru=C*H*Ph, J_{HP} = 11.7 Hz), 6.94-7.89 (m, Ru=CH(C_6H_5),

$P(C_6H_5)_3$), 5.08 (s, 5H, C_5H_5); ^{13}C (CD_2Cl_2) δ 128.61-133.57 (m, Ru=CH(C_6H_5), $P(C_6H_5)_3$), 94.84 (s, C_5H_5); ^{31}P NMR (CD_2Cl_2): δ 46.97 (s).

Preparation of [Cp(PPh_3)$_2$Ru=CHCO_2Et]BF_4 (37). Method 1: A solution of Cp(PPh_3)$_2$RuCl (250 mg, 0.344 mmol) in C_6H_6 (20 mL) was treated with $AgBF_4$ (68 mg, 0.349 mmol, 1.01 equiv) at room temperature for 40 min. The reaction mixture was filtered via cannula filtration to yield a clear orange solution, which was cooled to 10 °C in an ice water bath. EDA (53 µL, 0.504 mmol, 1.5 equiv) was dissolved in C_6H_6 (5 mL) and added dropwise to the reaction mixture, allowing nitrogen evolution to cease between additions. The resulting reaction mixture was left to stir 30 min at 10 °C, after which the solvent was removed *in vacuo*. The residue was dissolved in a minimum of C_6H_6 (~1-2 mL) and precipitated by the addition of pentane (~5 mL). Following cannula filtration, the residue was dried under vacuum overnight to yield 207 mg of an impure yellow brown solid (yield 70%). Method 2: A solution of Cp(PPh_3)$_2$RuCl (250 mg, 0.344 mmol) in C_6H_6 (5 mL) was treated with $AgBF_4$ (67 mg, 0.344 mmol, 1.0 equiv) 1.5 h at room temperature. The reaction mixture was filtered through a 5 µm filter in the drybox to yield a clear orange solution, and transferred to a Schlenk flask. EDA (38 µL, 0.361 mmol, 1.05 equiv) was added to the ruthenium solution via syringe, after which the reaction changed from orange to dark brown-orange. The reaction was left to stir 1.5 h, during which time a small amount of purple solid precipitated from the reaction mixture. The reaction mixture was filtered via cannula filtration, and the solid was dried under vacuum, during which time it turned pale gray. (The solution contained product as well.) Selected spectroscopic data: ^1H NMR (CD_2Cl_2): δ 15.46 ppm (t, 1H, Ru=C*H*CO_2Et, J_{HP} = 8.3 Hz), 7.44 (m, 6H, $P(C_6H_5)_3$), 7.25 (m, 12H, $P(C_6H_5)_3$), 6.96 (m, 12H, $P(C_6H_5)_3$), 5.14 (s, 5H, C_5H_5), 4.57 (q, 2H, CH_2CH_3, J_{HH} = 7.1 Hz), 1.56 (t, 3H, CH_2CH_3, J_{HH} = 7.1 Hz); ^{13}C NMR (CD_2Cl_2): δ 312.93 (s, Ru=*C*HCO_2Et), 180.07 (s, Ru=CH*C*O_2Et), 128.45-133.00 (m, $P(C_6H_5)_3$), 97.29 (s, C_5H_5); ^{31}P NMR (CD_2Cl_2): δ

44.39 (s); ^{19}F NMR (CD_2Cl_2): δ -151.6 (s) (± 5 ppm, spectrum not referenced). FAB MS: calculated for $C_{45}H_{41}P_2O_2Ru$: *m/e* 777.1619; found 777.1629.

Preparation of Crystals of 37. A solution of $Cp(PPh_3)_2RuCl$ (22.9 mg, 0.0315 mmol) in C_6D_6 was treated with $AgBF_4$ (6.1 mg, 0.0313 mmol, 0.99 equiv) at room temperature for 12 h. The reaction mixture was filtered through a 5 μm filter to yield a clear orange solution. EDA (3.5 μL, 0.0333 mmol, 1.06 equiv) was added via syringe and the NMR tube was shaken. Following overnight ^{13}C NMR accumulation, the NMR tube was found to contain a clear yellow solution that contained no metal carbene species along with purple crystals, which were analyzed by X-ray crystallography.

Preparation of $[Cp(PPh_3)_2Ru{=}CHTMS]BF_4$ (38). A solution of $Cp(PPh_3)_2RuCl$ (250 mg, 0.344 mmol) in C_6H_6 (20 mL) was treated with $AgBF_4$ (67 mg, 0.344 mmol, 1.0 equiv) at room temperature overnight. The reaction mixture was filtered through a 5 μm filter in the drybox to yield a clear orange solution. $TMSCHN_2$ (10 % in hexanes, 406 μL, 0.356 mmol, 1.03 equiv) was added dropwise to the reaction mixture over a period of about 5 min, allowing nitrogen evolution to cease between drops. The resulting reaction mixture was left to stir 90 min at room temperature, after which the solvent was removed *in vacuo*, yielding a black oil. This was dried under vacuum overnight during which time it solidified to yield 198 mg of a black-green solid (yield 67%). ^{1}H NMR (CD_2Cl_2): δ 20.55 (t, 1H, Ru=C*H*TMS, J_{HP} = 9.6 Hz), 6.85-7.50 (m, $P(C_6H_5)_3$), 5.35 (s, 5H, C_5H_5), 0.41 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (CD_2Cl_2): δ 381.67 (t, Ru=*C*HTMS, J_{CP} = 7.5 Hz), 128.20-134.86 ($P(C_6H_5)_3$), 96.12 (s, C_5H_5), 0.252 (s, $Si(CH_3)_3$); ^{31}P NMR (CD_2Cl_2): δ 46.07 (s). Elemental analysis: calculated for $C_{45}H_{45}P_2SiRuBF_4$: C, 62.57%; H, 5.25%; P, 7.17 %; found: C, 62.65%; H, 5.49%; P 7.20%. FAB MS: calculated for $C_{45}H_{45}P_2SiRu$: *m/e* 777.1803; found 777.1801.

Observation of $[Cp^*Ru]_2(\mu\text{-}CHPh)(\mu\text{-}Cl)_2$ (44). *Caution: Very rapid decomposition of phenyl diazomethane was observed during this reaction. Extreme care should be taken during any attempts at a preparative scale reaction.* An NMR tube was charged with $[Cp^*RuCl]_4$ (11.6 mg, 0.011 mmol) and C_6D_6 (0.5 mL) in the drybox, after which the NMR tube was removed from the drybox. Under a purge of argon, 1-2 drops phenyl diazomethane were added via glass pipet, accompanied by vigorous fuming. The NMR tube was quickly capped and shaken. Several different alkylidene species were initially formed (see text), but only **44** remained after the reaction mixture was left to sit overnight at room temperature. Note: When the reaction was run more concentrated (15-20 mg), a polymeric material was obtained. This was passed through a 5 μm filter, washing with CD_2Cl_2 to obtain **44**. Selected spectroscopic data: ^1H NMR (C_6D_6): δ 13.57 (s, $\mu\text{-}C\mathit{H}Ph$), 1.89, 1.56, or 1.32 (s, $C_5(C\mathit{H}_3)_5$); ^{13}C NMR (C_6D_6): δ 96.93, 96.57, 88.52, or 88.28 (s, $\mathit{C}_5(CH_3)_5$), 10.94, 10.76, or 9.79 (s, $C_5(\mathit{C}H_3)_5$).

Preparation of $[Cp^*Ru]_2(\mu\text{-}CHCO_2Et)(\mu\text{-}Cl)_2$ (45). A Schlenk flask was charged with $[Cp^*RuCl]_4$ (194 mg, 0.179 mmol) and CH_2Cl_2 (30 mL). EDA (110 μL, 1.05 mmol, 5.9 equiv) was added via syringe, and the reaction mixture was left to stir at RT for 25 min. The solvent was reduced under vacuum to 1 mL and pentane was added via cannula, causing a small amount of black solid to precipitate. The suspension was filtered via cannula filtration and the solid set aside. The filtrate was concentrated *in vacuo* to yield a black oil. The oil was dissolved in diethyl ether and filtered by cannula to remove a small amount of brown solid. The filtrate was concentrated *in vacuo* to yield 180.6 mg of a slightly impure dark green-black solid (yield 91%). ^1H NMR (C_6D_6): δ 11.89 (s, 1H, $\mu\text{-}C\mathit{H}CO_2Et$), 4.24 (q, 2H, $C\mathit{H}_2CH_3$, J_{HH} = 7.2 Hz), 1.52 (s, 30H, $C_5(C\mathit{H}_3)_5$), 1.24 (t, 3H, $CH_2C\mathit{H}_3$, J_{HH} = 7.2 Hz); ^{13}C NMR (C_6D_6)[78]: δ 186.33 (s, $\mu\text{-}\mathit{C}HCO_2Et$), 175.55 (s, $\mathit{C}O_2Et$), 97.77 (s, $\mathit{C}H_2CH_3$),[79] 86.69 (s, $\mathit{C}_5(CH_3)_5$), 59.36 (s, $CH_2\mathit{C}H_3$),[79] 10.15 (s, $C(\mathit{C}H_3)_5$).

Observation of $[Cp^*Ru]_2(\mu\text{-CHTMS})(\mu\text{-Cl})_2$ (46). Trimethylsilyl diazomethane (10% in hexanes, 105 mg, 0.092 mmol, 4 equiv) was added via syringe to a solution of $[Cp^*RuCl]_4$ (25 mg, 0.023 mmol) in CD_2Cl_2 (0.5 mL) or C_6D_6 (0.5 mL), and the reaction mixture was shaken. ^1H NMR (CD_2Cl_2): δ 14.13 (1H, s, μ-C*H*TMS), 1.60 (s, 30H, $C_5(CH_3)_5$), 0.30 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (C_6D_6): δ 210.70 (s, μ-*C*HTMS), 86.92 (s, $C(CH_3)_5$), 10.61 (s, $C(CH_3)_5$), 6.46 (s, $Si(CH_3)_3$).

Polymerization of Norbornene with 45 and 46. Norbornene (43.2 mg, 0.459 mmol, 58 equiv) was added to a solution of **45** (5 mg, 0.0079 mmol) or **46** (prepared *in situ*, 5 mg, 0.0079 mmol) in C_6D_6 (0.5 mL). The reaction was monitored by ^1H NMR as described in the text. In the case of **45**, polymer was observed after several hours and the reaction mixture had solidified after 24 h. In the reaction with **46**, only a trace of norbornene was visible after 2 days at room temperature.

Preparation of $[Cp^*Ru]_2(\mu\text{-CPh}_2)(\mu\text{-Cl})_2$ (47).[80] A 3-neck round-bottom flask was charged with $[Cp^*RuCl]_4$ (75 mg, 0.069 mmol) and THF (20 mL). In a Schlenk flask, Ph_2CN_2 (107 mg, 0.55 mmol, 8.0 equiv) was dissolved in THF (5 mL), and the resulting solution was transferred into the addition funnel via a polyethylene cannula. The diazo solution was added dropwise, allowing nitrogen evolution to cease between additions. After the addition was complete, the reaction mixture was left to stir at room temperature for an additional 30 min. The solvent was removed *in vacuo*, and the residue was extracted into 2:1 diethyl ether/pentane and filtered via cannula filtration. The filtrate was concentrated and dried under vacuum overnight to yield 23.1 mg of a black solid (yield 47%). The remainder of the product could be found in lower purity as a tan solid left behind during the extraction step. ^1H NMR (C_6D_6): δ 6.98-7.71 (m, μ-

$C(C_6\mathit{H}_5)_2)$, 1.13 (s, $C_5(C\mathit{H}_3)_5$); ^{13}C NMR (C_6D_6): δ 227.20 (s, μ-$\mathit{C}Ph_2$), 126.77-131.26 (μ-$C(\mathit{C}_6H_5)_2$), 87.68 (s, $\mathit{C}_5(CH_3)_5$), 9.08 (s, $C_5(\mathit{C}H_3)_5$).

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(47) Methanol insoluble material.

(48) It should be pointed out that **22b** was isolated while **29** was prepared and characterized *in situ,* and thus these two results may not be directly comparable.

(49) The 500 MHz ^{31}P NMR spectrum of an *in situ* reaction mixture carried out with excess PCy_3 does indicate the presence of small amounts of a couple other phosphorus-containing species, as well as free PPh_3 and free PCy_3.

(50) The magnitude of this chemical shift difference is not unreasonable. On changing from CD_2Cl_2 to C_6D_6, the carbene proton in **24** shifts from 19.56 to 19.28 ppm and that in **25** shifts from 19.77 to 19.14 ppm.

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(52) Based on our experience with the other ruthenium carbenes in this series, the spectrometer settings used are expected to be adequate to observe the carbene carbon of **32** at this concentration if it were present.

(53) The reaction was attempted with CuCl present prior to introduction of the diazo compound and with CuCl addition after reaction with the diazo compound. In neither case were carbene carbon resonances observed.

(54) This can also be used as a source of organic carbenes. See: Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry. Part B: Reactions and Synthesis*; Plenum Press: New York, 1983; pp. 429-430.

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time. Assignments were made on the basis of the relative intensities of the signals and by comparison with other analogous ruthenium carbenes in the same series.

(79) The resonances tentatively assigned to the ethyl carbons are unusually downfield. These seemed to be the most logical signals based on peak intensity. However, there were several smaller peaks (less intense than the quaternary carbonyl carbon) with chemical shifts in a more typical range. These were observed at 61.80, 61.28, 60.86, and 58.64 ($\mathit{C}H_2CH_3$) and 14.75, 13.92, 10.40, 9.91, and 9.70 ($CH_2\mathit{C}H_3$). These resonances do not correspond to diethyl maleate or diethyl fumarate, the olefinic carbons of which are not observed in this spectrum.

(80) This reaction can also be carried out in benzene.

Appendix

Structure Determination Summary for [Cp(PPh$_3$)$_2$Ru=CHCO$_2$Et]BF$_4$ (37)

Crystal Data

Empirical Formula	$C_{45}H_{41}BF_4O_2P_2Ru \cdot C_6H_6$
Color; Habit	Yellow/bronze plate
Crystal size (mm)	0.23 x 0.33 x 0.34
Crystal System	Monoclinic
Space Group	$P2_1/c$
Unit Cell Dimensions	$\underline{a}$ - 10.077(5) Å
	$\underline{b}$ - 24.241(7) Å
	$\underline{c}$ - 18.174(7) Å
	β - 96.690(0)°
Volume	4409(3) Å^3
Z	4
Formula weight	941.7
Density(calc.)	1.419 Mg/m^3
Absorption Coefficient	0.486 mm^{-1}
F(000)	1936

Data Collection

Diffractometer Used	Siemens P4
Radiation	MoKα ($\lambda = 0.71073$ Å)
Temperature (K)	163
Monochromator	Highly oriented graphite crystal
2θ Range	4.0 to 45.0°
Scan Type	θ–2θ
Scan Speed	Constant; 3.00°/min. in ω
Scan Range (ω)	1.20° plus Kα-separation
Background Measurement	Estimated from 96 step profile
Standard Reflections	3 measured every 97 reflections
Reflections Collected	2505
Independent Reflections	2234
Observed Reflections	2070 ($F > 2.0\sigma(F)$)
Absorption Correction	N/A

Solution and Refinement

System Used	Siemens SHELXTL PLUS (PC Version)
Solution	Direct Methods
Refinement Method	Full-Matrix Least-Squares
Quantity Minimized	$\sum w(F_o-F_c)^2$
Hydrogen Atoms	Riding model, fixed isotropic U
Weighting Scheme	$w^{-1} = \sigma^2(F) + 0.0010F^2$
Number of Parameters Refined	270
Final R Indices (obs. data)	$R_F = 7.4$ %, $R_{wF} = 8.1$ %
Largest and Mean Δ/σ	0.002, < 0.001
Data-to-Parameter Ratio	7.7:1
Largest Difference Peak	0.71 eÅ^{-3}
Largest Difference Hole	-0.62 eÅ^{-3}

Atomic Coordinates (x10^5) and Equivalent Isotropic Displacement Coefficients (Å^{2}x10^4)

	x	y	z	U(eq)
Ru(1)	20813(17)	8302(4)	20818(5)	284(9)
P(1)	17724(53)	17366(12)	15918(16)	216(27)
P(2)	2908(53)	8230(12)	27755(17)	271(28)
O(1)	7453(162)	-3835(40)	6843(65)	1071(89)
O(2)	23997(146)	1763(38)	4464(55)	521(79)
C(1)	36023(189)	1616(56)	22720(75)	464(41)
C(2)	42202(202)	5931(55)	18850(82)	473(43)
C(3)	42739(197)	10437(55)	23545(75)	418(40)
C(4)	37758(177)	9211(44)	30269(63)	262(32)
C(5)	33523(177)	3688(46)	29575(66)	299(33)
C(6)	9939(178)	4637(45)	13018(64)	317(34)
C(7)	13442(263)	420(61)	7873(83)	411(44)
C(8)	28460(210)	-2050(65)	-1272(84)	669(55)
C(9)	29371(207)	1248(69)	-8056(92)	801(62)
C(10)	16765(191)	22517(45)	23232(60)	204(30)
C(11)	4410(189)	24650(46)	24926(64)	242(32)
C(12)	4233(178)	28060(42)	30995(62)	241(32)
C(13)	16056(198)	29393(50)	35388(67)	283(34)
C(14)	28255(201)	27455(47)	33732(65)	266(33)
C(15)	28669(172)	23922(42)	27694(61)	241(33)
C(16)	31423(181)	19494(44)	10910(64)	246(32)
C(17)	36490(183)	24818(50)	11135(72)	368(36)
C(18)	46072(194)	26331(53)	6413(72)	408(39)
C(19)	49895(197)	22679(52)	1288(75)	470(42)
C(20)	44633(189)	17449(51)	968(72)	393(38)
C(21)	35677(183)	15777(48)	5703(63)	295(34)
C(22)	4191(181)	19060(45)	8630(65)	290(34)
C(23)	-566(179)	15084(46)	3279(62)	274(33)
C(24)	-9975(175)	16498(48)	-2650(66)	329(35)
C(25)	-14907(185)	21770(49)	-3299(70)	388(38)
C(26)	-9861(178)	25736(49)	1769(66)	339(36)
C(27)	-651(175)	24383(46)	7591(65)	294(34)
C(28)	8773(180)	9385(44)	37516(62)	271(33)
C(29)	12962(169)	14585(45)	39999(61)	259(32)
C(30)	17618(177)	15567(47)	47142(63)	305(34)

C(31)	18216(183)	11489(47)	52485(70)	343(36)
C(32)	14614(185)	6151(49)	50230(69)	333(36)
C(33)	9587(171)	5157(46)	42839(63)	289(34)
C(34)	-11168(169)	13035(41)	25820(58)	202(30)
C(35)	-16679(174)	16069(44)	31287(63)	264(33)
C(36)	-26894(188)	19795(51)	29245(71)	392(39)
C(37)	-31747(186)	20627(50)	22000(69)	368(37)
C(38)	-26928(190)	17387(49)	16588(74)	370(37)
C(39)	-17124(185)	13548(49)	18464(69)	352(36)
C(40)	-6044(249)	1480(44)	27604(66)	270(37)
C(41)	-19369(237)	1321(47)	28777(68)	298(38)
C(42)	-26155(191)	-3699(53)	28346(69)	424(41)
C(43)	-19547(263)	-8415(53)	26943(68)	382(43)
C(44)	-5980(264)	-8414(50)	26019(67)	360(41)
C(45)	872(189)	-3363(48)	26090(66)	363(37)
C(46)	53984(259)	7131(65)	51033(101)	730(60)
C(47)	57254(228)	8711(56)	58281(88)	520(44)
C(48)	69656(222)	10037(49)	61019(83)	402(38)
C(49)	80256(217)	9930(54)	56534(79)	482(44)
C(50)	77294(247)	8416(58)	49167(89)	536(46)
C(51)	64254(255)	7268(61)	46546(106)	630(52)
B(1)	39992(352)	-13896(73)	18973(103)	524(57)
F(1)	40808(114)	-19063(31)	15464(43)	565(25)
F(2)	48792(145)	-13997(42)	25425(64)	1027(38)
F(3)	44218(139)	-10120(41)	14157(59)	956(36)
F(4)	27181(165)	-12781(42)	20290(57)	886(39)

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

Interatomic Distances (Å)

Ru(1)-P(1)	2.378(3)	Ru(1)-P(2)	2.318(5)
Ru(1)-C(1)	2.230(16)	Ru(1)-C(2)	2.299(20)
Ru(1)-C(3)	2.267(19)	Ru(1)-C(4)	2.287(14)
Ru(1)-C(5)	2.225(13)	Ru(1)-C(6)	1.907(13)
Ru(1)-Cnt	1.920		

P(1)-C(10)	1.834(12)	P(1)-C(16)	1.815(17)
P(1)-C(22)	1.833(15)	P(2)-C(28)	1.825(12)
P(2)-C(34)	1.837(15)	P(2)-C(40)	1.867(16)
O(1)-C(7)	1.199(21)	O(2)-C(7)	1.332(28)
O(2)-C(8)	1.501(20)		

C(1)-C(2)	1.442(22)	C(1)-C(5)	1.393(19)
C(2)-C(3)	1.383(19)	C(3)-C(4)	1.406(21)
C(4)-C(5)	1.406(17)	C(6)-C(7)	1.456(21)
C(8)-C(9)	1.481(23)	C(10)-C(11)	1.415(26)
C(10)-C(15)	1.409(22)	C(11)-C(12)	1.380(16)
C(12)-C(13)	1.393(23)	C(13)-C(14)	1.382(27)
C(14)-C(15)	1.396(16)	C(16)-C(17)	1.387(18)
C(16)-C(21)	1.409(18)	C(17)-C(18)	1.413(24)
C(18)-C(19)	1.372(21)	C(19)-C(20)	1.373(19)
C(20)-C(21)	1.379(23)	C(22)-C(23)	1.413(16)
C(22)-C(27)	1.385(17)	C(23)-C(24)	1.393(19)
C(24)-C(25)	1.371(18)	C(25)-C(26)	1.387(18)
C(26)-C(27)	1.364(19)	C(28)-C(29)	1.388(16)
C(28)-C(33)	1.405(16)	C(29)-C(30)	1.349(16)
C(30)-C(31)	1.382(17)	C(31)-C(32)	1.393(17)
C(32)-C(33)	1.400(17)	C(34)-C(35)	1.402(18)
C(34)-C(39)	1.406(17)	C(35)-C(36)	1.387(21)
C(36)-C(37)	1.365(18)	C(37)-C(38)	1.390(20)
C(38)-C(39)	1.371(22)	C(40)-C(41)	1.384(35)
C(40)-C(45)	1.409(22)	C(41)-C(42)	1.394(21)
C(42)-C(43)	1.362(23)	C(43)-C(44)	1.397(37)
C(44)-C(45)	1.405(22)	C(46)-C(47)	1.375(24)

C(46)-C(51)	1.391(35)	C(47)-C(48)	1.330(30)
C(48)-C(49)	1.417(29)	C(49)-C(50)	1.387(21)
C(50)-C(51)	1.373(34)	B(1)-F(1)	1.412(20)
B(1)-F(2)	1.386(27)	B(1)-F(3)	1.368(25)
B(1)-F(4)	1.367(39)		

* Cnt is the centroid of the C(1)-C(5) ring.

Interatomic Angles (°)

P(1)-Ru(1)-P(2)	97.7(2)	P(1)-Ru(1)-C(6)	96.5(4)
P(2)-Ru(1)-C(6)	89.1(5)	P(1)-Ru(1)-Cnt	118.1
P(2)-Ru(1)-Cnt	121.8	C(6)-Ru(1)-Cnt	126.4

Ru(1)-P(1)-C(10)	111.9(4)	Ru(1)-P(1)-C(16)	112.1(4)
C(10)-P(1)-C(16)	106.1(7)	Ru(1)-P(1)-C(22)	122.1(4)
C(10)-P(1)-C(22)	105.9(7)	C(16)-P(1)-C(22)	96.9(7)
Ru(1)-P(2)-C(28)	110.1(6)	Ru(1)-P(2)-C(34)	121.6(4)
C(28)-P(2)-C(34)	104.1(6)	Ru(1)-P(2)-C(40)	113.8(6)
C(28)-P(2)-C(40)	104.5(6)	C(34)-P(2)-C(40)	101.1(8)

C(7)-O(2)-C(8)	119.5(12)	C(2)-C(1)-C(5)	107.9(12)
C(1)-C(2)-C(3)	105.1(14)	C(2)-C(3)-C(4)	112.2(13)
C(3)-C(4)-C(5)	105.0(11)	C(1)-C(5)-C(4)	109.8(12)
Ru(1)-C(6)-C(7)	130.0(15)	O(1)-C(7)-O(2)	123.5(16)
O(1)-C(7)-C(6)	123.3(21)	O(2)-C(7)-C(6)	113.2(14)
O(2)-C(8)-C(9)	107.4(12)	P(1)-C(10)-C(11)	121.9(11)
P(1)-C(10)-C(15)	117.9(12)	C(11)-C(10)-C(15)	119.9(11)
C(10)-C(11)-C(12)	119.1(14)	C(11)-C(12)-C(13)	120.5(16)
C(12)-C(13)-C(14)	121.3(12)	C(13)-C(14)-C(15)	119.2(15)
C(10)-C(15)-C(14)	119.9(15)	P(1)-C(16)-C(17)	123.3(11)
P(1)-C(16)-C(21)	117.6(10)	C(17)-C(16)-C(21)	118.4(14)
C(16)-C(17)-C(18)	119.9(13)	C(17)-C(18)-C(19)	120.7(13)
C(18)-C(19)-C(20)	119.1(16)	C(19)-C(20)-C(21)	121.5(13)
C(16)-C(21)-C(20)	120.3(12)	P(1)-C(22)-C(23)	120.6(10)
P(1)-C(22)-C(27)	121.9(10)	C(23)-C(22)-C(27)	117.1(12)
C(22)-C(23)-C(24)	120.7(11)	C(23)-C(24)-C(25)	120.2(11)
C(24)-C(25)-C(26)	119.2(13)	C(25)-C(26)-C(27)	120.8(12)
C(22)-C(27)-C(26)	121.8(11)	P(2)-C(28)-C(29)	120.5(8)
P(2)-C(28)-C(33)	122.9(9)	C(29)-C(28)-C(33)	116.6(10)
C(28)-C(29)-C(30)	122.1(10)	C(29)-C(30)-C(31)	122.1(11)
C(30)-C(31)-C(32)	118.0(11)	C(31)-C(32)-C(33)	119.7(11)
C(28)-C(33)-C(32)	121.4(11)	P(2)-C(34)-C(35)	123.9(9)
P(2)-C(34)-C(39)	118.2(10)	C(35)-C(34)-C(39)	117.9(13)

C(34)-C(35)-C(36)	119.7(11)	C(35)-C(36)-C(37)	121.7(14)
C(36)-C(37)-C(38)	118.9(14)	C(37)-C(38)-C(39)	120.6(12)
C(34)-C(39)-C(38)	120.8(13)	P(2)-C(40)-C(41)	119.9(10)
P(2)-C(40)-C(45)	119.0(17)	C(41)-C(40)-C(45)	121.2(14)
C(40)-C(41)-C(42)	119.6(14)	C(41)-C(42)-C(43)	119.7(19)
C(42)-C(43)-C(44)	121.9(15)	C(43)-C(44)-C(45)	119.1(15)
C(40)-C(45)-C(44)	118.3(19)	C(47)-C(46)-C(51)	116.3(21)
C(46)-C(47)-C(48)	122.4(21)	C(47)-C(48)-C(49)	121.2(15)
C(48)-C(49)-C(50)	117.9(19)	C(49)-C(50)-C(51)	118.6(21)
C(46)-C(51)-C(50)	123.3(18)	F(1)-B(1)-F(2)	107.5(17)
F(1)-B(1)-F(3)	105.4(16)	F(2)-B(1)-F(3)	109.7(22)
F(1)-B(1)-F(4)	111.1(21)	F(2)-B(1)-F(4)	112.3(17)
F(3)-B(1)-F(4)	110.5(17)		

Anisotropic Displacement Coefficients ($Å^2 x 10^4$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru(1)	440(26)	145(5)	262(6)	11(7)	29(7)	-10(4)
P(1)	235(76)	204(17)	213(17)	-29(19)	44(22)	-15(12)
P(2)	356(78)	154(16)	291(18)	-38(19)	-12(22)	-1(13)
O(1)	1889(239)	360(63)	954(93)	-313(79)	122(99)	-312(59)
O(2)	644(215)	536(62)	418(61)	-71(71)	209(76)	-257(47)

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

H-Atom Coordinates (x10^4) and Isotropic Displacement Coefficients (Å^{2}x10^3)

	x	y	z	U
H(1A)	3416	-207	2097	80
H(2A)	4517	575	1403	80
H(3A)	4620	1399	2240	80
H(4A)	3733	1162	3443	80
H(5A)	2937	168	3324	80
H(6A)	61	556	1242	80
H(8A)	2175	-483	-242	80
H(8B)	3679	-381	44	80
H(9A)	3196	-99	-1201	80
H(9B)	2097	300	-963	80
H(9C)	3605	402	-677	80
H(11A)	-369	2374	2184	80
H(12A)	-414	2944	3225	80
H(13A)	1563	3176	3959	80
H(14A)	3622	2856	3680	80
H(15A)	3705	2250	2650	80
H(17A)	3367	2746	1457	80
H(18A)	4958	3002	673	80
H(19A)	5626	2383	-194	80
H(20A)	4755	1488	-252	80
H(21A)	3214	1210	541	80
H(23A)	287	1139	367	80
H(24A)	-1329	1377	-623	80
H(25A)	-2149	2271	-736	80
H(26A)	-1319	2944	119	80
H(27A)	243	2720	1109	80
H(29A)	1300	1754	3649	80
H(30A)	2046	1923	4858	80
H(31A)	2107	1233	5759	80
H(32A)	1556	318	5375	80
H(33A)	681	150	4135	80
H(35A)	-1334	1556	3641	80
H(36A)	-3076	2180	3303	80
H(37A)	-3849	2335	2063	80
H(38A)	-3029	1792	1147	80

H(39A)	-1431	1115	1474	80
H(41A)	-2395	466	2977	80
H(42A)	-3537	-395	2918	80
H(43A)	-2425	-1186	2646	80
H(44A)	-158	-1184	2521	80
H(45A)	1009	-315	2525	80
H(46A)	4508	598	4923	80
H(47A)	5040	888	6153	80
H(48A)	7145	1105	6614	80
H(49A)	8921	1086	5854	80
H(50A)	8418	820	4595	80
H(51A)	6210	657	4135	80

Observed and Calculated Structure Factors for 37

h	k	l	10Fo	10Fc	10s
2	0	0	1418	-1473	7
3	0	0	1273	-1221	9
2	1	0	948	-928	8
1	2	0	551	532	7
2	2	0	855	-913	9
3	2	0	37	-82	-59
1	3	0	1169	-1145	6
2	3	0	1592	-1575	7
3	3	0	291	299	20
1	4	0	345	358	14
2	4	0	346	304	14
3	4	0	1715	1694	9
1	5	0	2011	-1923	8
2	5	0	145	-168	28
3	5	0	257	259	17
1	6	0	220	-192	21
2	6	0	346	-332	15
3	6	0	234	203	21
2	7	0	101	136	31
4	7	0	209	161	25
1	8	0	208	-229	25
2	8	0	358	366	16
3	8	0	433	448	16
4	8	0	139	73	33
1	9	0	915	924	12
2	9	0	2247	2097	10
3	9	0	193	-154	20
4	9	0	558	-570	15
1	10	0	308	-295	18
2	10	0	1055	-1072	12
3	10	0	80	-140	-44
4	10	0	480	464	15
1	11	0	1063	1001	13
2	11	0	386	413	19
3	11	0	94	-92	23
4	11	0	395	-405	18
1	12	0	442	593	19
2	12	0	544	-561	16
3	12	0	720	-721	15
4	12	0	581	568	17
1	13	0	865	-948	16
3	13	0	346	379	17
4	13	0	448	458	18
2	14	0	270	-293	24
3	14	0	545	-527	16
4	14	0	221	188	24
1	15	0	890	-885	17
2	15	0	463	-494	19
3	15	0	608	611	17
4	15	0	312	297	25
1	16	0	233	-366	27
2	16	0	287	328	20
3	16	0	137	199	28
4	16	0	289	-330	25
1	17	0	173	-207	29
2	17	0	311	-315	24
3	17	0	433	384	22
4	17	0	65	67	-62
1	18	0	451	-397	21
2	18	0	222	275	27
3	18	0	237	-272	25
4	18	0	688	-723	19
1	19	0	135	210	38
2	19	0	155	160	39
3	19	0	55	-97	-68
4	19	0	285	279	30
1	20	0	144	-231	48
2	20	0	464	491	24
3	20	0	405	488	27
4	20	0	438	-465	24
1	21	0	828	803	20
2	21	0	562	557	22
3	21	0	543	-555	21
4	21	0	423	-433	26
3	22	0	366	-385	23
1	23	0	301	314	32
3	23	0	243	-323	28
4	23	0	336	-341	28
1	24	0	616	617	23
2	24	0	462	-441	24
3	24	0	332	-296	30
4	24	0	338	270	28
1	25	0	229	-253	27
2	25	0	117	-148	54
3	25	0	195	23	35
-3	1	1	894	922	9
-2	1	1	681	-648	9
-1	1	1	2000	2027	4
2	1	1	189	121	23
3	1	1	238	-220	21
-3	2	1	51	46	-51
-2	2	1	522	529	11
-1	2	1	1235	-1182	6
1	2	1	2031	-2017	5
2	2	1	2101	2117	7
3	2	1	1176	1244	9
-3	3	1	427	-383	13
-2	3	1	628	-627	10
-1	3	1	60	27	-34
1	3	1	546	548	9
2	3	1	1095	-1115	8
3	3	1	169	-200	23
-3	4	1	177	-160	22
-2	4	1	831	-772	10
-1	4	1	438	400	10
1	4	1	305	-308	13
2	4	1	61	4	-48
3	4	1	710	675	11
-3	5	1	836	830	11
-2	5	1	254	-253	18
-1	5	1	1638	-1621	8
1	5	1	1938	1958	8
2	5	1	425	-456	14
3	5	1	745	-688	12
-3	6	1	346	-311	17
-2	6	1	715	688	11
-1	6	1	1186	1165	9
1	6	1	429	398	13
2	6	1	473	419	13
3	6	1	18	-88	-71
-3	7	1	547	597	12
-2	7	1	897	-927	11
-1	7	1	1344	-1326	10
1	7	1	704	725	11
2	7	1	1219	1102	10
3	7	1	436	400	15
4	7	1	911	-892	12
-3	8	1	467	425	15
-2	8	1	734	-660	12
-1	8	1	570	-577	12
1	8	1	870	800	11
3	8	1	180	-156	22
4	8	1	1056	1040	12
-3	9	1	493	-451	15
-2	9	1	700	-715	12
-1	9	1	220	-256	21
1	9	1	39	-5	-35
2	9	1	461	412	15
3	9	1	95	131	31
-3	10	1	350	-360	17
-2	10	1	672	-661	13
-1	10	1	125	-105	29
1	10	1	1303	1235	12
2	10	1	824	-829	13
3	10	1	400	-428	15
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1	15	13	23	-60	-91
2	15	13	267	238	26
3	15	13	214	224	31
4	15	13	97	-42	-62
-3	16	13	121	-147	48
-2	16	13	443	-461	22
-1	16	13	263	-188	38
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2	16	13	216	-158	37
3	16	13	449	-479	25
-3	17	13	280	-235	31
-2	17	13	159	212	46
-1	17	13	727	700	18
2	17	13	243	-307	30
-3	18	13	112	-133	-58
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-1	18	13	257	162	32
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2	18	13	191	-227	29
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-1	19	13	616	591	25
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3	0	14	729	-800	18
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1	3	14	152	-178	43
2	3	14	308	-387	27
3	3	14	25	-2	-98
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-2	4	14	205	147	23
2	4	14	228	166	35
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-1	5	14	346	338	24
1	5	14	256	-304	23
2	5	14	417	-451	23
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-2	6	14	628	617	17
1	6	14	709	-690	18
3	6	14	470	421	21
-3	7	14	482	455	20
-2	7	14	286	349	29
-1	7	14	240	-344	34
1	7	14	141	40	41
2	7	14	344	402	25
3	7	14	179	-204	39
-3	8	14	340	275	25
-2	8	14	152	220	42
-1	8	14	282	-288	27
1	8	14	253	-221	25
2	8	14	22	61	-90
3	8	14	226	296	33
-3	9	14	346	292	24
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-1	9	14	651	-619	19
1	9	14	450	387	26
2	9	14	640	627	20
3	9	14	271	-269	31
4	9	14	607	-612	22
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1	10	14	60	99	-70
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2	11	14	153	175	41
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2	12	14	182	-222	35
3	12	14	520	-499	24
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-2	13	14	97	-161	-55
-1	13	14	62	88	-76
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2	2	15	119	-154	55
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2	3	15	304	291	25
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-1	4	15	109	21	50
1	4	15	608	-598	19
2	4	15	64	-128	-35
3	4	15	376	391	27
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-2	5	15	514	466	20
-1	5	15	574	-603	19
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3	4	16	210	-217	46
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2	6	16	132	16	47
3	6	16	467	-430	24
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1	7	16	127	157	44
2	7	16	239	-202	35
3	7	16	105	-46	52
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4	8	16	67	57	-44
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2	3	17	313	-328	32
3	3	17	111	-145	51
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2	4	17	482	535	27
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-1	5	17	106	144	50
1	5	17	71	126	-68
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3	5	17	198	-164	43
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-2	6	17	221	-237	25
-1	6	17	54	-17	-77
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2	6	17	94	18	-61
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-1	7	17	188	148	27
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2	7	17	448	-475	24
3	7	17	397	-384	25
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-1	8	17	317	340	29
1	8	17	603	-565	24
2	8	17	251	-312	41
3	8	17	162	66	39
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2	9	17	140	-121	46
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2	10	17	230	-223	36
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-2	11	17	303	312	26
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-2	12	17	384	-328	24
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-1	0	18	746	-708	17
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3	1	18	76	-141	-72
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1	4	18	385	-379	26
2	4	18	266	-224	35
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1	5	18	59	0	-79
2	5	18	199	-148	43
-3	6	18	301	-208	29
-2	6	18	156	160	40
-1	6	18	164	168	40
1	6	18	417	-459	23
2	6	18	290	-298	32
-2	7	18	169	194	39
1	7	18	104	-6	-56
-2	8	18	87	135	-63
-1	8	18	91	141	-62
1	8	18	482	-461	28
-3	9	18	282	269	27
-2	9	18	273	236	30
-1	9	18	210	-156	40
-2	10	18	23	-20	-92
-1	10	18	127	-128	47
-2	1	19	345	-312	29
-3	2	19	507	-546	22
-2	2	19	128	104	53
-1	2	19	565	531	22
-3	3	19	265	253	30
-2	3	19	192	206	36
-1	3	19	155	-30	46
1	3	19	93	132	-66
-3	4	19	536	-432	22
-2	4	19	156	-154	42
-1	4	19	105	-79	-58
-2	5	19	284	200	32
-1	5	19	86	-161	-67
-1	6	19	139	-146	49

Appendix

Preliminary Investigations of

I. Carbonyl Olefination Mediated by Tungsten Alkylidene Complexes

and

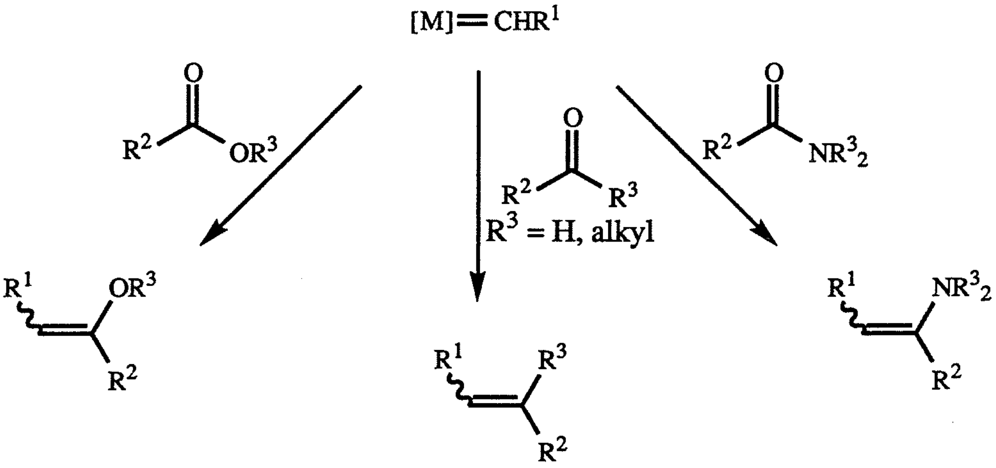
II. Its Application to Ring-Formation via Sequential Olefin Metathesis/Carbonyl Olefination of Esters

Introduction

The use of inorganic and organometallic reagents in organic synthesis has been a subject of intense study in recent years.[1, 2] Metal complexes can allow transformations to take place that do not otherwise occur with traditional organic reagents. In addition, the ability to vary non-reacting ligands attached to the metal center in many cases can allow for the incorporation of bulky or chiral ligands and thus provide a means of influencing the stereochemistry of the product obtained.

One organometallic reaction that has received a great deal of attention is olefin metathesis, a process that allows for the exchange of alkylidene moieties between a pair of double bonds.[3-7] A number of well-defined metathesis catalysts have been developed, including titanium and tantalum metallacyclobutane complexes and tantalum, molybdenum, tungsten, and rhenium alkylidene complexes.[4, 5, 8, 9] More recently, well-defined ruthenium carbene compounds have also been prepared.[10, 11] Many of these transition metal species are also effective reagents for the transfer of an alkylidene moiety to a carbonyl group (Scheme 1), a reaction that is analogous to the Wittig reaction. This dual

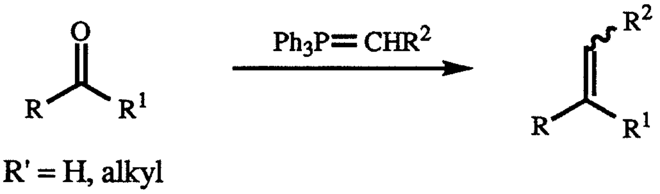
Scheme 1. Alkylidene Transfer to Carbonyl Compounds.



reactivity could potentially be exploited to allow for the development of novel metal-mediated organic transformations. This appendix describes preliminary investigations of carbonyl olefination by a series of tungsten alkylidene complexes as well as a novel ring-forming reaction that takes advantage of the double reactivity of metathesis catalysts of this type.[12]

I. Carbonyl Olefination Mediated by Tungsten Alkylidene Complexes

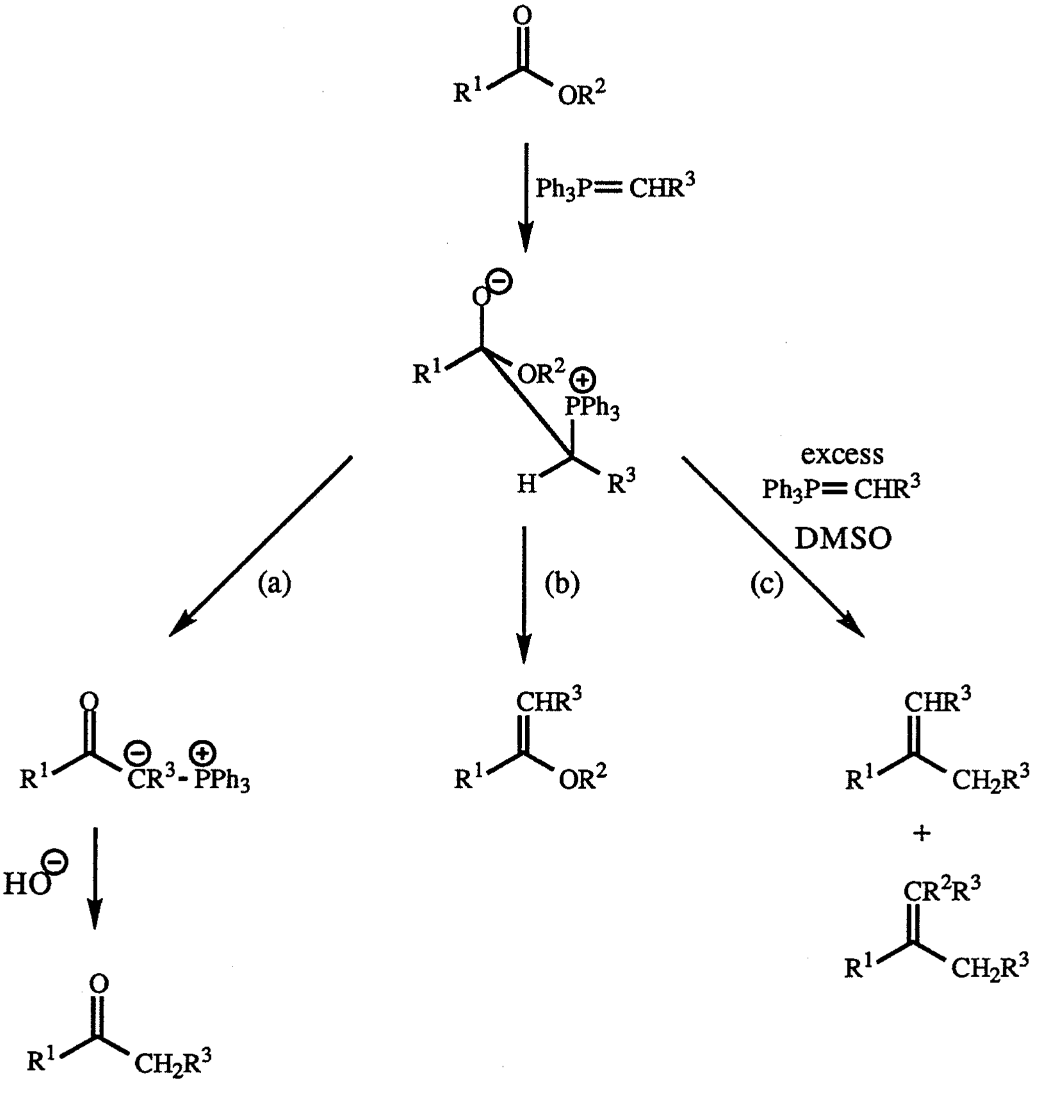
The traditional Wittig reaction makes use of a phosphorus ylide to convert an aldehyde or ketone to an alkene (Equation 1).[13-16] This reaction is extremely



(1)

important in organic chemistry, but its synthetic utility is limited for several reasons. First, the reaction is only effective with aldehydes and ketones. Different types of products are obtained upon reaction with other carbonyl functionalities. For example, there are three main reactive pathways that esters generally show towards phosphoranes (Scheme 2). Although some activated esters (for example, oxalic and cyanoacetic esters) can react with conjugated phosphoranes under certain conditions to produce a mixture of E and Z enol ethers (pathway b),[17-19] most esters react with Wittig reagents to yield acylated phosphoranes (pathway a), which can be converted by base hydrolysis to ketones.[20-23] Upon reaction of some esters with excess ylide under "salt-free" conditions or in a polar, aprotic solvent, pathway c is favored, leading to the formation of branched olefins.[24-26]

Scheme 2. Reactions of esters with phosphorus ylides.



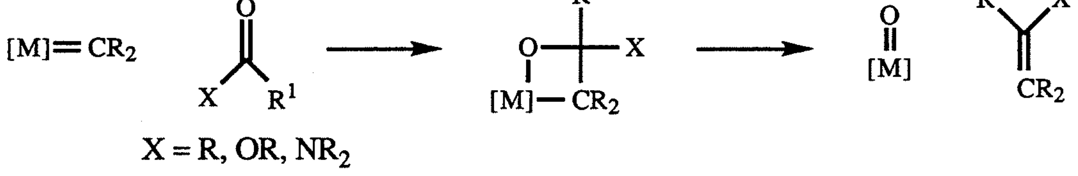
A second limitation of the conventional Wittig reaction is that the product is usually formed as a mixture of cis and trans olefins. Generally, Z olefins are preferred in the case of non-stabilized phosphoranes, while E olefins are favored with stabilized ylides.[14, 15] Several modifications have been developed to allow better control of product geometry;[27-32] however, many of these adaptations have limited applicability and the results are not always satisfactory.

The Wittig reaction is further limited by the sensitivity of phosphorus ylides to the steric environment about the carbonyl group.[33-35] Furthermore, due to the highly basic character of phosphoranes, proton abstraction tends to dominate with easily enolizable aldehydes and ketones, and asymmetric centers adjacent to the carbonyl are often scrambled.[16, 36-39]

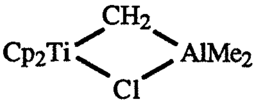
In recent years much progress has been made in overcoming these drawbacks through the use of reagents based on transition metal complexes. These include early transition metal alkylidene complexes based on tantalum,[40-42] zirconium,[43-45] titanium,[43] molybdenum,[46] and tungsten,[47, 48] as well as the Tebbe reagent and related titanacycles.[49-54] The non-basic character of these species makes them compatible with a wide variety of sensitive aldehydes and ketones that do not react cleanly with traditional Wittig reagents. In addition, many of the transition metal complexes are also effective at olefinating esters and amides. However, despite these successes, the availability of a large number of different alkylidene moieties remains limited, and E/Z selectivity is often low. Thus, the continued development of reagents for carbonyl olefination is important.

The mechanism of the transition metal mediated Wittig-like transformation is believed to be analogous to that of olefin metathesis. Following coordination of the carbonyl to the metal center, a metallaoxetane is formed, which can open in a productive manner to yield a metal oxo species and an olefin (Scheme 3).[1, 2, 40, 46, 51, 55]

Scheme 3. Mechanism of carbonyl olefination by metal carbene complexes.



Of the organometallic complexes that have been investigated, the Tebbe reagent (**1**) has probably been the one most frequently applied to organic synthesis.[49-53, 56, 57] Although this reagent and related titanacyclobutane complexes undergo reaction with a variety of functionalized carbonyls, only the titanium methylidene complex can be prepared, and thus the reaction is limited to methylene transfer.[51] A wider variety of alkylidenes can be incorporated into several other systems; for example, the zirconium analogues **2** exhibit similar chemistry and also react with imines and imidates in moderate to high yields (Scheme 4).[43-45]



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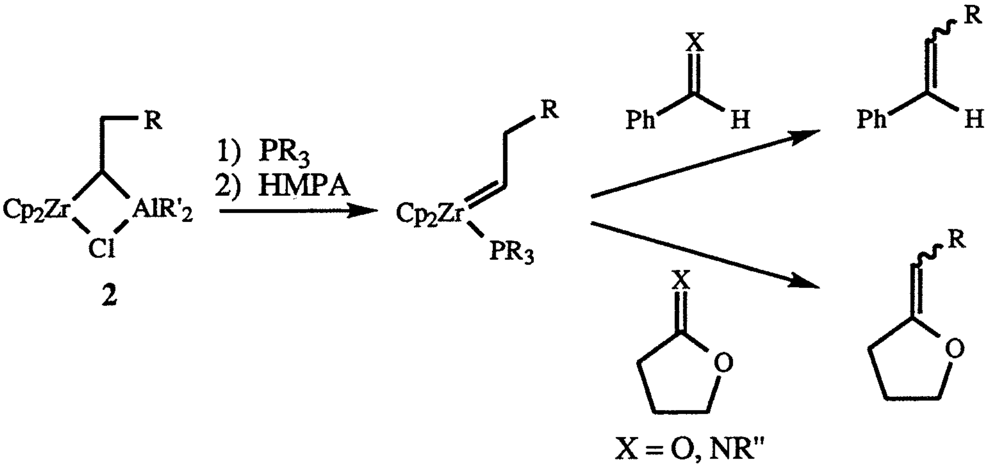
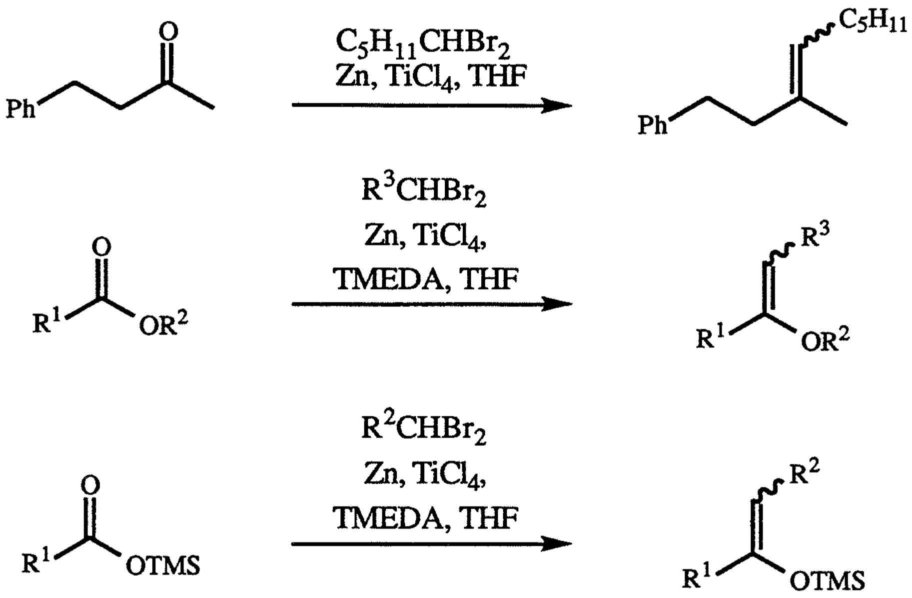
Scheme 4. Alkylidene Transfer from zirconium complexes.



Another transition metal reagent, an ill-defined system derived from 1,1-dibromoalkanes, zinc and titanium tetrachloride, appears quite promising (Scheme 5). Geminal dimetallic compounds are believed to be the active species. These reagents react

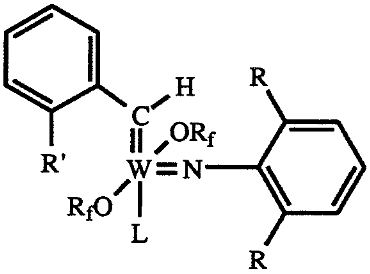
Scheme 5. Alkylidenation of carbonyl groups by zinc reagents.



with ketones to form olefins with low E/Z selectivity; however, in the presence of TMEDA they also react with esters and trimethylsilyl esters to generate enol ethers and trimethylsilyl enol ethers, respectively. These products are formed in good yield with a high preference for the Z configuration. The reaction with other carbonyl compounds has also been described,[58-64] as has the use of similar *gem*-dichromium.[65, 66]

Tungsten and molybdenum alkylidenes also exhibit this type of Wittig reactivity. Osborn has demonstrated the utility of $W(=CRR')X_2Y_2$ (R,R'= alkyl, aryl; X,Y = anionic ligands),[48] and Schrock has reported carbonyl olefination using complexes of the type $M(=CHR)(NAr)(OR')_2$ (M = W, Mo).[67] While the tungsten complexes are reactive with esters and amides, the molybdenum analogues are most effective with aldehydes.[68] In fact, aldehydes are frequently used as chain termination agents during the ring-opening metathesis polymerization of cyclic olefins using tungsten and molybdenum catalysts of this type[8, 9, 48, 68].

A number of new synthetic routes into tungsten alkylidene complexes have recently been developed in our laboratories.[69-72] These complexes are easier to prepare than many of the previous early transition metal alkylidene species and provide a source of reagents with different alkylidene moieties than are available from the other systems. Similar Wittig-like reactivity of these compounds would complement the results already obtained using other transition metal complexes and expand the scope of the reaction. Furthermore, a great deal of progress in the variability of the imido and alkoxide ligands has been made[69-72] and might allow for greater control of the E/Z selectivity in these reactions. Preliminary investigations indicated that the tungsten alkylidene **3b** can undergo Wittig-type reactions with aldehydes, esters and amides in high yield to form olefins, enol ethers and enamines, respectively.[69] Further examination of the reactivity of complexes **3a-e** with a variety of different carbonyl compounds has therefore been undertaken.[73]

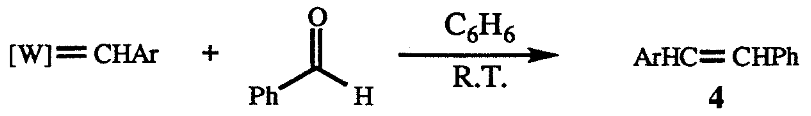


3a	R = H	R' = OMe	L = THF
3b	R = Me	R' = OMe	L = THF
3c	R = *i*-Pr	R' = OMe	L = THF
3d	R = Me	R' = H	L = PMe_3
3e	R = Me	R' = OMe	L = PMe_3

$R_f = CCH_3(CF_3)_2$

Results and Discussion

A series of ^1H NMR experiments in benzene-d_6 showed that carbenes **3a-c** react with benzaldehyde rapidly at room temperature to quantitatively yield a mixture of the cis and trans substituted stilbenes **4** (Equation 2). Compounds **3d-e** required higher temperatures (80 °C) and longer reaction times (4.5 h) to go to completion. Although E/Z



(2)

selectivity was low, the preference could be influenced by the steric bulk of the aryl imido ligand to favor either geometry (Table 1). These results indicate that it might be possible to design a ligand combination that would enable good control of the product geometry.

Table 1. Alkylidene transfer to benzaldehyde.[a,b]

Reagent	**% Trans**
3a	58
3b	54
3c	45
3d	53
3e	76
$PhHC=PPh_3$	68

[a] All reactions were carried out in benzene.
[b] All yields were quantitative.

The products of the reaction were isolated from the metal by passage through a short plug of silica and analyzed by ^1H NMR spectroscopy and GC/MS. Yields were determined relative to mesitylene, employed as an internal standard. The product geometry was assigned on the basis of GC retention times and by correlation to *cis*- and *trans*-stilbene. A large-scale reaction of benzaldehyde with catalyst **3a** resulted in the same product composition as obtained in the NMR tube reaction. Following removal of the metal by filtration through silica gel, the product was found to contain organic impurities due to decomposition of the tungsten reagent.[74]

A preliminary observation showed that a tungsten Wittig reagent of this type could be prepared *in situ* by combining a tungsten precursor with the ylide and using the resulting solution without isolation of the organometallic species. Reaction with benzaldehyde in this manner led in good yield to a product with E/Z selectivity comparable to that obtained with the isolated alkylidene.[75] This finding indicates that it may be possible to develop a one-pot procedure for carbonyl olefination, a modification that would make this reaction more attractive to synthetic organic chemists.

The reaction of **3a-c** with ethyl acetate in benzene gave similar results, although more vigorous conditions (80 °C, 12 h) were required for complete conversion (Equation 3) (Table 2). The products **5** were identified by ^{1}H NMR spectroscopy and GC/MS.

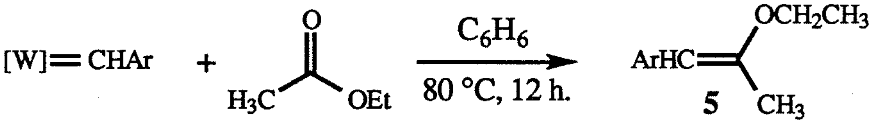


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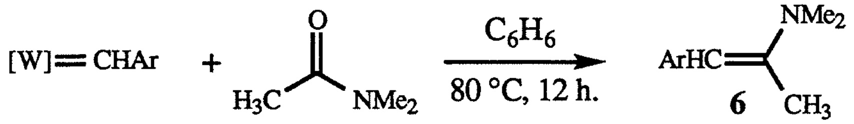
Table 2. Alkylidene transfer to ethyl acetate.[a,b]

Reagent	Product Ratio[c]	Yield, (%)
3a	42:58	91
3b	63:37	>99
3c	61:39	82
3d	----	N.R.
3e	----	N.R.

[a] All reactions were carried out in benzene.
[b] N.R. = no reaction.
[c] The absolute geometry of the enol ether products has not yet been determined.

Reagents **3d-e** failed to react, even upon heating to 100 °C overnight, and **3d** decomposed, as indicated by the disappearance of the carbene peak in the ^{1}H NMR spectrum. As was observed in the aldehyde case, E/Z selectivities could be altered by varying the substituents on the aryl imido ligand. The absolute geometry of the enol ether products obtained in this reaction has not yet been determined. Difficulties were encountered in isolating the products; a large amount of solvent was required to elute the enol ether through a short plug of silica, and the isolated product had an E/Z ratio which differed from the original sample. Compounds of this nature have been isolated by passage through basic alumina,[50, 52, 53, 58] but this method has not been examined.

The reaction of these tungsten reagents with dimethylacetamide was less straightforward (Equation 4). Complex **3a** gave only one enamine product (**6**) in 82%



6

(4)

yield. Compound **6** had a vinyl proton that resonated at δ 5.68 in the ^{1}H NMR spectrum. However, the results utilizing **3c** were inconsistent over several different trials. In one experiment, only this same enamine was observed, while in another run a second product with a vinyl hydrogen at δ 5.62 (**6**:secondary product = 0.6:1) also appeared. A third trial indicated only the original enamine and a different second product with a signal at δ 5.28 (**6**:secondary product = 1.9:1). It is not clear whether either of these additional resonances corresponds to the enamine with the opposite geometry about the double bond or to some other species. Again, attempts at isolating these products were unsuccessful. Only one trial each was done using **3b** and **3d**, but these also showed second resonances at δ 5.80 (**6**:secondary product = 16:1) and δ 6.18 (**6**:secondary product = 1:1) respectively, in addition to the signal at δ 5.68. It is possible that the steric bulk of the imido ligand affects the product distribution in these reactions. Complex **3e** failed to react under the conditions, and prolonged heating at 100 °C led only to carbene decomposition. Overall, the results obtained for dimethylacetamide were not reproducible and warrant further investigation.

An examination of these Wittig-type reactions with **3a-c** by ^1H NMR spectra taken at intermediate time intervals indicated that the reaction rate decreased as the steric bulk of the aryl imido group increased. The relative reactivities of the substrates decreased in the order aldehydes > esters > amides. This order is in agreement with that observed for the tungsten alkylidene complexes studied by Osborn.[48] Preliminary studies of the reactivity of **3a** with acetone and 2-butanone showed that these reactions were well-behaved under the conditions used, and the latter gave both E and Z products in approximately a 1:1 ratio.

A limited investigation of solvent effects was undertaken, and the results are summarized in Tables 3 and 4. Again E/Z selectivity was slight, but the ratio could be altered by varying the solvent. In the case of benzaldehyde, the preference for the Z isomer increased as the solvent polarity increased.

Table 3. Effect of varying the solvent in the reaction of **3a** with benzaldehyde.[a]

Solvent	% Trans
C_6H_6	58
CH_2Cl_2	56
THF	48

[a] All yields were quantitative.

Table 4. Effect of varying the solvent in the reaction of **3a** with ethyl acetate.

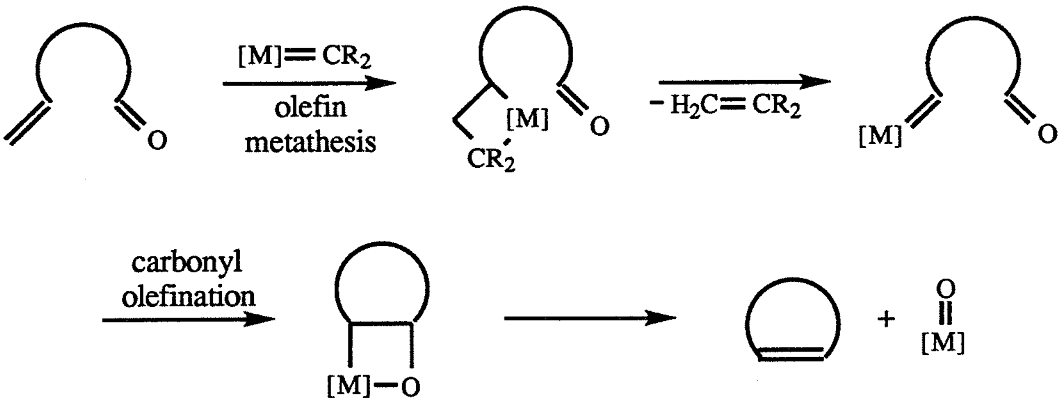
Solvent	Product Ratio[a]	Yield, (%)
C_6H_6	42:58	91
CH_2Cl_2	46:54	84

[a] The absolute geometry of the enol ether products has not yet been determined.

II. Ring-Formation via Sequential Olefin Metathesis/Carbonyl Olefination of Esters

The findings presented in the preceding section clearly demonstrate the potential of tungsten-mediated carbonyl olefination. One unique feature of these tungsten reagents is that they are also active olefin metathesis catalysts. We can take advantage of this dual reactivity to develop novel transformations that could not be accomplished with conventional Wittig phosphoranes. For example, the cyclization depicted in Scheme 6 can be accomplished by an olefin metathesis reaction followed by a carbonyl olefination. Clearly, a transition metal complex that exhibits greater reactivity towards olefins than carbonyl groups would be required. The development of such new methodologies for the preparation of cyclic and heterocyclic organic molecules would be of great value in organic synthesis.

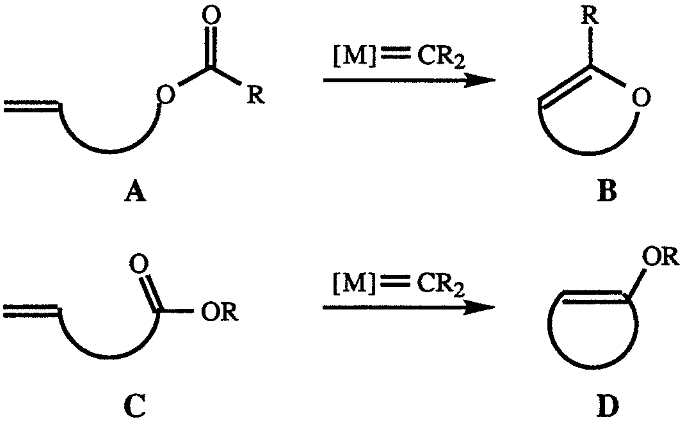
Scheme 6. Cyclization by sequential olefin metathesis/carbonyl olefination.



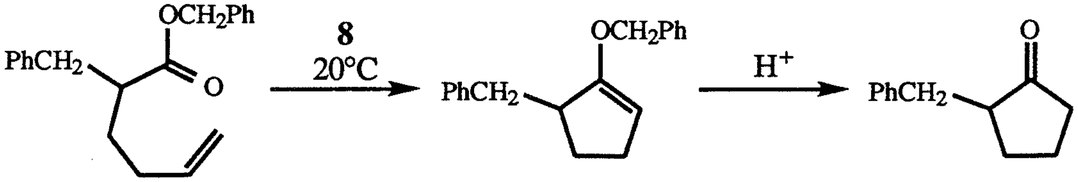
Some exploration of this type of cyclization chemistry has previously been carried out in our laboratories. The molybdenum alkylidene $Mo(=CHCMe_2Ph)(NAr)(OCMe(CF_3)_2)_2$ ($Ar = 2,6\text{-}(i\text{-}Pr)_2C_6H_3$) (7) has been employed for the preparation of a variety of five-, six-, and seven-membered cycloalkanes by cyclization of the corresponding unsaturated ketones.[76] Related reactions involving the use of **7**, as well as an isolated ruthenium carbene, to catalyze the cyclization of dienes to unsaturated carbocycles and heterocycles have also been investigated.[76-79]

It would be desirable to expand the scope of the sequential olefin metathesis/carbonyl olefination reaction to include other carbonyl functionalities, such as esters. Two different types of products could be formed, depending on the position of the double bond relative to the ester (Scheme 7). Starting materials of type **A** lead to the formation of heterocycles **B**, while esters **C** are converted into enol ethers **D**.

Scheme 7. Cyclization of esters by sequential olefin metathesis/ carbonyl olefination.



Unfortunately, attempts to accomplish the transformation **C** to **D** using **7** were unsuccessful (*vide infra*). Preliminary results (Equation 5) indicated that such a reaction could be accomplished using the more reactive tungsten analogue $W(=CHCMe_3)(NAr)(OCMe(CF_3)_2)_2$ (Ar = 2,6-(i-Pr)$_2C_6H_3$) (**8**);[76] therefore, the ability

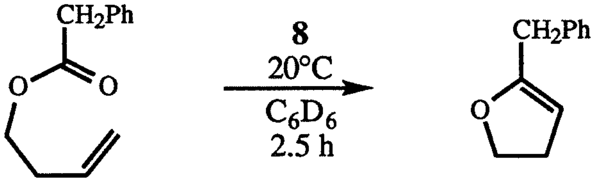


(5)

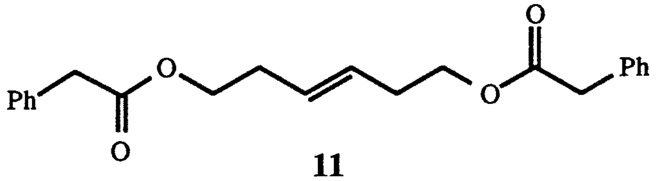
of this and other tungsten reagents to effect cyclizations of this type has been further examined.

Results and Discussion

Treatment of a 0.004 M benzene solution of ester **9** with 1.1 equiv tungsten alkylidene **8** for 3 h at room temperature resulted in the formation of the cyclic product **10** (Equation 6). The choice of reaction conditions is extremely important. When the reaction was run more concentrated (0.02 M), the dimer **11** was the major product detected, formed by metathesis coupling of **9** without subsequent carbonyl olefination. By varying the concentration, reaction time, and work-up procedures, the relative rates of the olefin metathesis and carbonyl olefination processes could be altered, leading to product distributions ranging from mostly **10** to essentially all **11**.



9 **10** **(6)**

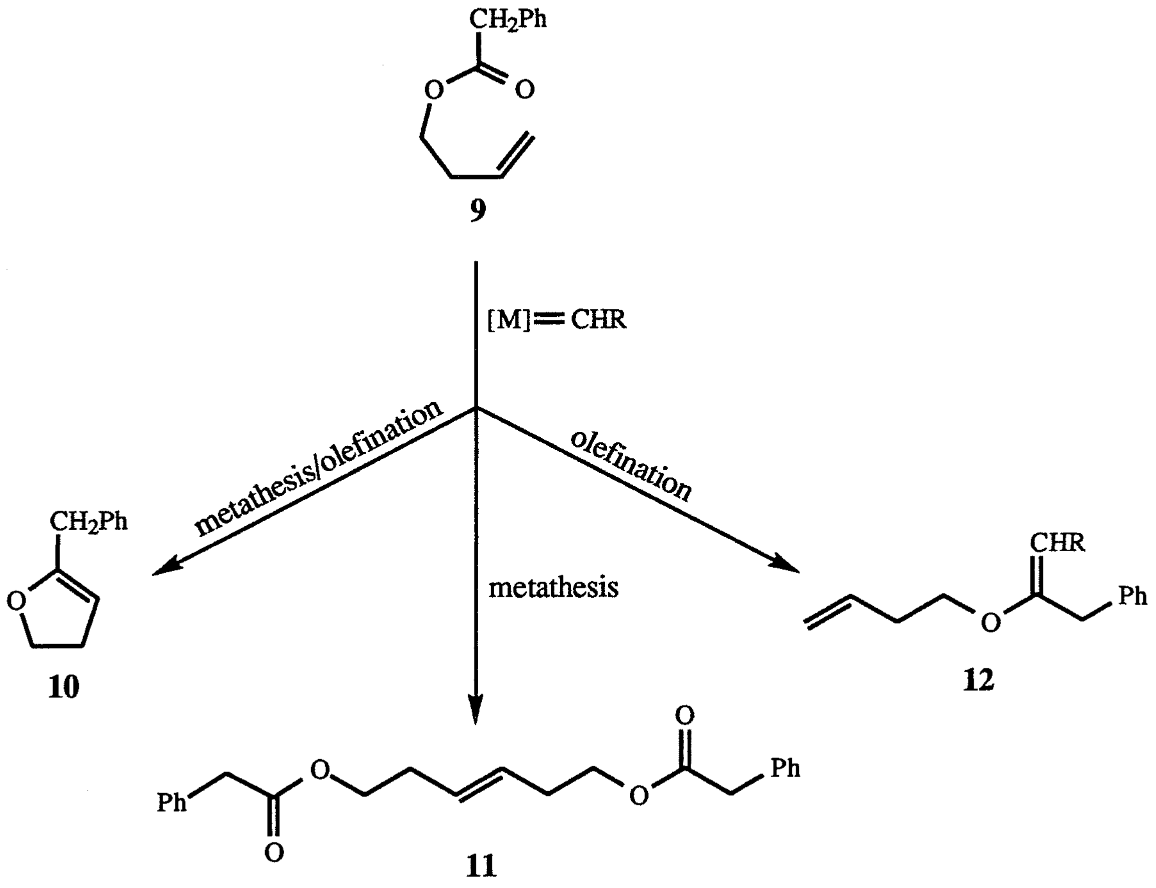


11

Methods for cleanly isolating products of this type were not fully investigated at the time these experiments were done. More recently, conditions for the purification of these and similar products, as well as their full characterization, have been developed[80] and will undoubtedly be of great utility for the continued study of these systems in the future. The reaction products described here were isolated by exposure to air followed by rapid passage through basic alumina, eluting with ethyl acetate. All compounds were obtained in impure form, contaminated by decomposition products of the tungsten reagent, in particular 2,6-diisopropylaniline. Attempts at purifying the product mixtures by more careful column chromatography appeared to result in decomposition of the desired product. The ^{1}H NMR spectra were rather difficult to interpret for many of the reaction mixtures; therefore, GC/MS was employed as the primary diagnostic tool for product identification.

One potential drawback of this cyclization chemistry is that **8** is difficult to prepare[81-85] and its high air sensitivity requires it to be used under conditions in which oxygen is rigorously excluded. Furthermore, the carbonyl olefination is a stoichiometric

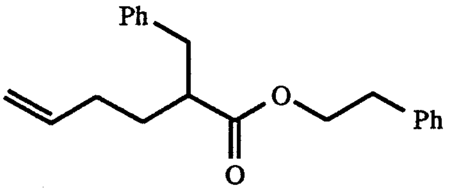
Scheme 8. Possible reaction pathways upon treatment of **9** with metathesis catalysts.



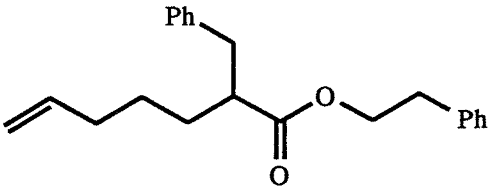
process that results in the formation of non-reactive metal oxo species. In order to make this novel transformation more attractive to synthetic organic chemists, it is important to identify other metathesis catalysts that might possess the required balance of metathesis versus olefination reactivity to promote this transformation. To favor the desired cyclization over the alternative pathways (Scheme 8), a complex is needed that will be more reactive with the olefin than the carbonyl but will still possess great enough reactivity to attack the ester functionality in an intramolecular fashion.

The optimal procedures determined to favor cyclization of **9** by **8** were investigated with a number of other more readily prepared metathesis catalysts. The results are summarized in Table 5. All products were identified by GC/Ms. In some cases, high molecular weight products were obtained that could not be positively identified. It was assumed that these corresponded to some type of reaction that involved metathesis coupling followed by a secondary reaction, perhaps olefination of the ester functionality. All such high molecular weight products are classified as dimeric in Table 5. It should be noted that while several reactions yielded only recovered starting material, this was likely due to deactivation of the metal complex rather than lack of reactivity. Overall, these data indicate that, despite its drawbacks, only tungsten alkylidene **8** possesses the right balance of reactivity to be of use for cyclizations of this type.

In addition to substrate **9**, ester **14** was also employed for some studies. However, the coupling products of **14** are of too high a molecular weight to be observed by GC/MS, and many of these experiments were inconclusive. The analogous substrate **15** was also prepared, but has not yet been studied under the cyclization conditions.

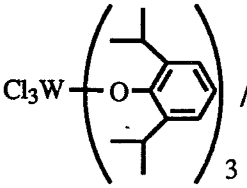
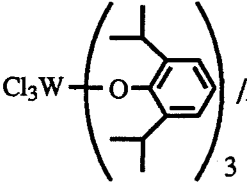


14



15

Table 5. Reaction of **9** with various metathesis catalysts.

Catalyst	**Organic Product**[a]
8	**10**
7	dimer
$WCl_6/SnMe_4$	dimer
$WCl_6/EtAlCl_2$	decomposition
3a	**12**
3b	dimer
3c	recovered **9** + dimer
3d	recovered **9**
3e	decomposition
 /$SnMe_4$ **13**	recovered **9** + decomposition
 /$EtAlCl_2$ **13**	decomposition

[a]Dimer indicates that **9** has undergone metathesis coupling. Secondary reactions may have also taken place; therefore, the product may not necessarily be **11**.

Conclusions and Further Work

Investigations of the reaction of the tungsten alkylidene complexes **3a-e** with carbonyl complexes have indicated that these species exhibit promising reactivity as Wittig analogues. Complexes **3a-c** were found to be particularly suited for alkylating a wide range of carbonyl functionalities, including esters and amides, although the reaction rate was slightly decreased by bulky substituents on the aryl imido ligands. Although only slight E/Z selectivity was achieved, the product distribution could be influenced by changes in the solvent and the ligands. These encouraging results indicate that it might be possible to find a combination of ligands and reaction conditions that might lead to a much greater control of product geometry. The effect of varying the alkoxide ligand has not yet been explored. The great flexibility of this ligand in terms of steric and electronic effects might hold the key to improved selectivity.

The ambiguous results obtained with dimethylacetamide remain to be examined further. Other amides should also be investigated to determine whether these difficulties are unique to this substrate. In addition, other carbonyl derivatives, including sensitive ketones and aldehydes that do not react cleanly under standard Wittig conditions, should also be studied in order to establish the generality of the alkylidenation reaction.

The ability of metathesis catalysts to transfer alkylidene moieties to esters has been exploited to develop a unique sequential metathesis/carbonyl olefination cyclization. The optimal conditions to favor the desired product were determined, and a study of different metathesis catalysts has identified **8** as the best reagent to effect this transformation. Several substrates were prepared, and explorations of the scope of this reaction are currently in progress.[86] In addition, other research in our laboratories has led to the development of a two-step procedure that avoids the stoichiometric use of **8** by first olefinating the ester with a more readily available reagent prior to cyclization of the resulting diene with a metathesis catalyst.[80]

Experimental

General. All manipulations involving air- and/or moisture-sensitive compounds were carried out using standard high vacuum or Schlenk techniques. Argon was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4Å molecular sieves. Solids were transferred and stored in a nitrogen-filled Vacuum Atmospheres glove box equipped with a MO-40-1 purification train, a DK-3E Dri-Kool conditioner, and a Dri-Cold Freezer.

Instrumentation. NMR spectra were recorded on a JEOL GX-400 (399.65 MHz ^{1}H, 61.25 MHz ^{2}H, 100.40 MHz ^{13}C) spectrometer or a GE QE-300 NMR spectrometer (300.19985 MHz ^{1}H, 75.49283 MHz ^{13}C). Proton chemical shifts are referenced to internal residual solvent protons. IR spectra were recorded on a Perkin-Elmer 1600 Series FTIR. GC/MS data were obtained on a Hewlett Packard HP 5890A GC/5970 MS (50°C for 2 min, increasing at 10°C per minute to 250°C, remaining at this temperature for 18 min).

Materials. Tungsten alkylidenes **3a-e** were a gift from Lynda K. Johnson. Dr. Gregory C. Fu provided catalysts **7** and **8** as well as substrate **9**. Tungsten complex **13** was prepared according to literature procedures.[87] WCl_6 (Aldrich) was heated at 85°C under vacuum for 11 h and sublimed 12 h at 125°C. Ethyl acetate and dimethylacetamide (Aldrich, anhydrous) were degassed by repeated freeze-pump-thaw cycles and stored under argon. Benzaldehyde was washed with 10% Na_2CO_3 and saturated Na_2SO_3, dried over $MgSO_4$, and distilled under reduced pressure. Methylene chloride-d_2 (Cambridge Isotope Laboratories) was vacuum transferred from calcium hydride and degassed by repeated freeze-pump-thaw cycles. Benzene, benzene-d_6, and THF-d_4 (Cambridge Isotope Laboratories) were vacuum transferred from sodium-benzophenone ketyl and degassed by repeated freeze-pump-thaw cycles. 5-hexenoic acid (Tokyo Kasei), 6-heptenoic acid

(Aldrich), phenethyl alcohol (Aldrich), and benzyl bromide (Aldrich) were used as received.

General procedure for ^1H NMR studies of alkylidene transfer to carbonyl compounds with tungsten alkylidenes 3a-e. The tungsten reagent (**3a-e**) (15 mg) was weighed into an NMR tube, followed by addition of the deuterated solvent (0.5 mL), the carbonyl compound (1.1 equiv), and a 0.646 M solution of mesitylene in C_6D_6 (0.33 equiv) as an internal standard. The NMR tube was shaken, and a ^1H NMR spectrum was obtained. Less reactive substrates (esters and amides) were heated at 80 °C for 12 hours, and another spectrum was obtained. Products (except **6**) were isolated by filtration through a short plug of silica. Yields and olefin geometries are reported in the text (Tables 1-4). For the products obtained from the *o*-methoxyphenyl alkylidene species (**3a-c, e**), the diagnostic ^1H NMR and GC/MS data are reported in Table 6.

Table 6. Characterization of products **4** - **6**.

Product[a]	**NMR Chemical Shifts**[b]		**GC/MS**
	Vinylic Protons (δ)	**Methoxy Protons (δ)**	***m/e* (M$^+$)**
4	---[c]	3.29, 3.31	210
5	5.86, 6.13	3.36, 3.37	192
6	5.68	3.40	---[d]

[a] Ar = *o*-methoxyphenyl

[b] In C_6D_6.

[c] Due to reagent and solvent signals of similar chemical shifts, the vinylic protons of the products **4** could not be positively identified.

[d] This product was not isolated.

Preparative scale reaction of benzaldehyde with 3a. Reagent **3a** (500 mg, 0.60 mmol, 1.1 equiv) was weighed into a Schlenk reaction flask under inert atmosphere and dissolved in benzene (5 mL). Upon addition of benzaldehyde (55 mL, 0.54 mmol), the solution changed from dark orange-brown to light orange-brown. The reaction, monitored by thin layer chromatography, was allowed to stir 10 h at room temperature. The flask was opened to the atmosphere and allowed to stir in air for an additional 25 min. The reaction mixture was filtered through a short column of alumina and concentrated on the rotary evaporator to yield **4** (Ar = *o*-methoxyphenyl) as a yellow oil that still contained decomposition products from the catalyst. Selected ^{1}H NMR data (C_6D_6): δ 3.29 (s, 1H), 3.31 (s, 1H). GC/MS: *m/e* 211 ($M^+ + 1$), 210 (M^+), 209 ($M^+ - 1$).

General procedure for the reaction of 9 or 12 with metathesis catalysts. A Schlenk flask was charged with the metal complex (1.1 equiv) and the substrate (0.02 mmol). Benzene (5 mL) was added and the reaction mixture was left to stir 3 h at room temperature. The flask was opened to the atmosphere and the contents were rapidly passed through a short plug of basic alumina, eluting with ethyl acetate, and analyzed by GC. Three signals with the molecular weights corresponding to **10** were observed. It was assumed that these resulted from ring-opening and/or isomerization of the product, either on the alumina or in the GC injector. These three signals appeared at retention times 8.80, 10.85, and 11.28 min, and each showed *m/e* 160 (M^+). The dimer **11** had a retention time of 22.58 min and showed *m/e* 352 (M^+).

Preparation of 14. A round bottom flask was charged with 5-hexenoic acid (0.50 g, 4.4 mmol), phenethyl alcohol (1.3 mL, 10.9 mol, 2.5 equiv) and a small amount of molecular sieves. Acetyl chloride (5 drops) was added and the reaction mixture was left to stir overnight at room temperature. Following chromatography on silica (5% ethyl acetate/hexanes), the intermediate phenethyl ester was isolated as a clear colorless oil (yield 79%). ^{1}H NMR (C_6D_6): δ 6.97-7.14 (m, 5H, C_6H_5), 5.54-5.63 (m, 1H, $CH{=}CH_2$), 4.89-4.95 (m, 2H, $CH{=}CH_2$), 4.16 (t, 2H, OCH_2, J_{HH} = 7.0 Hz), 2.66 (t, 2H, CH_2Ph,

J_{HH} = 7.0 Hz), 2.03 (t, 2H, $COCH_2$, J_{HH} = 7.4 Hz), 1.83 (q, 2H, $CH_2CH{=}CH_2$, J_{HH} = 7.1 Hz), 1.55 (quintet, 2H, $CH_2CH_2CH_2$, J_{HH} = 7.2 Hz). The intermediate phenethyl ester (1.3 g, 6.0 mmol) was added dropwise to a solution of LDA (0.65 g, 6.0 mmol, 1.0 equiv) in THF (200 mL) at -78°C. The reaction mixture was left to stir 2.5 h at -78°C, after which benzyl bromide (0.78 mL, 6.6 mmol, 1.1 equiv) was added. The reaction mixture was stirred 3 h at -78°C and left to warm slowly to room temperature overnight. The reaction mixture was concentrated and partitioned between water and ether. The aqueous layer was washed three times with ether. The combined ether layers were washed twice with water, dried over $MgSO_4$, filtered, and concentrated. The product was chromatographed on silica (5% ethyl acetate/hexanes) and dried under vacuum to yield 1.3 g of a clear, colorless oil (yield 73%). ^1H NMR (C_6D_6): δ 6.88-7.14 (m, C_6H_5), 5.54-5.67 (m, $CH{=}CH_2$), 4.89-4.97 (m, $CH{=}CH_2$), 4.09 (t, OCH_2), 2.84-2.93 (m), 2.52-2.69 (m), 1.38-2.0 (m).

Preparation of 15. The preparation was carried out as described for **14**, starting from 6-heptenoic acid. Intermediate phenethyl ester (yield 69%): ^1H NMR (C_6D_6): δ 7.00-7.14 (m, C_6H_5), 5.59-5.72 (m, $CH{=}CH_2$), 4.92-5.00 (m, $CH{=}CH_2$), 4.18 (t, OCH_2), 2.67 (t, CH_2Ph), 2.03 (t, $COCH_2$), 1.83 (q, $CH_2CH{=}CH_2$), 1.48 (quintet, $CH_2CH_2CH_2CH{=}CH_2$), 1.18 (quintet, $CH_2CH_2CH_2CH{=}CH_2$). **15** (yield 70%): ^1H NMR (C_6D_6): δ 6.88-7.12 (m. C_6H_5), 5.59-5.72 (m, $CH{=}CH_2$), 4.92-5.00 (m, $CH{=}CH_2$), 4.11 (t, OCH_2), 2.88-2.97 (m), 2.54-2.68 (m), 1.81-1.89 (m), 1.57-1.69 (m), 1.18-1.41 (m).

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(11) See Chapter 5.

(12) This appendix is not intended to describe a complete work. The first half, Carbonyl Olefination Mediated by Tungsten Alkylidene Complexes, was taken essentially intact from the Candidacy Report of Marcia B. France, California Institute of Technology, 1991.

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