Macromolecules **2002,** *35,* 48−53

Comparison of the Kinetics of Acyclic Diene Metathesis Promoted by Grubbs Ruthenium Olefin Metathesis Catalysts

Stephen E. Lehman, Jr., and Kenneth B. Wagener*

Department of Chemistry and Center for Macromolecular Science and Engineering, University of Florida, P.O. Box 117200, Gainesville, Florida 32611-7200

Received June 25, 2001; Revised Manuscript Received October 8, 2001

ABSTRACT: The kinetics of acyclic diene metathesis (ADMET) promoted by $(PCy_3)_2Cl_2RuCHPh$ (**2**), and the more recently developed catalyst **3**, which contains the 1,3-bis(mesityl)imidazolidene-2-ylidene (SIMes) ligand, were measured and compared. Complex **3** is clearly the more active catalyst at temperatures of 45−75 °C, while complex **2** is actually the faster catalyst at 30 °C. Although no induction period was observed for complex **2**, a conspicuous delay in activity was observed at the onset of ADMET with complex **3** at all temperatures studied. We propose that this behavior is due to the rates of phosphine dissociation for these catalysts, as is consistent with new mechanistic data in the context of other olefin metathesis reactions.

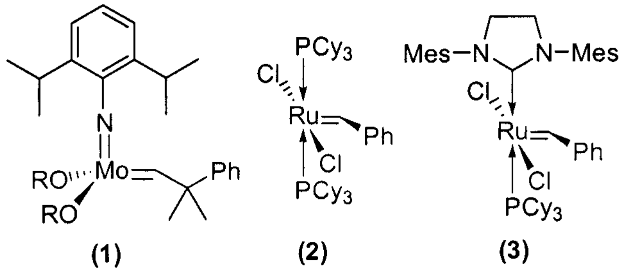
Introduction

Olefin metathesis has become a standard conversion in synthetic organic[1] and polymer chemistry,[2] and as such it is of interest to understand and predict the kinetics of these reactions with different olefin metathesis catalysts. Of these conversions, acyclic diene metathesis (ADMET) has been employed in our laboratory to synthesize polymers with unique architectures and structures.[3] Well-defined molybdenum and ruthenium carbene complexes have been used to initiate and catalyze these polymerizations (Chart 1).[4]

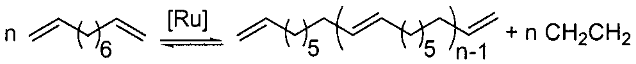
The highly active molybdenum complex **1**[5] initiated a renaissance in metathesis chemistry, and in the context of ADMET **1** is the best catalyst for the polymerization of hydrocarbons and other relatively nonpolar monomers. The more recent ruthenium complexes, such as **2**,[6] have been shown to be more stable to moisture, oxygen, and functionalized molecules. Furthermore, the ruthenium complex **3**, coordinated with a 1,3-bis(mesityl)imidazolidene-2-ylidene (SIMes) ligand, is more tolerant of polar and protic functionality and more active than **1** or **2** in a variety of olefin metathesis reactions.[7] For example, the rate of ring-opening metathesis polymerization (ROMP) of the low-strain olefin *cis,cis*-cycloocta-1,5-diene is much higher when initiated by **3** compared to **2** or even **1**.[7d]

Experiences in our laboratory with **3** have shown that it allows ADMET polymerization of a wider variety of functional monomers than **2**, most notably the solution polymerization of dienes containing amino acids.[8] Additionally, the liberation of ethylene from a mixture of **3** and 1,9-decadiene was observed to be much more vigorous at elevated temperature and ambient pressure than ever observed with **2** (Scheme 1). Intrigued by these observations, we undertook a comparative kinetic study of ruthenium complexes **2** and **3**, utilizing the ADMET of 1,9-decadiene as the basis reaction.

Chart 1. Popular Well-defined Olefin Metathesis Catalysts; R = $C(CF_3)_2(CH_3)$, Mes = 2,4,6-Trimethylphenyl



Scheme 1. ADMET of 1,9-Decadiene



1,9-Decadiene, the "benchmark" monomer for ADMET, was chosen for this study since it lacks polar or protic functional groups that could lead to complicating effects, such as complexation or reaction of the functional group with the catalyst. 1,9-Decadiene is well-known to undergo the desired polycondensation with the use of a variety of metathesis catalysts.[3i] This comparative study of catalysts **2** and **3** was undertaken in order to determine whether the trends reported in the context of other metathesis reactions, namely the dramatic increase in activity and unexpected temperature dependence of **3**, are also evident for ADMET and to what degree. Thus, 1,9-decadiene was the only monomer deemed necessary for this work. One method of evaluating the kinetics of condensation polymerization is to measure the volume of condensate produced during the course of the reaction.[9] This approach has been used previously for ADMET[10] and is employed herein to study the kinetics of the reaction by measuring the volume of ethylene gas released over time.

ADMET polymerization usually is conducted under high vacuum to remove the condensate, ethylene, thus driving the polymerization to high molecular weight. However, in the interest of rapid, simple, and reproducible data collection, this study was conducted at near-ambient pressures and without removing ethylene from the system. Under these conditions, an equilibrium between oligomeric diene and ethylene is established once an average degree of polymerization (DP) of 5−7 is attained.[11] Nevertheless, this study gives trends that correlate to ADMET under high vacuum or in solution leading to high polymer. This paper reports both the

10.1021/ma011094f CCC: $22.00

relative rate of acyclic diene metathesis with the catalyst **3** to that of catalyst **2** and the interesting temperature dependence on the activity of these catalysts. In addition, important differences in the initial stages of metathesis with the two catalysts are described, and a hypothesis involving new findings from the Grubbs group about the mechanism of olefin metathesis[12] is offered to explain these observations.

Experimental Section

General Considerations. Standard ^{1}H NMR (300 MHz) spectra were recorded in $CDCl_3$ solution on a Mercury series or Varian VXR-300 NMR superconducting spectrometer. Resonances were referenced to residual $CHCl_3$. Complex **2** was a gift from Materia Co. and was used as received. Complex **3** was synthesized according to the literature procedure.[7a] Both catalysts were stored in an argon-filled drybox. 1,9-Decadiene (Aldrich) was distilled from CaH_2 under reduced pressure into a Kontes flask equipped with a Teflon valve, degassed by three freeze−pump−thaw cycles, and stored in an argon-filled drybox. To speed data collection, 1,9-decadiene was portioned into small Teflon-capped vials in the drybox. Several of these vials were removed from the drybox and stored in a desiccator until use. Likewise, 30 mg quantities of catalysts **2** and **3** were transferred to vials and stored outside the drybox in a desiccator until use. All polymerizations were conducted in the bulk with a monomer-to-catalyst ratio of 450:1. Ethyl vinyl ether and 2,6-di-*tert*-butyl-4-methylphenol (BHT) were purchased from Aldrich and used as received. Chloroform (Fisher) was used as received.

Apparatus. A similar apparatus for the measurement of ethylene has been described previously;[10] however, important modifications used for this study warrant a complete description of the method. A temperature controller attached to a resistive wire in an oil bath was used to control the temperature of the reactions to within ±1 °C. The laboratory pressure was monitored with an electronic barometer (Fisher). The reaction chamber consisted of a standard 50 mL single-neck round-bottom flask with a 24/40 ground-glass joint. This was fitted with a custom-made glass tube with three glass stopcocks. The upper stopcock was connected to a female 14/20 ground glass joint. The side stopcocks at 45° from vertical were attached to short pieces of $^1/_4$ in. o.d. frosted glass tubing. The tubing from stopcocks A and C were connected to a vacuum-argon manifold and an inverted buret (graduated at 0.2 mL), respectively, both by way of brass Swagelok fittings and $^1/_8$ in. o.d. FEP tubing. The tubing from stopcock C was passed through a trough of water and into the inverted buret, such that the open end of the tubing remained over the water level of the buret (Figure 1).

This apparatus is airtight and can be left at slightly reduced pressure, that of the actual experimental conditions, overnight without any leaks. In addition, the setup time needed for a single kinetic trial is greatly reduced from the previously described method and allows for multiple experiments in 1 day.[13]

Procedure. An oven-dried flask containing a magnetic stir bar was attached to the custom-made glass fitting and allowed to cool in the oil bath under a stream of argon for 5 min; subsequently, 6.0 μmol of catalyst was weighed out on the bench and rapidly added to the flask. The apparatus was then evacuated and back-filled with argon three times, and a rubber septum was placed in the glass joint of stopcock B. With stopcock A closed and stopcocks B and C open, the water level in the buret was adjusted to 100.0 mL by means of a pipet bulb attached to the TFE stopcock on the buret. Water was then added to top off the trough of water. After approximately 2 min, the water level was readjusted to 100.0 mL. Then 0.50 mL (0.38 g, 0.54 mmol) of 1,9-decadiene was added by a disposable syringe through the rubber septum and stopcock B, such that the syringe needle protruded into the reaction flask. The syringe needle was then rapidly removed, stopcock B was closed, and a stopwatch was started. The level in the inverted buret was then marked at 10 s after injection of monomer, and subsequent time intervals appropriate to the temperature and catalyst were used. After productive metathesis had ceased, 1 mL of a chloroform solution containing 0.010 M ethyl vinyl ether and 0.0043 M 2,6-di-*tert*-butyl-4-methylphenol (BHT) was added and stirred until a homogeneous solution was attained. Ethyl vinyl ether terminates the polymerization by rapidly reacting with ruthenium carbene species to form a Fischer carbene which does not undergo further metathesis with alkenes,[12] while BHT is commonly used to inhibit oxidation of olefin-containing polymers. Measurements were repeated at least six times for each temperature−catalyst combination.

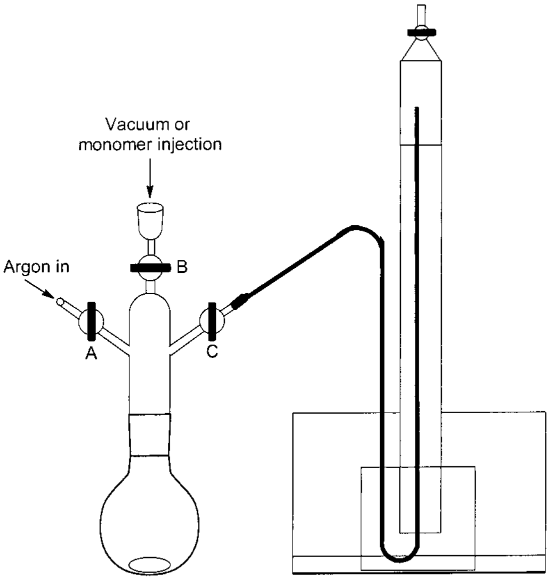


Figure 1. Apparatus for kinetics measurements.

Data Analysis. The amount of ethylene liberated at time t (N_e) was calculated with the ideal gas relation according to eq 1, in which R is the ideal gas constant. The initial volume of the system (V_0) was approximated by the volume of water required to fill the entire apparatus, and the volume of the system at time t (V_t) was calculated by adding V_0 to the change in the buret reading over the course of the experiment. The initial pressure of the system (P_0) was calculated by subtracting the pressure caused by the column of water in the inverted buret (density times height) from the pressure reading obtained from the laboratory barometer. The pressure of the system at time t (P_t) was calculated in the same manner, taking into account that the height of the column of water in the buret decreases over time. The effective internal temperature of the system (T) was estimated with the use of the ideal gas relation by observing the expansion of argon in the system as the apparatus was heated from room temperature to the temperature of the oil bath. Olefin metathesis promoted by ruthenium complexes is considered to be essentially thermoneutral[13] except when release of ring strain is involved, as in the ROMP of norbornene. ADMET has never been observed to be significantly endothermic or exothermic, and for these reasons the temperature of the system is assumed to be constant throughout the measurement.

$$N_e = [(P_t V_t) - (P_0 V_0)]/RT \tag{1}$$

The degree of polymerization (DP) was calculated by eq 2, where N_i, N_t, and N_e represent the initial amount (moles) of 1,9-decadiene, the number of moles of diene of any size (monomer, dimer, trimer, oligomer, etc.) at time t, and the number of moles of ethylene liberated at time t, respectively.

$$DP = N_i/N_t = N_i/(N_i - N_e) \tag{2}$$

The DP at each data point was then plotted vs time to generate kinetic curves. The DP vs time curves are not linear overall, so the initial rate of metathesis is defined as the slope of this curve during the average dimerization of the monomer (DP = 1 to DP = 2). The relative rate is defined as the ratio of the initial rate of metathesis with catalyst **3** to that with **2**.

In cases with a significant catalyst initiation period, signified by a low rate at the onset of reaction followed by a gradual increase to the maximum rate, the initial induction period was not included in the calculation of the rate. The end of the induction period was determined by visual inspection of the curves. To describe the longer initiation period observed with catalyst **3**, the derivative of the DP vs time curve was calculated by computer software, and the data during the induction period was fitted to a line. Thus, the slope attained was defined as the initiation rate.

The ^{1}H NMR spectra were used to spot-check the accuracy of the measurement by calculating the ratio of the integrals of internal olefinic protons (m, 5.30−5.45 ppm) to the sum of the end group olefinic protons (CH, m, 5.74−5.89 ppm and CH_2, m, 4.90−5.40 ppm), N_{int}/N_{end}. The average DP was then calculated by multiplying N_{int}/N_{end} by three and adding one, based on the stoichiometry of the oligomer. The DP estimated by NMR was consistent with that calculated from the measurement of ethylene. A minor amount (0−2 mol %, based on monomer) of *cis*-cyclooctene was observed as a multiplet at 5.66−5.69 ppm in some samples. The proton and carbon NMR spectra were consistent with the published spectra of polyoctenylene.[3i]

Results and Discussion

We have found that the ruthenium catalyst **3**, containing the SIMes ligand, promotes ADMET at a significantly higher rate than does **2** at temperatures of 45−75 °C. In fact, **3** is the faster catalyst at 75 °C by a factor of 6.5. On the other hand, this trend is reversed at 30 °C, where the activity of **2** is approximately twice that of **3**. In addition, catalyst **3** displayed a conspicuous delay in activity at the onset of reaction that was not observed with catalyst **2**.

Activity and Temperature Dependence of 2 and 3. The graph of the degree of polymerization vs time (Figure 2) is a pertinent representation of the kinetics of the ADMET reaction, for it directly tracks the formation of average dimer, trimer, tetramer, etc., and is thus a model for the stepwise formation of high polymer. The significantly higher activity of the SIMes-ligated catalyst **3** compared to catalyst **2** at elevated temperature is immediately apparent (Figure 2a). Table 1 displays the initial rates of ADMET and the relative rates of **3** vs **2** at each temperature and shows that catalyst **3** promotes productive metathesis from 2 to 6.5 times faster than catalyst **2** at elevated temperatures. This rate difference is important to note and is consistent with the report of the increased rate of ring-closing metathesis (RCM), where much higher yields of cyclized products were observed after a certain period of time when promoted by **3** vs **2**.[7a] Also evident from Figure 2 and Table 1 is the fact that **2** is the more active catalyst at 30 °C, which was previously reported in the context of RCM.[7a]

Figure 3 displays the temperature dependence of the initial rate of metathesis with both catalysts and shows that the activity of **3** is more temperature dependent than that of **2**. It is also apparent from Figure 3 that the difference in rate between the two catalysts increases with temperature. Our findings underscore the fact that condensation metathesis reactions with the 4,5-dihydroimidazol-2-ylidene catalyst **3** must be conducted at elevated temperatures to take advantage of this recent improvement in catalyst design.

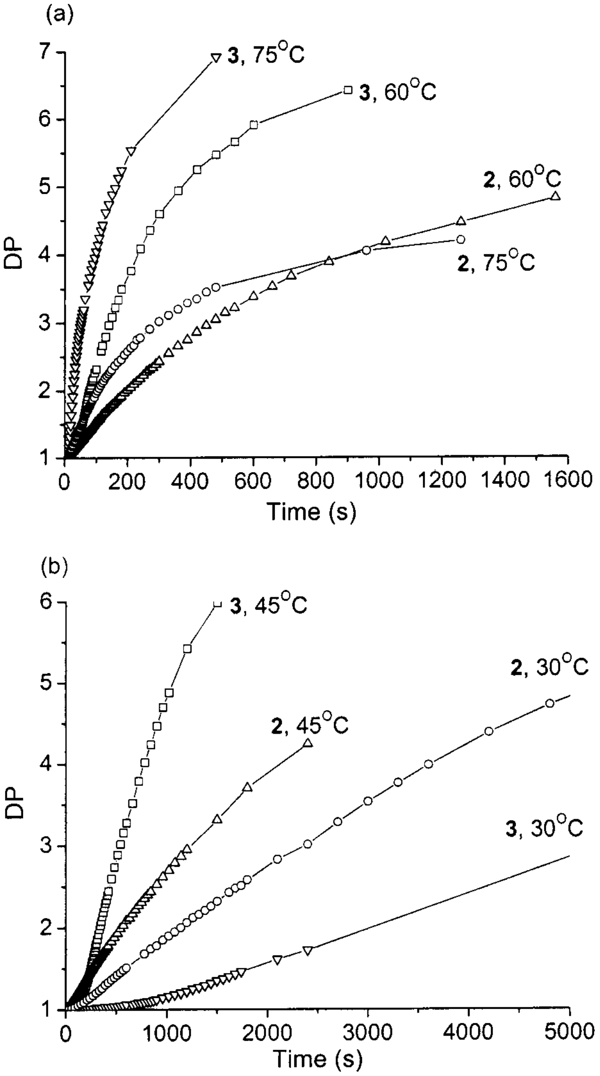


Figure 2. Typical degree of polymerization (DP) vs time data for ADMET of 1,9-decadiene with catalysts **2** and **3** at near-ambient pressure: (a) 60 and 75 °C; (b) 30 and 45 °C.

Table 1. Rate of ADMET of 1,9-Decadiene

		initial rate (10^{-3} DP s^{-1})[b]	
T (°C)	relative rate[a]	**2**	**3**
30	0.42 ± 0.21	1.0 ± 0.5	0.42 ± 0.05
45	1.9 ± 0.3	2.3 ± 0.4	4.4 ± 0.7
60	4.5 ± 0.6	5.1 ± 0.6	23 ± 3
75	6.5 ± 1.3	7.8 ± 1.5	51 ± 5

[a] Ratio of the rate of initial metathesis with **3** with respect to that with **2**. [b] The values given are the average of six trials and the uncertainty is given as the standard deviation of the rates. All measurements were taken in bulk monomer with a 450:1 monomer:catalyst ratio.

Initial Delay in Activity of 3. A conspicuous delay in productive metathesis with catalyst **3** was observed at the onset of reaction at all temperatures. This behavior is consistent with the observation[6e] that catalyst initiation for **3** is slower than that for **2**. In this context, "catalyst initiation" refers to the induction period before the maximum rate of metathesis is reached, not to be confused with the initiation of a chain polymerization such as ROMP. To illustrate, Figure 4 shows a portion of the DP vs time plot at 45 °C with

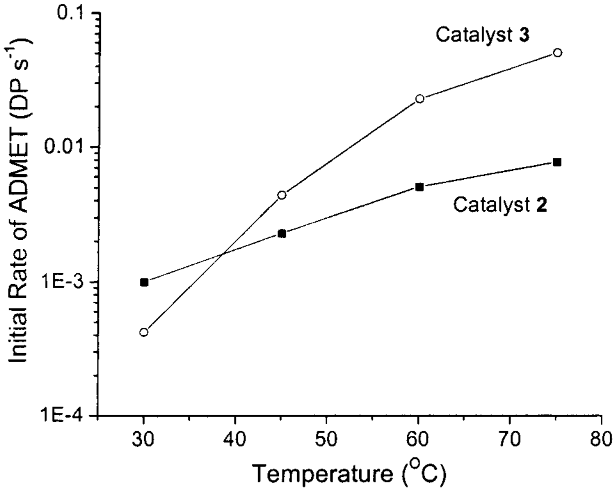


Figure 3. Temperature dependence of the initial observed rate of ADMET.

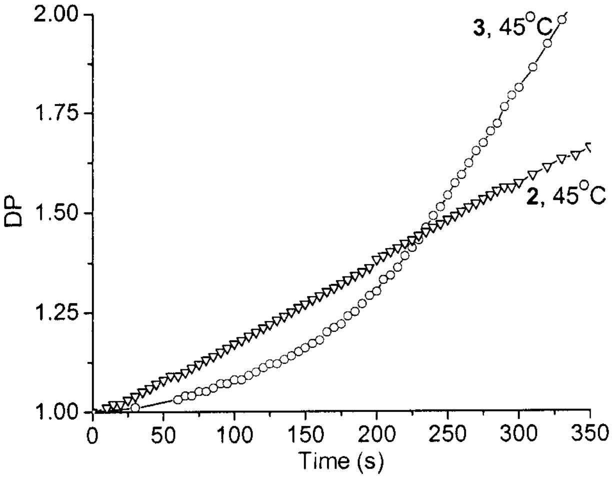


Figure 4. DP vs time data at low conversion.

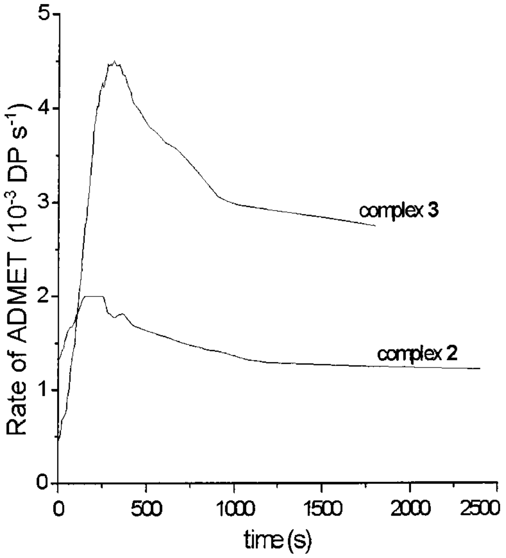


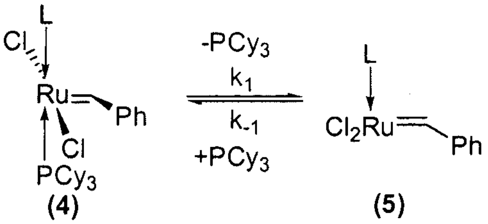
Figure 5. Time derivative of DP vs time graph at 45 °C. This graph was produced by calculating the derivative of the DP vs time plot at each point and then smoothing the data by the adjacent averaging technique.

Table 2. Gradual Rate Increase at Low Conversion with Catalyst 3

T (°C)	induction period[a] (s)	catalyst initiation rate[b] (10^{-3} DP s^{-2})
30	1800	0.00036 ± 0.00015
45	250	0.020 ± 0.003
60	70	0.39 ± 0.11
75	25	3.4 ± 0.7

[a] Time elapsed when maximum rate of ethylene production was attained. Estimated by visual inspection of the time derivative of the DP vs time graph (Figure 5). [b] Rate is given as the average of the data from at least six trials and uncertainties were estimated by the standard deviation of the data.

Scheme 2. Aspects of Phosphine Dissociation

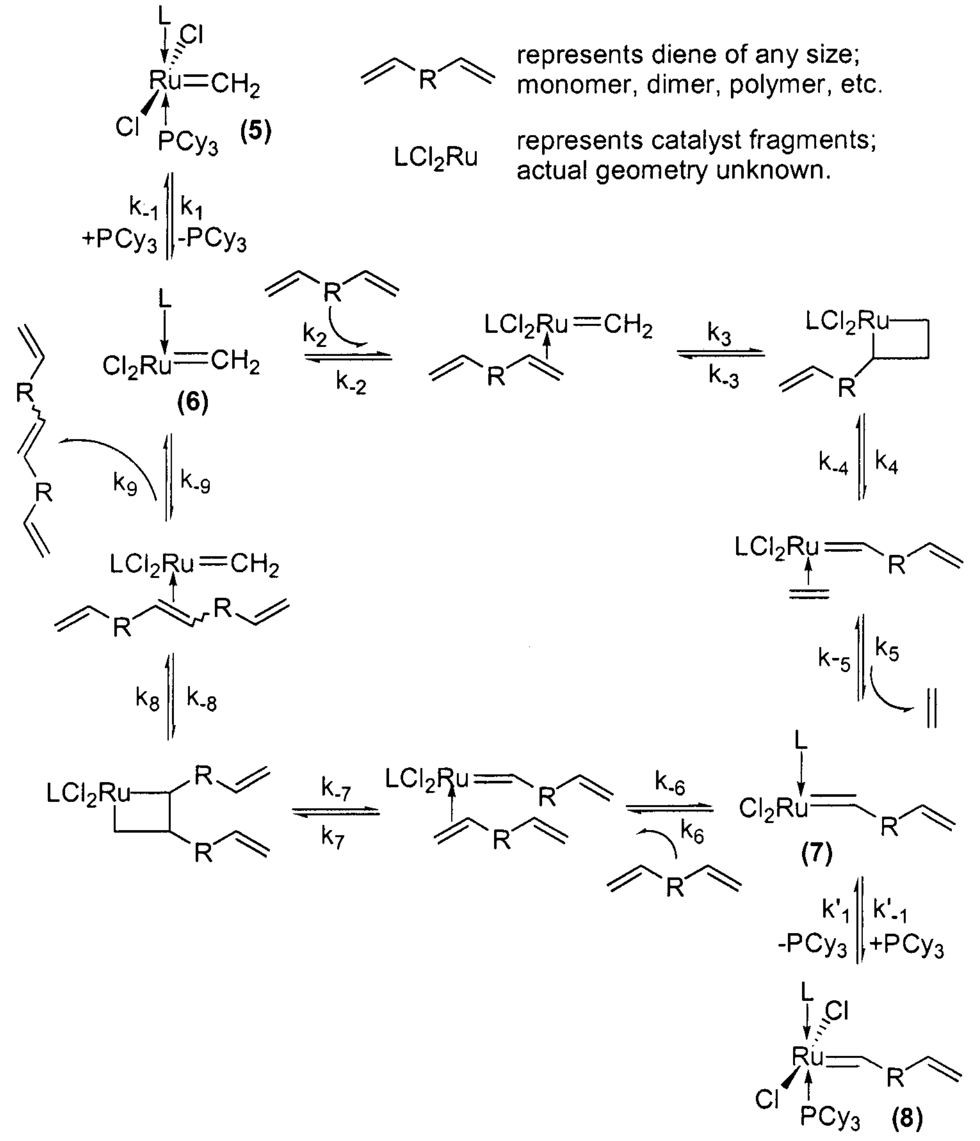


-Complex **5** is a much more active metathesis catalyst than complex **4**.
-Phosphine dissociation occurs before complexation of olefin.
-The rate of phosphine dissociation, k_d, is higher for **2** (L=PCy$_3$) than **3** (L=1,3-*bis*-mesityl-imidizolidene-2-ylidene).
-The actual geometry of **5** is unknown.

both catalysts. The rate of metathesis with **3** was somewhat retarded upon injection of monomer and then gradually increased to the maximum rate. In contrast, the rate with **2** was constant at the maximum value by the first data point at 10 s. We describe the rate of catalyst initiation as the slope of the time derivative of the DP vs time graph (Figure 5), and this quantity is given in Table 2 along with the time delay before the maximum rate of metathesis was attained (initiation time). Figure 5 shows that the rate of reaction for both catalysts goes through a maximum that is followed by a gradual decrease in the rate of metathesis.[15] Figure 5 also shows the significantly longer induction time of catalyst **3** compared to catalyst **2**. As seen in Table 2, the induction time decreases with increasing temperature. A delay in activity for **2** was observed only at 30 °C and to a very slight extent.[16]

We interpret the slower catalyst initiation for **3** to be a consequence of the rates of phosphine dissociation for the two complexes. A recent report from the Grubbs group has shown that the phosphine dissociation for both complexes is dissociative rather than associative[17] and that the rate of phosphine dissociation for complex **3** is actually *slower* than that of **2**.[12] Scheme 2 illustrates the general mechanism for the dissociative phosphine exchange of these complexes. Substantial evidence suggests that 14-electron intermediates, such as **5** in Scheme 2, which are produced by phosphine dissociation from the parent complex, are the most active catalytic species in these systems.[6e,7e,14] We propose that the rate of phosphine ligand dissociation from complex **2** is such that these 14-electron intermediates were present at steady-state concentrations almost immediately after injection of monomer, and therefore the maximum rate of metathesis was observed almost immediately as well. On the other hand, steady-state concentrations of the analogous intermediates for **3** were not attained until after the observed time delay due to the slower rate of

Scheme 3. Proposed Mechanism of Productive Metathesis



phosphine dissociation from complex **3**. Since these intermediates are the most active metathesis catalysts in these systems, the maximum rate of metathesis was not attained as quickly for **3** as for **2**, although **3** is clearly the more active of the two catalysts.

The current working mechanism of productive ADMET (Scheme 3) illustrates the critical role of phosphine dissociation in this chemistry. A report of slower phosphine dissociation for catalyst **3** is surprising and seems counterintuitive. The higher activity of **3** is due to a very high affinity of the corresponding intermediates **7** and **8** to bind and metathesize olefins once they are formed by the slower phosphine dissociation step. In contrast, the analogous intermediates derived from **2** have a higher probability of being trapped by free phosphine to regenerate complex **2** rather than undergoing metathesis.[12]

Our hypothesis that we are observing a longer initiation period for catalyst **3** due to the slower rate of phosphine dissociation is consistent with the current understanding of olefin metathesis promoted by these complexes, even though the steady-state concentrations of the 14-electron intermediates and the effect of solvent on the rates of phosphine exchange are not known. Regardless, the trends reported with the use of catalyst **3** in RCM, cross-metathesis (CM), and ROMP do extend to ADMET in that **3** is a more active catalyst than **2** and that temperatures of 45 °C and higher are necessary to exploit this advance in catalyst design.

Conclusions

The described method of kinetics measurement is rapid and simple to perform and is general in that other condensation olefin metathesis reactions, such as RCM and CM of terminal dienes, can be studied. This method also has the advantage of observing the very early stages of metathesis and thus has provided special insight into the initiation process for these catalysts.

The reported advantages of catalyst **3** were found to be applicable to ADMET. The SIMes-ligated catalyst **3** promotes ADMET considerably faster than **2** at temperatures of 45 °C and higher; just the opposite is observed at 30 °C. The activity of **3** is more dependent on temperature than that of **2**. The catalyst initiation for ADMET with **3** was observed to be much slower than that with **2** at all temperatures investigated, which we interpret to be consistent with new data[12] indicating that the rate of phosphine dissociation for complex **3** is slower than that of **2**.

Acknowledgment. We thank the National Science Foundation, Division of Materials Research (Grant DMR9806492), for financial support of this research and Dr. Krystyna Brzezinska, Dr. John Zoltevich, and Jason Smith for helpful discussions.

Note Added After ASAP Posting

This article was released ASAP on December 7, 2001, with an error in Figure 5 and ref 12. The correct version was reposted on December 11, 2001.

References and Notes

(1) (a) Bourgeois, D.; Pancrazi, A.; Ricard, L.; Prunet, J. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 726. (b) Hyldtoft, L.; Madsen, R. *J. Am. Chem. Soc.* **2000**, *122*, 8444. (c) Limanato, J.; Snapper, M. L. *J. Am. Chem. Soc.* **2000**, *122*, 8071. For recent reviews on RCM, see: (d) Wright, D. L. *Curr. Org. Chem.* **1999**, *3*, 211. (e) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413. (f) Fürstner, A. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 3012.

(2) (a) Claverie, J. P.; Viala, S.; Maurel, V.; Novat, C. *Macromolecules* **2001**, *34*, 382. (b) Trzaska, S. T.; Lee, L. B. W.; Register, R. A. *Macromolecules* **2000**, *33*, 9215. (c) Heroguez, V.; Amedo, E.; Grande, D. *Macromolecules* **2000**, *33*, 7241. (d) Myles, A. J.; Zhang, Z. R.; Liu, G. J.; et al. *Org. Lett.* **2000**, *2*, 2749. (e) Maynard, H. D.; Okada, S. Y.; Grubbs, R. H. *Macromolecules* **2000**, *33*, 6239. (f) Morita, T.; Maughon, B. R.; Bielawski, C. W.; Grubbs, R. H. *Macromolecules* **2000**, *33*, 6621. (g) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: London, 1997.

(3) (a) Watson, M. D.; Wagener, K. B. *Macromolecules* **2000**, *33*, 3196. (b) *Macromolecules* **2000**, *33*, 5411. (c) *Macromolecules* **2000**, *33*, 8963. (d) Smith, J. A.; Brzezinska, K. R.; Valenti, D. J.; Wagener, K. B. *Macromolecules* **2000**, *33*, 3781. (e) Gomez, F. J.; Wagener, K. B. *J. Organomet. Chem.* **1999**, *592*, 271. (f) Tindall, D.; Wagener, K. B.; Brzezinska, K. R. *Abstr. Pap. Am. Chem. Soc.* Part 2 **1999**, *218*, 413-POLY. (g) O'Donnell, P. M.; Wagener, K. B.; Brzezinska, K. R. *Abstr. Pap. Am. Chem. Soc.* Part 2 **1999**, *218*, 619-POLY. (h) Wolfe, P. S.; Gomez, F. J.; Wagener, K. B. *Macromolecules* **1997**, *30*, 714. (i) Brzezinska, K.; Wolfe, P. S.; Watson, M. D.; Wagener, K. B. *Macromol. Chem. Phys.* **1996**, *197*, 2065.

(4) The terms "initiate and catalyze" and "promote" are used because the initial benzylidene catalyst is lost in the first turnover to produce a ruthenium alkylidene and styrene. After metathesis with another terminal olefin, a ruthenium methylidene is produced. Thus, the ruthenium methylidene and alkylidene complexes are the actual catalysts in ADMET and other condensative metathesis reactions, RCM, and cross-metathesis. See Scheme 3.

(5) (a) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, M.; Dimare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875. (b) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158.

(6) (a) Schwab, P.; Grubbs, R. H.; Ziller, J. *J. Am. Chem. Soc.* **1996**, *118*, 100. (b) Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887. (c) Ulman, M.; Grubbs, R. H. *Organometallics* **1998**, *17*, 2484. (d) Ulman, M.; Grubbs, R. H. *J. Org. Chem.* **1999**, *64*, 7202. For a recent review of the L_2X_2Ru carbene metathesis catalysts, see: (e) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18.

(7) (a) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953. (b) Chatterjee, A. K.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 1751. (c) Chatterjee, A. K.; Morgan, J. P.; Scholl, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 3783. (d) Bielawski, C. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 2903. For information on ruthenium olefin metathesis catalysts with related ligands, see: (e) Jafarpour, L.; Nolan, S. P. *Organometallics* **2000**, *19*, 2055. (f) Briot, A.; Bujard, M.; Gouverneur, V.; Nolan, S. P.; Mioskowski, C. *Org. Lett.* **2000**, *2*, 1517. (g) Fürstner, A.; Thiel, O. R.; Ackermann, L.; Schanz, H.; Nolan, S. P. *J. Org. Chem.* **2000**, *65*, 2204. (h) Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674. (i) Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247. (j) Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2490.

(8) Hopkins, T. E.; Wagener, K. B. Submitted for publication.

(9) Odian, G. *Principles of Polymerization*, 3rd ed.; John Wiley & Sons: New York, 1991; pp 45−56.

(10) Wagener, K. B.; Brzezinska, K.; Anderson, J. D.; Younkin, T. R.; Steppe, K.; DeBoer, W. *Macromolecules* **1997**, *30*, 7363.

(11) The reversibility of olefin metathesis with these catalysts is well-documented. For the *retro*-ADMET depolymerization of 1,9-decadiene with **2**, see: (a) Watson, M. D.; Wagener, K. B. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 1857. (b) Watson, M. D.; Wagener, K. B. *Macromolecules* **2000**, *33*, 1494. In the context of RCM, see: (c) Smith, A. B., III; Adams, C. M.; Kozmin, S. A. *J. Am. Chem. Soc.* **2001**, *123*, 990. (d) Lee, C. W.; Grubbs, R. H. *Chem. Lett.* **2000**, *2*, 2145. (e) Xu, Z.; Johannes, C. W.; Houri, A. F.; La, D. S.; Cogan, D. A.; Hofilena, G. E.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1997**, *119*, 10302. (f) Marsella, N. J.; Maynard, H. D.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1101.

(12) (a) Sanford, M. S.; Ulman, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 749. (b) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543.

(13) The apparatus and procedure of ref 10 were developed to be compatible with highly moisture and air-sensitive early transition metal olefin metathesis catalysts.

(14) Adlhart, C.; Hinderling, C.; Baumann, H.; Chen, P. *J. Am. Chem. Soc.* **2000**, *122*, 8204.

(15) The fact that the rate of productive metathesis goes through a maximum and then gradually decreases could be due to a number of factors, such as the increasing viscosity of the reaction medium, decomposition of the catalyst, or the relative amounts of the various catalytic species.

(16) It is difficult to tell whether the slight inflection in the DP vs time graph for **2** at 30 °C is due to the same phenomenon as observed with **3** at all temperatures or if it is some artifact due to physical aspects of the measurement procedure.

(17) The terms associative and dissociative exchange refer to the ligand exchange mechanism. See: Jordan, R. L. *Reaction Mechanisms of Inorganic and Organometallic Systems*, 2nd ed.; Oxford University Press: New York, 1998; pp 34−48. These terms were also used to describe the number of phosphine ligands coordinated to the ruthenium during metalacyclobutane formation (ref 6b); that is not the intent here.

MA011094F