Transition Metal Carbenes: Controlled Ring-Opening Metathesis Polymerizations and Metathetical Reactions with Acyclic Olefins

Thesis by
Zhe Wu

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To My Parents

Acknowledgments

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ABSTRACT

Although strained cyclic olefins undergo facile ring-opening metathesis polymerization (ROMP) catalyzed by transition metal alkylidene or carbene complexes, there are few examples of living ROMP systems because the rate of the polymerization is much faster than that of the initiation. The phosphines reversibly bind to both the initial and the propagating tungsten or molybdenum alkylidene complexes, thus altering the rates of both initiation and the propagation. Due to the steric bulk difference of the propagating species and the initiating complexes, phosphines bind more strongly to the propagating alkylidene than to the initial alkylidene, which reduces the rate of propagation much more than that of the initiation and results in a living system. The kinetics and mechanism for both initiation and propagation have been studied. By using this living system, linear and near monodispersed polybutadiene and polyethylene can be synthesized. Block copolymers of both practical and theoretical interests can be prepared.

Metathesis of functionalized olefins using a molybdenum alkylidene complex was conducted. The metathesis of functionalized olefins is controlled by a fine balance between the coordination of olefins and that of the hetero-atoms. The formation of chelated alkylidene complexes during the metathesis of alkyl-3-alkenoate slows down the rate of productive metathesis. The formation of a stable chelated metallacyclobutane complex during the metathesis of N,N-dimethyl alkenamide prevent its productive metathesis.

Reactions of the late transition metal ruthenium carbene complexes with strained acyclic olefins and functionalized olefins are explored. Several α-hetero substituted carbene complexes and active ruthenium carbenes are synthesized through the metathesis of functionalized olefins and strained acyclic olefins, respectively. The mechanism for the rearrangement of alkoxy substituted ruthenium carbenes is determined by deuterium and ^{13}C labeling studies.

Perfect rubber (*cis*-1,4-polyisoprene) is synthesized by ROMP of 1-methylcyclobutene using a molybdenum alkylidene complex. New living polymerization systems of both bicyclo[3.2.0]heptene and bicyclo[4.2.0]octene are discovered using a ruthenium carbene complex. Narrow dispersed and regioselective alternating copolymers are synthesized through the ROMP of 3-methylcyclobutene and 3,3-dimethylcyclobutene.

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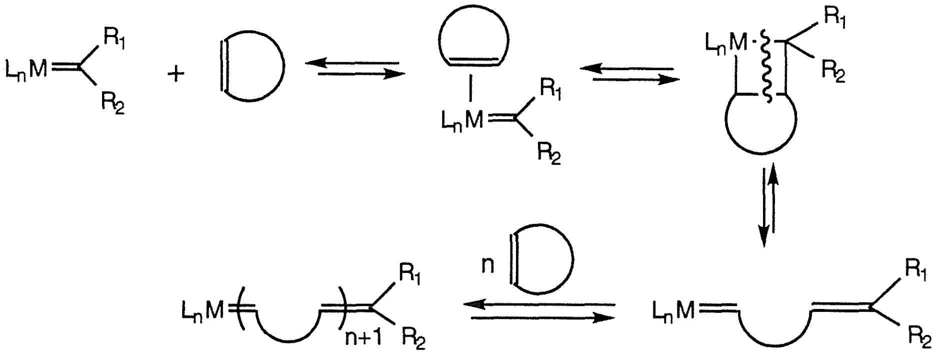
Chapter 1

Living Ring-Opening Metathesis Polymerization of Cyclobutene in the Presence of Lewis Bases

Introduction

Living polymerization is an ideal type of polymerization that has no chain transfer or chain termination during the time scale of the reaction and it has been the focus of polymer research since it was discovered.[1] Molecular weights of polymers as well as the bulk properties of materials can be controlled precisely by using living polymerization. Living polymerization technique also allows the facile preparation of block copolymers with the controlled structures and properties and provides the deepest insight to the mechanism of the polymerization as well.[1] There are several types of living polymerization known to date.[2] Among them living Ring-opening metathesis polymerization (ROMP) emerges as a new type of polymerization and holds a great promise.[3] ROMP involves the reaction of a transition alkylidene, carbene or metallacyclobutane complex with cyclic olefins in a (2+2) fashion as shown in Scheme 1. The release of ring-strain energy is usually the thermodynamic driving force for the polymerization.

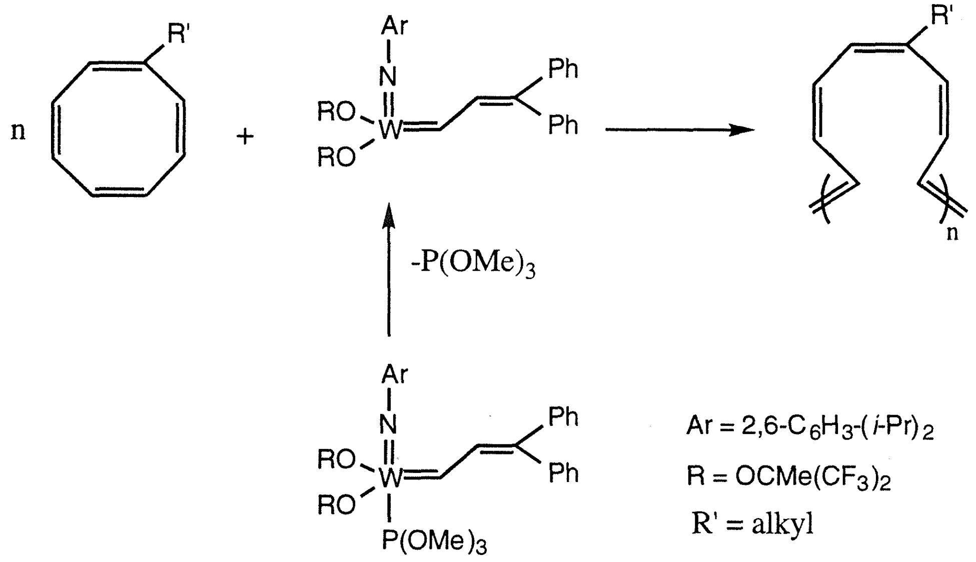
Scheme 1



Since the first report of a titanium metallacyclobutane complex catalyzed the living ROMP of norbornene, intensive efforts have been concentrated on developing new living catalysts and living polymerization systems. Strained olefin usually has to be used for the living ROMP in order to provide the driving force for the ring-opening process and to ensure the irreversibility of the propagation step, which is essential for achieving good control of polydispersity of the polymer. In the polymerization of strained olefins other than norbornene and its derivatives, broad polydispersities are usually obtained, which indicates that the rate of the propagation is much greater than that of the initiation.[4(a)] The slow decomposition of the propagating species in the time scale of the polymerization also contributes to the broadening of the polydispersity.[4]

The interest in the ROMP of cyclobutene stemmed from the structural equivalence of polycyclobutene with polybutadiene a precursor to polyethylene. Polyethylene is an important commercial material and monodispersed linear polyethylene has long been both a synthetic challenge and theoretical interest. Low polydispersity polyethylene has been synthesized by hydrogenation of 1,4-polybutadiene prepared by anionic polymerization of 1,3-butadiene. This approach results in branched polyethylene, since the polybutadiene produced by this technique contained C_2 branches as a result of low level 1,2-polymerization of 1,3-butadiene. ROMP should allow the preparation of the polybutadiene free of branches. The ROMP of cyclobutene should also provide an excellent system to study kinetic control of the polymerization and to further understand the mechanism of living polymerization.

The attenuation of the rate of the propagation relative to that of the initiation has been observed in the presence of Lewis bases, such as THF and quinuclidine.[5] For example, THF has been used to slow down the rate of polymerization of cyclooctatetraene (COT) sufficiently for fabrication. The presence of THF also prevents the formation of back-biting product.[6] In the polymerization of acetylene catalyzed by a molybdenum or tungsten alkylidene complex, the presence of quinuclidene not only bonded to but also modified the reactivity of the propagation and initiation rate. The rate for the polymerization of alkylthiolcyclooctenes using a tungsten alkylidene complex was found to be dependent on the coordination ability of alkylthiol group to the metal center.[7] In retro-aspect, it is found that the reactivity of a tungsten phosphite vinyl alkylidene complex can be greatly enhanced by the removal of a bound trimethylphosphite. The phosphite free complex catalyzes the ROMP of COT in a mild condition and yields polyacetylene with a narrow polydispersity (eq 1).[8]



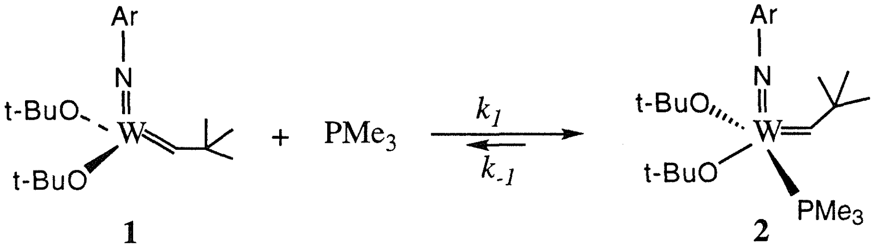
Ar = 2,6-C_6H_3-(*i*-Pr)$_2$
R = OCMe$(CF_3)_2$
R' = alkyl

(1)

In this chapter, polymerization of cyclobutene catalyzed by well-defined transition metal alkylidene complexes with or without the presence of donor ligands has been studied. Phosphines have been found to successfully attenuate the rate of the polymerization of cyclobutene and to allow the control of the polymerization, and to synthesize monodispersed polybutadiene and polyethylene. Kinetics and mechanism for the polymerization of cyclobutene in the presence of trimethylphosphine will be discussed in detail. The application of this living system to the synthesis of block coplolymers has also been examined.

Results and Discussion

Reversible Binding of Phosphines to Catalyst 1. Upon addition of one equivalent of PMe_3 to a 0.021 M toluene solution of 1, both the bound **2** and free **1** neopentylidene complexes are observed at room temperature by ^1H NMR spectroscopy.



(2)

Variable temperature NMR spectra indicate that the rate of phosphine exchange (eq 2) is slow compared to the NMR time scale at and below room temperature. Figure 1 shows that free phosphine peak (I) and bound phosphine peak (II) start to coalesce as the temperature increases from 0 to 60 °C. The binding constants K_f can be determined from

$$K_f = [WP]/([W]\,[P])^{9}$$

where [WP] = concentration of bound catalyst, [W] = concentration of free catalyst, and [P] = concentration of free phosphine. The Arrhenius plot for binding of PMe_3 to **1** shows a positive linear slope with excellent correlation ($\rho = 0.999$, Figure 2). As expected, the binding is exothermic ($\Delta H° = -15.8 \pm 1$ kcal/mol) with a large negative entropy factor ($\Delta S° = -40.7 \pm 3.7$ e.u.).

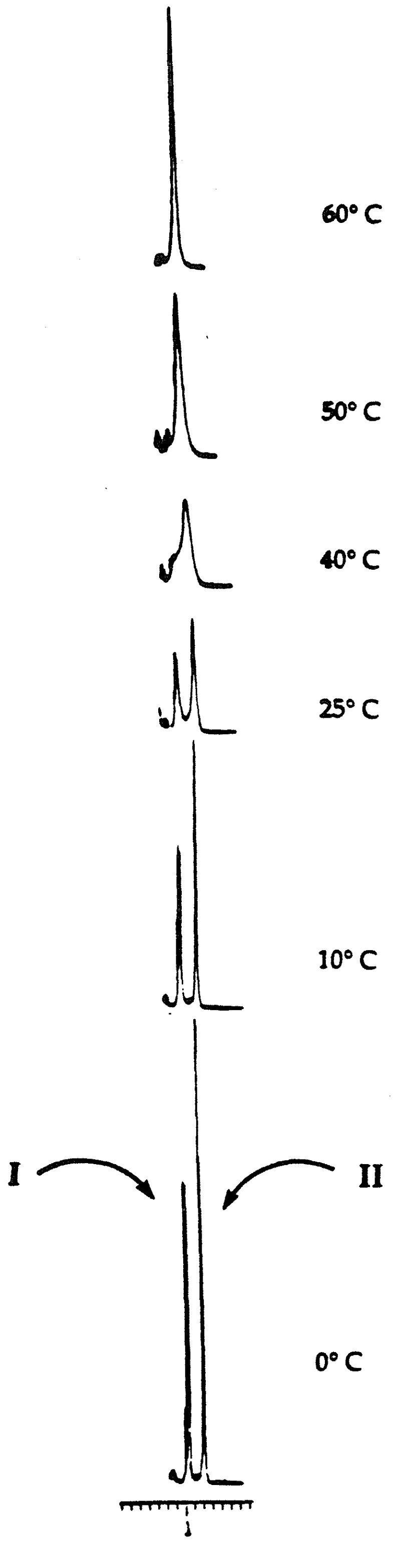


Figure 1. Variable temperature ^{1}H NMR spectra in the region of bound (I) and free PMe$_3$ (II).

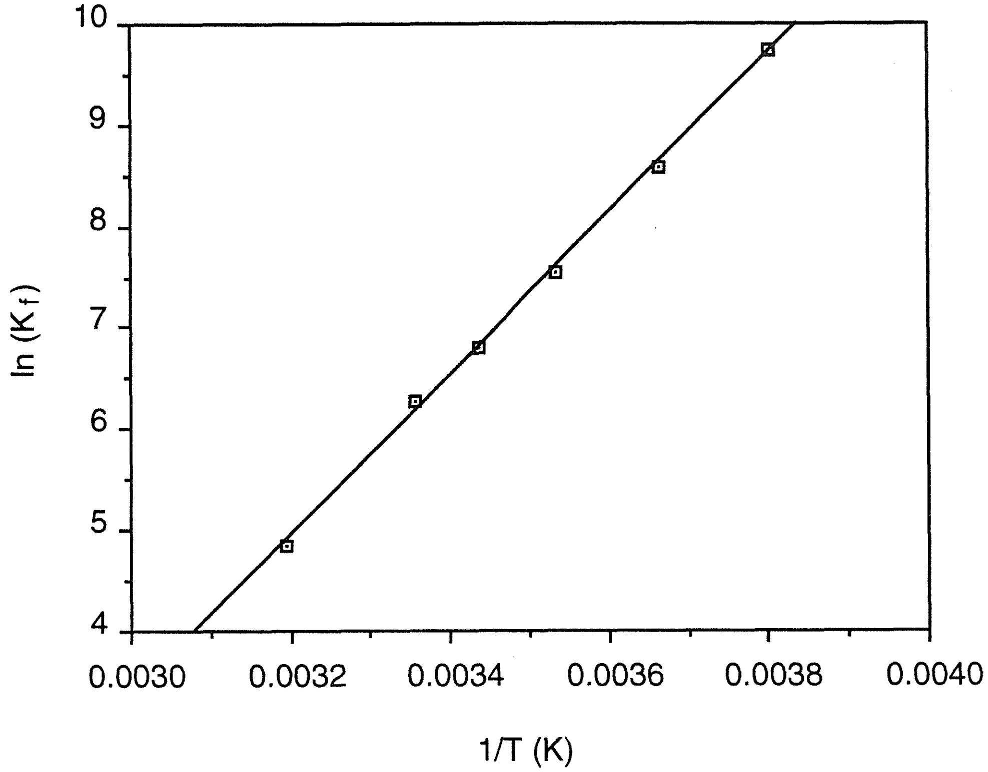


Figure 2. Arrhenius plot for the binding constants of eq 2.

In order to calculate the phosphine exchange rate, the T_1'S of the alkylidene protons for both free and bound complexes are measured using an inversion-recovery method. Values of T_1's at different temperatures are listed in Table I. The coordination of phosphine significantly increases the rate of relaxation of the alkylidene protons. At room temperature, the rate of complex formation k_1 and dissociation k_{-1} can be measured by a magnetization transfer experiment (Figure 3)[10] and are determined to be 358.7 $M^{-1}s^{-1}$ and 0.595 s^{-1}, respectively. The equilibrium constant (K_f = 603) determined from the ratio of these rate constants is within experimental error of the equilibrium constant (K_f = 536) measured directly by ^{1}H NMR spectroscopy.

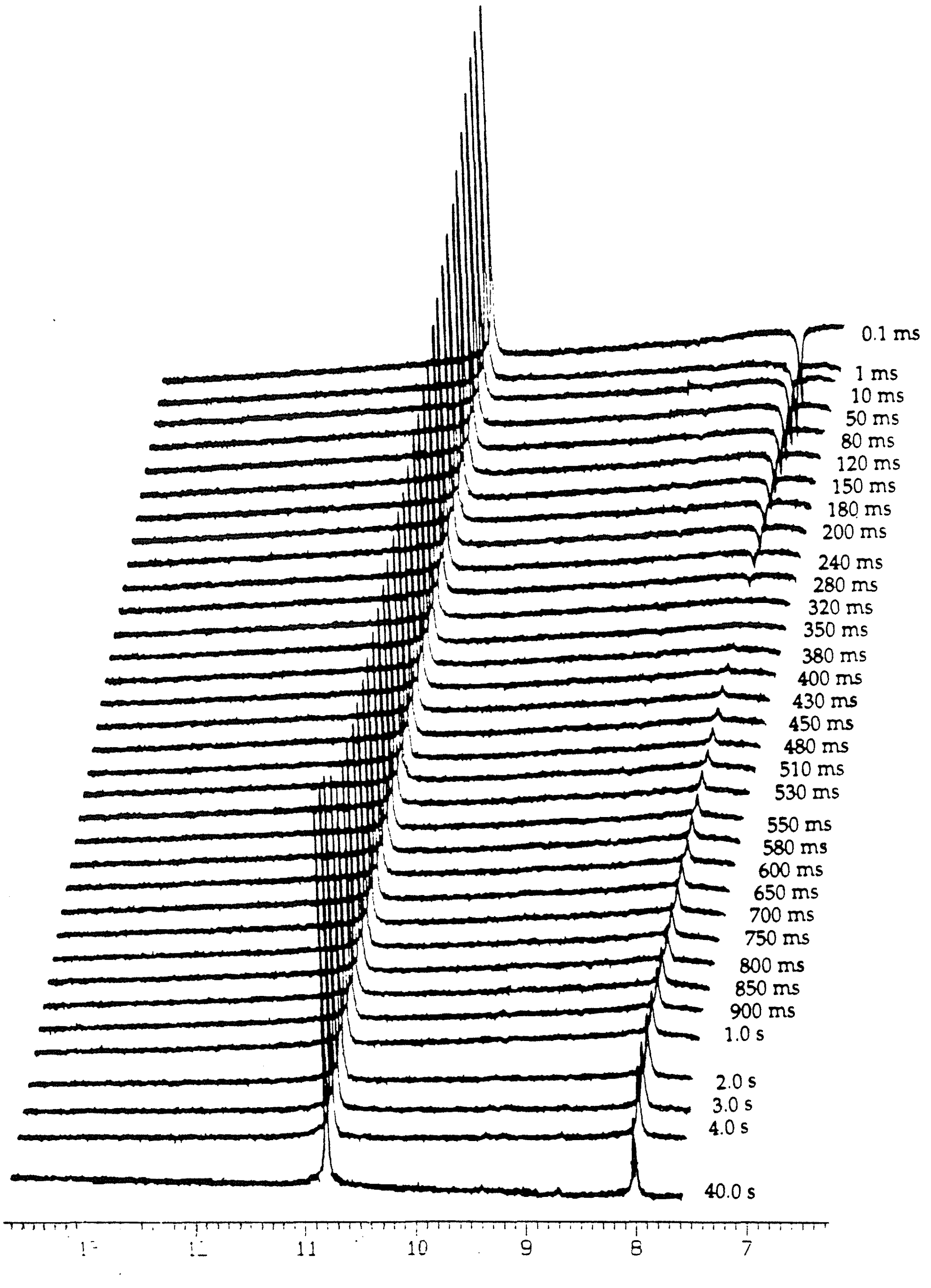


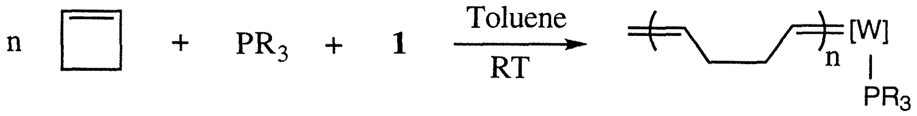
Figure 3. Inversion spin transfer for a mixture of **1** and **2** at 25 °C. Each spectrum consists of 8 scans: delay time τ_2 after selective inversion of the peak of **1** is shown. $\tau_1 = 0.444$ ms. The pulse sequence $\pi/2_x\ (\upsilon_x) - \tau_1 - \pi/2_{\pm x} - \tau_2 - \pi/2_{\pm x,\pm y}$ - acquisition is used.

Apart from PMe_3, we found that $PPhMe_2$ and PEt_3 also bind the catalyst **1** reversibly at room temperature. For example, when 5 equiv of $PPhMe_2$ or 11 equiv of PEt_3 is added to a toluene solution of **1**, new alkylidene resonances are observed at 10.81 ppm and 10.82 respectively. The binding constants (K_{eq}=7.6 for $PPhMe_2$; K_{eq}=1.5 for PEt_3) at room temperature are determined using the similar method described earlier.

Table I. T_1's for the Protons of Free and Bound Alkylidenes **1** and **2**.

Temp (°C)	0	10	25	40
T_1 - Free (sec)	2.7165	3.5873	4.7868	5.3808
T_1 - Bound (sec)	0.9493	1.0874	1.3204	1.7788

Polymerization of Cyclobutene in the Presence of Phosphines. In the presence of excess PMe_3, **1** catalyzes the polymerization of cyclobutene in toluene or benzene at room temperature. Precipitation in methanol and drying in vacuo affords a sticky polymer in greater than 85% isolated yield. ^{13}C NMR spectroscopy indicates that clean 1,4-polybutadiene is obtained with a blocky distribution of cis and trans double bonds[11] and a cis-to-trans ratio of 3.7:1. There is no evidence of branching by NMR or IR spectroscopy.



$PR_3 = PMe_3, PEt_3, PPMe_2$

As detailed below, molecular weight analyses and NMR spectroscopic data indicate that the polymerization is living. For example, the molecular weights of polybutadiene (as determined by gel permeation chromatography versus polystyrene standards) obtained from polymerizations with varying equivalents of cyclobutene are given in Table II. In all cases, the molecular weight is proportional to the monomer-to-catalyst ratio and narrow polydispersities are obtained (Figure 4). All samples prepared with these tungsten complexes show a small, high molecular weight peak, as reported in the first paper in this area.[12] The high molecular weight peak may be attributed to the presence of trace amount of oxygen in the system.[13]

Table II. Molecular Weight Analysis of Polymers

Equiv.'s of Cyclobutene	M_n (theory)	$M_n{}^a$ (GPC)	$M_n{}^b$ (GPC)	$M_w{}^a$	PDI
20	1082	3000	1600	3200	1.07[c]
50	2705	6900	3800	7100	1.03[c]
100	8120	12200	6900	16200	1.04[c]
200	10820	23200	12800	23900	1.03[c]
1500	81150	147000	82000	162100	1.1[d]
200	10820	24000	13000	24500	1.02[e]

[a] Based on calibration with polystyrene standards. [b] Based on calibration with polybutadiene standards (from Polyscience). A correction factor of 0.55 was calculated (Ref. 20). [c] Polymerization was performed in the presence of 10 equiv. of trimethylphosphine at room temperature. [d] Polymerization was performed at 0 °C in the presence of 75 equiv. of dimethylphenylphosphine. [e] Polymerization was performed by using catalyst **3** in the presence of 10 equivalents of PMe_3 at room temperature.

Reaction of one equivalent of cyclobutene with **1** in the presence of 5 equivalents of PMe_3 resulted in the initiation of 66% of the total catalyst.[14]

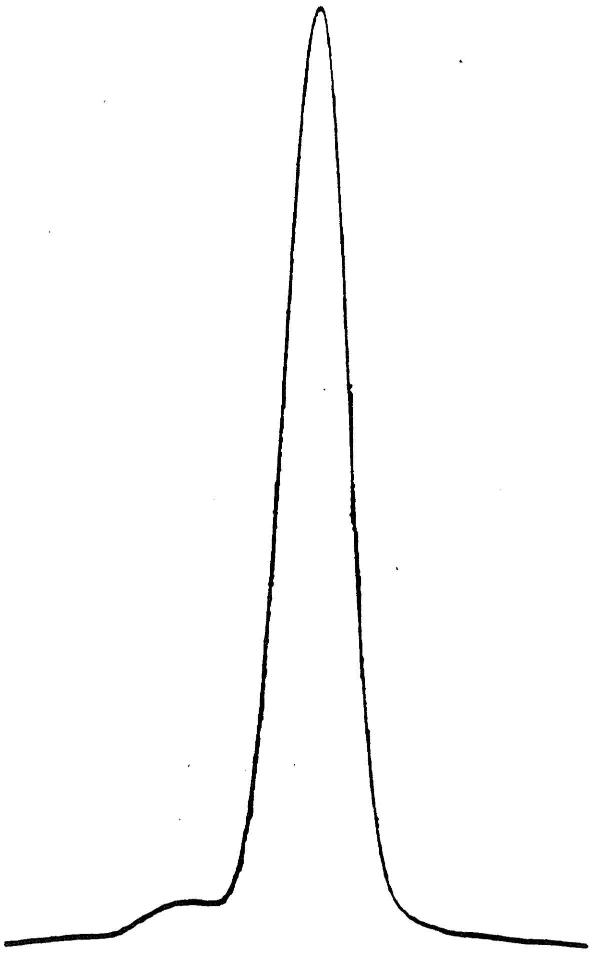


Figure 4. GPC trace of the polymer produced by ROMP of cyclobutene (200 equiv), using catalyst **1** in the presence of PMe3 (10 equiv).

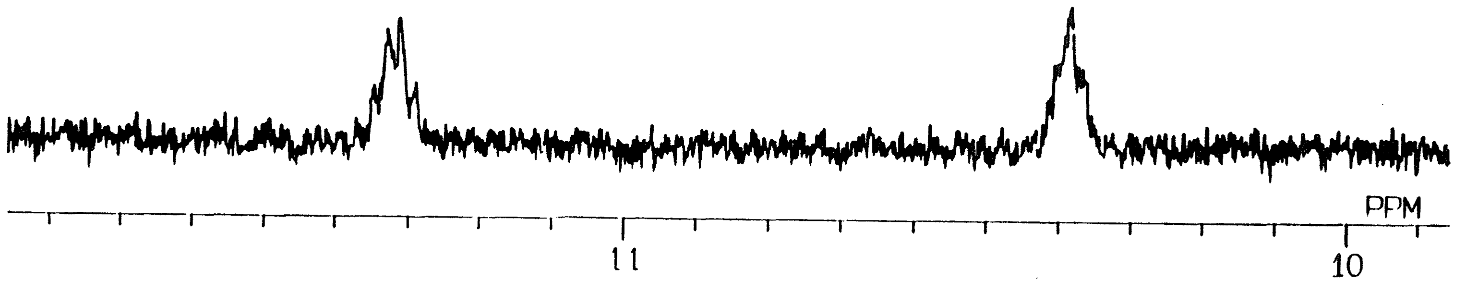


Figure 5. The Alkylidene region of ^{1}H NMR spectrum of living polybutadiene (20 equiv of cyclobutene).

With 20 equiv of cyclobutene, ^{1}H NMR spectroscopy shows that all of the initial alkylidene is converted to the propagating alkylidene. Two multiplets at 11.31 and 10.38 ppm are observed throughout the polymerization by ^{1}H NMR spectroscopy for H_α of the alkylidene ligand (Figure 5) and are attributed to the presence of two isomers of the propagating species.[5(b)] End-capping of the living polymer chain is accomplished by addition of excess benzaldehyde or acetone at room temperature.[15]

The propagating alkylidene is greatly stabilized by PMe_3. A sealed NMR tube containing 75 equivalents of cyclobutene and 5 equivalents of PMe_3 was monitored periodically by ^{1}H NMR spectroscopy. No change in the amount of propagating carbene was evident after storing the reaction mixture for two weeks at room temperature. After two months at room temperature, only 50% of the propagating carbene had disappeared, which may be due to either the slow decomposition of the catalyst itself or to the reaction of the catalyst with small amounts of impurities that were not detected by ^{1}H NMR spectroscopy.

The polymerization of cyclobutene was also studied in the presence of other phosphines, such as $PPhMe_2$, PPh_2Me and PEt_3. When 18 equiv of cyclobutene was added to a toluene solution containing 12 equiv of $PPhMe_2$ and 0.01M of **1**, all the starting alkylidene initiated and converted to the propagating alkylidenes evidenced by the new resonances at 11.34 and 10.48 ppm with a ratio of 1.1:1. However, when this polymerization was conduced at room temperature, a PDI of 1.5 was obtained. Lowering the reaction temperature to 0 °C, we obtained polymers having a PDI of 1.05 and a *cis/trans* ratio of 4.7:1. Polycyclobutene with excellent PDI can also be obtained using PEt_3 as a Lewis base. When 337 equiv of cyclobutene was

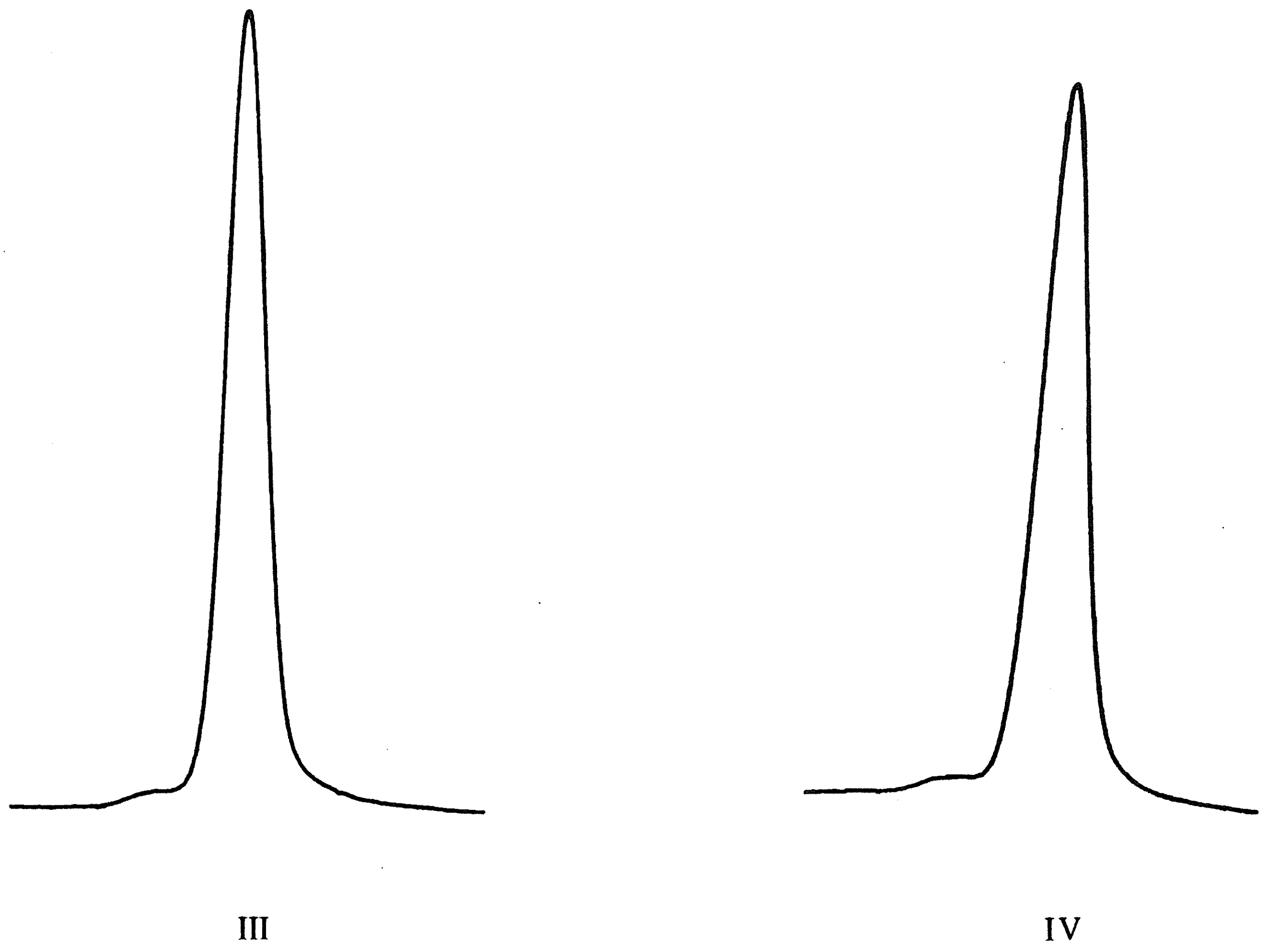


Figure 6. GPC traces of the polymer produced by ROMP of cyclobutene using catalyst **1** in the presence of $PPhMe_2$ (III) and PEt_3 (IV).

reacted with **1** in the presence of 14 equiv of PEt_3 at 0 °C, the polymer obtained had a molecular weight of 32000, a PDI of 1.05 and a cis-to-trans ratio of 4.57:1. The GPC traces for these polymerization are shown in Figure 6. The polymerizations of cyclobutene in the presence of $PPhMe_2$ and PEt_3 also exhibit the characteristics of living polymerization.

However, when the polymerization was carried out in the presence of weakly coordinated PPh_2Me (20 equiv) and 323 equiv of cyclobutene, the polymer resulted had a molecular weight of 41000 and PDI of 1.6.

The analogous molybdenum alkylidene complex **3** also catalyze the living polymerization of cyclobutene in the presence of PMe_3. For example, when 24 equiv of cyclobutene is added to a toluene-d_8 solution containing 0.01 M of **3** and 10 equiv of PMe_3, two resonances (triplets with $J_{H\text{-}H}$ = 8.3 and 7.3 Hz respectively) corresponding to the propagating species are observed at 12.82 and 12.55 ppm. The polymer isolated from the reaction of 150 equiv of cyclobutene in the presence of 10 equiv of PMe_3 has a molecular weight of 24000 and a PDI of 1.02.

Kinetic Data and Mechanism for the Cyclobutene Polymerization. The kinetic scheme for the polymerization of cyclobutene in the presence of PMe_3 is shown in Figure 7. In the proposed mechanistic scheme, a rapid equilibrium is first established between the phosphine-ligated and free neopentylidene complexes (eq 3). Cyclobutene reacts with one equivalent of free neopentylidene to form the propagating alkylidene (eq 4), which is then captured by PMe_3 (eq 5) to form the inactive phosphine adduct. Loss of phosphine regenerates the propagating alkylidene to continue the polymerization (eq 6). By ^1H NMR spectroscopy, it is observed that the initial neopentylidene is completely consumed before the propagating alkylidene begins to react with cyclobutene to form polymer.

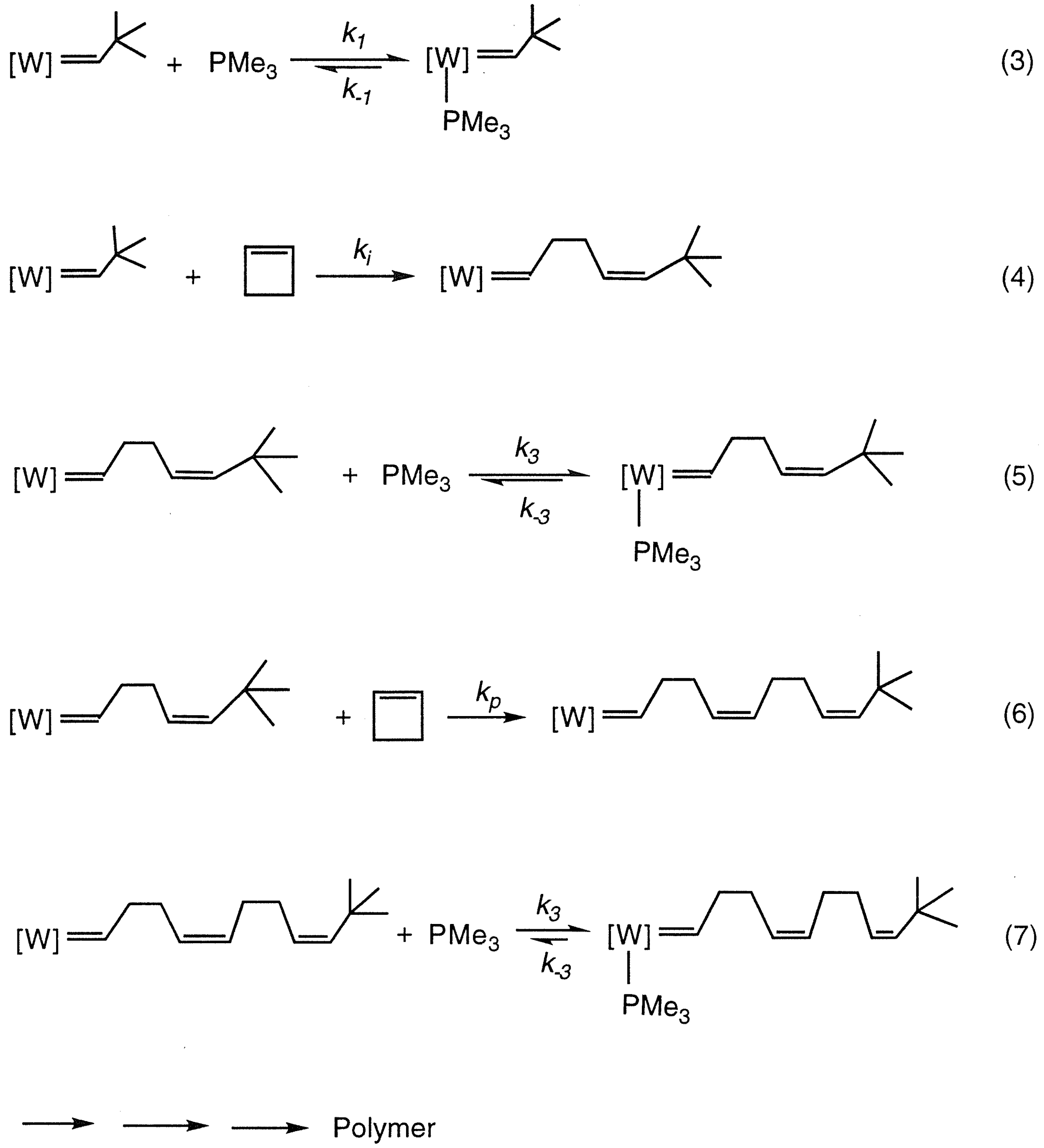


Figure 7. Kinetic scheme for the polymerization of cyclobutene catalyzed by **1**.

Derivation of the kinetic expressions for the initiation and propagation reactions is possible based upon the following observations and assumptions. First, since the large ring strain of cyclobutene is the driving force for the ring-opening process, the reactions shown in eqs 4 and 6 are irreversible and the rate of backbiting to form cyclooctadiene is negligible comparing to the rate of propagation. Second, it is reasonable to assume that all of the propagating alkylidenes have the same reactivity (k_p), irrespective of the polymer chain length. Third, experimental results at room temperature and below show that the association rate of PMe_3 is very large (i.e. $k_1 \gg k_{-1}$ and $k_3 \gg k_{-3}$). Therefore, it is reasonable to assume that the concentration of free catalyst in the system reaches a steady state during the polymerization, yielding the following expression for the propagation rate:

$$-\frac{d[M]}{dt} = \frac{k_p}{K'_f} \cdot \frac{[C_0][M]}{[P_0]-[C_0]} = k_{obs(p)}\,[M]$$

where K'_f = the binding constant of PMe_3 to the propagating species,

$[M]$ = monomer concentration, and

$k_{obs(p)} = (k_p/K'_f)[C_0]/\{[P_0]-[C_0]\}$.

$[P_0]$, $[C_0]$ = initial phosphine and catalyst concentrations

The following expression for the initiation rate is derived in a similar manner:

$$-\frac{d[WP]}{dt} = \frac{k_i}{K_f} \cdot \frac{[WP][M]}{[P_0]-[C_0]} = k_{obs(i)}\,[WP]$$

where K_f = the binding constant of PMe_3 to the initial species, and

$k_{obs(i)} = (k_i/K_f)[M]/\{[P_0]-[C_0]\}$.

The derived kinetic expressions are consistent with experimental observations. For example, the rates of the polymerization and initiation of cyclobutene were monitored by ^{1}H NMR spectroscopy at different temperatures and different phosphine concentrations. At low phosphine concentrations, the rate of initiation is too fast to be measured by NMR spectroscopy accurately. The disappearance of the phosphine-bound neopentylidene complex can be followed by ^{1}H NMR spectroscopy at higher PMe_3 concentrations. Plots of $\ln(M/M_0)$ versus time are linear throughout the course of the polymerization. The data fit the first order kinetic rate law as shown in Figure 8, and $k_{obs(p)}$ can be obtained at different phosphine concentrations and temperatures. Figure 9 shows a linear relationship between $k_{obs(p)}$ and $1/([P_0]-[C_0])$, enabling $k_{app(p)}$ to be obtained from the slope. When the concentration of the catalyst is doubled, the observed propagation rate is also doubled. Variation of the monomer concentration does not change the observed propagation rate constants. Similarly, the rate of disappearance of **2** is first order with respect to the concentration of **2** as shown in Figure 10. Figure 11 shows a linear relationship between $k_{obs(i)}$ and $1/([P_0]-[C_0])$, and $k_{app(i)}$ can be calculated from the slope. Doubling the concentration of the monomer doubles the observed initiation rate. The experimental data are in close agreement with the derived kinetic expressions. The rate of the polymerization is followed by ^{1}H NMR spectroscopy over a temperature range of 40 °C and the rate of the initiation is followed over a 35 °C range. Therefore, the activation parameters for both the propagation and initiation can be calculated from Erying plot as shown in Figure 12 and Figure 13.

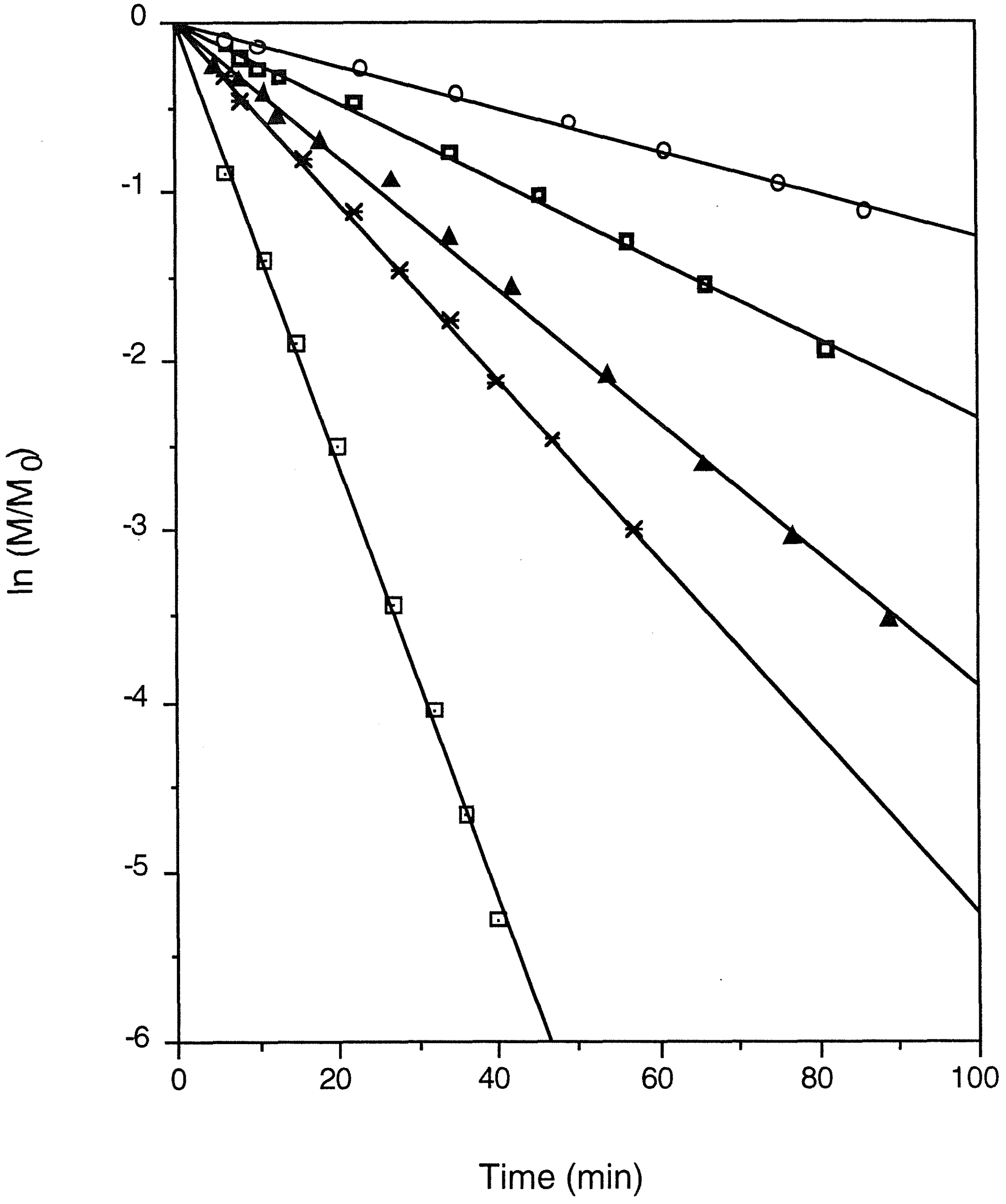


Figure 8. Kinetic data for the polymerization of cyclobutene by **1** at 25 °C.

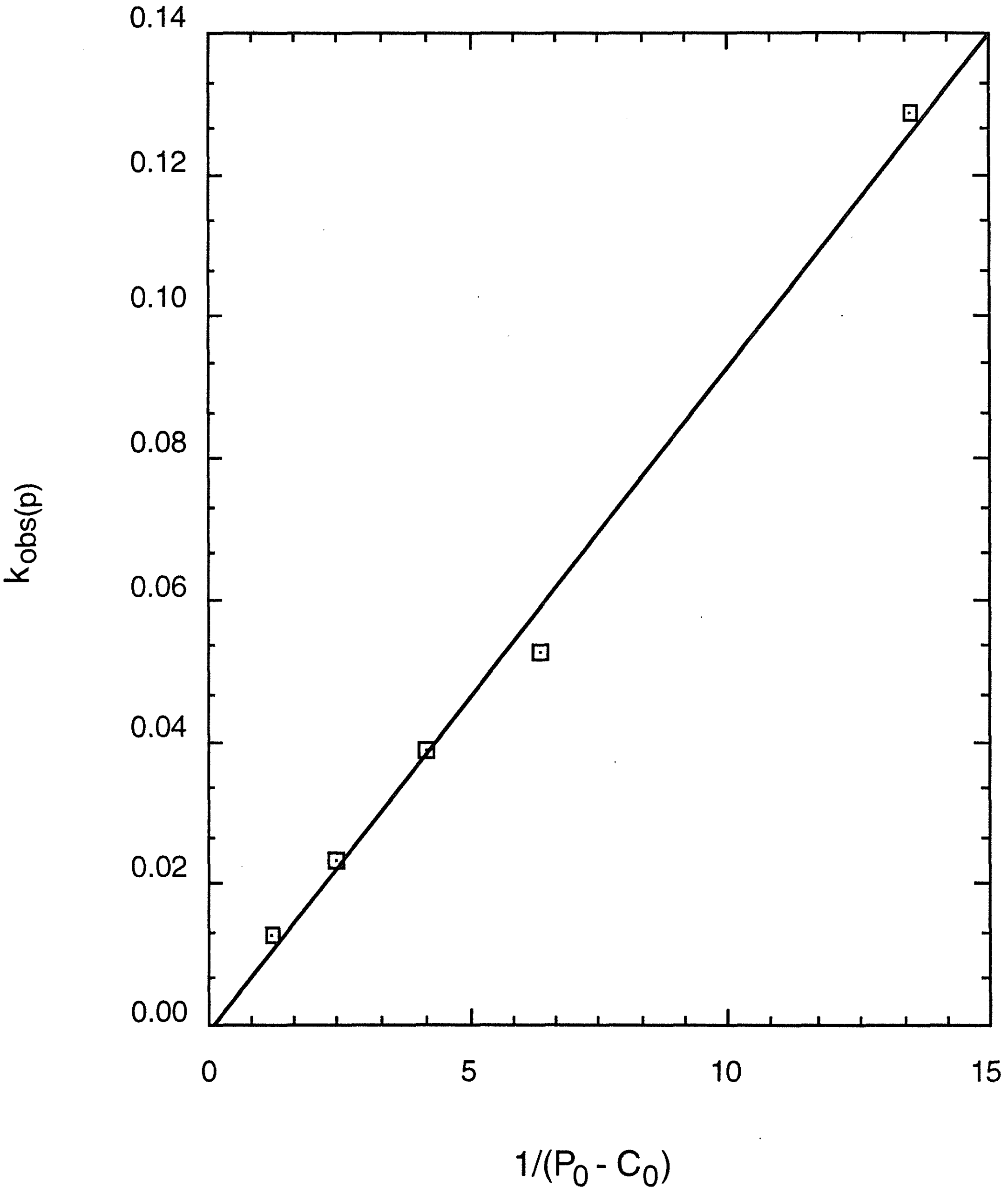


Figure 9. The change of observed rates with the concentration of phosphines at 25 °C.

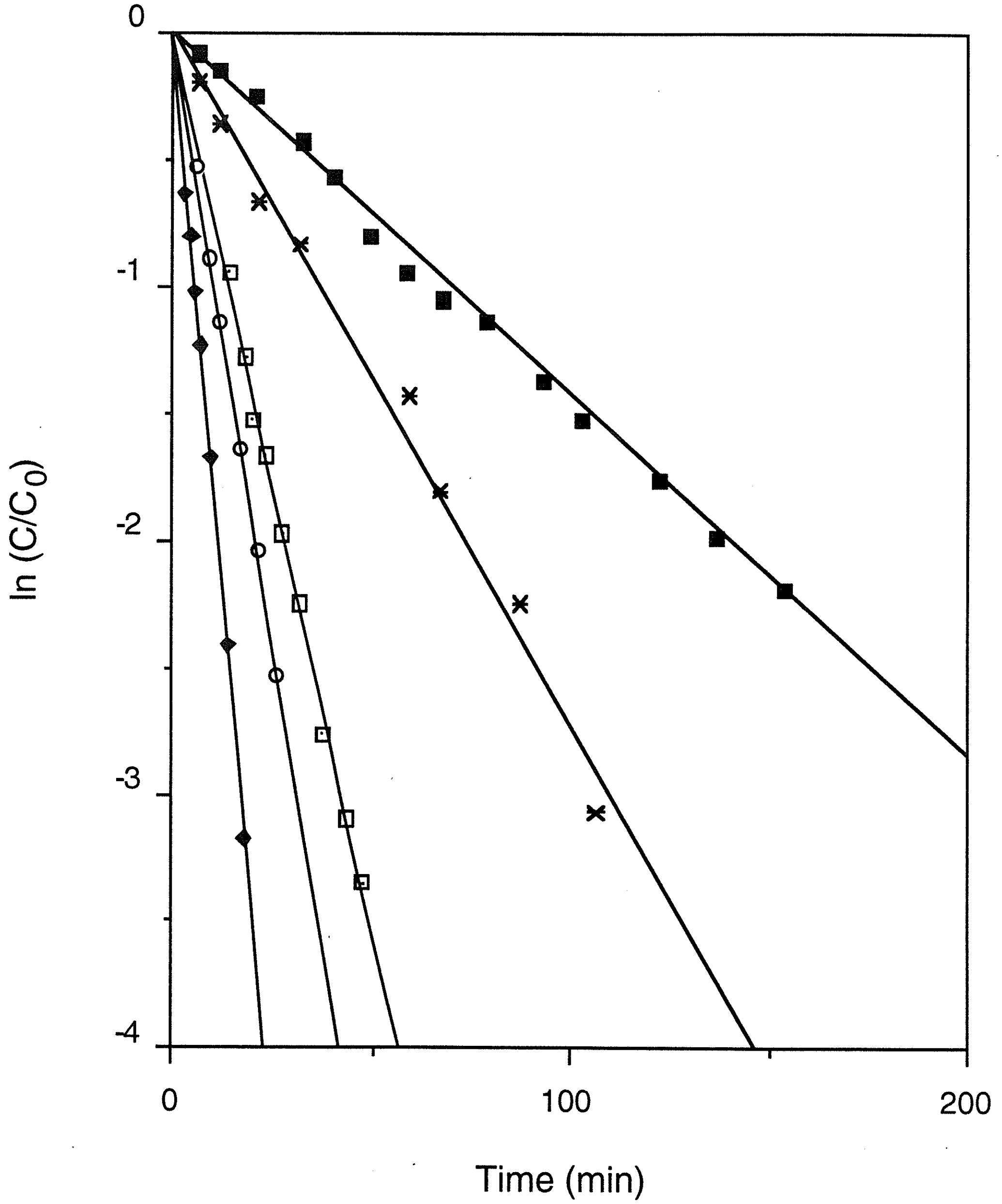


Figure 10. Kinetic data for the initiation of cyclobutene by **1** at -10 °C.

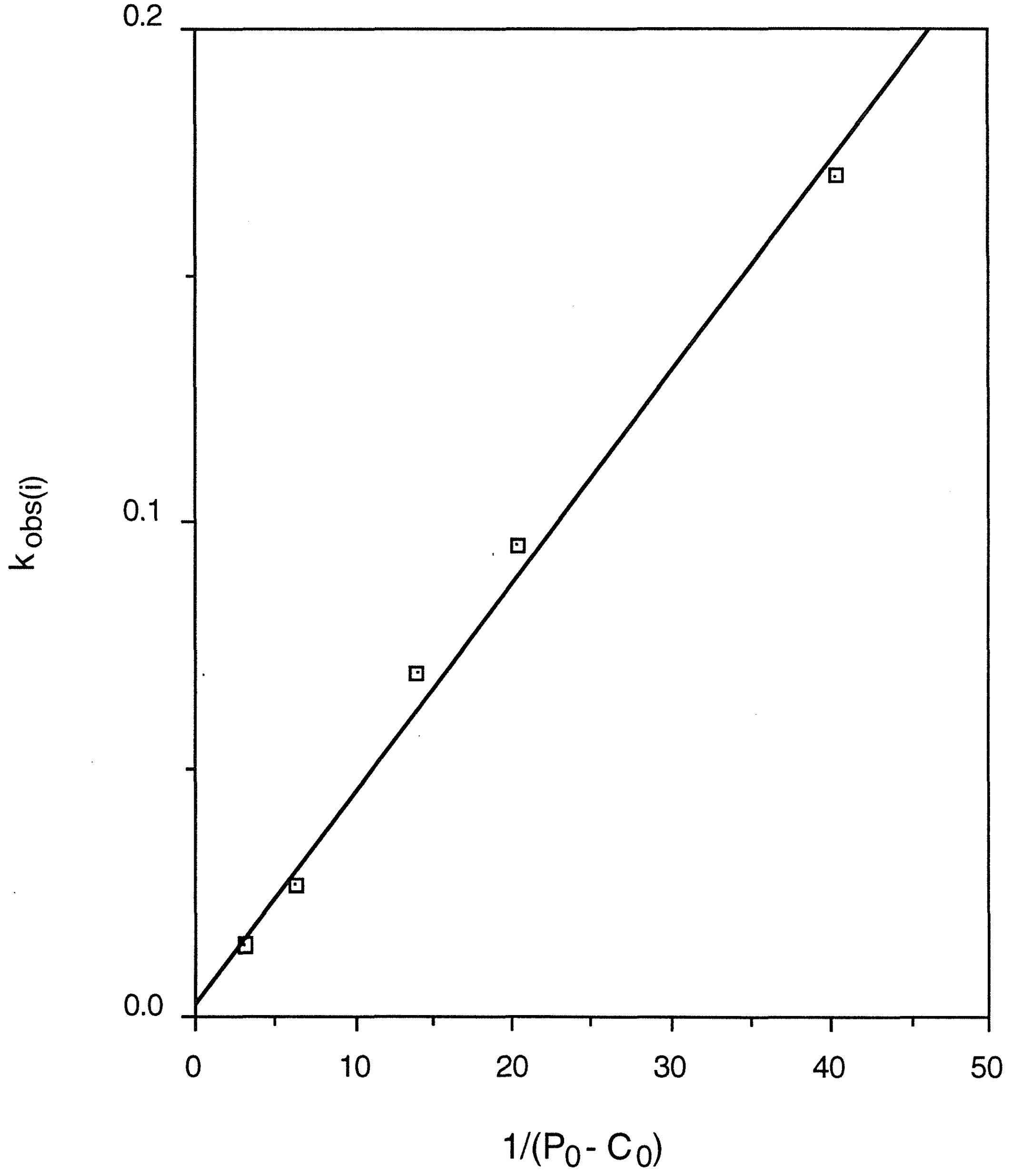


Figure 11. The change of observed initiation rates with phosphine concentrations at -10 °C.

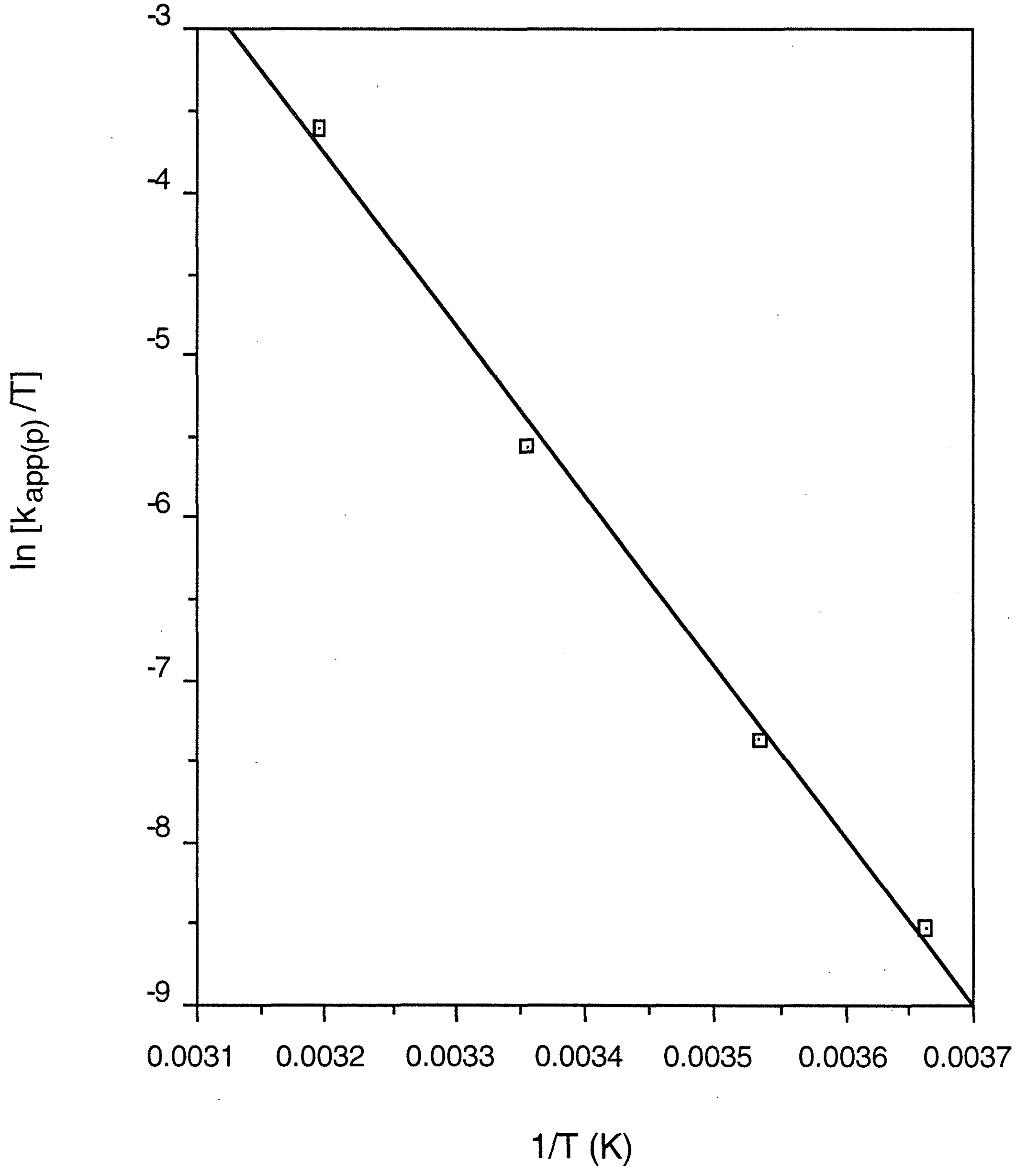


Figure 12. Erying plot for the propagation of cyclobutene polymerization catalyzed by **1**.

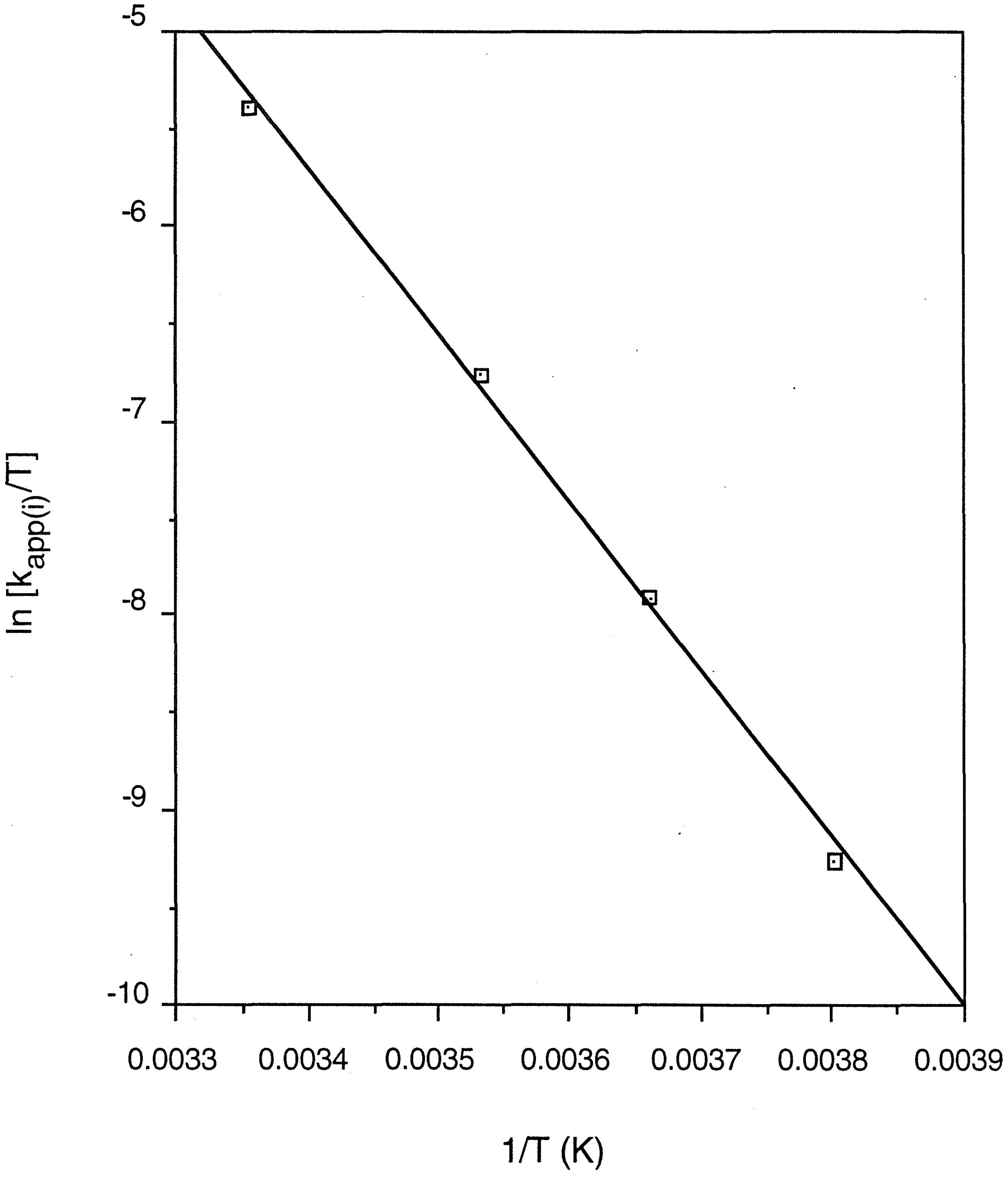
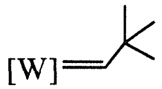


Figure 13. Erying plot for the initiation of cyclobutene polymerization catalyzed by **1**.



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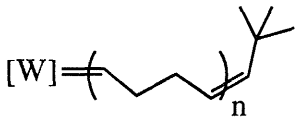


B

Table III. Kinetic Data for Polymerization and Initiation

Temp (°C)	-10	0	10	25	40
$k_{app(p)}=k_p/\mathrm{Kf}'$		0.05418	0.1804	1.159	9.124
$k_{app(i)} = k_i/\mathrm{K_f}$	0.02532	0.1014	0.3280	1.344	

$\Delta\Delta H^{\ddagger}_{(p)} = 20.9 \pm 2$ kcal/mol, $\Delta\Delta S^{\ddagger}_{(p)} = 4 \pm 8$ e.u., $\Delta\Delta G^{\ddagger}_{273K} = 19.8 \pm 3$ kcal/mol

$\Delta\Delta H^{\ddagger}_{(i)} = 17.1 \pm 1$ kcal/mol, $\Delta\Delta S^{\ddagger}_{(i)} = -8 \pm 4.8$ e.u., $\Delta\Delta G^{\ddagger}_{273K} = 19.4 \pm 2$ kcal/mol

The Role of Phosphines. The overall role of PMe_3 is that of a competitive inhibitor to the catalytic species, which effectively serves to reverse their relative reactivities by binding more strongly to the propagating alkylidene **B** than to the initiating neopentylidene **A**. Quantitatively, this is illustrated in Table III by a comparison of the apparent rate constants of initiation and propagation at several temperatures. The ratio of the observed rates for initiation and propagation is proportional to the ratio of the apparent rate constants, and hence, the observed initiation rate is larger than the observed propagation rate. Since the apparent rate constant is inversely proportional to the binding constant, PMe_3 binds more strongly to the propagating species than to the initiating species, thus reducing the propagation rate constant more than the initiation rate constant. The stronger binding of PMe_3 to the propagating alkylidene **B** ($K'_f \approx 10^5$ at 25 °C) than to the initiating neopentylidene **A** ($K_f \approx 500$) results from the steric bulkiness of the neopentylidene ligand disfavoring phosphine association. Further evidence for the importance of steric factors in regulating the polymerization is provided by the molybdenum neopentylidene complex Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (Ar=2,6-diisopropylphenyl) **3**.[16] Complex **3** is electronically different from its tungsten analog **1**, but should show the same relative difference in steric bulk of the propagating alkylidene and initiating neopentylidene. This complex also gives narrow polydispersity polybutadiene from the polymerization of cyclobutene in the presence of PMe_3 (Table II). We believe that the great stabilization of the propagating alkylidene by the binding of phosphine is another important factor for the resulting of a living polymerization. The above explanations have been mainly focusing on the thermodynamics and its effect to the kinetic process. The regulation of the polymerization by PMe_3 can also be envisaged from the kinetic perspective. As shown in Figure 7, if the rate of phosphine reacting with the first insertion product (eq 5) is much faster than that of the cyclobutene reacting with the first insertion product (i.e., $k_3\,[PMe_3] \gg k_p\,[M]$), and as along as the initiation rate and propagation rate constants do not differ significantly, all the initial alkylidene should initiate before the propagation starts. This assumption should also lead to a living polymerization system, which is consistent with the experimental observations.

In the polymerization of cyclobutene, the addition of strongly donating Lewis bases (PMe_3, PMe_2Ph or PEt_3) as shown in Table IV is necessary to reverse the relative magnitudes of the observed rates of initiation and propagation. There is no evidence for the cyclic oligomers that should be in equilibrium with polycyclobutene or polycyclooctadiene. The bound phosphine completely suppresses back-biting reactions, as was found with THF in the COT polymerization reactions.[6] This can also be understood from the following aspects: (i) The four-coordinated alkylidene complex is an active species for metathesis, therefore the five-coordinated trigonal bipyramid phosphine or THF complexes require first to dissociate the bound phosphine or THF in order to react with an olefin. (ii) Complex **1** has been shown to be a very poor catalyst for the metathesis of acyclic olefins.[12]

Table IV. ROMP of Cyclobutene by **1** in the Presence of Different Phosphines.

Lewis Bases	Monomer/ Catalyst	*Cis/Trans*	[a]M_n (theory)	[b]M_n(GPC)	PDI	Catalyst initiated (%)
$PPhMe_2$	189 (25 °C)	4:1	10230	7500	1.10	100 %
	209.3 (0 °C)	4.74:1	11323	9300	1.04	100%
PEt_3	236.5 (25 °C)	4.21:1	12973	12500	1.11	100%
	336.6 (0 °C)	4.57:1	18208	18600	1.04	100%
PPh_2Me	322.9	4:1	17468	24000	1.60	<10%

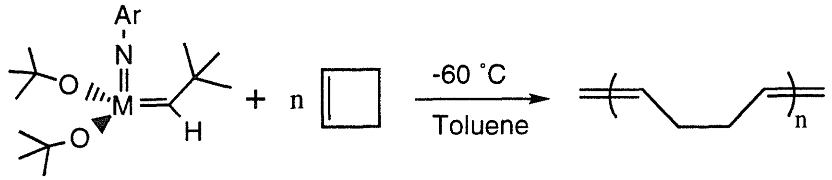
[a] Based on the ratio of initially added monomer and catalyst. [b] Polybutadiene purchased from Polyscience was used as a standard for the measurement.

Polymerization of Cyclobutene in the Presence of Weak Lewis Bases. In the presence of quinuclidene, the rate of the polymerization is reduced markedly. For example, when 12 equiv of cyclobutene was added to a solution containing **1** and 6 equiv of quinuclidene at -78 °C, no polymerization was observed. When the temperature was increased to -40 °C, the polymerization started and it took 66 minutes for the reaction to complete. A total of 71% of the initial alkylidene was consumed and the propagating alkylidenes were observed at 9.11 and 9.75 ppm. Cyclobutene

(155 equiv) was polymerized by **1** in the presence of 6 equiv of quinuclidene to give a polymer having a molecular weight of 22000 and a PDI of 1.4. It apparently that the polymerization of cyclobutene can be regulated to certain extent by the presence of quinuclidene.

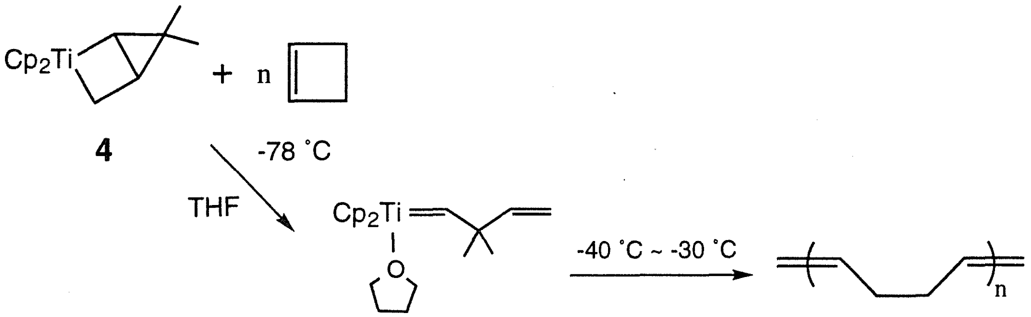
The polymerization of cyclobutene was also investigated in the presence of oxygen based donor ligands, such as THF, and 1-methyl THF. For example, cyclobutene was rapidly polymerized in the presence of 5 equiv of THF or 20 equiv of 1-methyl THF. The propagating species were observed in both cases at 8.45 ppm with the intensities of 56% and 26% relative to those of the starting alkylidenes respectively. However, the polymerization is not controllable in the presence of 1-methyl THF and much higher molecular weight than that of the calculated value is usually obtained. When the polymerization of 275 equiv of cyclobutene is carried out in neat THF solution, the polymer obtained has a PDI of 2.0. THF tends to bind weakly with both the starting and the propagating tungsten alkylidene species[6], thus it only slightly affects the rate of the polymerization.

Polymerization of of Cyclobutene in the Absence of Lewis Bases. Since cyclobutene has a strain energy of 29.8 kcal/mol,[17] it can be polymerized rapidly by several well-defined transition metal alkylidenes (eq 8). The initiation of cyclobutene polymerization by molybdenum or tungsten alkylidene complexes starts at -60 °C and the polymers produced have high molecular weights and broad polydispersities ($M_n > 100000$; PDI = 2~3). The polymers obtained have ~ 87% and ~ 83% of *cis* double bond configuration in the backbone, respectively, when molybdenum and tungsten alkylidenes are employed as initiators.



(8)

M= Mo, W
Ar = 2,6-di-*i*-pr-C_6H_4

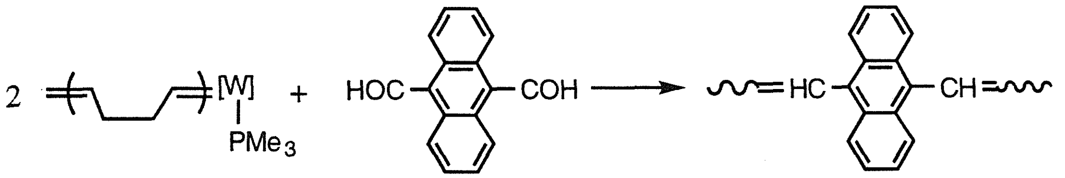


(9)

Cyclobutene can also be polymerized by a titanacyclobutane complex **4** in THF or toluene. As indicated in eq 9, a sealed NMR tube containing **4** and cyclobutene was photolyzed at -78 °C for a short period of time, then the reaction mixture was warmed up to -40 °C and the polymerization was monitored by ^{1}H NMR spectroscopy. The polymer (PDI = 2.3) obtained has relatively low molecular weight compared to those obtained using tungsten or molybdenum complexes as initiators. The kinetics of the polymerization was followed by ^{1}H NMR spectroscopy and the rate of the polymerization was first order with respect to the monomer concentration.[18] This is in contrast to the result of **4** catalyzed polymerization of norbornene in which the rate of the polymerization is zero order with respect to the monomer concentration.[24(b)] This observation implies that the formation of titanium metallabicyclobutane intermediate is the rate-determining step during the polymerization of cyclobutene.

Polymers with high molecular weights and broad polydispersities obtained when **1** and **3** are used indicate that the rate of the polymerization is much faster than that of the initiation. Low molecular weight obtained using titanacyclobutane **4** as initiators may be attributed to the decomposition of the titanium carbene propagating species during the course of the polymerization.

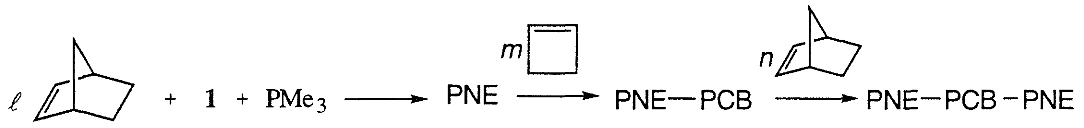
Reaction of Living Polycyclobutene with Aldehyde or Ketone. Compounds containing anthracene moiety are important fluorescence or luminescence materials. The idea of incorporation of anthracene moiety into the polymer backbone has the important consequences in terms of understanding the local mobility of the polymer chain or serving as a polymeric luminescence probe in various applications.[19] The preparation of monodispersed polybutadiene or polyethylene with a fluorescence moiety in the center of the polymer chain is of great interest and has not been realized. Here, we would like to use anthracene dialdehyde to couple with a living polycyclobutene in a Wittg-like reaction as shown in eq 10. The polymer can be prepared by addition of 0.5 equiv of dialdehyde to a solution of living polybutadiene prepared by polymerizing cyclobutene in the presence of PMe_3. GPC shows two peaks corresponding to a major coupled polymer peak and a minor homo polymer peak. The molecular weight of the coupled polymer is twice as much as that of the homopolymer and exhibits narrow polydispersities. The homopolymer resulted from the incomplete coupling might be separated from the coupled polymer by fractional precipitation technique.



(10)

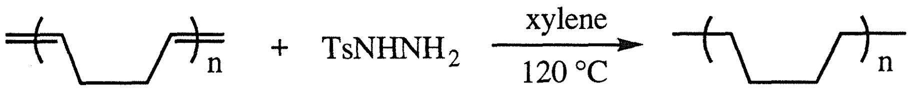
The living polycyclobutene can also react with acetone. The reaction, however, is extremely slow and requires extended time to reach completion even in the presence of large excess of acetone.

Reaction of Living Polycyclobutene with Norbornene. The most convenient way for the preparation of block copolymers of the type A-B or A-B-A is the sequential addition of monomers to a living polymerization system.[1] The interest in the block copolymer formed by polynorbornene and polybutadiene lies that the material is a potential thermoplastic after hydrogenation, since the hydrogenated polymer contains hard (polyethylene) and soft (hydrogenated polynorbornene) segments in the backbone. The narrow dispersity of the copolymer should render the material exhibiting phase separation property in the micro phase domain. In this section, we would like to demonstrate the formation of block coplolymers employing the living polycyclobutene and polynorbornene systems. As shown in eq 11, when 5 equiv of PMe_3 was added to a toluene solution of polynorbornene prepared by polymerizing 26 equiv of norbornene with **1** (0.008 M), two alkylidene species were observed at 11.21 and 10.29 ppm corresponding to the PMe_3 bound propagating alkylidenes of polynorbornene. When 32 equiv of cyclobutene was added to the above solution, all the resonances corresponding to the propagating species of polynorbornene were displaced by two new resonances at 11.30 and 10.38 ppm corresponding to the propagating species of polycyclobutene. When the polymerization was complete, another 35.5 equiv of norbornene was added into the mixture, the two propagating species corresponding to polycyclobutene disappeared and resonances corresponding to the propagating species of polynorbornene reappeared. This observation indicates that it should be possible to prepare polynorbornene-polycyclobutene-polynorbornene triblock copolymer with ease. The preparation of diblock copolymers of polynorbornene and polycyclobutene was also investigated by either adding cyclobutene to a living polynorbornene with the presence of PMe_3 or in a reverse manner. For example, 48 equiv of norbornene was polymerized in toluene followed by sequential addition of 9 equiv of PMe_3 and 18 equiv cyclobutene. The diblock polymer obtained has a molecular weight 17200 and a PDI of 1.04. Reversing the order of addition, such as 16 equiv of cyclobutene being polymerized in the presence of 10 equiv of PMe_3 followed by the addition of 48 equiv of norbornene, produced a diblock copolymer with M_n = 23700 and PDI = 1.08.



(11)

On the basis of the diblock experiment, we felt that a better order of addition for preparing this type of block copolymer would be to add cyclobutene to the living polynorbornene solution in the presence of PMe_3. Since PMe_3 binds more strongly to the propagating species of polycyclobutene than to that of polynorbornene due to the steric reason, the rate of the first insertion of cyclobutene to form the block copolymers will be faster than that of the self propagation to form polycyclobutene block. The diblock prepared in this manner will expect to have a narrow polydispersity and better-defined molecular structures. In the formation of both diblock copolymers, high molecular weight traces were also observed by GPC, which were consistent with the observation made before when this type of catalyst was employed in the ROMP of strained olefins.[12]



(12)

M_n = 85000
PDI = 1.1

Hydrogenation of Polycyclobutene and Characterization of Polyethylene. Near monodispersed polybutadiene can be prepared by ROMP of cyclobutene in the presence of PMe_3. The polymer was characterized by both ^1H and ^{13}C NMR and IR spectroscopy. The spectroscopy data are consistent with a perfect linear polybutadiene.[20] The polybutadiene can be readily hydrogenated to saturated polyethylene using tosylhydrazide in xylene at 120 °C (eq 12). Analysis of ^1H (δ 1.56 ppm) and ^{13}C (δ 29.82 ppm) NMR spectroscopy data (in $C6D_5Cl$, 100 °C) of the resulting hydrogenated polymer is consistent with a perfect linear polyethylene and free of branches.[21] IR spectroscopy shows the absence of C-H stretching at 3002.1 CM^{-1} is another evidence for the complete hydrogenation. The resulting polyethylene exhibits a melting point at 126 °C measured by differential scanning calorimetry (DSC) as shown in Figure 14. Powder X-ray diffraction pattern (Figure 15) of the sample indicates that the polyethylene is highly crystalline. The crystallinity is calculated to be greater than 95%.[22]

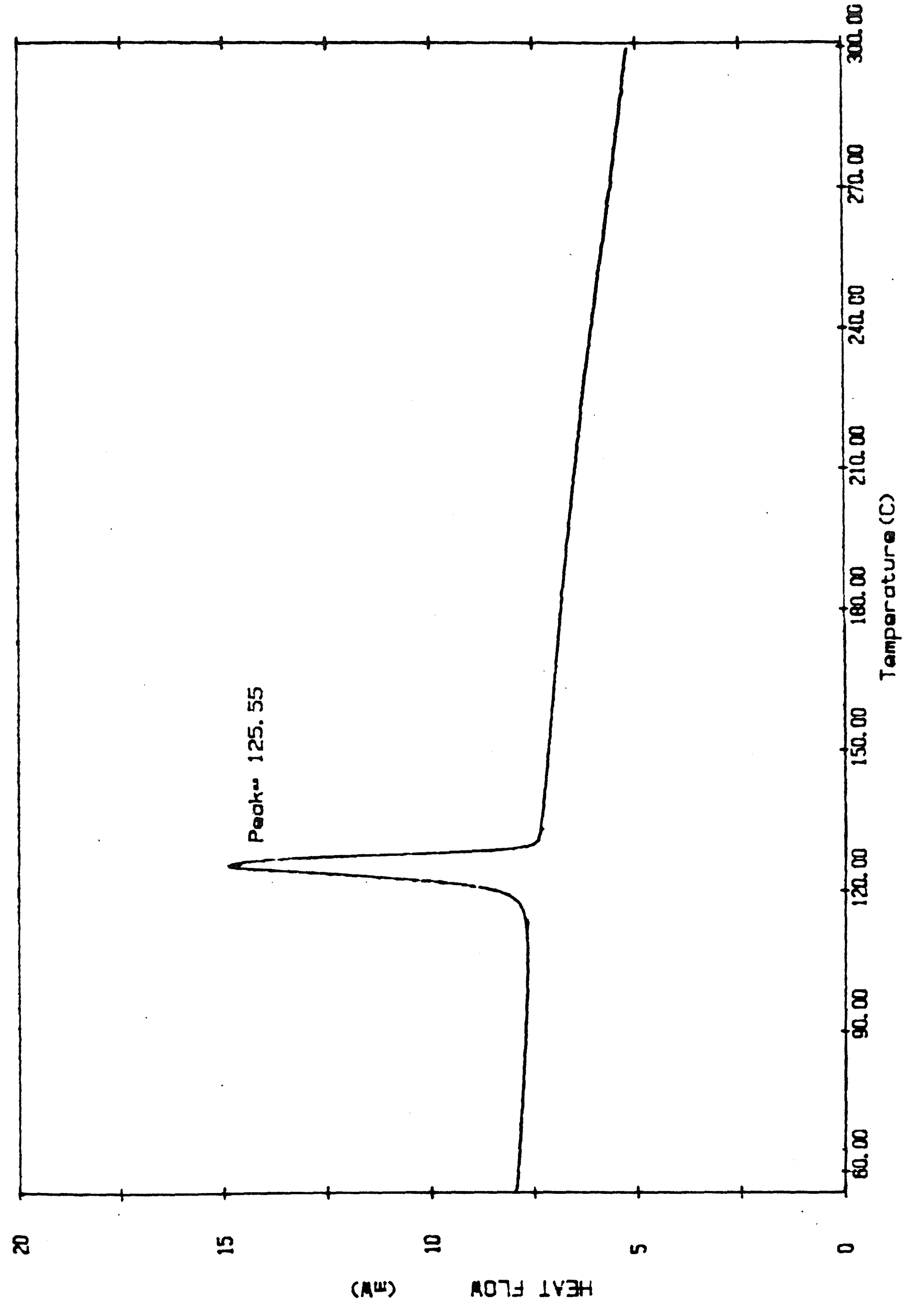


Figure 14. DSC profile of polyethylene prepared via hydrogenation of polycyclobutene.

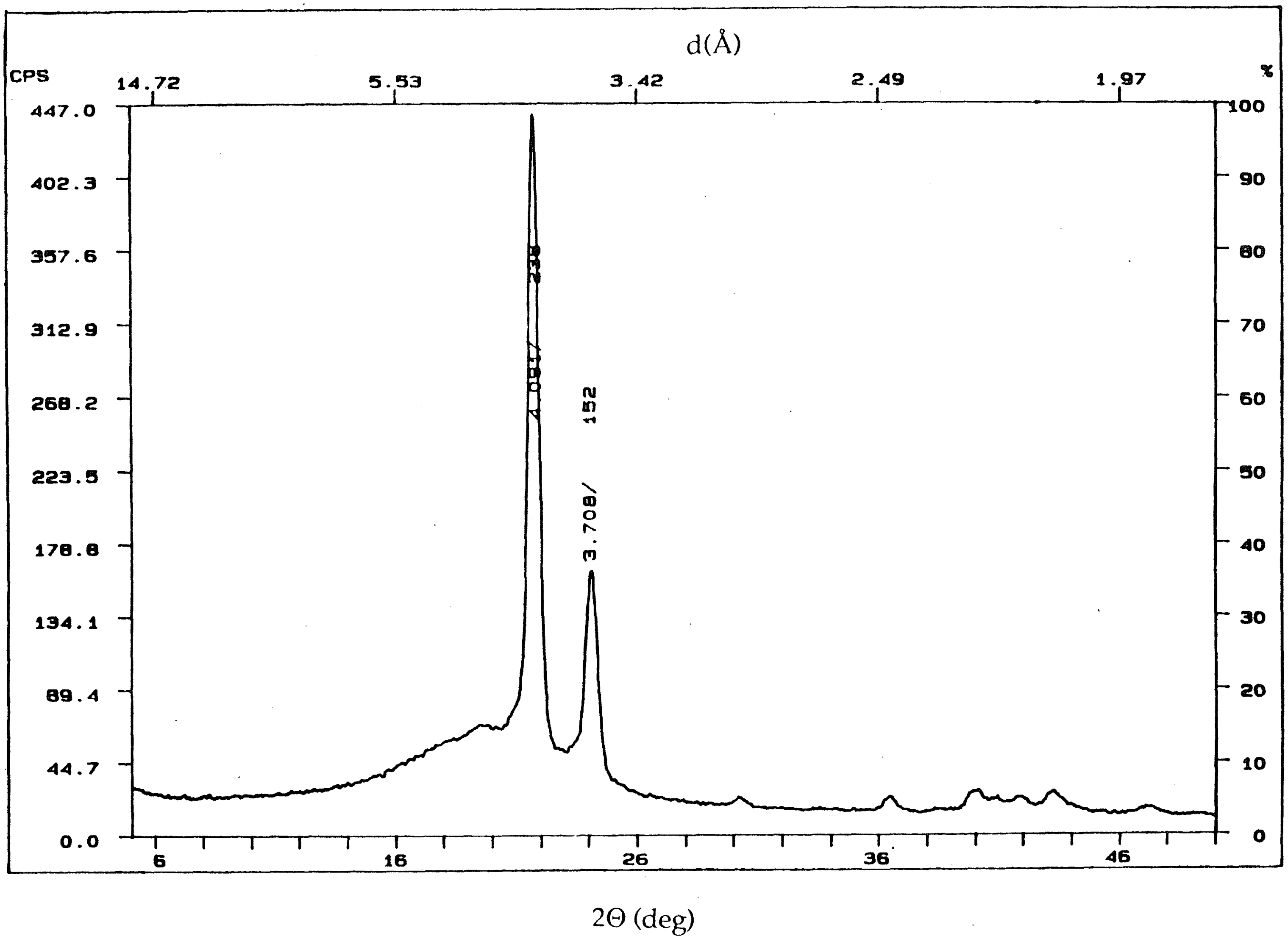


Figure 15. Powder X-ray diffraction data of polyethylene prepared by hydrogenation of polycyclobutene.

Conclusion:

In summary, the polymerization of cyclobutene catalyzed by **1** in the presence of PMe_3 exhibits the six characteristics[23] of a living polymerization: (i) well-defined kinetics, (ii) linear increase of molecular weight with percent monomer conversion, (iii) irreversible propagation steps, and (iv) the absence of chain termination and transfer steps, and (v) complete and rapid initiation. (vi) formation of block copolymers. This living polymerization results in near monodispersed and predetermined molecular weights. The polymerization of cyclobutene by **1** or **3** clearly indicates that the large ring-strain energy of the monomer is a necessary, but not sufficient, condition for achieving nearly monodispersed polymer. The large ring strain only ensures that the polymerization is irreversible but does not determine the relative magnitude of the propagation and initiation rates. In this study, control of these rates is enabled by the addition of reversibly bound Lewis bases, which alter the amount of active species in the system without varying their intrinsic reactivities. As demonstrated by the related studies with other monomers and Lewis bases, the reactivity of the monomer and the complexing ability of the base must be matched. The rate of ROMP in the presence of a Lewis base is the product of a rate and equilibrium constant. For a reasonably unreactive monomer, a weak ligand is sufficient to have a major effect. As the monomer becomes more reactive, a stronger base is needed to lead to the required balancing of the rate constants. This living system has resulted in the preparation of perfectly linear and near monodispersed polybutadiene, which upon hydrogenation, gives linear, narrow dispersed polyethylene. The formations of block copolymers and reaction with aldehyde or ketone using this living system have also been accomplished.

Experimental Section

General Procedures. All manipulations of air and/or moisture-sensitive compounds were carried out using standard Schlenk or vacuum-line techniques or in a N_2-filled drybox. Argon was purified by passage through a column of BASF RS-11 (Chemlog) and Linde 4Å molecular sieves. ^1H NMR spectra were recorded on a JEOL GX-400 MHz (399.65 MHz ^1H; 100.4 MHz ^{13}C; 61.25 MHz ^2H) spectrometer. T_1 was measured using standard pulse sequence. Magnetization transfer experiments were performed according to published procedures.[10] Gel permeation chromatography (GPC) utilized Shodex KF-803, KF-804, and KF-805 columns and a Knauer differential refractometer. All GPC analyses were performed on a 0.5% W/V solution of polymer in dichloromethane. An injection volume of 0.1 ml and a flow rate of 1.5 ml/min. were used. Calibration was based on narrow dispersity polystyrene standards (Polyscience) ranging from M_n=3,550 to 600,000. Powder X-ray diffraction was performed on a Scintag/USA PAD V powder X-ray diffractometer using CuK_α radiation. Infrared spectra were recorded using a Perkin-Elmer 1600 series FT-IR spectrometer. Gas chromatography was performed using a Hewlett-Packard HP 5890 Series II Gas Chromatography equipped with 30 mm SE-30 (OV-1) capillary column and a HP 3396 Series II integrator. Differential scanning calorimetry and thermal gravimetric analysis were performed on a Perkin-Elmer PC Series DSC7 and TGA 7, respectively. Photolysis was performed with a 450 watt high pressure mercury Hanovia lamp. Pyrex immersion well was used.

Materials. $Cp_2Ti(CH_2CHCH)(C(CH_3)$,[24] W(CH-*t*-Bu)(O-*t*-Bu)$_2$(NAr)[12,25] Mo(CH-*t*-Bu)(O-*t*-Bu)$_2$(NAr)[16] (Ar=2,6-diisopropylphenyl) were prepared according to literature procedures. Dichloromethane-d_2 was dried over CaH_2. Benzene and toluene were distilled from sodium benzophenone ketyl.

Norbornene and PMe_3 were distilled from Na. Acetone-d_6 was dried over B_2O_3. Benzaldehyde was washed with 10% Na_2CO_3 and saturated Na_2SO_3, then dried over $MgSO_4$, and distilled under reduced pressure. Xylene was dried over 4Å molecular sieves. Methanol was distilled from Mg turnings. All of the purified solvents were stored under Ar in a flask with a Teflon valve.

Synthesis of Cyclobutanol.[26] To a one-liter round bottom flask, was added 520 ml of water, 50 ml of 37% concentrated hydrochloric acid and 50 g of cyclopropane methanol. The mixture was then heated to 88 °C and refluxed for three hours. After cooled down to room temperature, the flask was immersed into an ice-water bath, and 20.8 g of NaOH and 5.8 g of Na_2CO_3 were added to neutralize the solution. 400 ml of ether was added and the mixture was subjected to continuous liquid-liquid extraction for 36 hours. Evaporation off the solvent yields cyclobutanol (90%) containing 3-butenol (7%), which was separated by either a spinning-band column distillation or flash column chromatography on 10% $AgNO_3$/silica gel using pentane as eluent. The spectroscopic data are consistent with those in the literature.

Synthesis of Cyclobutyl Tosylate.[26] A 250 ml three-neck round bottom flask was charged with 16.6 g of cyclobutanol and 103 ml pyridine. The flask was chilled to 0 °C and 46.3 g of *p*-toluenesulfonyl chloride is added in small portions over a 20-minute period. After the addition, the mixture was allowed to stir at room temperature for 12 hours and then for an additional 6 hours at 32 °C. The reaction mixture was poured into a beaker containing a HCl-ice-H_2O solution under stirring. The aqueous phase was extracted with ether until it is clear. Ether solution was dried with $NaSO_4$. A yellow oil (95.4%) was obtained after evaporating the solvent and pumping the residue under high vacuum for 3 hours. The spectroscopic data are consistent with those in the literature.

Preparation of Cyclobutene.[26] Inside the N_2-filled dry box, 65.3 g of *t*-BuOK was weighed into a 3-neck one liter flask and 233 ml of DMSO was added outside the dry box to dissolve the *t*-BuOK. Cyclobutyl tosylate (49 g) was dissolved into 59 ml DMSO and transferred into a 250 ml dropping funnel. The outlet of the flask was connected to two cold traps. The flask containing *t*-BuOK and DMSO was heated to 70 °C under Ar and at this temperature, cyclobutyl tosylate was added dropwise in 10 minutes. After the addition, the mixture was stirred at 70 °C for two hours to ensure that the reaction was complete. The first trap was then allowed to warm to room temperature and cyclobutene collected boiled over into the second trap and left some high boiling stuff in the first trap. The product in the second trap was then distilled at -40 °C to a flask equipped with a Teflon valve to give the product (9.2 g, 77.4%). Spectroscopic data are the same as those reported in the literature.

Synthesis of Perdeuterated Trimethyl Phosphine.[27] To an oven-dried 500 ml three-neck flask, was added 4.098 g Mg powder and 250 ml of n-butyl ether. The mixture was then flushed with Ar. In another 250 ml flask, 25 g of CD_3I dissolved in 30 ml of n-butyl ether was degassed and added dropwise into an ether mixture containing Mg/butyl with a narrow pore cannular at room temperature. After the addition, the mixture was stirred at room temperature for another 0.5 hour and cooled down to 0 °C. To the above Gringard solution, 20.01 g of $P(p\text{-toyl})_3$ was added slowly via a cannular. After the addition, the solution was warmed to room temperature and stirred for an hour. The mixture was then fractionally distilled through a helices-packed column at 175 °C (oil bath temperature) under atmospheric pressure and the fraction boiled at 35 °C was collected (2.5 g, 50%).

General Procedure for NMR Tube Reactions. Catalyst was weighed and added to an NMR tube in the dry box and dissolved in calculated amount of solvent and capped with a rubber septum. The tube was brought out and cooled to -78 °C in a dry ice-acetone bath. The liquid reagent was added from a gas tight syringe and the tube was shaken well at -78 °C before being transferred to the NMR probe. In a reaction where sealed NMR tube was required, the catalyst was weighed into an NMR tube equipped with a ground glass joint and a Teflon valve in the dry box. Outside the dry box on a high vacuum line deuterated solvent was vacuum-transferred into the tube. The reagent was then vacuum-transferred on top of the frozen solvent and the tube was sealed by flame. The tube was kept at liquid nitrogen temperature and quickly thawed at -78 °C with shaking and then transferred into the NMR probe, the spectrum was recorded at the desired temperature.

General Procedure for the Polymerization of Cyclobutene. Inside a nitrogen filled dry box 3~5 mg of catalyst was weighed and dissolved with 0.5 ~ 1.0 ml of toluene into a small flask equipped with a Teflon valve and ground glass joint. The flask was brought out of the box and calculated amount of cyclobutene was vacuum transferred into the flask at 77 K. The flask was thawed at the desired temperature and stirred for a certain length of time. The reaction mixture was either quenched by addition of 30 equiv benzaldehyde or added directly into a rapidly stirring methanol. The polymer collected can be further purified by either reprecipitation into methanol or passing through a short column of silica gel.

NMR Tube Polymerization of Cyclobutene Using 4. In the dry box, 4.8 mg of **4** was weighed into an NMR tube equipped with a Teflon valve. The tube was brought out of the dry box and 0.6 ml of toluene and 42 mg of cyclobutene were vacuum-transferred into the NMR tube sequentially at liquid nitrogen temperature. The tube was sealed under high vacuum at 77K and kept at this temperature. The tube was thawed at -78 °C in a dry ice isopropanol bath and photolyzed at this temperature for 5 minutes. The tube was then rapidly transferred into the NMR probe cooled to -78 °C. The spectra were recorded and the reaction was monitored at different temperatures. The polymer was collected by precipitation into methanol and dried in vacuo.

Polymerization of Cyclobutene in the Presence of PMe_3. A typical experiment was done in a small flask with a Teflon valve. The flask was charged with ~3 to 5 mg of catalyst dissolved in ~ 0.5 to 1.0 ml of benzene or toluene containing ~5 to 10 equiv of phosphine in the drybox. The mixture was then degassed at liquid nitrogen temperature and cyclobutene was vacuum-transferred onto it. After mixing well at -78 °C, the reactants were warmed up to room temperature and stirred for about an hour. The resulting polymer solution was added dropwise into a rapidly stirring methanol containing a small amount of BHT. The precipitated polymer was collected and dried in vacuo overnight, yield >80%.

General Procedure for the Polymerization of Cyclobutene in the Presence of other Lewis Bases. The procedures were similar to that employed for the polymerization in the presence of PMe_3, except 10 ~ 20 equiv or more Lewis bases were used.

Kinetics of the Polymerization with 1. A typical kinetic run: Stock solutions of 1.6 M cyclobutene, 4.112 M $P(CD_3)_3$ and 0.0907 M catalyst in toluene-d_8 were prepared. NMR tubes were charged with aliquots of the stock solutions, diluted with additional toluene-d_8 to provide 0.5 ml total volume. The tubes were kept at -78 °C before being rapidly transferred into the NMR probe. The spectra were recorded at the desired temperatures during certain time intervals. The disappearance of the olefinic protons of cyclobutene at 5.9 ppm was monitored with respect to the mesitylene internal standard at different phosphine and catalyst concentrations for over 3 half lives ($\rho \geq 0.998$). Similarly, the disappearance of the bound-catalyst alkylidene proton resonance at 10.85 ppm was monitored at different phosphine and monomer concentrations over 3 half lives. The first order plots have $\rho \geq 0.996$. Least square analyses of first order plots of $\ln[M/M_0]$ vs. time and $\ln[C/C_0]$ vs. time yielded $k_{obs(p)}$'s and $k_{obs(i)}$'s. Linear Erying plots for both propagation and initiation have $\rho = 0.996$ and 0.997. Activation parameters were obtained from least square analyses of $\ln(k_{app(p\ or\ i)}/T)$ vs. $1/T$ plots.

Reaction of Polycyclobutene with Aldehyde and Ketone. (A) Reaction with 9,10-anthracene Dialdehyde: In the dry box, 0.0031 g of catalyst **1** was dissolved in 0.8 ml toluene in a small flask equipped with a Teflon valve. After added 10 equiv of PMe_3, the flask was brought out of the dry box and 53.4 mg (183 equiv) of cyclobutene was added. The mixture was then stirred at room temperature for 1.5 hours and 57.46 μl of 0.0469 M 9,10-anthracenedialdehyde in pyridine was then added via a gas tight syringe. The solution gradually changed into red and was stirred at room temperature for 3 hours. The resulting solution was then added into methanol and the polymer collected was analyzed by GPC, which showed two peaks corresponding to the coupled polymer ($M_n = 54000$, PDI = 1.06) and homopolymer ($M_n = 27000$, PDI = 1.05).

(B) Reaction with Acetone: In the dry box, 0.0027 g of catalyst **1,** 0.4 ml of toluene and 8.3 equiv of PMe_3 were weighed into an NMR tube. The tube was brought out of the dry box and 0.15 ml of 1.6 M cyclobutene solution was added via a gas tight syringe at -78 °C. The reaction was then monitored by ^1H

NMR spectroscopy. When the reaction was nearly complete (99%), 10 ul of acetone-d_6 was added into the tube via syringe. After 7 hours the polymer was isolated by precipitation into methanol. The end group was observed by ^{2}H NMR spectroscopy. ^{2}H NMR (66.7 MHz, $C6H_6$) δ 1.57, 1.65. Integration against an internal standard showed that 83% of the polymer was end-capped by acetone.

Observe the Formation of Tri-block Copolymers. Inside the dry box, 0.0023 g of catalyst **1** was weighed into an NMR tube, and dissolved with 0.5 ml toluene-d_8. 2 µl PMe_3 and 25 mg of norbornene were added into the tube sequentially. The tube was brought out of the dry box and the reaction was monitored by ^{1}H NMR spectroscopy. When the polymerization was complete in half an hour, 1.3 ml of 1.6 M cyclobutene in toluene-d_8 was added via a syringe. Upon the completion of this reaction, 13 mg of norbornene was added into the NMR tube again. After reaction, the solution was precipitated into methanol and polymer collected showed two GPC traces. The minor higher molecular weight trace showed M_n = 184000, PDI = 1.05 and the main lower molecular weight peak (triblock copolymer) shows M_n = 8300, PDI = 1.08.

Preparation of Diblock Copolymers. Inside the drybox, a small flask equipped with a Teflon valve was charged with 0.003 g of catalyst **1** and 0.4 ml toluene. To the above solution, 23.6 mg of norbornene dissolved in 0.3 ml toluene was added via a syringe. After the mixture was stirred at room temperature for 0.5 hr, 40 ul of toluene containing 1.2 M PMe_3 was added by syringe followed by 48.3 mg of cyclobutene via vacuum-transfer. The resulting mixture was stirred at room temperature for 0.5 hr and then quenched by addition of 10 ul benzaldehyde. The content of the flask was added dropwise into a rapidly stirring methanol. The polymer was collected, dried in vacuo overnight (70%) and was analyzed by GPC (M_n = 17200, PDI = 1.04).

Hydrogenation of Polycyclobutene. In a small schlenk tube, 68 mg of polybutadiene was dissolved in 3.0 ml of xylene. To the above solution was added 1.5 g (6.4 equiv of relative to the repeating units) of tosyl hydrazide and trace amount of BHT. The mixture was then degassed twice via a freeze-pump-thaw cycle and a reflux condenser was assembled under Ar. The Schlenk tube was heated to 110 °C, while at 98 °C, a homogeneous solution resulted and nitrogen started to evolve. The solution was stirred at 110 °C ~ 120 °C for 3 hours until the evolution of nitrogen stopped. The solution was cooled down to room temperature and precipitated into methanol. The polymer collected was washed with dilute HCl and hot water several times. The white cotton-shape material was further purified by redissolving in hot cyclohexane and reprecipitated into methanol. The polymer was dried in vacuo overnight, yield 60 mg (85%). ^{1}H NMR (400 MHz, C_6D_5Cl) δ 1.56. ^{13}C NMR (100.4 MHz, C_6D_5Cl) δ 29.82. Anal. calcd for $(CH_2)_n$: C, 85.7; H, 14.3. Found: C, 85.6; H, 13.94.

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(9) The ratio [WP]/[W] can be accurately determined by ^{1}H NMR integration. Concentration of the unbound phosphine can be calculated using the equation

$$[P] = [P_0] - [C_0]/\{1 + [W]/[WP]\}$$

where $[P_0]$ and $[C_0]$ are the initial phosphine and catalyst concentrations.

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(15) The ^{1}H NMR spectrum of the polymer end-capped with benzaldehyde shows two olefinic doublets at 6.42 and 6.31 ppm with H-H coupling constants of 13.18 and 16.11 Hz, corresponding to cis and trans isomers respectively. When acetone-d_6 is used, the ^{2}H NMR spectrum of the resulting polymer shows two peaks at 1.65 and 1.57 ppm for the inequivalent perdeuterated methyl end groups.

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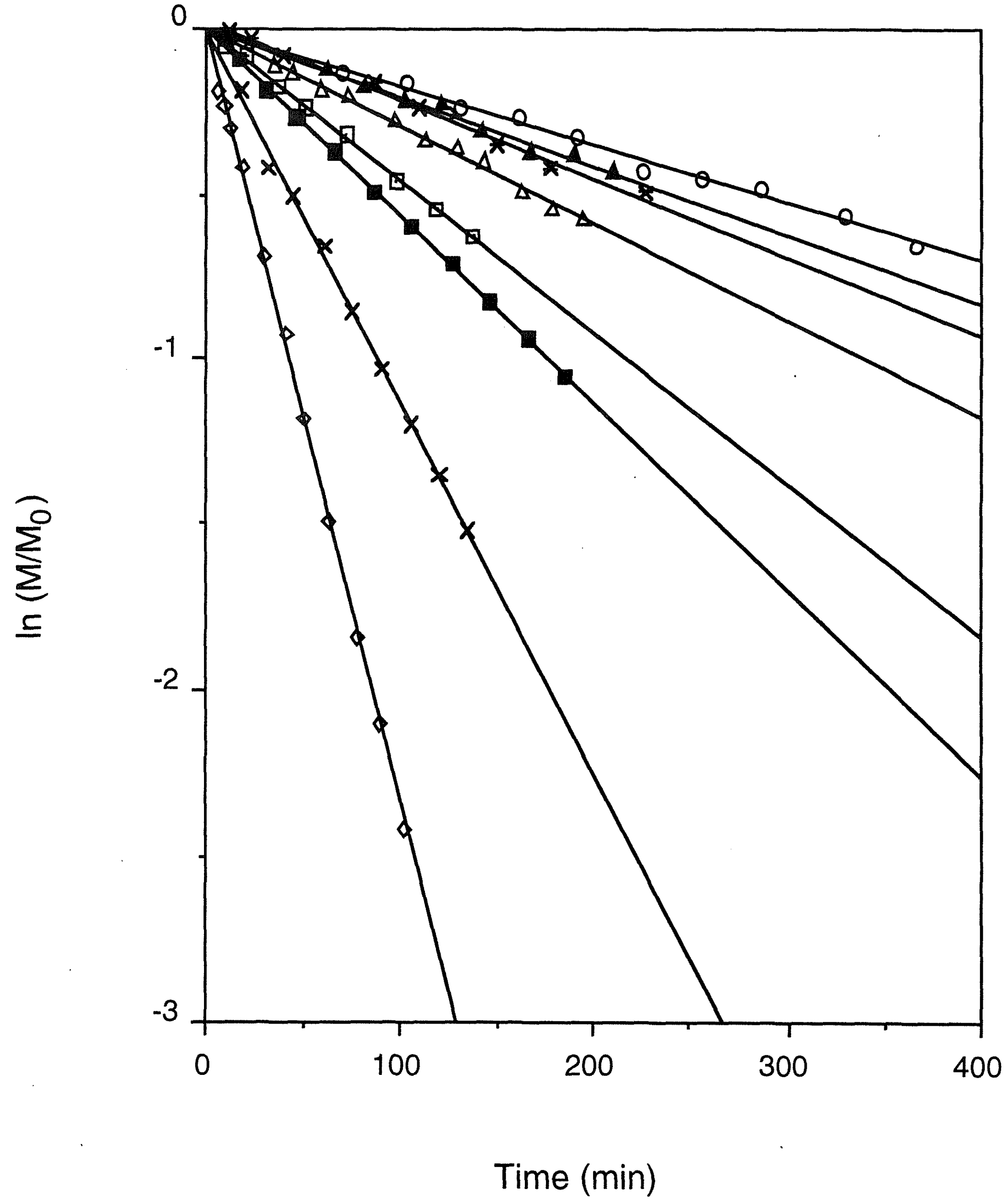
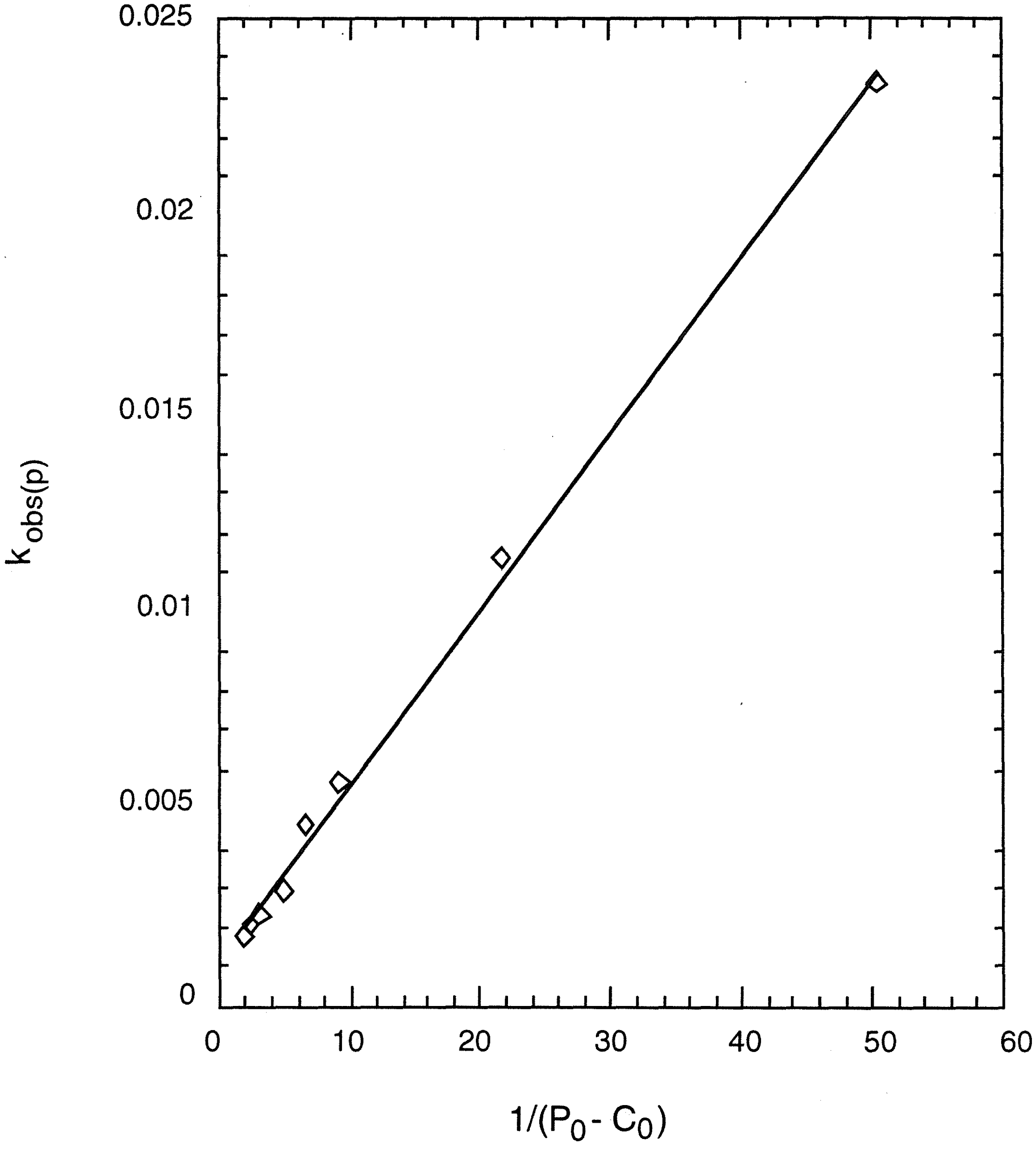
Appendix

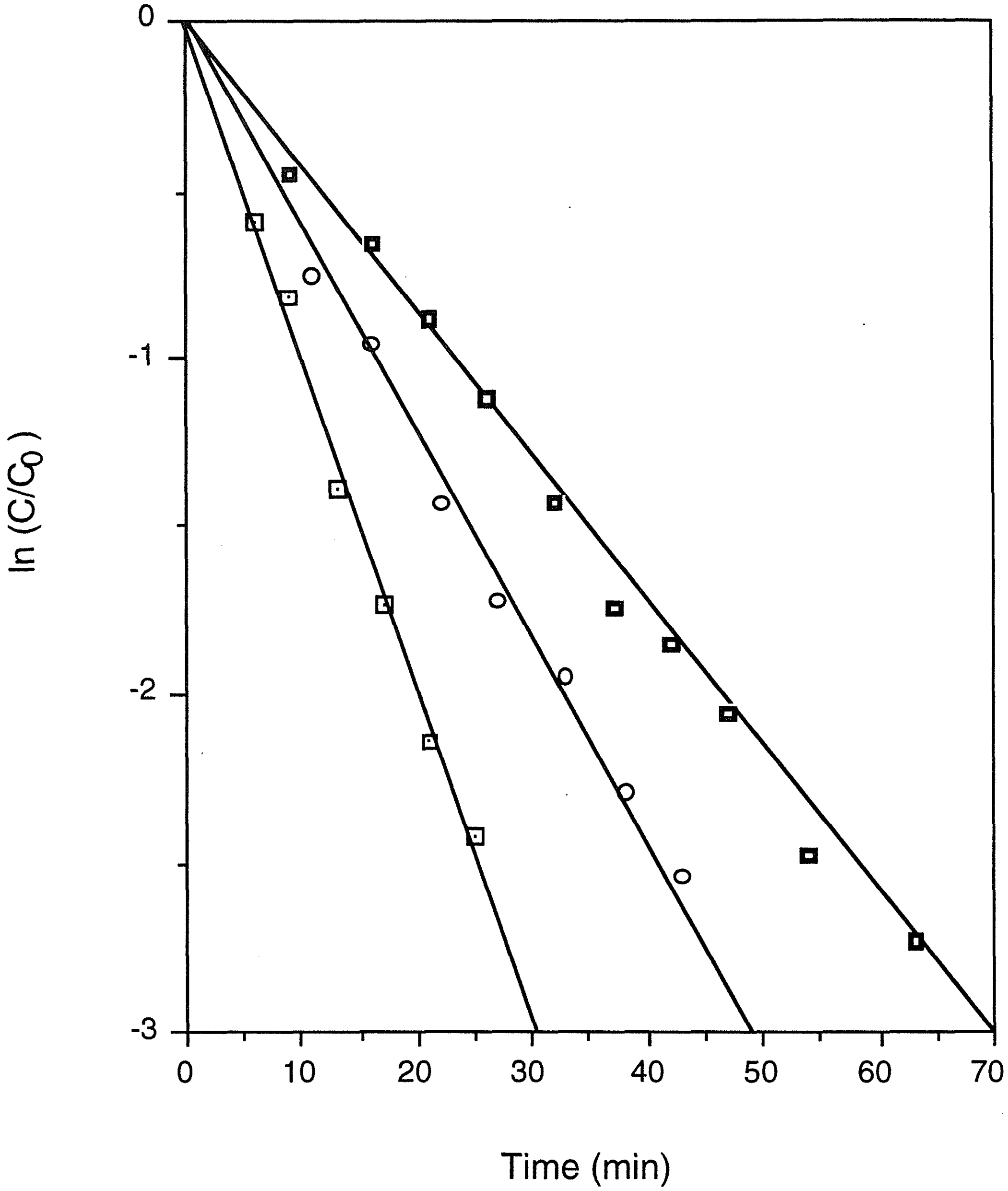
Kinetic Data for the Polymerization of Cyclobutene at Different Temperatures.



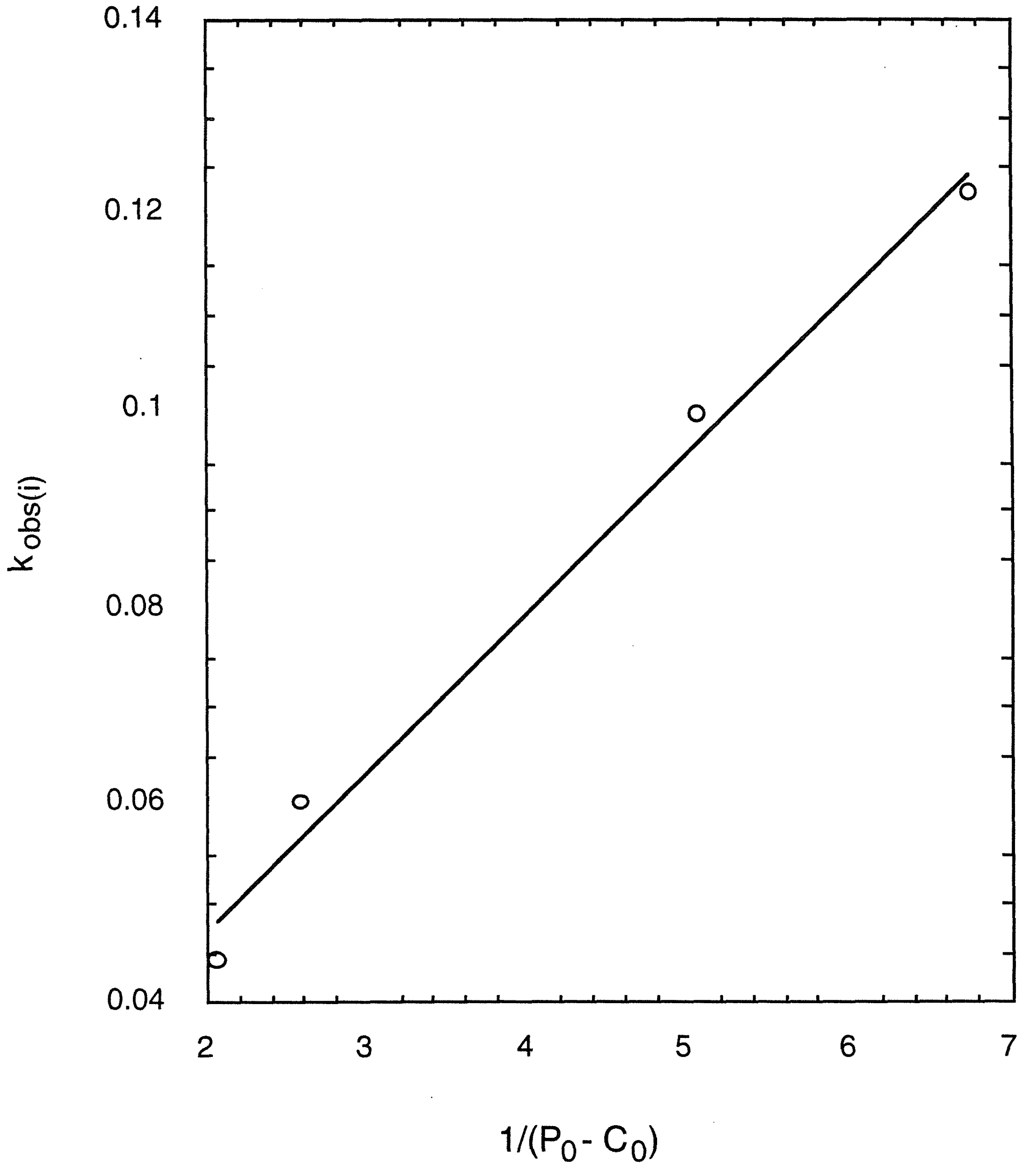
Graph 1. Kinetic data for the polymerization of cyclobutene by **1** at 0 °C



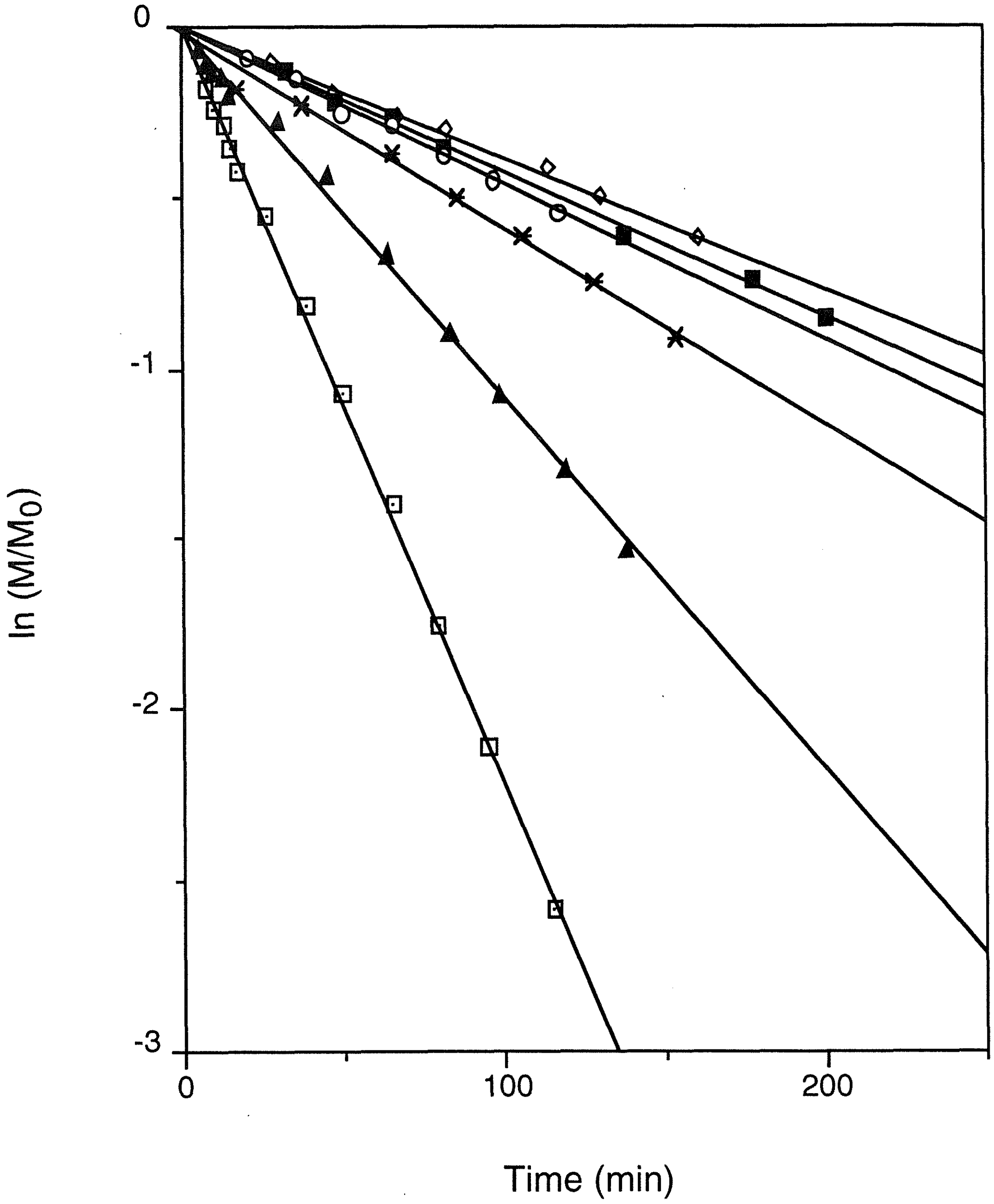
Graph 2. The change of observed propagation rate with phosphine concentrations at 0 °C.



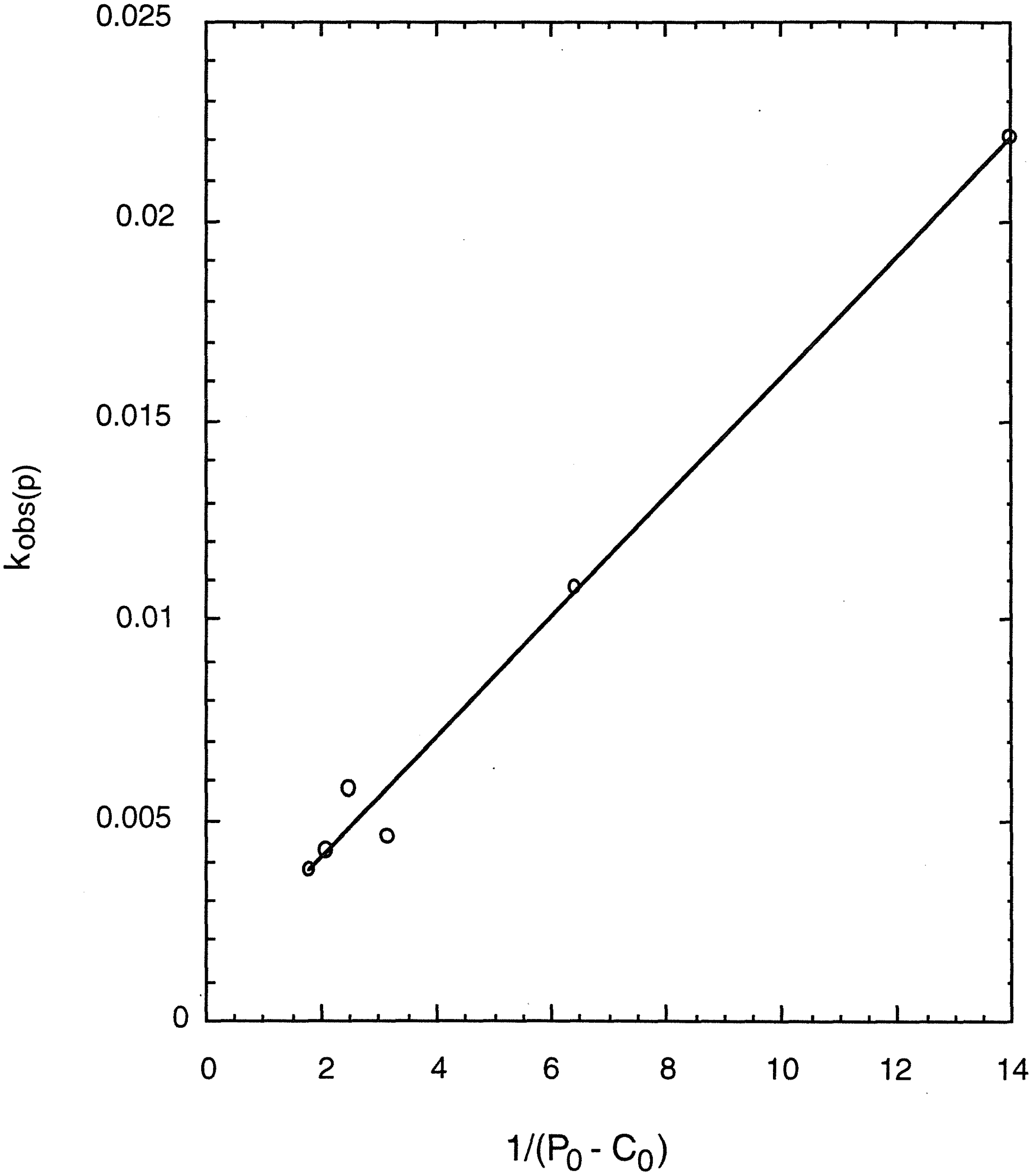
Graph 3. Kinetic data for the initiation of cyclobutene polymerization by **1** at 0 °C



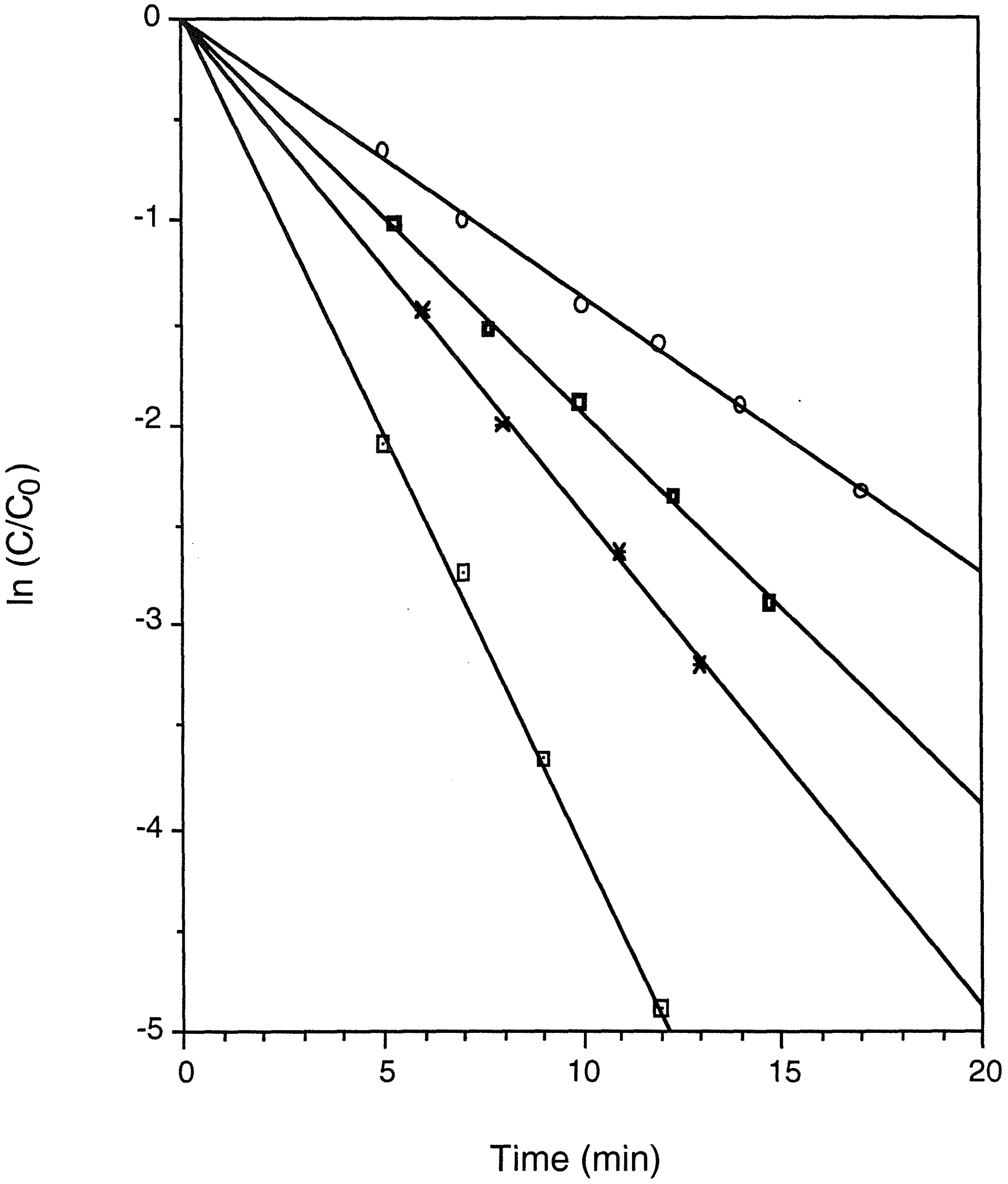
Graph 4. The change of observed initiation rates with phosphine concentrations at 0 °C.



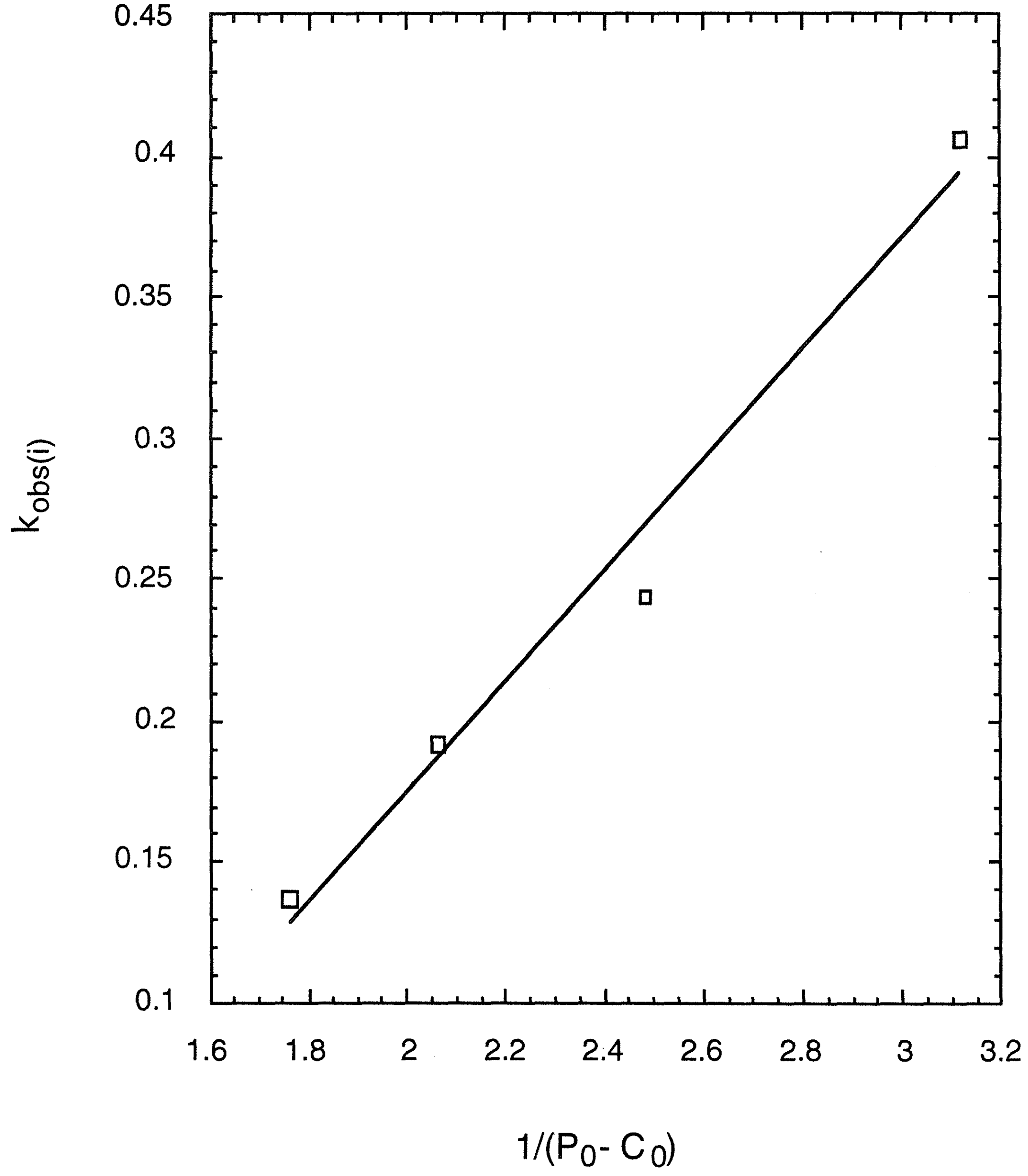
Graph 5. Kinetic data for the polymerization of cyclobutene by **1** at 10 °C



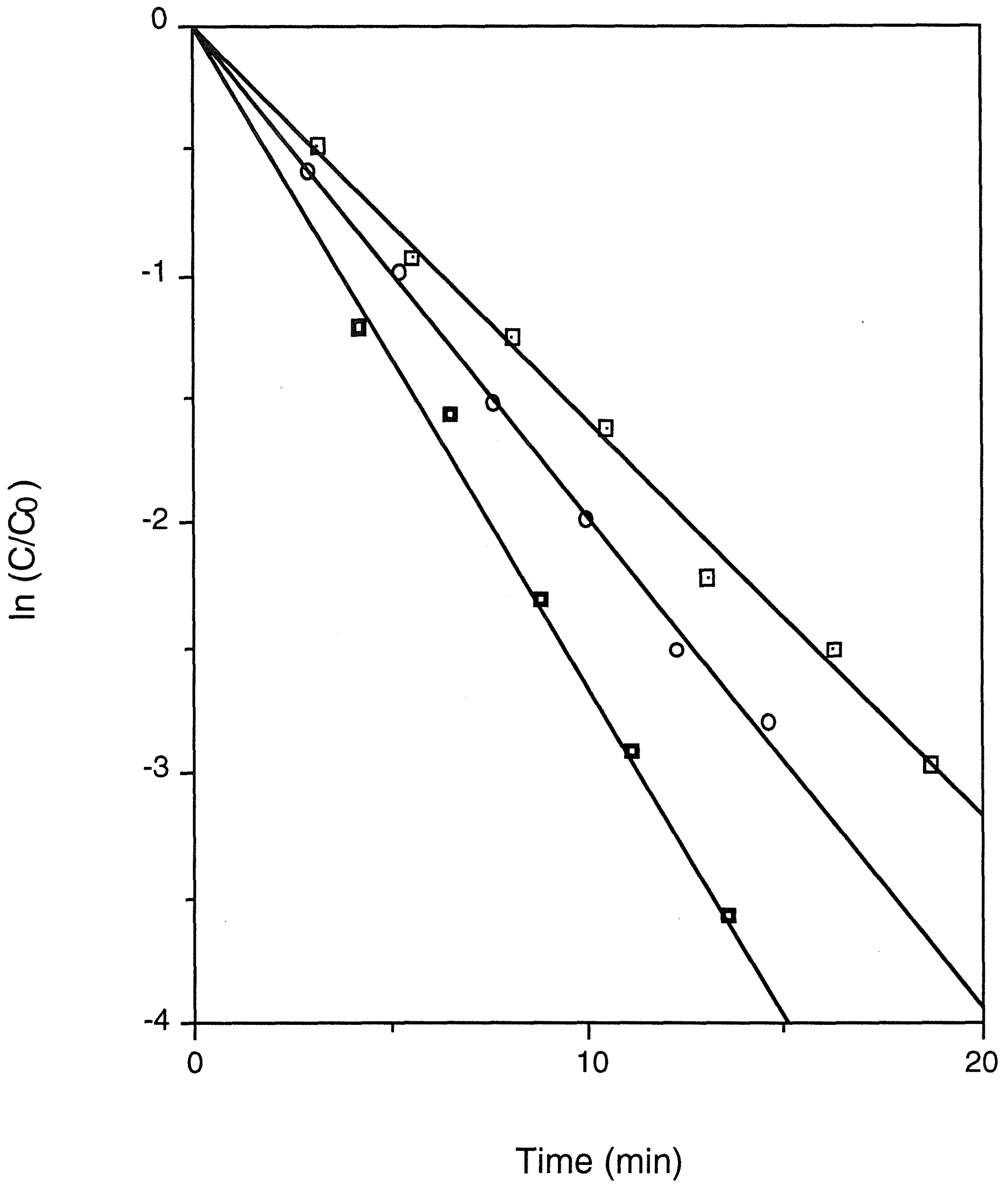
Graph 6. The change of observed propagation rates with phosphine concentrations at 10 °C.



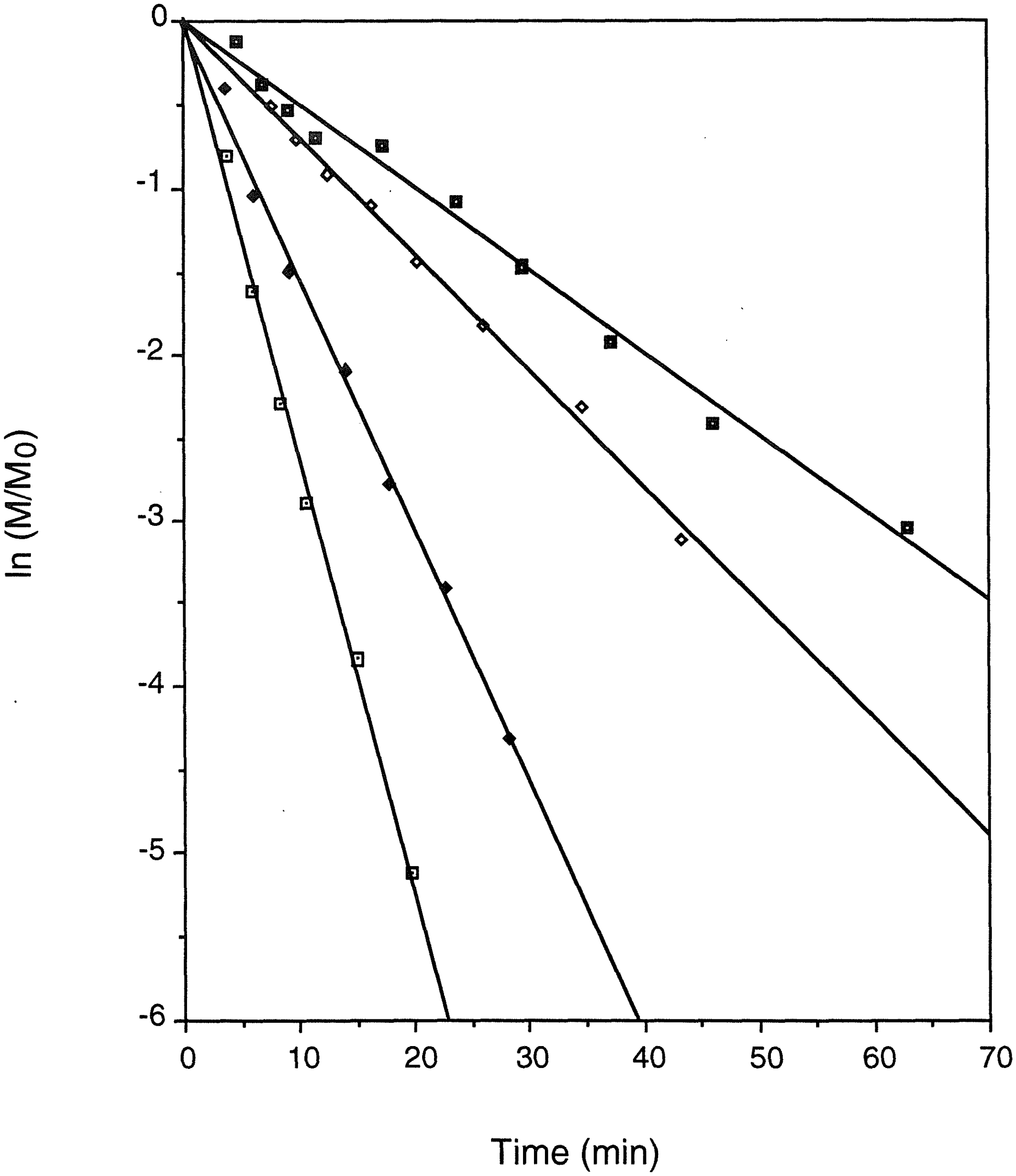
Graph 7. Kinetic data for the initiation of cyclobutene by 1 at 10 °C.



Graph 8. The change of observed initiation rates with phosphine concentrations at 10 °C.



Graph 9. Kinetic data for the initiation of cyclobutene by **1** at 25 °C.



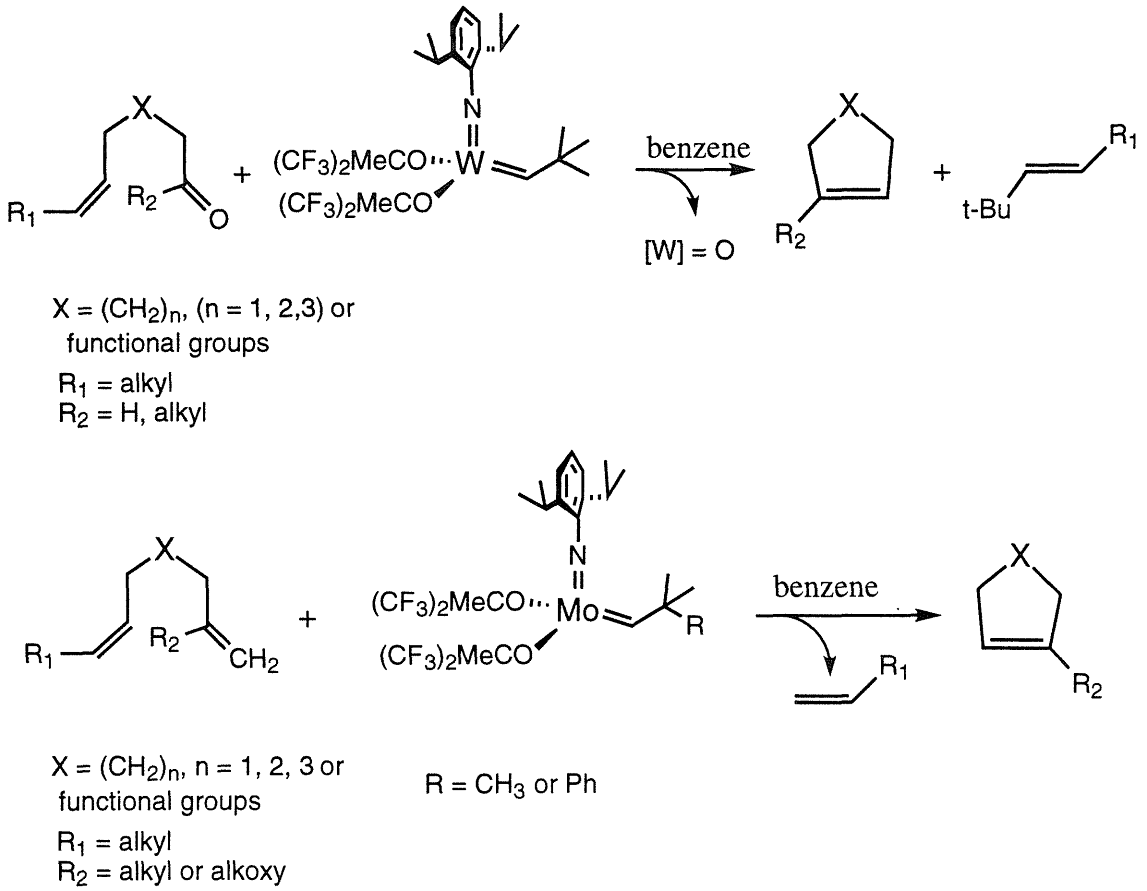
Graph 10. Kinetic data for the polymerization of cyclobutene by **1** at 40 °C.

Chapter 2

Metathesis of Functionalized Olefins Using a Molybdenum Alkylidene Complex

Introduction

One of the most promising synthetic applications of the metathesis reaction is to olefins bearing polar functional groups. A possible metathesis of functionalized olefins would be very important as a means of preparing in a single step of various mono- and difunctional derivatives of hydrocarbons.[1] The metathesis of functionalized olefins also has considerable commercial values in terms of dimerization of unsaturated olefins, for example the metathesis products of nitrile or esters might be used as precursors to adipic acid. Successful examples for dimerization of unsaturated esters have been reported based on cationic rhodium alkyl system.[2] Unfortunately, most homogeneous classical metathesis catalysts are easily poisoned by hetero functional groups; therefore, most metathesis reactions of functionalized olefins were carried out in heterogeneous system.[3] The drawbacks of these systems are the reproducibility, sensitivity to the experimental conditions and the difficulty for mechanistic studies, which hinder the systematic designing of other new catalytic systems. In the past decade, a number of well-defined transition metal alkylidene, metallacyclobutane and carbene complexes have been synthesized.[4,5,6,7] Tremendous advances have been realized for both the understandings of metathesis reactions and the applications to the synthesis of new materials.[8] Since the reactivity of these well-defined complexes can be tuned by changing both the coordinating ligand and the metal, certain functionality can be tolerated.[9] More recently, the metal alkylidene complexes have been used successfully in organic synthesis through an intramolecular cyclization process (Scheme 1). The driving force for this process is probably the increase of entropy since low-boiling olefins, such as ethylene, are generated during the reaction.[10]

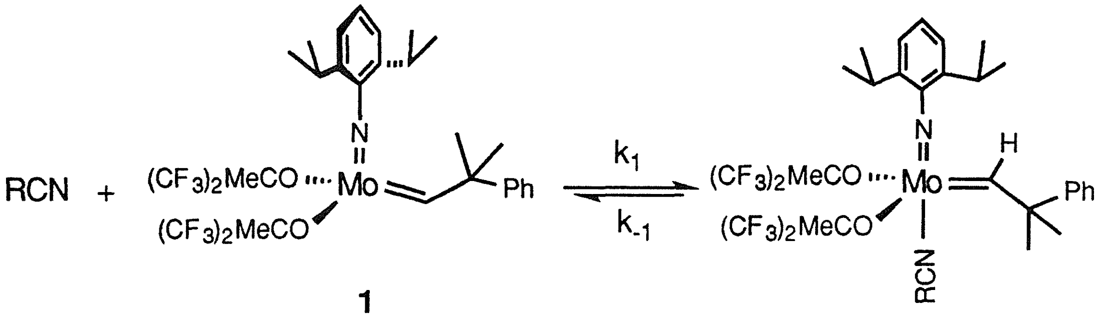


Scheme 1. Ring-Closing Metathesis Reaction (RCM).

Recently, Ishii and co-workers reported the production of 2-butene-1,4-dicarboxylic diester from the dimerization of alkyl-3-alkenoate esters using $MoCl_5/SnR_4$ as catalyst, and this reaction was believed to occur through an olefin metathesis pathway.[11] However, the exact mechanism is unclear. This result has inspired us for an investigation of the metathesis of functionalized olefin, which is much less studied and less understood. An exploration of the metathesis of functionalized olefins not only will allow us to gain more fundamental knowledge of the high oxidation state transition metal alkylidene system, but also will provide us a better understanding of the ring opening-metathesis polymerization (ROMP) process as well as the ring-closing metathesis (RCM) reactions.

In this chapter, the reactions of a well-defined molybdenum alkylidene complex **1** (eq 1) with unsaturated esters and nitriles will be examined. The selection of this catalyst is based on the fact that **1** has reasonable tolerance to functionality and is active in metathesizing acyclic olefins.[12]

Results and Discussion



1 **2** (1)

$$R = \begin{cases} CH_3,\ CH_3CH_2CH_2CH_2 \\ CH_3CH{=}CHCH_2,\ CH_3CH_2CH{=}CH \\ CH_2{=}CHCH_2CH_2 \end{cases}$$

Reversible Binding of Nitrile to 1. Nitriles have been found to bind reversibly to **1** in benzene or toluene as shown in eq 1. As an example, when two equiv of acetonitrile was added to a benzene solution containing 0.01M of **1** at room temperature, two resonances were observed in the alkylidene region at 13.85 and 12.15 ppm by ^{1}H NMR spectroscopy, which corresponded to the bound and free alkylidenes. The signal of the acetonitrile bound alkylidene (δ 357.9) was also observed by ^{13}C NMR spectroscopy. The presence of equilibrium was further demonstrated by varying the temperature and concentration of the reaction mixture. For example, at low temperature, more bound alkylidene **2** was observed. When the concentration of the nitrile was increased, more bound alkylidene was also detected by ^{1}H NMR spectroscopy. In a special circumstance, when 20 equiv of acetonitrile was added to a solution of **1** in benzene, only the resonance of bound alkylidene was observed by ^{1}H NMR spectroscopy. A list of chemical shifts for H_α of the nitrile bound alkylidenes is shown in Table I.

Table I. H_α Resonances of Nitrile Bound Alkylidenes.

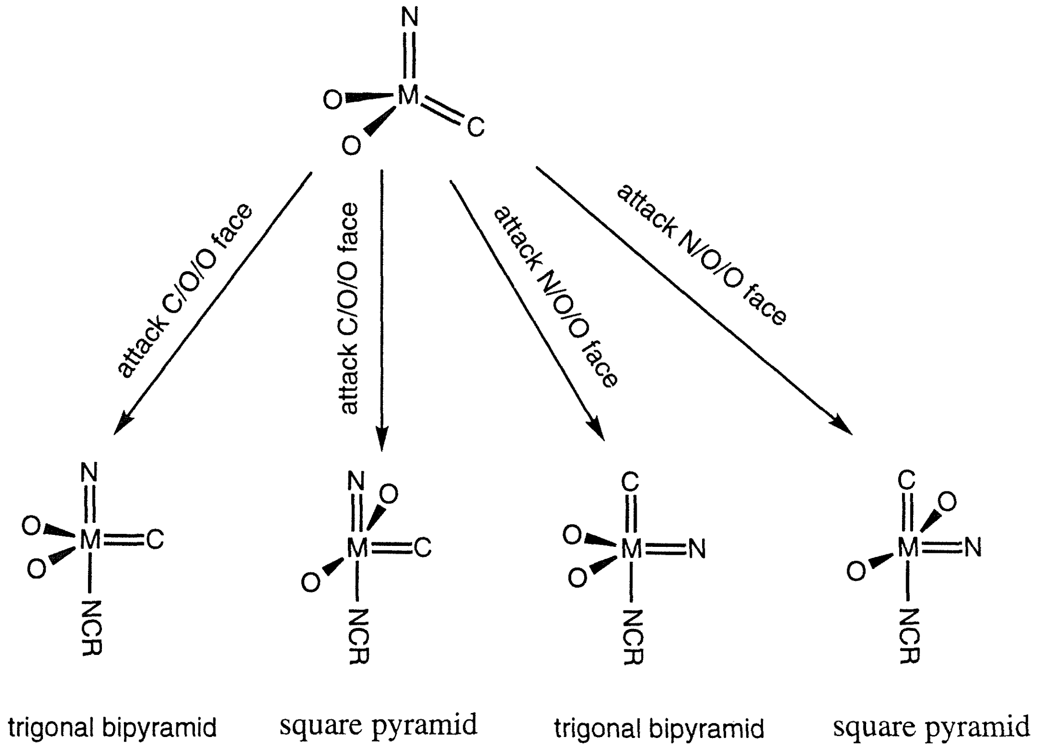
Nitriles	δ (ppm)
CH_3CN	13.85
$CH_3(CH_2)_2CN$	13.89
$CH_3CH_2CH{=}CH_2CN$	13.92
$CH_3CH{=}CHCH_2CN$	13.88
$CH_2{=}CH\text{-}CH_2CH_2CN$[a]	13.32

[a] Observed at - 78 °C.

The change of resonances of other protons in **1** upon binding was also evident. For example, the resonance of methine proton on the imido group of the nitrile bound complex **2** (R = CH_3) was observed at 4.2 ppm as a broad peak and only one methyl resonance of the isopropyl group of the imido ligand was observed at 1.3 ppm ($J_{H\text{-}H}$ = 6.89 Hz) at room temperature by ^1H NMR spectroscopy. These observations indicated the presence of rapid rotation of the aryl group around the C-N bond. Also, only one alkoxide resonance in **2** (R = CH_3) was observed at 1.9 ppm. The above data suggested that complexes of type **2** were achiral. Therefore, the nitrile was either *trans* to the imido or alkylidene by attacking either C/O/O or N/O/O faces of catalyst **1** (Scheme 2).[13]

The structure of the nitrile bound alkylidene complex was further studied by nOe experiments. When the H_α of acetonitrile bound alkylidene was irradiated, a strong nOe enhancement was observed for the methine proton on the imido group. This indicated that the alkylidene was in an anti conformation with the neopentyl substituent pointing away from the imido group.[12(a)] Further evidence for the anti rotamer conformation comes from the low temperature

NMR experiments. When a toluene solution containing 0.5 equiv of acetonitrile and 0.03 M of **1** was cooled down to -78 °C, a new resonance was observed at 13.53 ppm by ^{1}H NMR spectroscopy. The ratio of bound alkylidene, new resonance and free alkylidene were 5.17:2.8:1. As the temperature was lowered to -90 °C, the ratio changed to 3.78:4.48:1. On the basis of the analogy with a molybdenum and quinuclidene system,[13] we assigned the new resonance as the syn rotamer with the alkylidene proton pointing away from the imido ligand, which was believed to be a kinetic product of the reaction.[14] This was further supported by the following observations: When 5 equiv of acetonitrile was added to a pre-cooled toluene solution of **1** at -78 °C and the NMR spectrum was recorded immediately at this temperature, only the resonance corresponding to the syn rotamer and free alkylidene were observed by ^{1}H NMR spectroscopy.



Scheme 2. The Coordination of Nitriles to C/O/O or N/O/O Faces of **1**.[13]

The relaxation rate for the H_α of bound and free alkylidenes was also measured by an inversion-recovery experiment. The H_α of the free alkylidene has a T_1 of 1.84 s and the T_1 for the H_α of acetonitrile bound alkylidene is 0.76 s. The shorter T_1 for bound alkylidene proton indicated that the coordination of nitrile accelerated the rate of the relaxation through space interactions. Attempt to measure the exchange rate by magnetization transfer experiments was not successful, which indicated that the rate of exchange was too slow compared to the rate of relaxation. In order to probe the binding of nitrile to **1** ^{13}C labeled CH_3C^*N was used. There was, however, no chemical shifts difference observed for bound and free acetonitrile by ^{13}C NMR spectroscopy.

Metathesis of Unsaturated Nitriles. When 2 equiv of *cis*-2-pentenenitrile was added to a benzene solution containing 0.01 M of **1** at room temperature, no metathesis reaction was observed even with prolonged reaction time and heating conditions. This can be understood from the electronic factors, since the double bond next to the nitrile group is deactivated due to the presence of strong electronic withdrawing effect of the adjacent cyano functionality. This lack of metathesis for 2-pentenenitrile is also consistent with the results obtained by Mol using a heterogeneous Re_2O_7/Al_2O_3 catalytic system.[14]

Since *cis*-2-pentenenitrile bound reversibly to **1** (eq 1), the equilibrium constants for this reversible binding process was measured at several different temperatures and the enthalpy and entropy for binding could be estimated $\Delta H^\circ \approx$ 3 kcal/mol, $\Delta S^\circ \approx -6$ e. u. The Arrhenius plot for the binding is shown in Figure 1. The small enthalpy also indicates the weak binding of nitrile to the alkylidene.

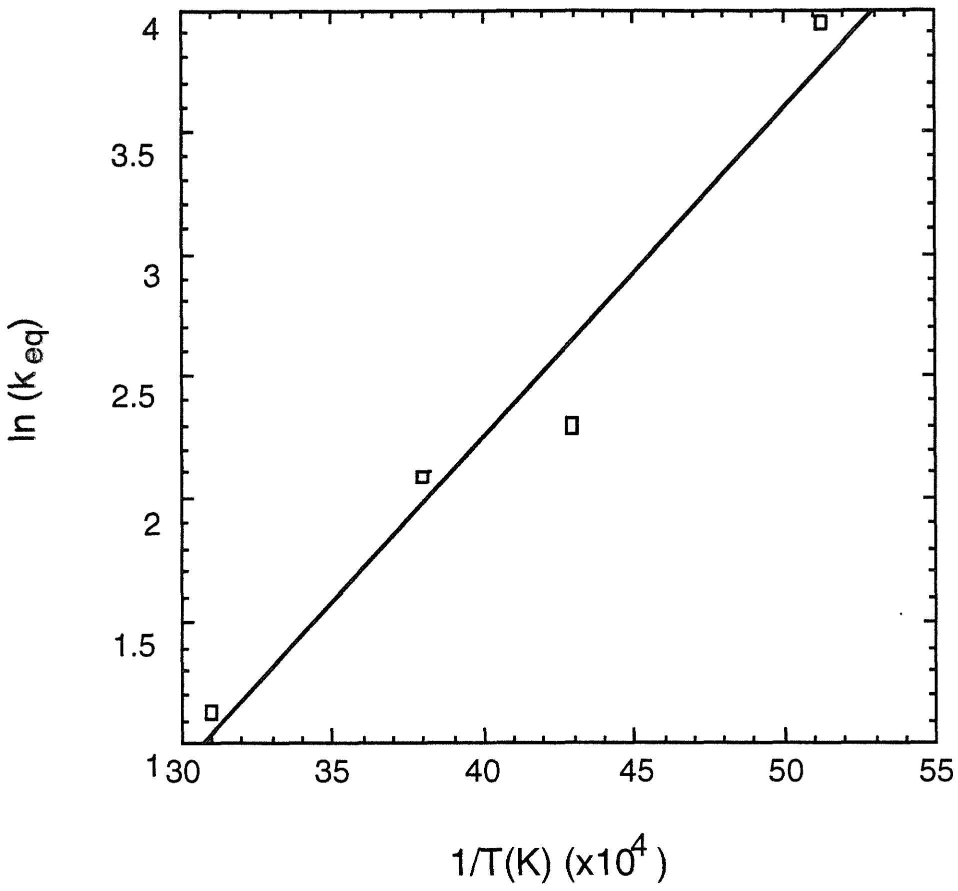
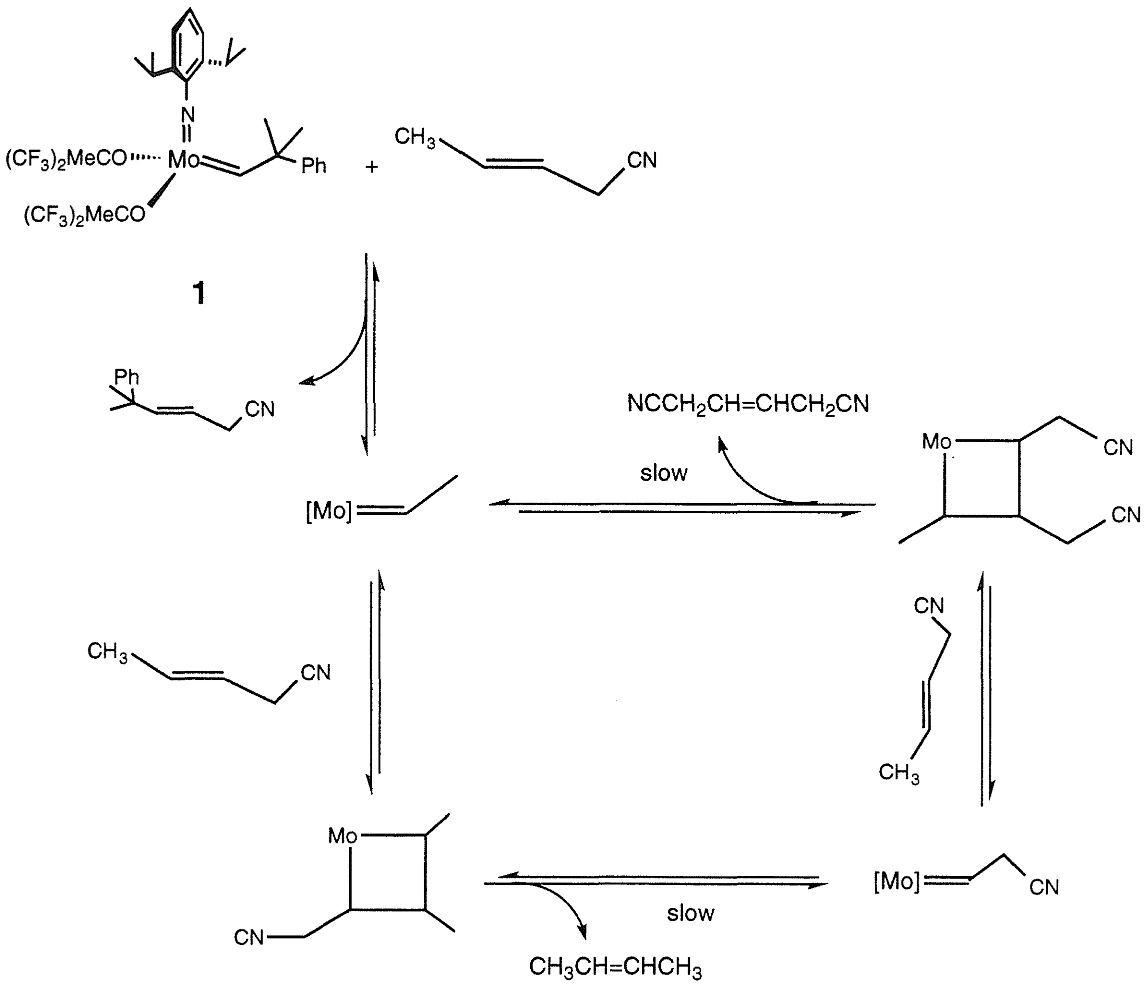


Figure 1. Arrhenius plot of the binding of 2-pentenenitrile to **1**.

We also investigated the metathesis of 3-pentenenitrile and hoped that an enhanced reactivity would be realized. Indeed the reaction proceeded at room temperature and the turn over number is 0.15/hr measured by ^{1}H NMR spectroscopy. After 33 hours, ~ 50% of the catalyst was consumed and extended reaction time did not produce more 3-hexyl-1,6-dinitrile. In contrast, the turnover number for the metathesis of *cis*-2-pentene by **1** is 250/min.[4(a)] The difference in turnover numbers reflexes that the coordination of nitrile significantly reduces the rate of metathesis by competing with the olefin for coordination. Compound 5-methyl-5-phenyl-3-hexenenitrile was identified from the analysis of the reaction mixture using high resolution mass spectroscopy. This suggested that the first step of the reaction involved the formation of a trisubstituted metallacyclobutane with the cyano group next to the neophyl group as shown in Scheme 3. The driving force for the overall reaction is perhaps the formation of volatile 2-butene. The change of dinitrile concentration with time was followed by ^{1}H NMR spectroscopy to the equilibrium point (50% conversion) and the initial rate for the formation of dinitrile was zero-order with respect to the concentration of 3-pentenenitrile. However, when the reaction was followed at 60 °C, the initial rate law deviated from zero-order. Since this reaction kinetics was only followed to the point, which corresponded to 50% conversion of the starting nitrile, therefore, only an approximate and qualitative meaning might be extracted from such studies. It did imply that the initial metathesis of 3-pentenenitrile could involve a slow cleavage of metallacyclobutane intermediates in the rate determining step and the metallacyclobutane was probably stabilized by the coordination of nitrile.[16] At higher temperature, the rate for the cleavage of metallacyclobutane became faster resulting in the initial rate law being deviated from zero-order.

Scheme 3



We reasoned that the relatively slow rate of metathesis for 3-pentenenitrile might also partly be ascribed to its possession of stericly more hindered internal double bond. Therefore, 3-butenenitrile was employed for a similar reaction. When 2 equiv of 3-butenenitrile was added to a solution of 0.01 M of **1** in toluene at room temperature, a triplet alkylidene was immediately observed at 12.4 ppm ($J_{H\text{-}H}$ = 10.6 Hz), corresponding to the H_α resonance of 1-cyanopropylidene.[12(a)] The intensity of this triplet alkylidene and the initial alkylidene was 1:1. The new alkylidene decomposed within hours. The decomposition is probably assisted by a β-hydride abstraction or followed by a bimolecular decomposition pathway.[17]

The metathesis of 4-pentenenitrile (4-PN) was also investigated at room temperature and the initial metathesis product was 3-methyl-3-phenyl-1-butene. No new alkylidene was observed by ^1H NMR spectroscopy. Only reversible binding of the nitrile with **1** existed at -78 °C as revealed by ^1H NMR spectroscopy and the metathesis reaction started as the temperature increased to 0 °C.

Table II shows a comparison of the relative rates of the dinitrile formation for several different unsaturated nitriles. These data demonstrate that the rates for conversion to dinitriles follow the order of 4-PN ~ 3PN > 5-hexenenitrile > 6-heptene nitrile > 3-butenenitrile >> 2-pentenenitrile. These results are also consistent with those obtained using a heterogeneous system.[15] The low turnover of 3-butenenitrile is probably attributed to the ease of decomposition of the cyanopropylidene. The high turnover number for 3-pentenenitrile compared to 3-butenenitrile can be understood from two aspects: (i) A trisubstituted metallacyclobutane intermediate is formed during the reaction, and the rate determining step may be the cleavage of metallacyclobutane intermediate. Since the rate for cleavage of trisubstituted metallacyclobutane is much faster than the disubstituted analog, a higher turnover is expected for 3-pentenenitrile.[16] (ii) The active species from the metathesis of 3-pentenenitrile is a molybdenum ethylidene, which is much more stable during the course of the reaction than methylidene derived from terminal alkenenitriles.[18]

Table II. Reactions of different unsaturated nitriles with **1**.

Nitriles[a]	2-PN[b]	3-PN[b]	3-BN[c]	4-PN[b]	5-HEXN[d]	6-HEPN[e]
dinitrile conversion(%)	0	67.5	47.6	70	61.8	56.3

[a] Reactions were carried out at 60 °C for six hours and the initial ratio of nitrile-to-catalyst was 4.

[b] PN is an abbreviation for pentenenitrile.

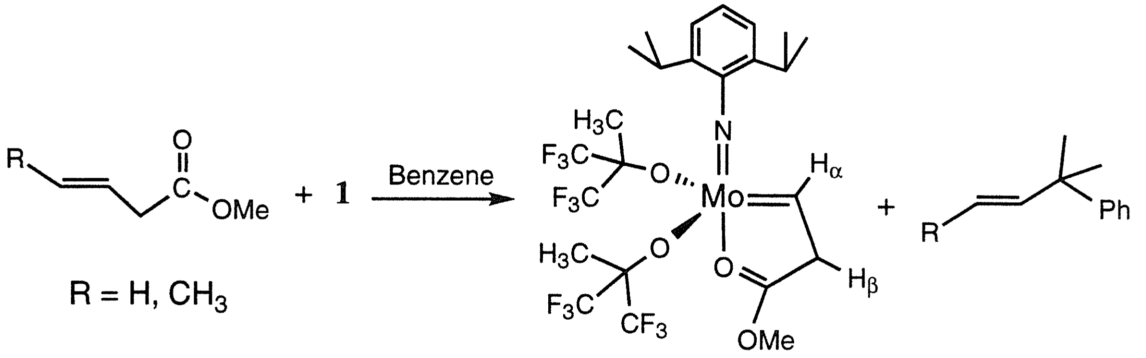
[c] 3-BN: 3-butenenitrile.

[d] 5-HEXN: 5-hexenenitrile.

[e] 6-HETN: 6-heptenenitrile.

Metathesis of Unsaturated Esters. When 3.4 equiv of methyl 2-pentenoate was added to a 0.01 M solution of **1** in benzene, no reaction was observed by ^{1}H NMR spectroscopy even with the increase of temperature. This could be attributed to the deactivation effect of the electronic withdrawing ester group on the double bond similar to the metathesis of 2-pentenenitrile (vide infra).

In order to remove the conjugation of ester group with the double bond, methyl-3-pentenoate was used. When 4.7 equiv of methyl 3-pentenoate was added to a toluene solution of **1**, No apparent reaction was observable by ^{1}H NMR spectroscopy after the reaction mixture was left at room temperature for 12 hours. After the reaction mixture was heated to 50 °C for 12 hours, a triplet resonance was observed at 11.77 ppm (J_{H-H} = 4.6 Hz) and 1,6-dimethyl-3-hexenoate also formed in a total of 44% conversion. The new alkylidene complex **3** was probably stabilized by the formation of a chelated



3

(2)

metallacyclopentane with the oxygen of the carbonyl group coordinated to the metal center (eq 2).[21] The productive metathesis observed also indicated the dissociation of the coordinated carbonyl. The slow reactivity was also partly attributed to the bulky internal double bond of 3-pentenenitrile. For example, when **1** was treated with 2 equiv of terminal unsaturated nitrile (methyl-3-butenoate) in toluene at room temperature, both rapid formation of ethylene and diester were observed. Low temperature NMR experiments indicated that the metathesis of methyl-3-butenoate with **1** to form **3** started at -10 °C and the reaction was completed in 0.5 hour at 0 °C. Only small amount of ethylene was detected at this temperature. A comparison of relative reactivities of the internal unsaturated ester versus the terminal ones is shown in Table III.

Table III. Reaction of Unsaturated Esters with **1**.

Esters[a]	methyl-3-butenoate	methyl-3-pentenoate	methyl-3-pentenoate[b]
Conversion to Diesters (%)	57	3.8	7.4

[a] Reactions were carried out at 60 °C for six hours.

[b] *cis*-2-heptene was used during the metathesis.

The geometry of the chelated metallacycle **3** was determined to be anti[19] by a nOe experiment. For example, when H_α of the alkylidene was irradiated, a strong nOe enhancement (22%) was observed for methine resonance of the isopropyl group. The coordination of the carbonyl group was trans to the imido ligand since the two alkoxides are equivalent. The resonances of methine and methyl of the isopropyl group were observed at 4.22 and 1.34 ppm, respectively. The structure was characterized spectroscopically by IR, ^1H and ^{13}C NMR spectroscopy, including decoupling, COSY and DEPT experiments. Typical NMR spectroscopic data are shown in Table IV.

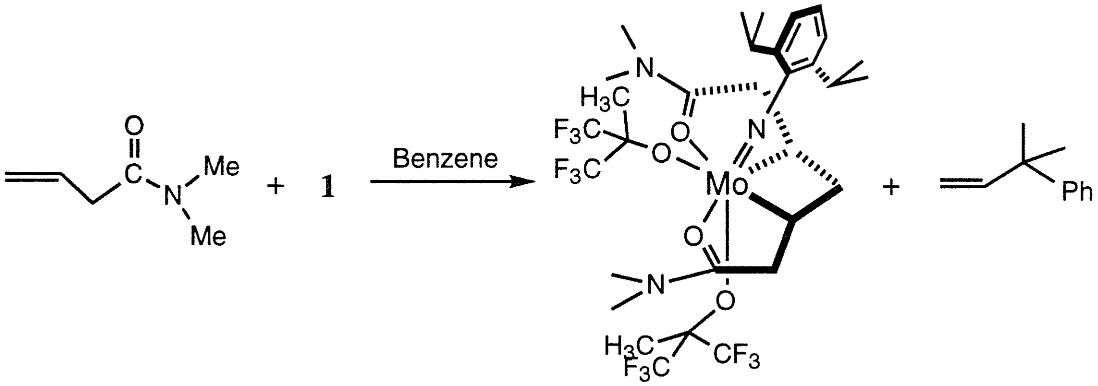
Table IV. Selective NMR Data of **3**

$\delta\ H_\alpha\ (J_{H\text{-}H})$	$\delta\ H_\beta\ (J_{H\text{-}H})$	$\delta\ C_\alpha\ (J_{C\text{-}H})$	$\delta\ H_\beta\ (J_{C\text{-}H})$
11.77 (4.6)	4.2 (4.6)	263.8 (159.8)	47.5 (133.2)

A slight increases in $J_{C\text{-}H}$ (133.2 Hz) for the β–carbon (sp^3 carbon) may correlate with the increasing of electron deficiency of the adjacent α-carbon due to the coordination. Further evidence to support the coordination of C=O to molybdenum was the change of C=O stretching frequency from 1752 cm^{-1} (free ester) to 1679 cm^{-1} (coordinated carbonyl) observed by IR spectroscopy. Attempt to obtain a single crystal structure of the compound was not successful.

The metathesis of methyl-4-pentenoate was also studied. When 3.5 equiv of methyl-4-pentenoate was added to a 0.01 M solution of **1** in benzene, all the starting alkylidene was consumed and the slow formation of dimethyl-1,8-dioctenoate was observed. It seemed that methyl-4-pentenoate behaved similarly as a normal olefin and the binding of the carbonyl group to the initial alkylidene was not detected, perhaps due to the steric reasons.[20]

The metathesis of N,N-dimethyl-3-butenamide was also studied with the hope that more basic carbonyl group will stabilize the high oxidation state complex. When N,N-dimethyl-3-butenamide was reacted with **1** (eq 1), we believed that a metallacyclobutane complex formed and both carbonyl groups of the amide were coordinated to the metal center, which was determined by comparing with the NMR data of some known chelated molybdenum and tungsten metallacyclobutane complexes.[22] The coordination of the carbonyl groups to the metal center was demonstrated by the down field shift of the carbonyl resonance (δ(CO) = 186.4 ppm) in ^{13}C NMR spectrum and low wave number shift of C=O stretching frequency (υ_{CO} = 1594 cm^{-1}) in IR spectrum. (In amides δ(CO) $\approx$ 170 and υ_{CO} $\approx$ 1680-1630 cm^{-1}). The compound was characterized by



4

(3)

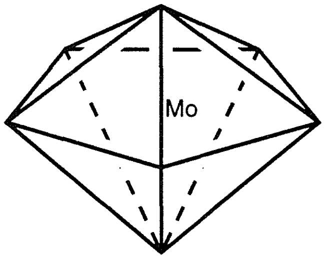
both proton and carbon NMR spectroscopy. Some typical NMR data are listed in Table V. Two methine protons of the imido groups are equivalent, but the two methyl groups from the same isopropyl group are not equivalent. The chemical shifts of α-protons of the metallacyclobutane are also equivalent. These data suggest the existence of a plane symmetry across the imido group and metallacyclobutane. The inequivalence of the two methyl groups of the same isopropyl group can be attributed to the restricted rotation of imido ligand. The ^1H NMR spectrum of compound **4** is shown in Figure **2**.

Table V.[a] Selective NMR Data for **4**.

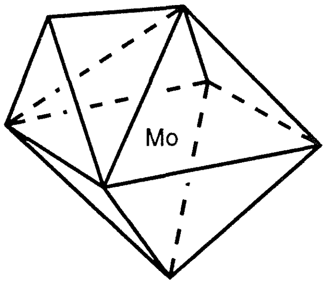
δ H_α	δ $H_{\beta1}$; δ $H_{\beta2}$	δ C_α ($J_{C\text{-}H}$)	δ C_β ($J_{C\text{-}H}$)
1.68 (quintet)	3.67 ; 2.93 (pseudo quartet)	23.53 (140.3)	34.85 (130.5)

[a] The chemical shifts and coupling constants listed in the table are in ppm and Hz respectively.

The ^1H and ^{13}C resonances of **4** were assigned by a combination of decoupling, ^1H-^1H COSY and ^1H-^{13}C COSY experiments and the structure of **4** was determined from nOe experiments. Since the compound has seven coordinating ligands, possible geometries of the complex will be either a capped octahedral or pentagonal bipyramid.[23] Since there



Pentagonal Bipyramaid



Capped Octahedron

is a plane symmetry across the metallacycle as derived from the NMR data, the carbons associated with the metallacycle must be at the equatorial positions and the alkoxide or the imido group will be either on the cap or the apical position. If the complex chooses a pentagonal bipyramid structure, then there are two possible configurations (Figure 3) with the imido being cis or trans to one of the

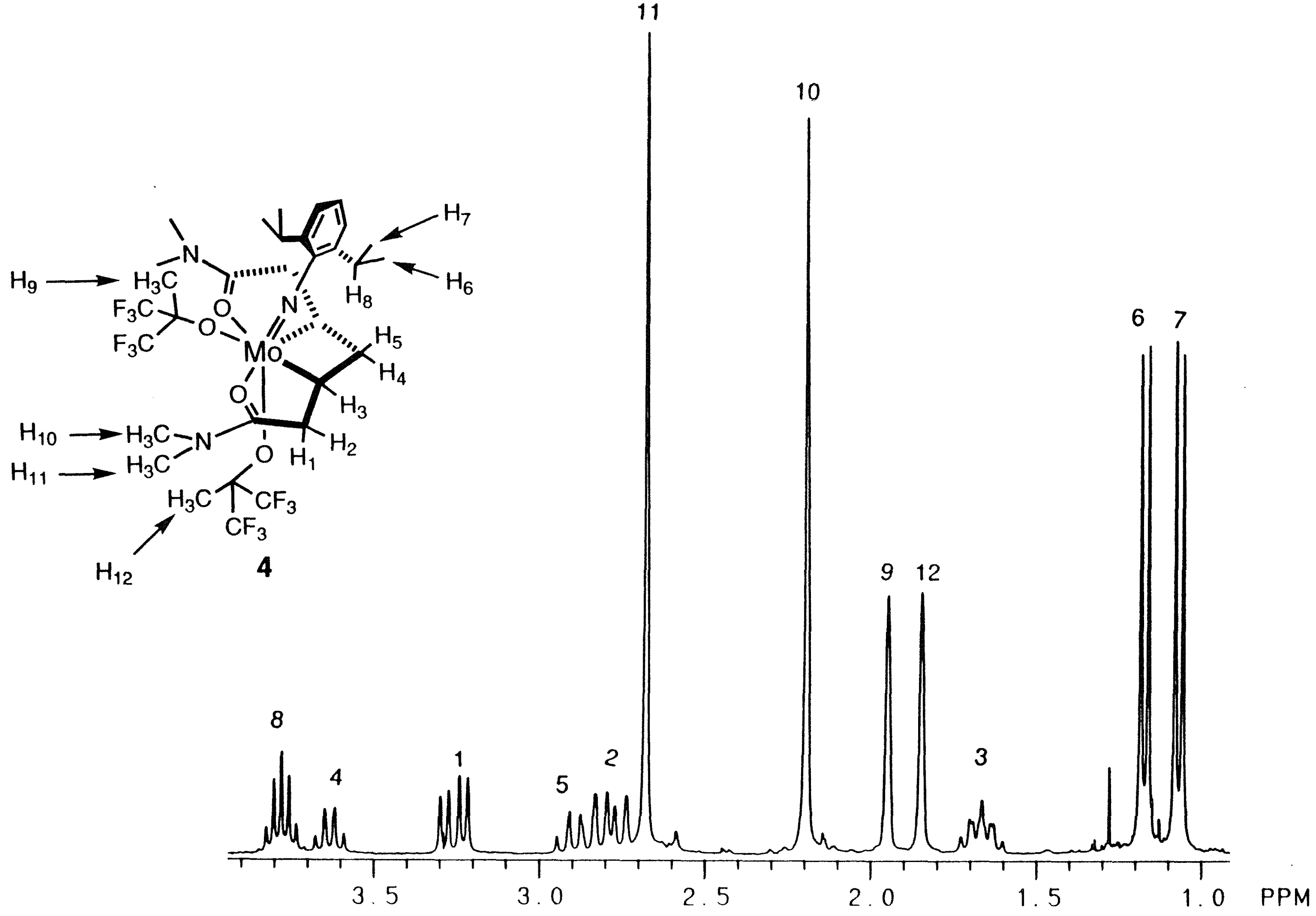


Figure 2. The ^{1}H NMR spectrum of **4**

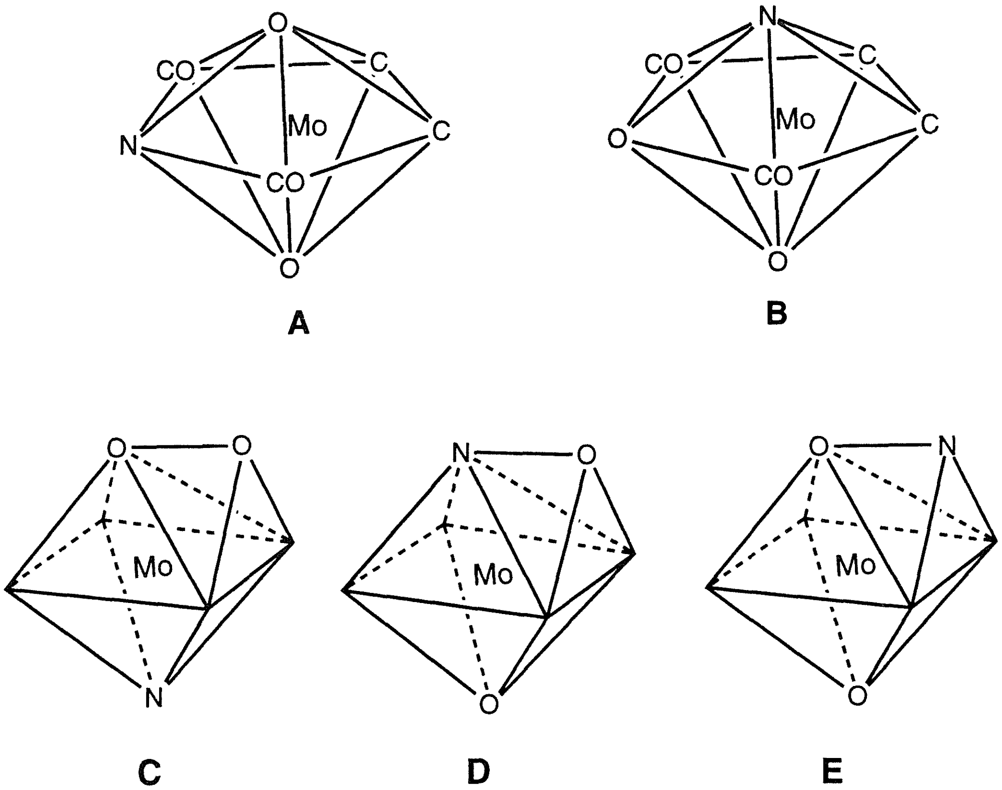


Figure 3. The possible structures for a seven-coordinated molybdenum complex **4**. (N, O and CO represent imido, alkoxide and carbonyl groups respectively. Each of **C**, **D** and **E** has two possible isomers depending on which way that the cap lies with respect to the metallacyclobutane.

alkoxides. If the complex adopts a capped octahedral geometry, there are six possible structures (Figure 3). NOe experiments suggest that one of the alkoxide is trans to the other one and away from the imido ligand. Structure **E** with the imido group on cap position and on the side of metallacyclobutane is the most favorable structure based the nOe data. For example, when the more upfield alkoxide resonance was irradiated, 8.13% enhancement of methine resonance was observed. When the α-proton of the metallacycle was irradiated, a strong enhancement of methine proton resonance (36.3%) was observed. When the resonance of one of the methyl groups on the imido ligand was irradiated, a 4%

enhancement of the β-proton resonance was observed. The precise structure assignment of **4** will await a single crystal X-ray structure analysis.

The tendency for the formation of a metallacyclobutane over a metal alkylidene complex as the electron density of the metal center increase is most likely due to the electronic reasons since the steric repulsion is actually increased. If we envision that the metal center in the metallacyclobutane complex gaining more positive charge compared to the metal alkylidene complex, then the increase of the donating ability of the coordinating ligand will favor the formation of a metallacyclobutane.[24] This proposal is consistent with the findings in titanacyclobutane chemistry, where an electron-donating substituent on a Cp ring slowed loss of an olefin from TiC_3 ring.

Conclusion. The metatheses of unsaturated nitriles and esters are controlled by a fine balance between the coordination of olefin and the binding of functional group to the metal center. Terminal nitriles or esters react much faster than the internal ones. Unsaturated nitriles reversibly bind to the metal center, which reduces their rates of metathesis compared to normal olefins. The decomposition of the propagating alkylidene species is another factor that contributes to the low turnover in the metathesis of nitriles. Especially in the use of 3-alkenenitrile, the β-hydrogen elimination may be a major pathway for the decomposition of cyano substituted alkylidene species. The slow reaction of unsaturated ester compared to the corresponding olefin may be the result of carbonyl bound more strongly to the active alkylidene species than to the starting alkylidene.[25] The metathesis reaction of alkyl-3-alkenoate with **1** is slow due to the chelation effect of the carbonyl group to the metal center, which results in the formation of a much less reactive chelating alkylidene **3**. Increasing the donating ability of the carbonyl group favors the formation of a stable inactive chelated metallacyclobutane complex **4**, such as the metathesis of 3-butenamide.

Experimental Section.

General Procedures. All manipulations of air- and/or moisture-sensitive compounds were carried out using standard Schlenk or vacuum-line techniques or in an N_2-filled drybox. Argon was purified by passage through a column of BASF RS-11 (Chemlog) and Linde 4Å molecular sieves. ^1H and ^{13}C NMR spectra were recorded on a QE-300 MHz or QE Plus-300 MHz spectrometer. T_1 was determined by an inversion-recovery pulse sequence. Hewlett 5890 Gas Chromatography was used for routine analysis.

Materials. Catalyst **1** was synthesized according to the published procedure.[12] Petroleum ether, benzene and toluene were distilled from sodium benzophenone ketyl. DMSO was distilled from CaH_2.

General Procedures for NMR Tube Reactions. In a nitrogen-filled dry box, catalyst **1** was weighed into an NMR tube and dissolved into calculated amount of solvent. The tube was then capped with a rubber septum and the reactants (nitrile or ester) were added through a gas-tight syringe either in or outside the drybox at the desired temperature. The NMR spectra were recorded at the desired temperature and time.

Synthesis of 5-Hexene Nitrile.[26] 5-bromo-1-pentene (10 g) was first dissolved in 50 ml DMSO in a 250 ml round bottom flask. To the above flask, KCN (6.1 g) dissolved in 5 ml of hot water was added dropwise. The rate of the addition was maintained so that the temperature of the reaction mixture was below 40 °C. The solution started to turn red, yellow and then white as the addition continued and a precipitate formed. After addition, the temperature was increased to 65 °C. After two hours, the conversion was 55% and the mixture was stirred at 65 °C overnight. On the second day, the content of the flask was poured into 1000 ml water and the aqueous phase was extracted several times with ether until it was clear. The etherate was then washed with water and evaporated off solvent to give a yellow oil. Fractional distillation of the yellow oil under house vacuum (~110 torr) at 110 °C yielded a colorless liquid (4.8 g, 77%), which was pure by GC.

Synthesis of 6-Heptene Nitrile.[26] Similar procedure for the synthesis of 5-hexene nitrile was used here. 6-bromo-1-hexene (5 g) was dissolved in 20 ml DMSO and added into a 100 ml 3-necked round bottom flask. To the flask, an aqueous solution of KCN (2.8 g) was added dropwise and the rate of addition was controlled so that the temperature was below 40 °C. After the addition, the mixture was stirred at room temperature for 0.5 hour and at 60 °C for an hour. The reaction was monitored by GC. After the reaction was complete, the mixture was cooled down to room temperature and poured into water. The aqueous solution was extracted several times with ether and the etherate was washed with H_2O and then evaporated off solvent to yield an oil (2.7 g, 81%), which was pure by GC.

Synthesis of Methyl-3-butenoate.[27] 3-butenoic acid (20 g) and $BF_3 \bullet 2MeOH$ (52 ml), were added into a 3-neck 500 ml round bottom flask containing 250 ml methanol. The mixture was refluxed for 0.5 hour and cooled down to room temperature. The content of the flask was poured into H_2O and extracted with petroleum ether several times. The organic was distilled to yield a colorless liquid (4.3 g, 20%), which was pure by GC.

Synthesis of Chelating Alkylidene Complex 3. In a nitrogen-filled dry box, catalyst **1** (109.4 mg) was dissolved in 7 ml of petroleum ether and cooled to -40 °C. Methyl-3-butenoate (16 ul, 17.5 mg) was added, then the mixture was allowed to warm up to room temperature and was stirred for 0.5 hour. Pump off all the volatiles in high vacuum to give a yellow solid in essentially quantitative yield: ^1H NMR (300 MHz, C_6D_6) δ 11.77 (t, 1H, $J_{H\text{-}H} = 4.6$ Hz), 4.22 (septet, 2H), 4.13 (d, 2H, $J_{H\text{-}H} = 4.6$ Hz), 3.40 (s, 3H), 1.34 (d, 12H, $J_{H\text{-}H} = 6.9$ Hz), 1.27 (s, 6H).

^{13}C NMR (75 MHz, C_6D_6) δ 263.8 (alkylidene α carbon, $J_{C\text{-}H}$ = 159.8 Hz) 47.5 (alkylidene β carbon, $J_{C\text{-}H}$ = 133.2 Hz).

Synthesis of N,N-dimethyl-3-butenamide.[28] 3-butenoic acid (1.0 ml), oxalyl chloride (0.91 ml) and 30 ml benzene were added into a 100 ml round bottom flask. Catalytic amount of DMF (10 ul) was added to the flask and the gas bubble was generated immediately. The mixture was stirred until the bubble stopped. In another 100 ml round bottom flask, $NHMe_2$ (~2.0 ml) was condensed at 0 °C and diluted with 10 ml of benzene. To this solution, 3-butenoyl chloride was added through a cannular at 0 °C. After the addition, the mixture was stirred at room temperature for 15 minutes. and then the content was poured into H_2O. The organic layer was separated and the aqueous layer was extracted with ethyl acetate three times. The organics were combined and evaporated off solvent to give a yellow oil pure by NMR. The yellow oil was further purified by kugelhror distillation to yield a colorless oil (0.8 g, 63%): ^1H NMR (300 MHz, $CDCl_3$) δ 5.9 (m, 1H), 5.15 (m, 2H), 3.14 (d, 2H, $J_{H\text{-}H}$ =6.6 Hz) 3.02 (s, 3H), 2.96 (s, 3H).

Synthesis of Chelated Metallacyclobutane 4. Compound **1** (0.515g) was dissolved in 15 ml of benzene in a 100 ml Schlenk flask. N,N-dimethyl-butenamide (0.16 g) was added dropwise through a gas-tight syringe. After the addition, the mixture was stirred at room temperature for half an hour. The resulting brown-reddish solution was removed off all the volatiles under high vacuum to give an analytically pure compound by NMR. The brown solid was redissolved in minimal amount of benzene, and pentane was added dropwise to precipitate the product as a yellow powder (0.3 g, 53%): ^1H NMR (300 MHz, C_6D_6) δ 3.79 (septet, 2H) 3.67 (m, 1H, β proton of the metallacycle), 3.23 (dd, 2H, $J_{H\text{-}H}$ =7.7 Hz), 2.93 (m, 1H, β proton of the metallacycle), 2.79 (dd, 2H, $J_{H\text{-}H}$ = 10.4 Hz), 2.623 (s, 6H, CH_3 of amide), 2.10 (s, 6H CH_3 of amide), 1.98 (s, 6H, CH_3 of alkoxide), 1.87 (s, 6H, CH_3 of alkoxide), 1.17 (d, 6H, CH_3 of isopropyl, $J_{H\text{-}H}$ = 6.83 Hz), 1.07 (d, 6H, CH_3 of isopropyl, $J_{H\text{-}H}$ = 6.83 Hz). ^{13}C NMR (75 MHz, C_6D_6) δ 186.4 (coordinated carbonyl), 150.2 (Ph), 150.4 (Ph), 127.0 ($J_{C\text{-}H}$ = 160 Hz, Ph), 124.1 ($J_{C\text{-}H}$ = 158 Hz, Ph), 81.3 ($J_{C\text{-}F}$ = 27 Hz, CF_3), 41.9 ($J_{C\text{-}H}$ = 124 and 126 Hz, CH_2), 38.6 (CH_3), 35.5 (CH_3), 34.9 ($J_{C\text{-}H}$ = 131 Hz, β carbon of the metallacycle), 27.1 (CH of isopropyl), 25.8 (CH_3 of isopropyl), 24.1 (CH_3 of isopropyl), 23.5 ($J_{C\text{-}H}$ = 140 Hz, α carbon of the metallacycle), 19.1 (CH_3 of alkoxide), 17.2 (CH_3 of alkoxide). Anal. Calcd for $MoC_{31}H_{43}F_{12}N_3O_4$: C, 44.03; H, 5.13; N, 4.97. Found: C, 44.10; H, 5.11; N, 4.88.

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Chapter 3

Metathetical Reactions of Ruthenium Carbene Complexes

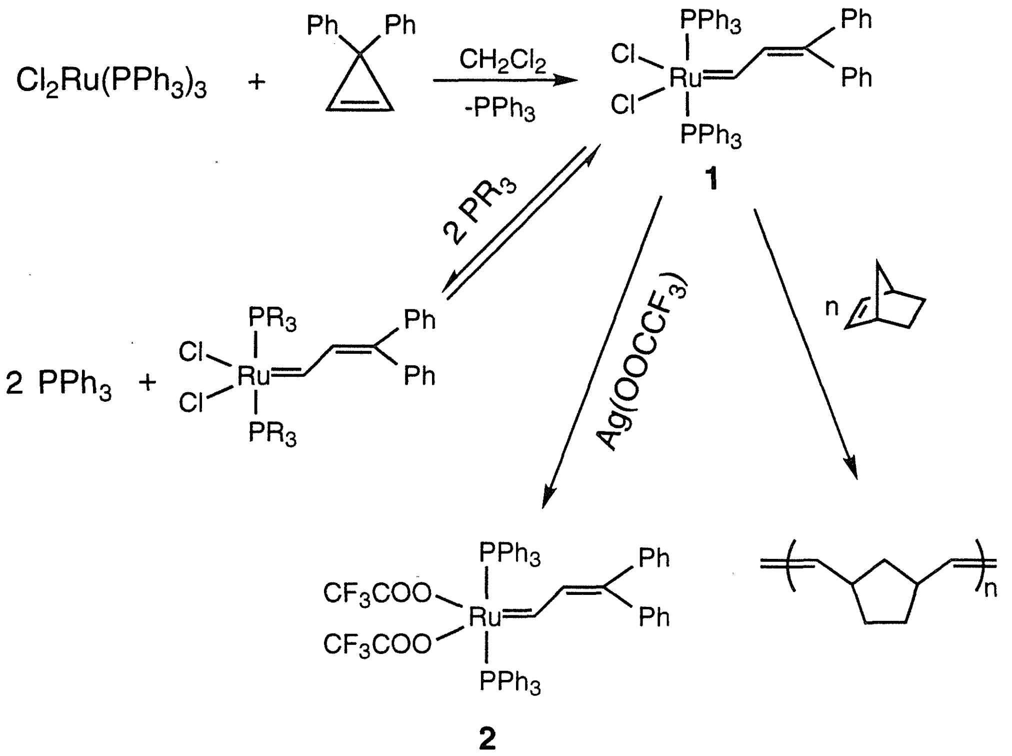
Introduction

Well-defined, high oxidation state, early transition metal alkylidene and metallacyclobutane complexes have been demonstrated to be extremely useful for the preparation of new materials via the ring-opening metathesis polymerization (ROMP) of cyclic olefins and in the synthesis of bioactive molecules through the ring-closing metathesis (RCM) or Wittig-like reactions.[1,2] However, these complexes have limited tolerance to acidic proton and polar functional groups. In contrast, late metal carbene complexes, such as those based on ruthenium, are stable to MeOH or H_2O and a variety of polar functional groups. Some ruthenium (II) salts, such as $RuCl_3$ and $Ru(H_2O)_6(Tos)_2$ have been shown to catalyze the ROMP of norbornene, 7-oxonorbornene and their derivatives in the aqueous media.[3] The mechanism of the polymerization is believed to involve a metal-carbene active species.[3]

In the literature, there are several known ruthenium carbene complexes, such as ruthenium vinylidene and ruthenium methylidenes, which were synthesized by the rearrangement of the alkyne complexes and by the reaction of diazo alkane with coordinately unsaturated species, respectively.[4,5] Unfortunately, most of these complexes are 18e species with strong π-acceptor ligands bound to the metal center and are inactive toward the metathesis of normal olefins.

Although the methodologies for the synthesis of early transition metal alkylidene complexes have been well documented based on α-proton abstraction, alkylidene transfer reactions via phosphorane and the ring-opening of cyclopropenes,[6,7,8] little had been successful for applying the similar methodologies in the synthesis of late metal carbenes. Until very recently, the methodologies of ring-opening cyclopropenes and carbene transfer via diazoalkanes have been used successfully in the Grubbs lab for the preparation of active late transition metal carbene complexes, such as ruthenium, rhodium and iridium carbenes.[9] As shown in Scheme 1, ruthenium vinyl carbene complex **1** was synthesized by the reaction of a precursor with 3,3-diphenylcyclopropene.[9] Complex **1** also catalyzed the living ROMP of norbornene. This is the first time that a late transition metal carbene complex was observed to react directly with an olefin in a [2+2] metathesis fashion. However, there are several fundamental questions associated with **1** and **2** which remain unanswered, such as the identity of active species during the metathesis reaction and the nature of the metal carbene bond. For example, the experimental observations are (i) The increase of steric bulk of the phosphine ligand enhances the metathesis reactivity of **1**[9(c)] and (ii) the presence of excess phosphine slows down the rate of metathesis.[10] The rate of the reaction was also greatly accelerated when one of the phosphines was removed by complexing with copper chloride.[11] These experimental evidences suggest that the phosphine dissociates during the reaction.[10]

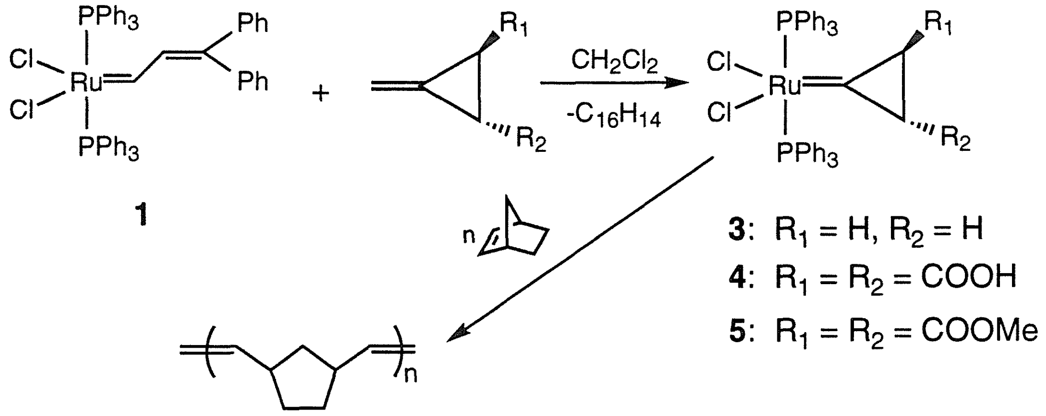
In this chapter, the metathesis reactivities of complexes **1** and **2** with strained acyclic olefins and functionalized acyclic olefins will be explored, with the goal of understanding more about the fundamental aspects of the ruthenium carbene complexes. This investigation may lead us to gain some insights into the reaction mechanism of **1** and **2** in metathesis.



Scheme 1. Formation of Ruthenium Vinyl Carbene Complexes through the Ring-Opening of 3,3-diphenylcyclopropene.

Results and Discussion

Reaction of Complex 1 with Methylenecyclopropane, Methylenecyclobutane and Their Derivatives. Although catalyst **1** has been shown to be an active catalyst for the living ROMP of norbornene,[9(b)] it is unreactive with unstrained olefins. We reasoned that this lack of reactivity may originate from the electronic properties of the metal center. Therefore, only strained-cyclic olefins, which are both good π donors and acceptors will react with **1** in a process favored thermodynamically by the release of ring-strain energy. On the basis of this consideration, we looked into some reactive acyclic olefins.

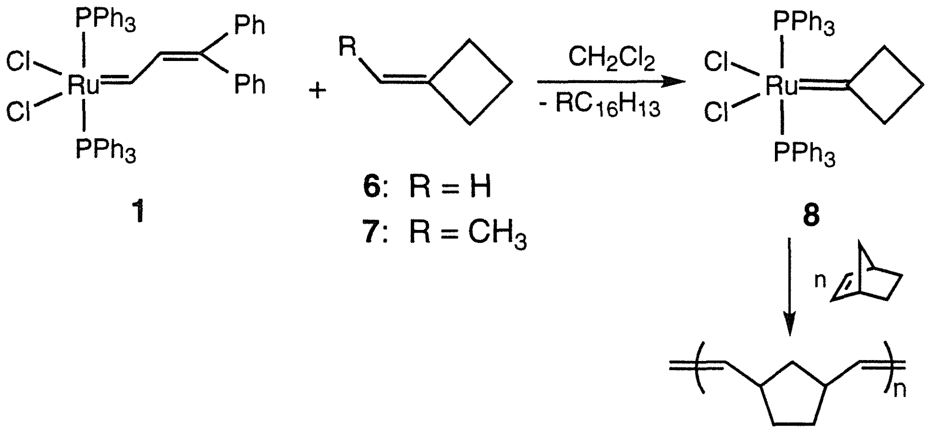


3: $R_1 = H, R_2 = H$
4: $R_1 = R_2 = COOH$
5: $R_1 = R_2 = COOMe$

(1)

As shown in eq 1, when **1** was treated with 1.1 equiv of methylenecyclopropane in CH_2Cl_2, a quantitative conversion of the starting material to complex **3** was observed by ^1H NMR spectroscopy. **3** was also isolated and characterized spectroscopically. Analysis of ^{13}C NMR data reveals that the tetrasubstituted carbene carbon resonances at 306.5 ppm, which is more down field than that of the vinylcarbene **1** (288.9 ppm). 3-methylenecyclopropane-trans-1,2-dicarboxylic acid can also react with **1** in a similar fashion in THF to form complex **4**. The chemical shift of H_β was observed at 1.44 ppm by ^1H NMR spectroscopy.[12] We found when **1** was treated with two equiv of the corresponding 3-methylenecyclopropane-trans-1,2-dimethyl dicarboxylate[13] in CH_2Cl_2, a clean formation of complex **5** was observed by ^1H NMR spectroscopy and the chemical shift of the H_β in complex **5** was at 1.79 ppm. The ^{31}P NMR spectroscopy reveals a singlet resonance at 29.6 ppm. **3** can also be used to initiate the polymerization of norbornene in a living fashion. For example, when 11 equiv of norbornene was added to a solution of **3** in CH_2Cl_2, a resonance (quartet) corresponding to the propagating species of polynorbornene was observed at 17.6 ppm by ^1H NMR spectroscopy. Therefore, complexes **4** and

5 might be used as initiators in the synthesis of narrow dispersed polymers having carboxylate functionality at the end of the polymer chain.



(2)

Catalyst **1** can also react with methylenecyclobutane as shown in eq 2. When a 0.01M solution of **1** was treated with two equiv of methylenecyclobutane in CD_2Cl_2 at room temperature, the formation of complex **8** was observed by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. The tetrasubstituted carbene signal was observed at 344.5 ppm by ^{13}C NMR spectroscopy. **1** can also react with a trisubstituted olefin, such as ethylenecyclobutane **7** (eq 2). The metathesis of a trisubstituted olefin is quite unusual even in the use of strong electrophilic high oxidation state alkylidene complexes.[14] **8** can also be used to initiate a living ROMP of norbornene similar to that of **1**.

The structure of **8** was also confirmed by a single crystal X-ray analysis. The typical bond lengths and angles are listed in Table 1. The length (1.830(4) Å) of the ruthenium carbon double bond is shorter than that (1.887(7) Å) of **1**, which indicates a relatively stronger bond for **8**. This can be understood from the absence of adjacent p-orbital in **8**, as present in complex **1** to compete with the metal d_{π}-orbital for the same bonding p-orbital on the carbene carbon. The structure of **8** is a distorted trigonal bipyramid (Figure 1) with the two chlorides

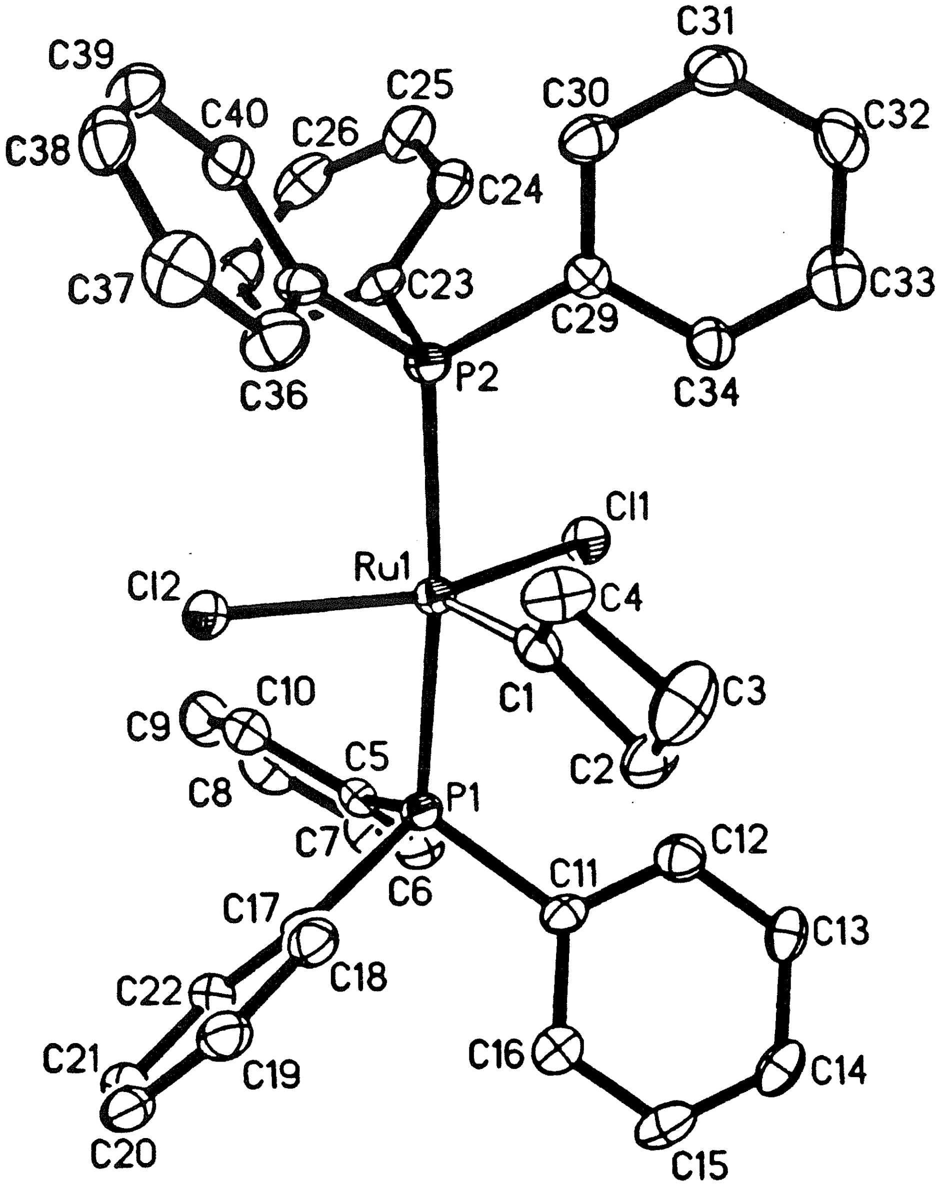


Figure 1. ORTEP plot of Cl2Ru(PPh3)2(C(CH2)3) **8**. Thermal ellipsoids are drawn at the 50% probability.

Table 1. Selected Bond Lengths an Angles for **8**.

Bond lengths (Å)			
Ru(1)-P(1)	2.386(1)	Ru(1)-P(2)	2.375(1)
Ru(1)-Cl(1)	2.370(1)	Ru(1)-Cl(2)	2.352(2)
Ru(1)-C(1)	1.830(4)	P(1)-C(5)	1.826(4)
P(1)-C(11)	1.837(4)	P(1)-C(17)	1.833(4)
P(2)-C(29)	1.843(4)	P(2)-C(35)	1.836(5)
Bond Angles (deg)			
Ru(1)-C(1)-C(2)	133.8(4)	Ru(1)-C(1)-C(4)	134.6(4)
P(1)-Ru(1)-P(2)	170.9(1)	P(1)-Ru(1)-Cl(1)	90.4(1)
P(2)-Ru(1)-Cl(1)	87.4(1)	P(1)-Ru(1)-Cl(2)	88.9(1)
P(2)-Ru(1)-Cl(2)	88.7(1)	Cl(1)-Ru(1)-Cl(2)	150.4
P(1)-Ru(1)-C(1)	94.0(2)	P(2)-Ru(1)-C(1)	95.2(2)
Cl(1)-Ru(1)-C(1)	104.5(1)	Cl(2)-Ru(1)-C(1)	105.1(1)
Ru(1)-P(1)-C(5)	109.8(2)	Ru(1)-P(1)-C(11)	122.2(1)
C(5)-P(1)-C(11)	102.7(2)	Ru(1)-P(1)-C(17)	113.5(2)
C(5)-P(1)-C(17)	104.9(2)	C(11)-P(1)-C(17)	101.9(2)
Ru(1)-P(2)-C(23)	106.5(2)	Ru(1)-P(2)-C(29)	118.3(2)
C(23)-P(2)-C(29)	105.3(2)	Ru(1)-P(2)-C(35)	122.1(2)
C(23)-P(2)-C(35)	101.3(2)	C(29)-P(2)-C(35)	101.0(2)
C(2)-C(1)-C(4)	91.6(3)	C(1)-C(2)-C(3)	88.7(4)
C(2)-C(3)-C(4)	90.8(4)	C(1)-C(4)-C(3)	88.6(4)

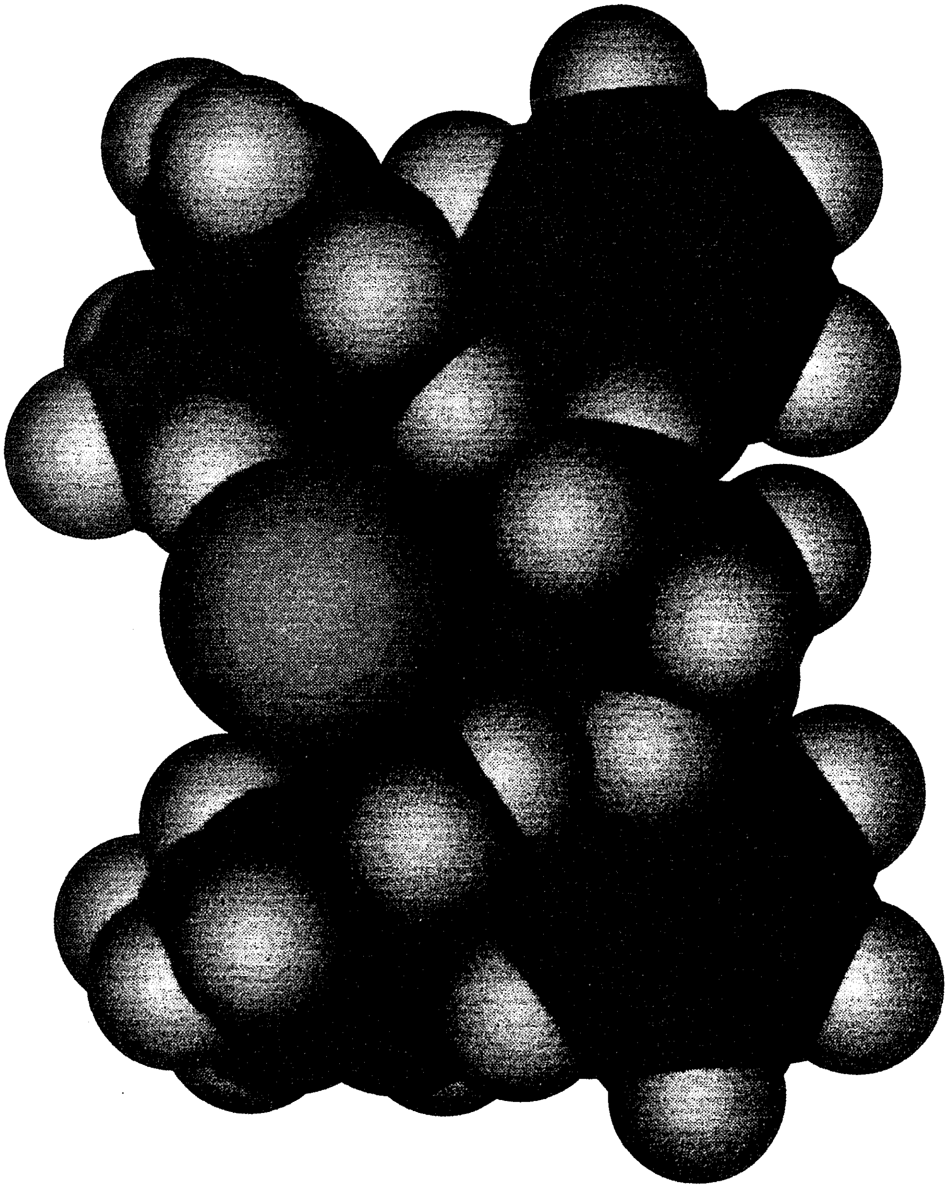


Figure 2. The 3-dimensional view of **8** from the direction bisecting Cl-Ru-C angle.

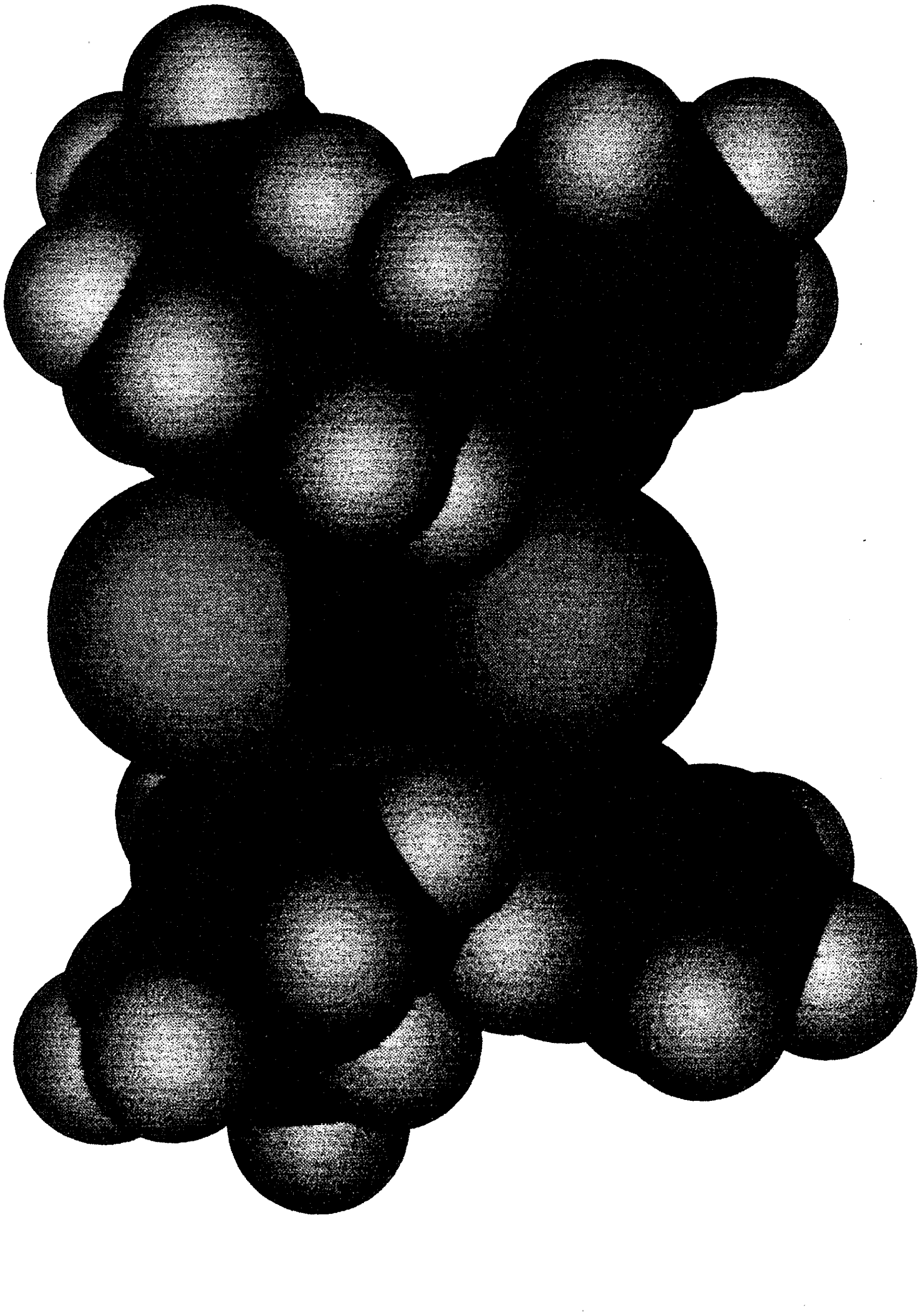
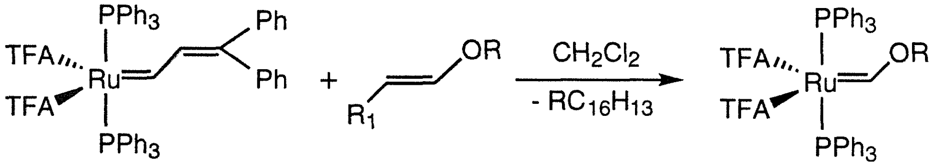


Figure 3. The 3-dimensional view of **8** from the direction bisecting Cl-Ru-Cl angle.

and the carbene carbon in the equatorial plane and the two phosphines in the axial positions, bending slightly away from the carbene carbon. The angles between phosphines and carbons are slightly larger than 90° (95.2(2)° and 94.0(2)°). The cyclobutane ring bisects the angle of P-Ru-Cl (the dihedral angel Cl_1-Ru-C_1-C_4 is -59.1(0.5)°). This is a result of the crystal packing force and that the cyclobutyl ring tilts in order to minimize the steric interaction of CH_2 groups with the bulky triphenyl phosphine ligands.[15] Figure 2 and 3 show two views of a 3-dimensional space filling drawing of **8** based on its crystal structure data. Apparently, the open coordination site is *trans* to the carbene and the incoming olefin has to bind *trans* to the carbene; therefore, it is difficult to form a metallacyclobutane.[16] This may partially explain why complex **1** is much less reactive toward normal olefins. The reaction of **1** with strained olefin is favored by the release of strain energy upon coordination. Kinetically, reactions of **1** with methylenecyclobutane and methylenecyclopropane are favored because the activation energies of the reactions are lowered due to the release of angle-strain energy in the transition state.[17] The thermodynamic driving force for these reactions are the release of exo-double bond strain energy of methylenecyclobutane and methylenecyclopropane.[17]

Metathesis of Vinyl Ethers and Ethyl Vinyl Acetate with 1 and 2. Both terminal and internal vinyl ethers can be metathesized by complexes **1** or **2**. When a 0.01 M solution of **2** in CD_2Cl_2 was treated with 2 equiv of ethyl vinyl ether for several hours, a yellow solution resulted (eq 3). The formation of the new carbene species was observed by ^1H NMR spectroscopy of a triplet resonance (H_α) at 14.49 ppm (J_{H-P} = 4.71 and 4.86 Hz). The slight difference of the two coupling constants reflected that the two phosphines were not perfect equivalent with respect to the carbene proton. ^{13}C NMR spectroscopy revealed the resonance of the alkoxy substituted carbene carbon at 297.5 ppm and a single peak was observed at 44.2 ppm by ^{31}P NMR spectroscopy.

However, when complex **1** was treated with ethyl vinyl ether in a similar manner, only the organic product 1,1-diphenyl-1,3-butadiene was observed from the metathesis and no new carbene species were detected by ^{1}H NMR spectroscopy. The reaction was not complete even with prolonged reaction time and heating conditions. The ethoxy carbene species derived from **1** was most likely unstable and decomposed during the course of the reaction. The decomposition of the alkoxy substituted carbenes derived from **1** was believed through a bimolecular decomposition pathway[18]. This was further suggested by the following experiment: A sealed NMR tube containing 0.02 M of **1** and 1.2 equiv of ethyl vinyl ether was left at room temperature for 48 hours and the volatiles were collected by vacuum transfer technique. A clean formation of 1,2-diethoxyethylene was observed by ^{1}H NMR spectroscopy in 50% conversion relative to the starting material. This observation supported the bimolecular decomposition mechanism. The organometallic species from the decomposition might be some dimeric species and were not identified.



2

R_1 = H or CH_3

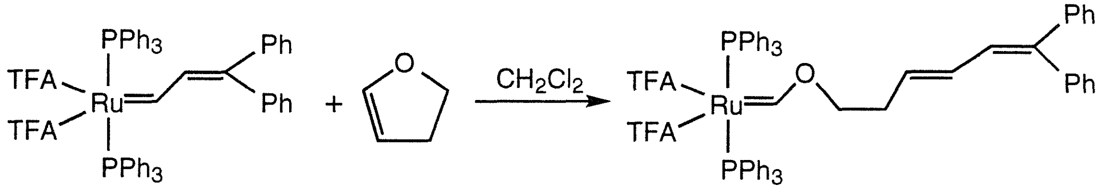
9: R = Et, CH_2Ph

10: R = $COCH_3$

(3)

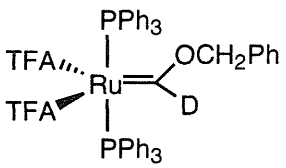
Complex **2** can also react with ethyl vinyl acetate in a metathesis fashion. When a 0.01 M solution of **2** in CD_2Cl_2 was treated with 1.5 equiv of ethyl vinyl acetate, a new carbene species, a triplet resonance, was observed at 13.75 ppm

($J_{H\text{-}P}$ = 1.6 Hz) by ^{1}H NMR spectroscopy. However, the reaction proceeded much slower than that of **2** reacting with ethyl vinyl ether. The resulting carbene decomposed during the reaction since the intensity of the resulting carbene proton resonance was also much lower than that expected and the decomposition was also suggested by the complex ^{31}P NMR spectrum. Complex **2** can also react with 2,3-dihydrofuran to form a ring-opened product as shown in eq 4. Two triplet resonances were observed at 14.49 ppm ($J_{H\text{-}P}$ = 4.96 Hz) and 14.55 ppm ($J_{H\text{-}P}$ = 4.9 Hz) corresponding to the carbene proton of **11**. There was, however, no further productive metathesis even with prolonged reaction time or heating conditions. In contrast to the high oxidation state complexes,[19] the electron withdrawing ligand stabilized hetero substituted ruthenium carbenes.

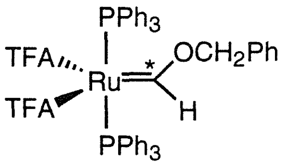


2 **11** (4)

Observation of the Rearrangement of the Alkoxy Carbene Complex. When an alkoxycarbene complex, such as **9** generated by the reaction of **2** with vinyl alkyl ether was left at room temperature, the carbene resonance slowly disappeared and a hydride resonance was observed at -17.5 ppm by ^{1}H NMR spectroscopy. After several days at room temperature, slow disappearance of the hydride resonance was also observed. The increase of the temperature accelerated this process. In order to understand this rearrangement, both deuterium and ^{13}C labeled complexes **12** and **13** were synthesized. Therefore, the reaction can be followed by ^{2}H and ^{13}C NMR spectroscopy.

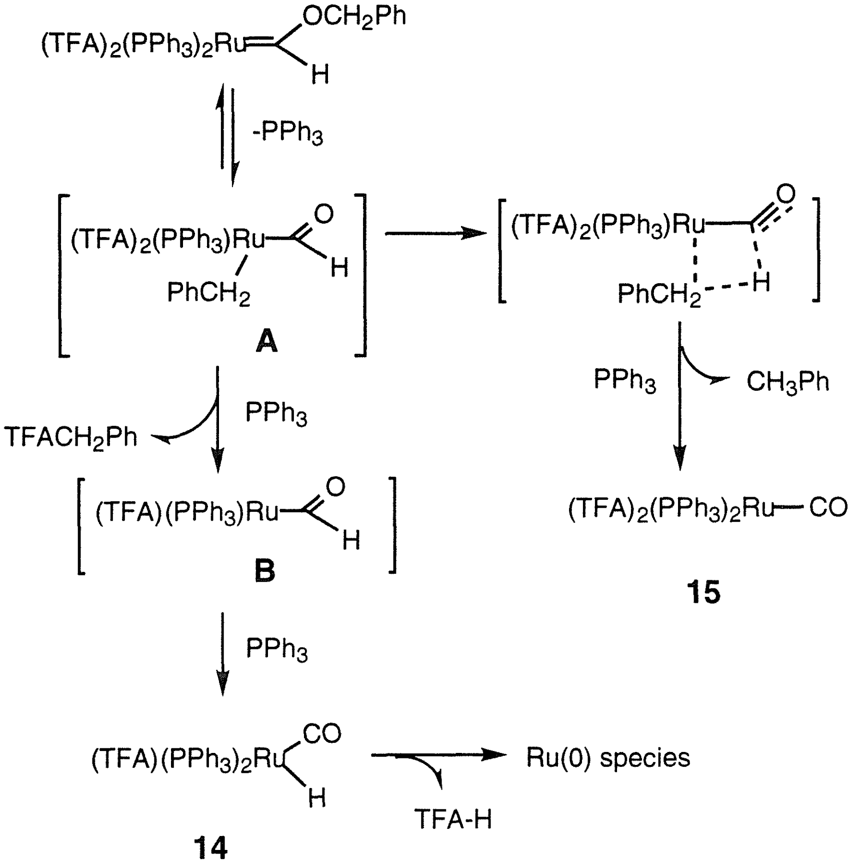


12



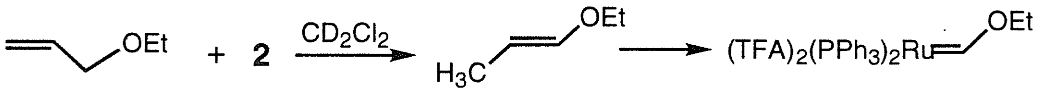
13

When a sample containing **12** was left at room temperature for 12 hours, we observed the formation of ruthenium hydride species (δ -17.5 ppm by ^{2}H NMR) and the formation of ruthenium carbonyl species by IR (1969.8 cm^{-1}) spectroscopy. Benzyl trifluoroacetate (m/e = 204) and $PhCH_2D$ (m/e = 92) were identified by GC/MS. When **13** was left at room temperature for 24 hours, ruthenium carbonyl resonances were observed at δ 205.1 (**14**, $J_{C\text{-}P}$ = 14.4 Hz), δ 204.8 (**15**, $J_{C\text{-}P}$ = 14.1 Hz) and 203 - 203.5 (multiplets) by ^{13}C NMR spectroscopy. On the basis of these observations, one of the possible decomposition pathways was proposed in Scheme 2. The first step involved a β–alkyl elimination to generate a ruthenium (IV) high energy formyl intermediate **A**, which can rapidly eliminate a benzyl trifluoroacetate to yield a Ru (II) formyl complex **B**, which further undergoes facile rearrangement to a ruthenium carbonyl complex **14**. **A** can also undergo reductive elimination of an alkane to form a carbonyl complex **15**.[20]

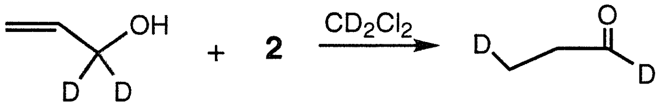


Scheme 2. Possible Decompositon Pathways of Bis-trifluoroacetate Bis-triphenylphosphine Ruthenium Alkoxy Carbenes.

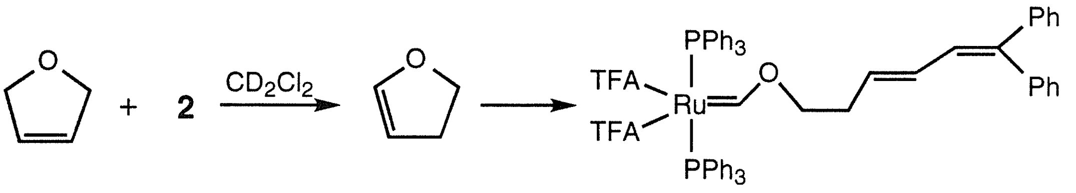
Observation of the Isomerization of Allylic Ether and Allylic Alcohol. Complex $Ru(H_2O)_6(Tos)_2$ not only has been known to be an active catalyst for the ring-opening metathesis polymerization of 7-oxonorbornene and its derivatives in polar or aqueous media, but also has been shown to catalyze the isomerization of allylic ether or alcohols in a protic solvent.[21] The mechanisms for the isomerization of olefins may involve the initial formation of a metal allyl hydride or metal alkyl hydride intermediates.[22] We have conducted the reaction of complex **2** with allylic ethers or allylic alcohols as shown in eqs 5, 6 and 7. When a 0.01 M solution of **2** in CD_2Cl_2 was treated with 2 equiv of allyl ethyl ether for 4 hours at 40 °C, all the starting olefins were isomerized to ethyl 1-propenyl ether and the metathesis product, ethoxy carbene complex was also observed evidenced by the resonance at 14.5 ppm. Similarly, when a 0.01 M solution of **2** was treated with 20 equiv of 2,5-dihydrofuran in CD_2Cl_2 at room temperature overnight, 88% of the starting material was converted to 2,3-dihydrofuran. When a 0.01 M solution of complex **2** in CD_2Cl_2 was treated with 20 equiv of 1,1-dideutero allylic alcohol at room temperature for 24 hours, a clean formation of 1,3-dideutero propyl aldehyde was observed in 67% conversion.[22(b)]



(5)



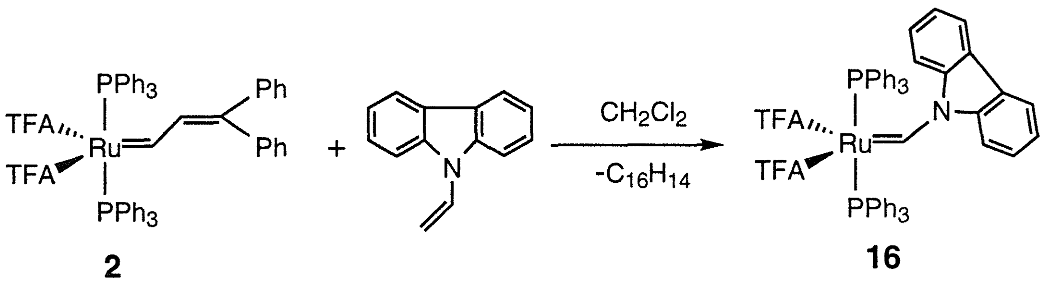
(6)



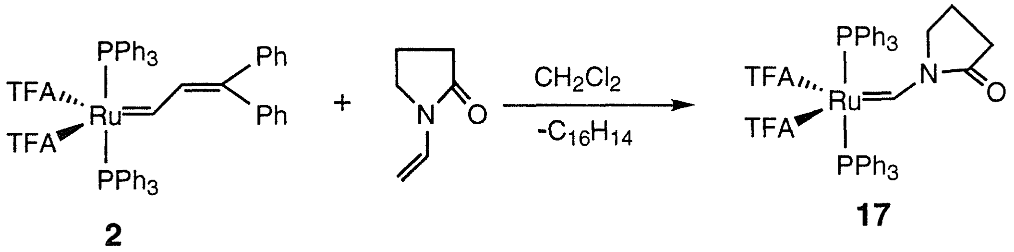
(7)

11

Reaction of Alkylamino Substituted Terminal Olefins with Complex 2. Complex **2** can react with 9-vinylcarbazole or 1-vinyl-2-pyrolidinone in CH_2Cl_2 to yield the corresponding nitrogen substituted carbene species (eqs 8 and 9). When a 0.015 M solution of **2** in CD_2Cl_2 was treated with 4 equiv of 9-vinylcarbazole for 48 hours at 40 °C, a new carbene resonance was observed at 13.47 ppm ($J_{H\text{-}P}$ = 11.5 Hz) by ^1H NMR spectroscopy and 253.1 ppm by ^{13}C NMR spectroscopy. The compound was isolated and fully characterized spectroscopically. In a similar manner, 1-vinyl-2-pyrolidinone can also react with complex **2** to yield the corresponding carbene species characterized by ^1H NMR spectroscopy (δ 14.33; $J_{H\text{-}P}$ = 1.93 and 1.66 Hz). However, these reactions proceed much slower than those of the corresponding alkyl vinyl ether and ethyl vinyl acetate reacting with **2**, which are probably due to the lower electron donating ability of the nitrogen in this particular situation, caused by the extended electron delocalization on to phenyl ring as in vinylcarbazole and the delocalization over carbonyl as in vinylpyrolidinone. Faster reaction would be anticipated if **2** were treated with alkylenamines.



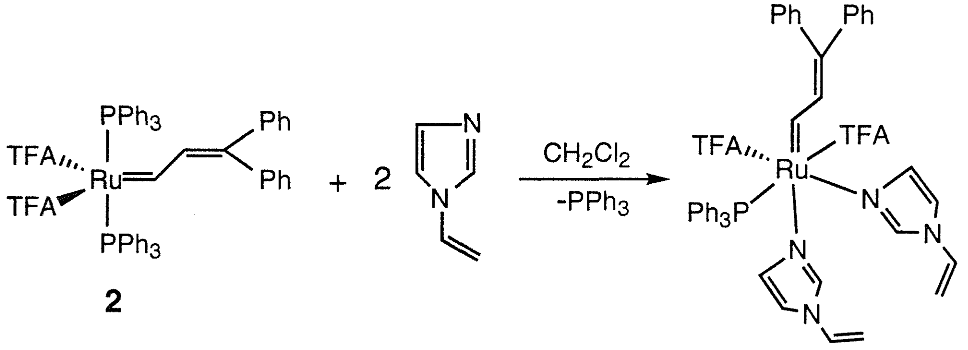
(8)



(9)

Complex **2** can also react with 1-vinylimidazole (eq 10). However, instead of the expected metathesis reaction, one imidazole coordinates to the metal center and the other displaces one of the phosphines. The structure of the complex **23** was supported by ^{1}H and ^{13}C NMR data, and was further confirmed by both elemental analysis and high resolution mass spectroscopy data. For example, when a 0.01 M solution of **2** in methylene chloride was treated with 2 equiv of vinyl imidazole, a new vinylcarbene resonance was observed immediately at δ 19.65 (H_α, $J_{H\text{-}P}$ = 11.7; 10.1 Hz), δ 8.43 (H_β, $J_{H\text{-}H}$ =12.97 Hz) by ^{1}H NMR spectroscopy. The resonances at δ 47.6, δ -75.5 were also observed by

^{31}P and ^{19}F NMR spectroscopy respectively. The spectroscopic data supports the structure of **18** (Scheme 3) with the imidazole *trans* to the carbene. After 24 hours, 20 equiv of vinyl imidazole was added and a triplet resonance was observed at 18.5 ppm ($J_{H\text{-}P}$ = 12.8 Hz) and a doublet at 8.34 ppm (H_β, $J_{H\text{-}H}$ = 3.76 Hz). The coupling pattern of the proton spectrum indicated that only one phosphine was bound to the metal center. This was further supported by ^{31}P NMR data, which showed a singlet resonance at 41.7 ppm and free phosphine signal at -4.9 ppm. The ^{13}C NMR data indicated that the phosphorus was *cis* to the carbene ($J_{C\text{-}P}$ = 13.83 Hz). The ^{19}F NMR spectrum showed two resonances at -75.20 and -75.98 ppm.

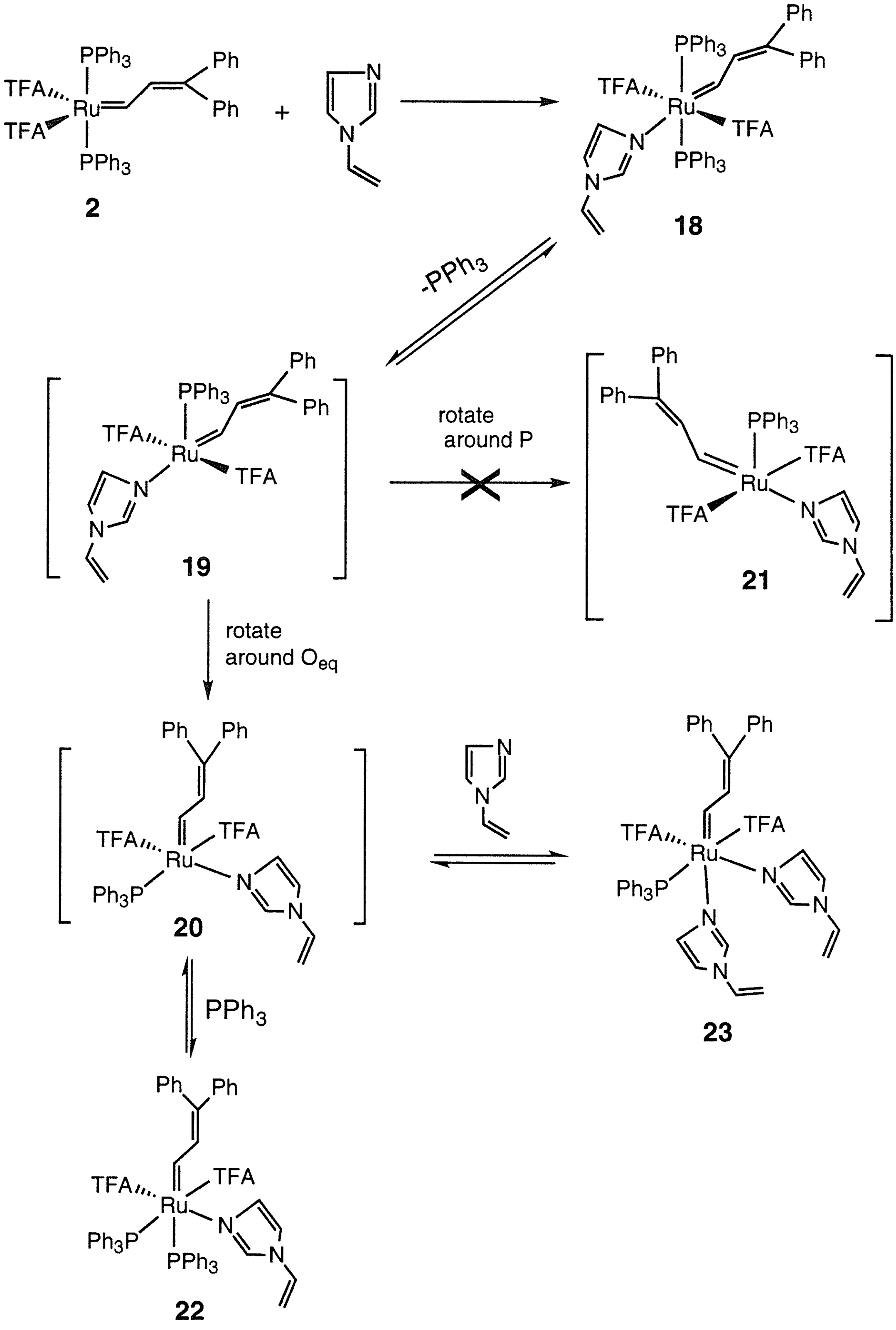


2

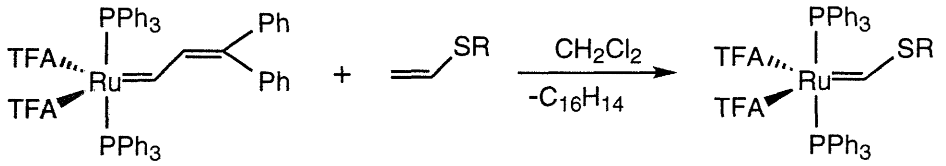
23

(10)

Scheme 3


PPh3
TFA
Ru
TFA
PPh3
Ph
Ph
2
+
N
N
18
-PPh3
19
rotate around P
21
rotate around Oeq
20
PPh3
22
23

On the basis of the experimental data, we have proposed the reaction mechanism as shown in Scheme 3. The first step involves the coordination of base to the metal center *trans* to the carbene forming an octahedral complex **18**, which undergo extremely fast exchange of phosphine in the NMR time scale to form intermediate **19**, which can undergo facile Berry pseudo rotation[23] around O to form intermediate **20**. Intermediate **20** can be trapped either by phosphine or vinylimidazole to form **22** or **23**. In the presence of large excess of vinyl imidazole, **23** is the only product observed. Pseudo rotation about P can be ruled out, since the resulted intermediate **23** has two equivalent trifluoromethyl groups. The finding of aromatic amine displacement of the phosphine is significant in terms of understanding the olefin metathesis mechanism catalyzed by this type of ruthenium carbene complex. We can easily envision that an olefin is likely to react with **1** or **2** in a similar manner by coordinating to the metal first in the direction *trans* to the carbene, then lose one of the phosphines to generate the active species. In order to further probe the reaction mechanism, future work may involve the confirmation of the structure of **23** by a single crystal X-ray analyses and reaction of **2** with imines, which are even closer electronically to olefin than the aromatic nitrogen bases



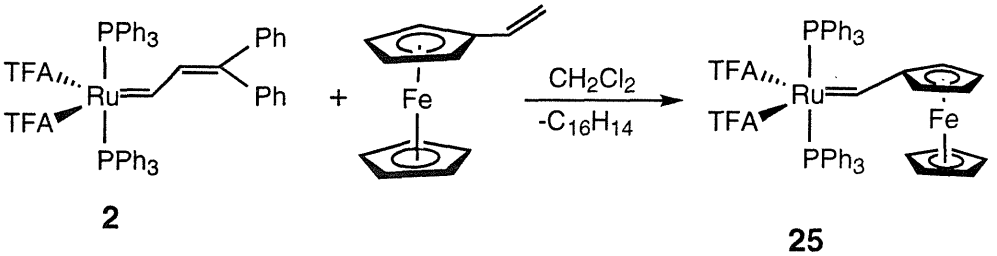
R = Ph or CH_2Ph

2

24. R = CH_2Ph

(11)

Reaction of Complex 2 with Vinyl Sulfide. When a 0.01 M solution of **2** was treated with the commercially available phenyl vinyl sulfide at 40 °C for several hours, a new carbene resonance was observed at 16.3 ppm. However, the reaction was sluggish and the conversion was low. Prolonged reaction time resulted in the slow conversion of the desired products to other species evidenced by the appearance of messy resonances in the carbene region. We reasoned that this kind of reactivity might be related to the electronic effect of the phenyl group on the sulfur atom. Therefore, benzyl vinyl sulfide[24] was synthesized. The reaction of complex **2** with benzyl sulfide was quite clean (eq 11). The reaction was completed at room temperature in 24 hours by stirring of **2** in the presence of excess benzyl vinyl sulfide. The alkylthiol substituted carbene complex **24** was stable at room temperature and was characterized by proton (δH_α, 17.43 ppm), carbon (δC_α, 306.6 ppm) and phosphorus (32.53 ppm) NMR spectroscopy as well as high resolution mass spectroscopy.



2 **25** (12)

Reaction of Complex 2 with Other Functionalized Terminal Olefins. Accumulated evidences indicated that the reactivity of **2** with olefins depends strongly on the hetero substitutents of the olefins and the electron donating group activates the adjacent double bond to undergo the metathesis reaction with **2**. With this idea in mind, vinyl ferrocene whose double bond activated by the electron rich Cp rings and vinyl silane or vinylsiloxane whose double bond activated by the more electron donating silicon atom should react with **2** in a metathesis fashion. This is indeed the case. When a 0.01 M solution of **2** in CD_2Cl_2 was reacted with 2 equiv of vinyl ferrocene at 40 °C for 30 hours, a 36% conversion of the product was observed by ^1H NMR spectroscopy (δ 18.9 ppm).

Extended reaction time did not drive the reaction further. It would be interesting to look at the reactions of other derivatives of **2** that possess different bulky phosphine ligands with vinyl ferrocene. The reactions of **2** with silyl substituted olefins were also explored. Vinyl trimethylsilane or vinyl trimethylsiloxane reacted rapidly with **1** or **2** to give the initial organic product from the metathesis as 1,1-diphenyl-1,3-butadiene. However, the resulting carbenes decomposed to unidentified products.

Conclusion

In summary, the studies of metathesis of acyclic olefins by **1** and **2** have revealed that these complexes are active in metathesizing strained acyclic olefins and functionalized olefins as well as isomerizing alkyl allylic ether and allylic alcohols. The reactions are favored both kinetically and thermodynamically by the release of double bond strain energy. Complex **2** with more electron withdrawing trifluoro acetate ligand has higher reactivities with functionalized olefins. More electron donating hetero atoms activate the olefins for metathesis with **2**. The reactions of **2** with α-hetero substituted olefins suggest that the carbene carbon is electron deficient. The α-alkoxy substituted complex of type **1** undergoes a bimolecular decomposition, while the α–alkoxy substituted carbene complexes of type **2** decomposes through a β–alkyl elimination by the formation of ruthenium carbonyl species as a driving force. Reactions of **2** with aromatic amine Lewis bases reveal that the phosphine is labile and the Lewis bases initially coordinate trans to the carbene. Although the hetero substituted ruthenium carbene complexes are not active catalysts in ROMP or metathesis of other olefins, they are a new type of complexes, which offer the potential to further modify the surrounding ligands; for example, the incorporation of CO into the coordination sphere of the metal center, we may find uses in organic synthesis.[25] Future work will involve the reaction of other types of carbene complexes that have different phosphine ligands with various functionalized acyclic olefins. In order to probe the reaction mechanism, 2-alkenyl imidazole or 2-alkenyl pyridine may be used to react with the complex of type **2** with the hope of forming a carbene-olefin or metallacyclobutane intermediates. Detailed molecular orbital (MO) calculations on **1** and **2** or other related complexes should also be carried out.

Experiment

General Procedures. All manipulations of air- and/or moisture-sensitive compounds were carried out using standard Schlenk or vacuum-line techniques or in a N_2-filled drybox. Argon was purified by passage through a column of BASF RS-11 (Chemlog) and Linde 4Å molecular sieves. NMR spectra were recorded on a JEOL GX-400 MHz (399.65 MHz ^1H; 100.4 MHz ^{13}C; 61.25 MHz ^2H; 161.85 MHz ^{31}P) spectrometer or on a QE Plus-300 MHz (300.1 MHz ^1H; 75.33 MHz ^{13}C) spectrometer. The chemical shifts of the phosphorus and fluorine resonances were determined relative to the phosphoric acid and trichlorofluoro methane standards respectively. Infrared spectra were recorded using a Perkin-Elmer 1600 series FT-IR spectrometer. Gas chromatography was performed using a Hewlett-Packard HP 5890 Series II Gas Chromatography equipped with 30 mm SE-30 (OV-1) capillary column and a HP 3396 Series II integrator. Elemental analysis was performed by Oneida Research Corporation microanalysis group. Low-resolution mass spectroscopy analyses were performed on a Hewlett-Packard model 5970 mass selective detector in conjunction with a Series 5890 GC equipped with a 15 mm capillary column and a Hewlett-Packard model 3390A integrator. High-resolution FAB mass spectroscopy analyses were performed at Mass Spectrometry Facility at the University of California, Riverside.

Materials. Catalyst **1** and **2** were synthesized according to the published procedure. Methylenecyclobutane and methylenecyclopropane were distilled from lithium aluminum hydride. CH_2Cl_2, DMSO were distilled from CaH_2. All the other common solvents used were distilled from Na-benzylphenone ketyl. All the other materials were either dried and distilled or degassed before use. Deuterated compounds were purchased from Cambridge Isotope Lab. All the other commercially available compounds were purchased from Aldrich chemical company.

Preparation of Bis(triphenylphosphine)dichlororuthenium Cycloproplene Carbene 3. Inside the drybox, complex **1** (102 mg, 0.138 mmol) was dissolved in 5 ml of CH_2Cl_2. The flask was brought out of the drybox and connected to a vacuum line. Methylenecyclopropane (46.6 mg, 0.86 mmol) was condensed into the schlenk flask at 77K. The reaction mixture was allowed to warm up to room temperature and stirred for 3 hours. During this period, the solution started to change from dark green to red. The reaction mixture was then concentrated and pentane was added dropwise to precipitate a red powder. The supernatant was cannulated away, and the residue was washed twice with 2x5 ml of pentane and dried in vacuo. (49 mg, 57%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.52 (m, 12H), 7.46 (m, 12H), 7.38 (m, 12H), 0.622 (s, 4H, β–proton). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 306.5 (Pseudo quartet, J_{C-P} = 13.8, 15.8 Hz) 134.9 (t, J_{C-P} = 5.9 Hz), 132.4 (t, J_{C-P} = 20.7 Hz, quartnary carbon of Ph) 130.4, 128.5 (t, J_{C-P} = 3.9, 4.9 Hz) 31.6 (t, J_{C-P} = 6.7 Hz, CH_2 of cyclopropyl). ^{31}P NMR (161.85 MHz, CD_2Cl_2) δ 29.95.

Preparation of Bis(triphenylphosphine)dichlororuthenium Cyclobutylene Carbene 8. Inside an N_2-filled glove box, complex **1** (105.7 mg, 0.1189 mmol) was weighed into a small schlenk flask and dissolved in 5 ml of methylene chloride. Methylenecyclobutane (55 ul, 0.6 mmol) was added via a gas-tight syringe under stirring. The flask was capped with a rubber septum and brought out of the drybox. The solution was stirred at 30 °C for 0.5 hour and then at room temperature for 4.5 hours. All the volatiles were removed under vacuum and the residue was dissolved in minimal amount of CH_2Cl_2, then pentane was added dropwise via a cannular to precipitate a red powder. The supernatant was cannulated away, and the solid was washed twice with pentane and dried by vacuum (60 mg, 62%). X-ray quality crystal may be obtained by slow diffusion of pentane into CH_2Cl_2. ^1H NMR, (CD_2Cl_2) δ 7.55 (m, 12H, Ph), 7.46 (m, 12H, Ph), 7.39 (m, 12H, Ph), 2.66 (t, $J_{H\text{-}H}$ = 7.42 Hz, Cyclobutyl), 2.31 (quartet, $J_{H\text{-}H}$ = 7.42 Hz). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 344.49 (t, $J_{C\text{-}P}$ = 10.5 Hz), 135.06 (t, $J_{C\text{-}P}$ = 5.56, 5.42 Hz), 132.08 (t, $J_{C\text{-}P}$ = 20.3 Hz), 130.38, 128.42 (t, $J_{C\text{-}P}$ = 4.36 Hz), 68.09 (t, $J_{C\text{-}P}$ = 7.32 Hz, β–carbon of cyclobutyl), 18.44 (γ-carbon of cyclobutyl). ^{31}P NMR (161.85 MHz, CD_2Cl_2) 30.1.

General Procedure for the NMR Tube Reactions. In the drybox, complex **1** or **2** was weighed into an NMR tube and dissolved into 0.5~0.6 ml CD_2Cl_2. The tube was capped with a rubber septum and calculated amount of olefins was added via a gas-tight syringe. The tube was then shaken vigorously and brought out of the drybox. The tube was either left standing at room temperature or put into a preheated oil bath at the desired temperature. The reaction was monitored by ^1H NMR spectroscopy at different time intervals.

Preparation of Ethylenecyclobutane 7. In the drybox, ethylenetriphenylphosphorane (4.15, 14.3 mmol) was weighed into a 100 ml 3-necked round bottom flask. The flask was capped with rubber septa and brought out of the box, then 25 ml dry DMSO was added. Cyclobutanone (1.06 ml, 14.2 mmol) was degassed and dissolved in 3 ml DMSO was added into the phosphorane dropwise via a cannular in 20 minutes. As the addition continued, the solution started to turn orange and a precipitate formed. The precipitate redissolved again as the reaction continued. After addition, the mixture was stirred at room temperature for 0.5 hours. All the volatiles were vacuum-transferred into a flask equipped with a Teflon valve. The compound collected was washed with H_2O and dried with $MgSO_4$, then vacuum-transferred again. Pure compound (690 mg, 59%) was obtained after distillation from NaH. ^1H

NMR (300 MHz, CD_2Cl_2) δ 5.06 - 5.09 (m, 1H, olefinic), 2.59 - 2.65 (m, 4H, CH_2), 1.92 (quintet, 2H, CH_2), 1.45 - 1.53 (m, 3H, CH_3).

Synthesis of 1-d_1-benzyl Formate. Deuterated sodium formate (0.88 g, 12.7 mmol), benzyl bromide (1.51 ml, 12.7 mmol) and 13 ml of HMPA were added together in a 25 ml round bottom flask. The mixture was stirred at room temperature for 60 hours. The content of the flask was then poured into 100 ml H_2O. The organic phase was separated and the aqueous phase was extracted several times with ether. The etherate was washed with H_2O, saturated NaCl solution and dried with $MgSO_4$. Evaporation of solvent yielded a yellow oil. A colorless oil (1.72 g, 87%) was obtained after purification by flash chromatography on silica gel using pentane-ether (100:3) as eluent. ^1H NMR (300MHz, C_6D_6) δ 7.2 - 7.3 (m, 5H, Ph), 5.1 (s, 2H, CH_2).

Synthesis of 1-^{13}C-benzyl Formate. ^{13}C enriched formic acid (>99%), 10 ml of benzene, DBU (1.61ml, 10.5 mmol) and benzyl bromide (1.38 ml, 11.6 mmol) were added into a 25 ml round bottom flask in order. The mixture was heated to 80 °C and refluxed at this temperature for 2 hours, and the reaction was monitored by TLC. The reaction mixture was then cooled down to room temperature and poured into 100 ml H_2O. The organic layer was separated and the aqueous phase was extracted several times with ether. The etherate was washed with H_2O, saturated NaCl solution and dried with $MgSO_4$. Evaporation of solvent yielded a yellow oil. A colorless oil (1.2 g, 82.3%) was obtained after purification by flash chromatography on silica gel using pentane-ether (100:3) as eluent. ^1H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, 1H, $J_{H\text{-}C} = 226.2$ Hz), 7.30 - 7.39 (m, 5H), 5.21 (d, 2H, $J_{H\text{-}C} = 3.3$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.8 (carbonyl), 129.8, 129.4, 128.5, 128.3, 65.7 (d, $J_{C\text{-}H} = 2.2$ Hz, CH_2).

Preparation of 1-d_1-vinyl Benzyl Ether. In the drybox, Tebbe reagent (4.3 g, 15.1 mmol) was weighed into a 100 ml round bottom flask and dissolved with

24 ml CH_2Cl_2. The flask was capped with a rubber septum and brought out of the drybox. In another 100 ml round bottom flask 1-d_1-benzyl formate was dissolved in a mixed solvent of CH_2Cl_2/THF (18 ml : 6 ml) containing 100 ul pyridine. Both flasks were cooled down to -40 °C. Tebbe reagent was added into the ester solution via a cannular in 0.5 hour. After the addition, the flask was warmed up to room temperature and stirred for another 0.5 hour, then was cooled back down to -10 °C. A 15% NaOH solution was added to quench the reaction, and the mixture was filtered through a pad of celite to remove the solid. The filtrate was concentrated, and 200 ml of pentane was added under rapid stirring to generate more solid. The mixture was filtered through the celite, and the filtrate was passed through a neutral alumina column using pentane as an eluent. Evaporation of the solvent yielded a yellow oil (1.02 g, 61%), which was pure by NMR. ^1H NMR (300 MHz, $CDCl_3$) δ 7.4 (m, 5H, Ph), 4.8 (s, 2H, CH_2), 4.32 (m, 1H), 4.10 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.3 ($J_{C\text{-}D}$ = 27.7 Hz), 136.8, 128.4, 127.8, 127.5, 87.0 (CH_2), 69.9 (CH_2).

Synthesis of 1-^{13}C-benzyl Ether. Similar procedure used for the preparation of deuterium labeled compound was employed here, and a yellow oil (0.66 g, 56%) was obtained. ^1H NMR (300 MHz, $CDCl_3$) δ 7.3 - 7.38 (m, 5H, Ph), 6.88 (dd, 0.5H, $J_{H\text{-}C}$ = 181.9 Hz), 6.27 (dd, 0.5H, $J_{H\text{-}C}$ = 181.9 Hz), 4.77 (d, 2H, $J_{H\text{-}D}$ = 3.1 Hz, CH_2), 4.27 - 4.34 (m, 1H, CH_2), 4.07 - 4.11 (m, 1H, CH_2). ^{13}C (75 MHz, $CDCl_3$) δ 151.6, 136.8, 128.5, 127.9, 127.5, 87.3 (d, $J_{C\text{-}C}$ = 78.8 Hz, CH_2), 70.1 (CH_2).

Synthesis of $(TFA)_2(PPh_3)_2Ru(^{13}CHOCH_2Ph)$ 13. In the drybox, complex **2** (90.4 mg, 0.086 mmol) was weighed into a small schlenk flask and dissolved in 10 ml of CH_2Cl_2. ^{13}C labeled vinyl benzyl ether (40 ul, 0.29 mmol) was added. The flask was capped with a rubber septum and brought out of the drybox. The solution was stirred at room temperature for 2 hours until the color of the solution turned to yellow. All the volatiles were removed by vacuum and the residue was washed twice with cold pentane, then the supernatant was carefully cannulated away. The solid was dried by vacuum and a yellow powder (60 mg, 65%) was obtained. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 14.81 (t, $J_{H\text{-}P}$ = 4.26 Hz, carbene proton), 14.29 (t, $J_{H\text{-}P}$ = 4.34, carbene proton), 4.44 (s, CH_2). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 297.46 (t, $J_{C\text{-}P}$ = 11.2 Hz, $J_{C\text{-}H}$ = 158 Hz, α–carbene carbon), 163 ($J_{C\text{-}P}$ = 37.14 Hz, ester carbonyl), 112.9 (quartet, $J_{C\text{-}F}$ = 288.6 Hz, CF_3), 84.1 (d, $J_{C\text{-}C}$ = 3.8 Hz, CH_2). ^{31}P NMR (161.85 MHz, CD_2Cl_2) 35.5 (d, $J_{P\text{-}C}$ = 11.1 Hz).

Synthesis of $(TFA)_2(PPh_3)_2Ru(CDOCH_2Ph)$ 12. Similar procedure used for the synthesis of ^{13}C labeled compound was employed here. ^{2}H NMR (61.25 MHz, CD_2Cl_2) 14.58.

Reaction of 2 with 2,3-dihydrofuran. In the drybox, **2** (6.6 mg, 6.3×10^{-3} mmol) and 2,3-dihydrofuran (1.0 ul, 0.013 mmol) were combined in CD_2Cl_2. The mixture was heated at 40 °C for 15 minutes and a bright yellow solution resulted. The NMR spectrum was recorded. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 14.49 (t, $J_{H\text{-}P}$ = 4.96 Hz, carbene proton), 14.55 (t, $J_{H\text{-}H}$ = 4.9 Hz, carbene proton), 6.7 (d, 1H, $J_{H\text{-}H}$ = 10.74 Hz, CH), 6.24 (dd, 1H, $J_{H\text{-}H}$ = 11.23 and 14.92 Hz, CH), 5.84 (pseudo quartet, 1H, CH), 4.37 (t, 2H, $J_{H\text{-}H}$ = 6.6 Hz, CH_2 adjacent to oxygen), 2.51 (Pseudo quartet, 2H, CH_2). ^{31}P NMR (161.85 MHz, CD_2Cl_2) δ 44.17.

Synthesis of $(TFA)_2(PPh_3)_2Ru(CHN(C_{12}H_8))$ 16. In the drybox, complex **2** (50 mg, 0.048 mmol) and 9-vinylcarbazole (18.8 mg, 0.096 mmol) were weighed into a small flask equipped with a Teflon valve and dissolved with 5 ml CH_2Cl_2. The reaction mixture was then stirred at 40 ~ 50 °C for 38 hours and a clear reddish-brown solution resulted. All the volatiles were removed by high vacuum and the residue was redissolved into minimal amount of CH_2Cl_2 and cooled down to -78 °C. Pentane was added dropwise via a cannular to the CH_2Cl_2 solution under rapid stirring to generate a fine precipitate. The supernatant was cannulated away carefully and the remaining was washed twice with pentane and dried in vacuo to yield a yellow powder (40 mg, 80%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 13.51 (t, 1H, $J_{H\text{-}P}$ = 11.5 Hz). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 253.11 (t, $J_{C\text{-}P}$ = 16 Hz). ^{31}P NMR (161.85 MHz, CD_2Cl_2) δ 50.41. Anal. Calcd for $C_{53}H_{39}F_6NO_4P_2Ru$: C, 61.75; H, 3.813; N, 1.36. Found: C, 61.57; H, 3.87; N, 1.04. FAB-HRMS: m/z calcd for $C_{51}H_{38}F_3NO_2P_2Ru$ (M^+-TFA), 917.1373; found 917.1321.

Synthesis of (TFA)$_2$(PPh$_3$)$_2$Ru(CHN(COCH$_2$CH$_2$CH$_2$)) 17. Similar procedure used for the synthesis of compound **16** was employed here. The mixture was stirred at 40 ~50 °C for 72 hours and the product (33 mg, 66%) was isolated in a similar manner. ^{1}H NMR (300MHz, CD_2Cl_2) δ 14.33 (t, 1H, $J_{H\text{-}P}$ = 1.93 and 1.66Hz). ^{31}P NMR (161.85 MHz, CD_2Cl_2) δ 34.17.

Synthesis of (TFA)(PPh$_3$)Ru(vinylimidazole)$_2$Ru(CHCHCPh$_2$) 23. Inside the dry box, **2** (97.1 mg, 0.093 mmol) was weighed into a small schlenk flask and dissolved with 5 ml of CH_2Cl_2. Vinylimidazole (10.2 ul, 0.113 mmol) was added to the flask via a gas-tight syringe. The flask was then capped with a rubber septum and brought out of the dry box. The mixture was stirred at 40 °C for 7 hours and all the volatiles were removed under high vacuum. The residue was redissolved in minimal amount of benzene and the product was precipitated out by dropwise addition of pentane. The supernatant was cannulated away and the product was further purified by dissolving in minimal amount of CH_2Cl_2 and cooling it down to -78 °C. Ether was then added dropwise to the solution to precipitate a green powder (60 mg, 57%), which was dried in vacuo. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 18.5 (t, 1H, $J_{H\text{-}P}$ = 12.83 Hz, carbene α–proton), 8.34 (d, 1H, $J_{H\text{-}H}$ = 3.76 Hz, carbene β–proton). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 321.59 (d, $J_{C\text{-}P}$ = 13.83 Hz, $J_{C\text{-}H}$ = 141.4 Hz). ^{31}P NMR (161.85 MHz, CD_2Cl_2) δ 41.7. Anal. Calcd for $C_{47}H_{39}N_4O_4F_6PRu$: C, 58.2; H, 4.05; N, 5.78. Found: C, 58.5; H, 4.52;

N, 6.24. FAB-HRMS: m/z calcd for $C_{45}H_{39}F_3N_4O_2PRu$ (M^+-TFA), 857.1806; found, 857.1815.

Preparation of Benzyl Vinyl Sulfide. Benzyl disulfide (6.19 g, 24.6 mmol) was dissolved in 30 ml THF in a 250 ml round bottom flask. The solution was degassed by bubbling Ar through for 10 minutes. Vinylmagnesium chloride (60 ml, 0.1 M) was added to the above solution slowly via a syringe. The mixture was stirred at room temperature for 5 hours. The progress of the reaction was monitored by TLC. The reaction was quenched by the addition of 15% NaOH/H_2O solution at 0 °C and the mixture was then filtered through a pad of celite. THF was evaporated off and the residue was extracted with ether. The etherate was washed with NaOH/H_2O solution and dried with Na_2SO_4. Evaporation of solvent yielded a yellow oil, which was distilled by a kugelrohor to give a colorless oil (2.4 g, 65%). ^1H NMR (300 MHz, CD_2Cl_2) δ 7.26 - 7.36 (m, 5H, Ph), 6.39 (dd, 1H), 5.12 - 5.2 (m, 2H), 3.92 (s, 2H, CH_2).

Synthesis of $(TFA)_2(PPh_3)_2Ru(CHSCH_2Ph)$ 24. In the dry box, **2** (87.6 mg, 0.084 mmol) was weighed into a small schlenk flask and dissolved in 5 ml of CH_2Cl_2. Vinyl benzyl sulfide (40 ul, 0.27 mmol) was added and the schlenk flask was capped with a rubber septum and brought out of the dry box. The mixture was stirred at room temperature for 48 hours and the resulting reddish-brown solution was pump off to dryness. The residue was dissolved in minimal amount of CH_2Cl_2 and the flask was cooled down to -78 °C. Pentane was added dropwise via a cannular to crash out a red powder, which was washed twice with cold pentane. The product (40 mg, 48%) was isolated after drying in vacuo. ^1H NMR (300 MHz, CD_2Cl_2) δ 17.43 (t, 1H, J_{H-P} = 3.91 and 3.41 Hz, carbene α-proton), 3.7 (s, 2H, CH_2). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 306.6 (t, J_{C-P} = 10.99 and 8.31 Hz, J_{C-H} = 152.9 Hz), 47.06 (CH_2). ^{31}P NMR (161.85 MHz, CD_2Cl_2) δ 32.53. Anal. Calcd for $C_{47}H_{38}O_4F_6P_2SRu$: C, 57.85; H, 3.92. Found: C, 58.31; H, 3.75.

FAB-HRMS: m/z calcd for $C_{46}H_{38}F_3O_2P_2SRu$ (M^+-TFA), 875.1063; found, 875.1074.

X-ray Data Collection, Structure Determination and Refinement for $Cl_2(PPh_3)_2Ru(C(CH_2)_3)$.[26] A red-orange crystal of approximate dimensions 0.17 x 0.26 x 0.32 mm was oil-mounted on a glass fiber and transferred to the Siemens P3 automated four-circle diffractometer that is equipped with a modified LT-2 low temperature system. The determination of Laue symmetry, crystal class, unit cell parameters and the crystal's orientation matrix were carried out by previously described methods similar to those of Churchill. Low-temperature (158K) intensity data were collected via a θ-2θ scan technique with Mo K_α radiation.

All 5376 data were corrected for absorption and for Lorentz and polarization effects and placed on an approximately absolute scale. Any reflection with I(net)<0 was assigned the value $|F_o| = 0$. The systematic absences observed were *0k0* for *k = 2n + 1* and *h0l* for *l = 2n + 1*; the diffraction symmetry was 2/m. The centrosymmetric monoclinic space group $P2_1/n$, a non-standard setting of $P2_1/c$ [C^5_{2h}; No. 14] is therefore uniquely defined.

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

The structure was solved by direct methods and refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with d(C-H) = 0.96 Å and U(iso) = 0.08Å. There is one molecule of dichloromethane present in the asymmetric unit. Refinement of positional and thermal parameters led to convergence with $R_F = 4.0\%$; $R_{wF} = 4.4\%$ and GOF = 1.33 for 433 variables refined against those 4197 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier synthesis showed no significant features, $\rho(\max) = 0.77e\text{Å}^{-3}$.

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(12) The reaction is sluggish because the catalyst is only partially soluble in THF. However, THF is the only reasonable choice for both **1** and **4**.

(13) 3-methylenecyclopropane-*trans*-1,2-dimethyl dicarboxylate was synthesized by 3-methylenecyclopropane-*trans*-1,2-dicarboxylic acid with excess diazomethane generated from diazald (N-methyl-N-nitroso-*p*-

toluenesulfonamide and KOH/ethanol/H_2O (5g/10 ml/8 ml) using a mini-Diazald apparatus purchased from Aldrich chemical company.

(14) For example, alkylidene complex $((CF_3)_2CH_3CO)_2$(2,6-di-*i*-pr-ArN)W(CH-*t*-Bu) does not react with 2-methyl-2-butene.

(15) (a) For example, in the cyclohexyl analog $(Cl)_2(PCy_3)_2Ru(CHCHCPh_2)$, the plane that contains the vinyl carbene moiety is nearly perpendicular to the Ru-P bond (the dihedral angle ($\angle$ P-Ru-C_1-C_2) is 83.5°). (b) Supplementary material from Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9858.

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(18) The general decomposition pathways for alkylidene complexes usually involve (i) rearrangement of alkylidenes to olefins (for Nb and Ta). (ii)

rearrangement of metallacyclobutane to olefins via β-hydride elimination. (iii) bimolecular coupling of alkylidenes to give olefins. For detail discussions see: Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991,** *39*. 1. (b) Vaughan, G. A.; Toreki, R.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1993,** *115,* 2980.

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(20) (a) The final ratio of the benzyl trifluoroacetate and toluene generated from the decomposition is 8.5:1 indicating that the reductive elimination of a benzyl trifluoroacetate proceeds much faster. (b) For a review of transition metal formyl complexes, see: Gladysz, J. A. *Adv. Organomet. Chem.* **1982,** *20,* 1. (c) Tam, W.; Lin, G. Y.; Gladysz, J. A. *Organometallics* **1982,** *1,* 525.

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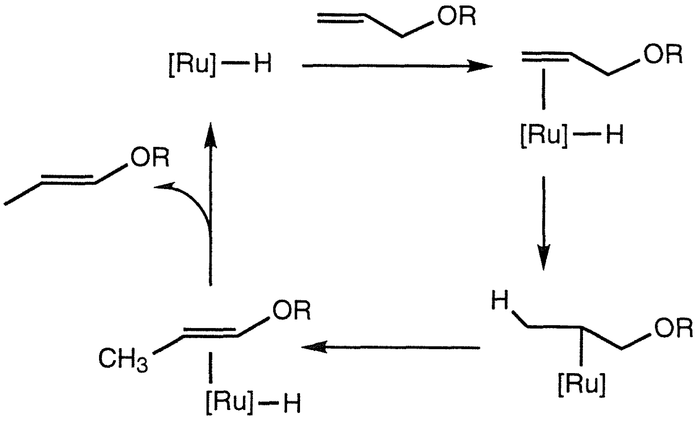
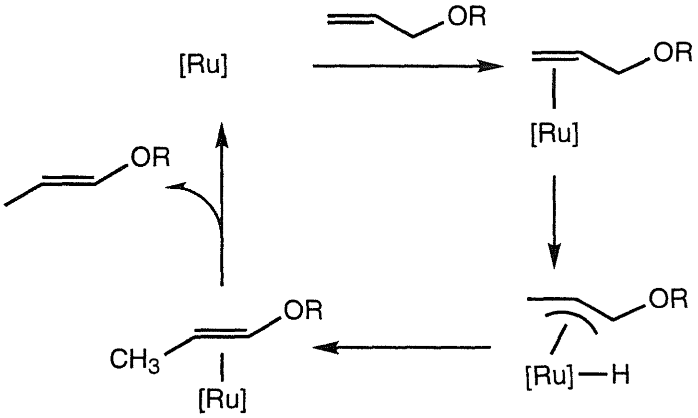
(22) (a) Two possible pathways for olefin isomerization.



Path **I**



Path **II**

(b) In the first step of the isomerization, the ruthenium hydride is probably generated through path II.

(23) The Berry pseudo rotation mechanism has been proposed for alkylidene complexes of trigonal bipyrimad geometries. For discussions see: (a) Feldman, J.; Davis, W. M.; Thomas, J. K.; Schrock, R. R. *Organometallics* **1990**, *9*, 2535. (b) Bazan, G. C.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378.

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Appendix.

Crystal Structure Data for $(PPh_3)_2(Cl)_2Ru(C(CH_2)_3)$ (8).

Formula: $C_{40}H_{36}P_2Cl_2Ru \bullet CH_2Cl_2$ Fw: 835.5

Color, habit: Red/orange prism Size: 0.17x0.26x0.32

Temperature: 158 K

Crystal System: Monoclinic Space Group: $p2_1/n$ [C^5_{2h}; No. 14]

a = 14.075(4) Å β = 103.17(2)° D_{calcd} = 1.483 (g/cm^3)

b = 15.632(2) Å V = 3742.8(13) Å^3 Z = 4

c = 17.471(3) Å Scan Type: Omega

Diffractometer: Siemens P3 (R3m/V System) Scan With: 1.2°

Radiation: Mo Kα (λ = 0.710730 Å) with oriented graphite monochrometer

Data Collected: $+h$, $+k$, $\pm l$ Scan Speed 4.0 deg/min (in ω)
2θ range (deg): 4.0 to 45 Reflections Collected: 5376

μ(Mo K_α), mm^{-1} = 0.811 Absorption Correction: Semi-empirical
No. of Variables : 433 R_F = 4.0%, R_{wF} = 4.4%

Reflections with $|F_o| > 3.0\sigma(|F_o|)$: 4197 Goodness of fit: 1.33

Atomic coordinates (x10^5) and equivalent isotropic displacement coefficients (Åx10^4)

	x	y	z	U(eq)
Ru(1)	21544(3)	7122(2)	20287(2)	167(1)
P(1)	8544(8)	6563(7)	26969(6)	182(4)
P(2)	33129(8)	5919(7)	12358(6)	186(4)
Cl(1)	28208(8)	-5656(7)	26612(6)	230(4)
Cl(2)	10995(8)	14147(7)	9787(6)	259(4)
C(1)	27993(32)	15697(29)	26493(26)	224(16)
C(2)	29097(35)	18125(32)	35115(26)	306(18)
C(3)	36369(42)	25065(35)	34049(29)	433(21)
C(4)	34548(36)	23054(30)	25217(28)	301(18)
C(5)	1107(30)	-2946(28)	23917(25)	187(15)
C(6)	-1001(34)	-8837(30)	29231(28)	273(17)
C(7)	-6401(35)	-16103(32)	26584(30)	335(19)
C(8)	-9854(35)	-17484(32)	18586(31)	338(19)
C(9)	-7894(35)	-11748(32)	13231(30)	331(18)
C(10)	-2414(33)	-4476(30)	15796(27)	271(17)
C(11)	10753(31)	6110(28)	37741(25)	193(15)
C(12)	18579(33)	1386(29)	42059(26)	257(17)
C(13)	20357(35)	1107(30)	50238(25)	261(17)
C(14)	14304(35)	5479(29)	54129(26)	267(17)
C(15)	6497(38)	10133(30)	49892(27)	301(18)
C(16)	4713(34)	10469(29)	41761(26)	242(16)
C(17)	24(31)	15558(27)	24640(24)	179(15)
C(18)	3839(34)	23791(29)	25014(25)	244(17)
C(19)	-2156(35)	30866(31)	23491(25)	271(17)
C(20)	-12251(37)	29807(32)	21392(26)	291(18)
C(21)	-16109(34)	21668(31)	20893(25)	261(17)
C(22)	-10002(32)	14544(29)	22501(25)	221(16)
C(23)	30995(32)	-4440(28)	7424(24)	197(15)
C(24)	38386(35)	-10367(30)	7515(25)	252(17)
C(25)	36252(39)	-18071(30)	3480(27)	318(18)
C(26)	26841(40)	-19862(33)	-539(27)	340(19)
C(27)	19408(39)	-14063(33)	-617(28)	352(19)
C(28)	21473(34)	-6393(31)	3425(26)	275(17)
C(29)	46197(30)	5990(25)	17255(24)	165(15)
C(30)	53338(34)	7146(29)	12998(27)	262(17)

Atomic coordinates (x10^5) and equivalent isotropic displacement coefficients (Åx10^4)

C(31)	63167(35)	7093(32)	16757(27)	313(18)
C(32)	65941(34)	5851(32)	24807(29)	325(19)
C(33)	58862(35)	4740(31)	29081(29)	322(18)
C(34)	49010(33)	4800(29)	25333(26)	234(16)
C(35)	33021(31)	13095(28)	4018(25)	205(16)
C(36)	32233(37)	21789(31)	4771(29)	331(19)
C(37)	33024(38)	27266(33)	-1332(30)	386(20)
C(38)	34310(35)	23982(34)	-8318(29)	347(20)
C(39)	34899(35)	15304(34)	-9211(28)	325(19)
C(40)	34186(33)	9822(32)	-3187(26)	278(17)
C(41)	54672(40)	14062(39)	56154(32)	491(22)
Cl(3)	42907(12)	9816(12)	53959(9)	636(7)
Cl(4)	59381(12)	15479(10)	47869(10)	622(7)

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

Interatomic Distances (Å) with Esd's

Ru(1)-P(1)	2.386(1)	Ru(1)-P(2)	2.375(1)
Ru(1)-Cl(1)	2.370(1)	Ru(1)-Cl(2)	2.352(1)
Ru(1)-C(1)	1.830(4)		

P(1)-C(5)	1.826(4)	P(1)-C(11)	1.837(4)
P(1)-C(17)	1.833(4)	P(2)-C(23)	1.827(4)
P(2)-C(29)	1.843(4)	P(2)-C(35)	1.836(5)

C(1)-C(2)	1.527(7)	C(1)-C(4)	1.522(7)
C(2)-C(3)	1.532(8)	C(3)-C(4)	1.538(7)
C(5)-C(6)	1.387(7)	C(5)-C(10)	1.413(6)
C(6)-C(7)	1.386(7)	C(7)-C(8)	1.388(7)
C(8)-C(9)	1.369(8)	C(9)-C(10)	1.389(7)
C(11)-C(12)	1.396(6)	C(11)-C(16)	1.397(7)
C(12)-C(13)	1.394(6)	C(13)-C(14)	1.385(7)
C(14)-C(15)	1.383(6)	C(15)-C(16)	1.386(6)
C(17)-C(18)	1.390(6)	C(17)-C(22)	1.384(6)
C(18)-C(19)	1.380(7)	C(19)-C(20)	1.394(7)
C(20)-C(21)	1.378(7)	C(21)-C(22)	1.396(6)
C(23)-C(24)	1.390(7)	C(23)-C(28)	1.397(6)
C(24)-C(25)	1.393(7)	C(25)-C(26)	1.379(7)
C(26)-C(27)	1.382(8)	C(27)-C(28)	1.388(7)
C(29)-C(30)	1.392(7)	C(29)-C(34)	1.389(6)
C(30)-C(31)	1.390(6)	C(31)-C(32)	1.385(7)
C(32)-C(33)	1.386(8)	C(33)-C(34)	1.392(6)
C(35)-C(36)	1.372(7)	C(35)-C(40)	1.403(7)
C(36)-C(37)	1.391(7)	C(37)-C(38)	1.374(8)
C(38)-C(39)	1.370(8)	C(39)-C(40)	1.379(7)

C(41)-Cl(3)	1.744(6)	C(41)-Cl(4)	1.738(6)

Interatomic Angles (Deg.) with Esd's

P(1)-Ru(1)-P(2)	170.9(1)	P(1)-Ru(1)-Cl(1)	90.4(1)
P(2)-Ru(1)-Cl(1)	87.4(1)	P(1)-Ru(1)-Cl(2)	88.9(1)
P(2)-Ru(1)-Cl(2)	88.7(1)	Cl(1)-Ru(1)-Cl(2)	150.4(1)
P(1)-Ru(1)-C(1)	94.0(2)	P(2)-Ru(1)-C(1)	95.2(2)
Cl(1)-Ru(1)-C(1)	104.5(1)	Cl(2)-Ru(1)-C(1)	105.1(1)
Ru(1)-P(1)-C(5)	109.8(2)	Ru(1)-P(1)-C(11)	122.2(1)
C(5)-P(1)-C(11)	102.7(2)	Ru(1)-P(1)-C(17)	113.5(2)
C(5)-P(1)-C(17)	104.9(2)	C(11)-P(1)-C(17)	101.9(2)
Ru(1)-P(2)-C(23)	106.5(2)	Ru(1)-P(2)-C(29)	118.3(2)
C(23)-P(2)-C(29)	105.3(2)	Ru(1)-P(2)-C(35)	122.1(2)
C(23)-P(2)-C(35)	101.3(2)	C(29)-P(2)-C(35)	101.0(2)
C(2)-C(1)-C(4)	91.6(3)	C(1)-C(2)-C(3)	88.7(4)
C(2)-C(3)-C(4)	90.8(4)	C(1)-C(4)-C(3)	88.6(4)
P(1)-C(5)-C(6)	122.7(3)	P(1)-C(5)-C(10)	118.5(3)
C(6)-C(5)-C(10)	118.7(4)	C(5)-C(6)-C(7)	120.4(4)
C(6)-C(7)-C(8)	120.2(5)	C(7)-C(8)-C(9)	120.5(5)
C(8)-C(9)-C(10)	119.9(5)	C(5)-C(10)-C(9)	120.3(4)
P(1)-C(11)-C(12)	120.2(4)	P(1)-C(11)-C(16)	121.0(3)
C(12)-C(11)-C(16)	118.8(4)	C(11)-C(12)-C(13)	120.4(5)
C(12)-C(13)-C(14)	120.0(4)	C(13)-C(14)-C(15)	120.0(4)
C(14)-C(15)-C(16)	120.3(5)	C(11)-C(16)-C(15)	120.5(4)
P(1)-C(17)-C(18)	118.3(3)	P(1)-C(17)-C(22)	123.2(3)
C(18)-C(17)-C(22)	118.5(4)	C(17)-C(18)-C(19)	121.3(4)
C(18)-C(19)-C(20)	119.8(4)	C(19)-C(20)-C(21)	119.3(4)
C(20)-C(21)-C(22)	120.5(4)	C(17)-C(22)-C(21)	120.4(4)
P(2)-C(23)-C(24)	122.9(3)	P(2)-C(23)-C(28)	117.7(3)
C(24)-C(23)-C(28)	119.4(4)	C(23)-C(24)-C(25)	119.7(4)
C(24)-C(25)-C(26)	120.3(5)	C(25)-C(26)-C(27)	120.6(5)
C(26)-C(27)-C(28)	119.4(4)	C(23)-C(28)-C(27)	120.6(5)
P(2)-C(29)-C(30)	121.2(3)	P(2)-C(29)-C(34)	119.6(4)
C(30)-C(29)-C(34)	119.1(4)	C(29)-C(30)-C(31)	120.6(4)
C(30)-C(31)-C(32)	120.0(5)	C(31)-C(32)-C(33)	119.6(4)
C(32)-C(33)-C(34)	120.5(4)	C(29)-C(34)-C(33)	120.1(5)
P(2)-C(35)-C(36)	121.0(4)	P(2)-C(35)-C(40)	120.5(3)
C(36)-C(35)-C(40)	118.4(4)	C(35)-C(36)-C(37)	120.9(5)
C(36)-C(37)-C(38)	120.0(5)	C(37)-C(38)-C(39)	119.7(5)
C(38)-C(39)-C(40)	120.8(5)	C(35)-C(40)-C(39)	120.1(5)

Cl(3)-C(41)-Cl(4)	112.9(3)

Anisotropic displacement coefficients (Å^{2}x10^{4})

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru(1)	182(2)	166(2)	163(2)	3(2)	57(2)	3(2)
P(1)	185(6)	204(7)	164(6)	-2(5)	56(5)	-15(5)
P(2)	195(7)	190(7)	184(6)	11(5)	69(5)	4(5)
Cl(1)	267(6)	192(6)	237(6)	21(5)	66(5)	39(5)
Cl(2)	269(7)	303(7)	207(6)	73(5)	59(5)	45(5)
C(1)	195(25)	218(26)	252(26)	45(21)	37(21)	23(21)
C(2)	298(29)	369(31)	253(27)	-104(24)	64(23)	-112(23)
C(3)	561(37)	379(33)	322(31)	-209(29)	23(28)	-81(25)
C(4)	368(31)	198(27)	378(30)	-111(23)	170(25)	-78(23)
C(5)	148(24)	208(25)	202(25)	28(20)	32(20)	1(20)
C(6)	284(28)	293(30)	257(27)	-12(23)	90(22)	-7(22)
C(7)	325(30)	272(30)	419(33)	-69(24)	106(26)	39(25)
C(8)	244(29)	257(29)	505(35)	-41(23)	66(26)	-67(26)
C(9)	304(30)	301(30)	355(30)	-1(25)	5(24)	-78(26)
C(10)	254(27)	286(29)	271(28)	43(23)	57(22)	-7(22)
C(11)	184(24)	231(26)	184(24)	-61(21)	84(20)	-18(20)
C(12)	265(28)	258(28)	260(27)	1(23)	88(22)	16(22)
C(13)	310(28)	278(28)	177(25)	-11(23)	17(22)	70(21)
C(14)	386(31)	254(28)	164(24)	-86(24)	65(23)	26(21)
C(15)	463(33)	261(28)	223(27)	-4(25)	168(25)	-7(22)
C(16)	278(28)	225(27)	231(26)	-36(22)	72(22)	-7(21)
C(17)	218(26)	198(26)	153(23)	-1(21)	111(20)	-14(19)
C(18)	241(27)	309(30)	192(25)	-20(23)	67(21)	2(21)
C(19)	351(31)	248(28)	226(26)	60(24)	90(23)	-4(22)
C(20)	385(33)	310(31)	199(26)	106(25)	110(23)	15(22)
C(21)	215(26)	339(31)	228(26)	35(24)	50(21)	-45(22)
C(22)	213(27)	236(27)	218(25)	19(22)	58(21)	-14(20)
C(23)	256(27)	195(26)	160(23)	-17(21)	89(20)	25(19)
C(24)	289(29)	274(28)	195(25)	29(23)	58(22)	50(21)
C(25)	483(35)	219(28)	243(27)	85(25)	66(25)	-5(22)
C(26)	551(37)	265(29)	223(27)	-49(28)	126(26)	-32(23)
C(27)	426(34)	378(33)	243(28)	-145(28)	57(25)	-48(24)
C(28)	253(27)	345(30)	232(26)	-30(24)	64(22)	9(23)
C(29)	174(24)	104(23)	212(24)	-11(19)	36(20)	-47(18)
C(30)	297(29)	269(28)	239(25)	-42(23)	100(22)	-65(22)
C(31)	253(28)	418(32)	291(29)	-103(25)	111(23)	-73(24)

Anisotropic displacement coefficients ($\AA^2 x 10^4$)

C(32)	198(27)	395(33)	357(31)	-90(24)	9(24)	-11(24)
C(33)	306(31)	320(30)	331(29)	-50(24)	51(25)	66(23)
C(34)	212(27)	256(28)	227(26)	-10(21)	34(21)	37(21)
C(35)	209(26)	210(27)	221(25)	16(20)	103(20)	27(21)
C(36)	435(33)	277(31)	304(29)	8(25)	134(25)	48(24)
C(37)	473(35)	264(30)	440(34)	-23(26)	143(28)	138(26)
C(38)	289(30)	447(36)	298(30)	-55(26)	51(24)	147(26)
C(39)	297(30)	443(35)	255(28)	-39(26)	107(23)	82(25)
C(40)	257(28)	339(29)	238(27)	25(23)	59(22)	77(23)
C(41)	450(36)	528(39)	447(35)	-110(31)	3(29)	-23(30)
Cl(3)	594(11)	862(13)	427(9)	-311(9)	67(8)	-18(9)
Cl(4)	693(11)	509(10)	787(12)	-44(8)	423(10)	-89(9)

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 (Åx10^4)

	x	y	z	U
H(2A)	3166	1362	3872	800
H(2B)	2327	2050	3622	800
H(3A)	4285	2376	3695	800
H(3B)	3460	3080	3510	800
H(4A)	3143	2758	2185	800
H(4B)	4025	2105	2363	800
H(6A)	140	-787	3476	800
H(7A)	-798	-2003	3033	800
H(8A)	-1345	-2258	1674	800
H(9A)	-1046	-1268	772	800
H(10A)	-100	-53	1200	800
H(12A)	2272	-162	3930	800
H(13A)	2571	-214	5323	800
H(14A)	1561	534	5977	800
H(15A)	237	1309	5269	800
H(16A)	-76	1362	3881	800
H(18A)	1077	2460	2621	800
H(19A)	31	3661	2408	800
H(20A)	-1640	3473	2018	800
H(21A)	-2306	2098	1945	800
H(22A)	-1275	890	2211	800
H(24A)	4493	-904	1024	800
H(25A)	4117	-2231	345	800
H(26A)	2531	-2519	-327	800
H(27A)	1288	-1528	-347	800
H(28A)	1640	-230	343	800
H(30A)	5146	807	743	800
H(31A)	6806	787	1378	800
H(32A)	7266	574	2756	800
H(33A)	6075	384	3466	800
H(34A)	4414	421	2835	800
H(36A)	3128	2409	964	800
H(37A)	3260	3334	-71	800
H(38A)	3477	2778	-1253	800
H(39A)	3584	1303	-1409	800
H(40A)	3455	374	-385	800
H(41A)	5884	1030	5977	800
H(41B)	5454	1947	5873	800

Observed and Calculated Structure Factors for $(PPh_3)_2(Cl)_2Ru(C(CH_2)_3)$ (8)

h	k	l	10Fo	10Fc	10s
2	0	0	834	-850	5
4	0	0	653	-675	7
6	0	0	55	-123	-44
8	0	0	405	-473	10
10	0	0	993	985	11
12	0	0	203	-227	18
14	0	0	588	610	15
2	1	0	335	-317	7
3	1	0	313	314	8
4	1	0	1915	-1856	6
5	1	0	386	412	9
6	1	0	313	-331	10
7	1	0	999	-999	8
8	1	0	1388	1405	9
9	1	0	1290	1306	10
10	1	0	677	-685	11
11	1	0	126	-68	31
12	1	0	133	-73	33
14	1	0	159	122	26
0	2	0	1970	1952	4
1	2	0	2000	-2024	4
2	2	0	541	-555	6
3	2	0	784	-774	7
4	2	0	1471	1443	7
5	2	0	572	-578	8
6	2	0	198	-221	16
7	2	0	268	-248	12
8	2	0	466	-478	10
9	2	0	448	429	11
10	2	0	638	649	12
12	2	0	255	-265	17
13	2	0	186	159	22
14	2	0	497	492	16
1	3	0	219	240	10
2	3	0	2759	-2763	6
3	3	0	550	-538	8
4	3	0	863	881	7
5	3	0	443	453	9
6	3	0	688	-728	9
7	3	0	262	-268	12
8	3	0	1466	1460	9
9	3	0	106	174	27
10	3	0	985	-994	11
11	3	0	212	-221	18
12	3	0	250	256	17
13	3	0	213	190	22
14	3	0	165	-135	30
0	4	0	1675	-1660	6
1	4	0	1173	-1177	6
2	4	0	1091	-1078	7
3	4	0	216	-205	12
4	4	0	556	566	8
5	4	0	525	-553	9
6	4	0	1286	1270	8
7	4	0	273	-247	13
9	4	0	577	548	11
10	4	0	403	-428	13
11	4	0	100	145	-44
12	4	0	85	68	-47
14	4	0	143	-71	38
1	5	0	157	-158	14
2	5	0	139	-130	15
3	5	0	113	172	28
4	5	0	1278	1262	8
5	5	0	280	-293	11
6	5	0	1532	-1477	9
7	5	0	741	719	10
8	5	0	1288	1281	10
9	5	0	936	-909	11
10	5	0	754	-772	12
11	5	0	319	299	15
12	5	0	434	399	16
13	5	0	105	-104	-43
0	6	0	2169	-2112	7
1	6	0	90	-69	-31
2	6	0	826	826	8
3	6	0	127	-71	18
4	6	0	504	-547	10
5	6	0	16	-6	-65
7	6	0	276	-248	15
8	6	0	521	534	12
9	6	0	72	43	-48
10	6	0	186	202	21
11	6	0	279	-278	17
12	6	0	274	273	21
13	6	0	117	-58	39
1	7	0	423	394	10
2	7	0	900	-890	9
3	7	0	216	173	14
4	7	0	388	338	11
5	7	0	314	-303	12
6	7	0	261	222	15
7	7	0	1058	1045	11
8	7	0	355	354	14
9	7	0	557	-592	13
10	7	0	241	273	20
11	7	0	318	319	18
12	7	0	199	192	22
13	7	0	389	-421	17
0	8	0	2156	-2147	8
1	8	0	583	594	10
2	8	0	1138	1138	9
3	8	0	193	195	16
4	8	0	968	-968	10
5	8	0	679	687	10
6	8	0	173	195	20
7	8	0	111	37	35
8	8	0	126	115	35
9	8	0	420	-421	14
10	8	0	456	-427	14
12	8	0	406	394	16
13	8	0	198	-232	24
1	9	0	112	99	29
2	9	0	195	182	16
3	9	0	117	-17	27
4	9	0	854	-842	10
5	9	0	444	427	13
6	9	0	556	553	12
7	9	0	366	350	15
8	9	0	397	-433	14
9	9	0	623	-623	13
10	9	0	416	419	16
11	9	0	22	52	-87
12	9	0	389	-400	18
0	10	0	1774	-1766	10
1	10	0	772	785	10
2	10	0	346	354	14
3	10	0	540	-551	11
4	10	0	202	211	18
5	10	0	536	513	13
8	10	0	75	-94	-54
9	10	0	440	-435	15
10	10	0	423	-426	16
11	10	0	286	265	20
1	11	0	126	-89	29
2	11	0	823	818	11
3	11	0	264	-281	16
4	11	0	91	-15	-39
5	11	0	703	704	12
6	11	0	490	486	13
7	11	0	277	-303	20
8	11	0	1128	-1074	12
10	11	0	560	584	16
11	11	0	121	-37	40
0	12	0	412	414	14
1	12	0	611	604	12
2	12	0	223	-200	18
3	12	0	103	-133	-40
4	12	0	235	243	19
5	12	0	218	-208	21
6	12	0	311	-318	17
7	12	0	137	-150	36
8	12	0	66	-65	-58
1	13	0	367	339	15
2	13	0	274	277	16
3	13	0	523	-514	14
5	13	0	585	559	13
6	13	0	208	207	21
7	13	0	680	-674	14
8	13	0	875	-836	14
9	13	0	743	752	15
0	14	0	1261	1267	12
1	14	0	161	-152	24
2	14	0	803	-826	13
3	14	0	527	511	15
4	14	0	175	127	25
5	14	0	265	-231	20
6	14	0	272	-265	22
1	15	0	143	109	33
3	15	0	550	-577	15
4	15	0	140	68	33
5	15	0	121	-115	-50
6	15	0	148	-110	33
0	16	0	737	755	14
1	16	0	496	-558	14
2	16	0	609	-622	14
3	16	0	486	461	17
4	16	0	183	177	29
-13	0	1	606	-662	13
-11	0	1	823	831	11
-9	0	1	436	445	11
-7	0	1	1329	-1341	8
-5	0	1	143	-171	17
-3	0	1	807	-841	6
1	0	1	660	-2733	-4
3	0	1	3159	3267	5
5	0	1	2106	-2075	7
7	0	1	1343	-1325	8
9	0	1	1750	1730	10
11	0	1	915	-906	11
13	0	1	615	598	13
-14	1	1	77	-66	-53
-13	1	1	328	358	17
-12	1	1	308	-298	17
-11	1	1	256	221	16
-10	1	1	394	404	12
-9	1	1	759	-775	10
-8	1	1	732	-741	9
-7	1	1	392	429	11
-6	1	1	1056	1062	8
-5	1	1	873	-838	7
-4	1	1	180	-140	13
-3	1	1	381	376	7
-2	1	1	321	-307	7
-1	1	1	51	-151	-22
1	1	1	1013	-1016	4
2	1	1	2057	-2075	5
3	1	1	218	-211	11
4	1	1	69	20	-37
5	1	1	468	455	9
6	1	1	658	630	8
7	1	1	298	354	11
8	1	1	1266	1249	9
9	1	1	450	-459	11
10	1	1	285	-251	15
11	1	1	225	192	22
12	1	1	109	31	35
13	1	1	294	-280	18
14	1	1	181	-169	25
-14	2	1	322	-352	17
-13	2	1	62	80	-55
-12	2	1	185	193	20
-9	2	1	446	-456	11
-8	2	1	561	-560	10
-7	2	1	266	-293	13
-6	2	1	171	186	13
-5	2	1	939	927	7
-4	2	1	369	347	9
-3	2	1	495	-501	7
-2	2	1	730	722	6
-1	2	1	1026	981	5
0	2	1	2094	-2121	23
1	2	1	2129	-2184	5
2	2	1	1412	1426	5
3	2	1	994	970	6
4	2	1	411	-387	9
5	2	1	204	-217	13
6	2	1	338	321	11
7	2	1	190	-177	15
8	2	1	714	743	10
9	2	1	654	644	11
10	2	1	996	-989	11
11	2	1	563	-593	13
12	2	1	170	183	20
13	2	1	428	414	17
-14	3	1	145	199	37
-13	3	1	209	-170	21
-12	3	1	97	-69	-41
-11	3	1	631	608	13
-10	3	1	278	-225	19
-9	3	1	1156	-1180	10
-8	3	1	883	-865	10
-7	3	1	1710	1744	9
-6	3	1	96	-19	31
-5	3	1	412	-456	10
-4	3	1	632	606	8
-3	3	1	817	793	7
-2	3	1	1496	1507	6
-1	3	1	271	264	10
0	3	1	409	-374	12
1	3	1	212	182	11
2	3	1	328	325	9
3	3	1	2210	2213	6
4	3	1	628	599	8
5	3	1	114	-82	25
6	3	1	473	-501	10
7	3	1	2142	2111	9
8	3	1	133	147	18
9	3	1	1337	-1368	10
10	3	1	133	109	33
11	3	1	317	326	16
12	3	1	222	199	19
13	3	1	296	-312	18
14	3	1	20	0	-81
-14	4	1	348	-323	16
-13	4	1	254	244	21
-11	4	1	538	-531	13
-10	4	1	105	-146	32
-9	4	1	222	-215	15
-8	4	1	131	88	17
-7	4	1	1025	966	9
-6	4	1	876	835	9
-5	4	1	241	274	12
-4	4	1	855	801	8
-3	4	1	1329	1266	7
-2	4	1	151	-102	16
-1	4	1	876	-875	6
0	4	1	1923	-1922	9
1	4	1	782	-791	7
2	4	1	497	459	8
3	4	1	223	236	12
4	4	1	87	-134	-33
5	4	1	226	230	12
6	4	1	33	-70	-60
7	4	1	467	434	11
8	4	1	626	639	11
9	4	1	234	-282	17
10	4	1	268	-248	17
11	4	1	82	-130	-49
12	4	1	79	162	-54
13	4	1	20	-27	-82
14	4	1	154	-160	36
-13	5	1	409	-370	15
-12	5	1	515	488	14
-11	5	1	364	378	16
-10	5	1	511	-497	13
-9	5	1	756	-741	11
-8	5	1	644	653	11
-7	5	1	2770	2768	9
-6	5	1	891	-885	9
-5	5	1	604	-600	9
-4	5	1	504	491	9
-3	5	1	347	-356	10
-2	5	1	179	169	13
-1	5	1	447	417	9
0	5	1	304	-289	7
1	5	1	937	905	7
2	5	1	1584	1542	7
3	5	1	2097	2076	7
4	5	1	419	-393	10
5	5	1	551	-580	10
6	5	1	93	141	-34
7	5	1	1452	1415	9
8	5	1	789	-796	11
9	5	1	794	-789	11
11	5	1	685	693	13
12	5	1	86	-127	-51
13	5	1	187	-195	21
-13	6	1	70	144	-57
-12	6	1	379	-382	16
-11	6	1	18	-12	-73
-10	6	1	283	288	17
-9	6	1	366	401	13
-8	6	1	621	624	12
-7	6	1	620	624	10
-6	6	1	482	474	11
-5	6	1	1325	-1295	9
-4	6	1	149	112	15
-3	6	1	180	202	15
-2	6	1	101	-46	28
-1	6	1	674	-673	8
0	6	1	848	-859	6
1	6	1	2386	2311	7
2	6	1	494	499	9
3	6	1	322	-370	11
4	6	1	372	329	11
5	6	1	122	95	21
6	6	1	441	-449	11
7	6	1	303	332	13
8	6	1	307	334	15
9	6	1	640	-622	12
10	6	1	83	-35	-46
11	6	1	651	636	12
12	6	1	102	-99	-45
13	6	1	530	-525	15
-12	7	1	382	404	16
-11	7	1	129	-8	34
-10	7	1	631	-419	14
-9	7	1	319	-320	16
-8	7	1	1417	1399	11
-7	7	1	110	-98	35
-6	7	1	912	-930	10
-5	7	1	473	471	11
-4	7	1	693	-644	9
-3	7	1	984	971	8
-2	7	1	87	26	-33
-1	7	1	209	226	17
0	7	1	650	-652	9
1	7	1	700	643	9
2	7	1	1149	1130	8
3	7	1	468	-460	10
4	7	1	521	-521	10
5	7	1	577	-544	10
6	7	1	594	570	11
7	7	1	166	157	31
8	7	1	743	-758	11
9	7	1	91	-160	-46
10	7	1	361	334	16
11	7	1	138	128	35
12	7	1	213	-235	23
-13	8	1	374	370	18
-12	8	1	146	-168	38
-11	8	1	135	-68	34
-10	8	1	118	-52	34
-9	8	1	602	597	12
-7	8	1	487	509	13
-6	8	1	143	-163	22
-5	8	1	1343	-1320	10
-4	8	1	250	267	13
-3	8	1	1101	1089	9
-2	8	1	1034	-1008	9
-1	8	1	950	-924	9
0	8	1	353	346	8
1	8	1	1776	1757	8
2	8	1	63	-55	-42
3	8	1	1143	-1131	9
4	8	1	467	487	11
5	8	1	42	-13	-55
6	8	1	251	229	16
7	8	1	265	287	16
8	8	1	558	-538	13
9	8	1	938	-921	12
10	8	1	203	-232	24
11	8	1	516	508	14
12	8	1	364	-367	16
-12	9	1	193	244	24
-11	9	1	330	-338	16
-10	9	1	19	47	-74
-9	9	1	614	603	13
-8	9	1	821	803	12
-7	9	1	1053	-1047	11
-5	9	1	646	666	11
-4	9	1	260	-297	14
-3	9	1	605	565	10
-2	9	1	86	-109	22
-1	9	1	490	477	11
0	9	1	477	-514	7
1	9	1	83	-39	-36
2	9	1	523	504	11
3	9	1	1254	-1227	10
4	9	1	376	-351	12
5	9	1	402	408	13
6	9	1	377	-386	13
7	9	1	395	-401	15
8	9	1	198	-189	19
9	9	1	320	285	16
10	9	1	95	63	-48
11	9	1	239	-206	23
-12	10	1	157	-115	27
-11	10	1	224	-220	21
-10	10	1	180	209	25
-9	10	1	630	-629	15
-8	10	1	221	-215	20
-7	10	1	261	242	17
-6	10	1	664	-684	12
-5	10	1	141	-90	30
-4	10	1	855	846	11
-3	10	1	220	213	14
-2	10	1	637	-641	11
-1	10	1	1171	-1136	10
0	10	1	1051	1028	7
1	10	1	531	543	11
2	10	1	610	-600	11
3	10	1	176	-155	17
4	10	1	17	112	-68
5	10	1	311	346	14
6	10	1	210	184	25
7	10	1	232	259	19
8	10	1	122	162	40
9	10	1	603	587	13

Observed and Calculated Structure Factors for $(PPh_3)_2(Cl)_2Ru(C(CH_2)_3)$ (8)

h	k	l	10Fo	10Fc	10s
10	10	1	537	549	15
11	10	1	363	388	19
-11	11	1	236	-211	24
-10	11	1	131	19	35
-9	11	1	1148	1139	13
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Observed and Calculated Structure Factors for $(PPh_3)_2(Cl)_2Ru(C(CH_2)_3)$ (8)

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Observed and Calculated Structure Factors for $(PPh_3)_2(Cl)_2Ru(C(CH_2)_3)$ (8)

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7	12	4	283	264	17
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6	13	4	502	463	15
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-7	14	4	141	102	26
-6	14	4	897	-883	13
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-2	14	4	375	-414	16
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6	14	4	359	326	18
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-7	0	5	946	-1011	8
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9	0	5	672	652	12
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-14	1	5	854	816	13
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-11	1	5	426	464	13
-10	1	5	559	-562	12
-9	1	5	380	-391	12
-8	1	5	82	17	-28
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-6	1	5	457	414	10
-5	1	5	551	539	9
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-2	1	5	788	-780	7
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11	1	5	170	-156	27
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11	2	5	644	-651	13
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-12	3	5	212	-251	20
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-7	3	5	873	859	9
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6	3	5	300	-303	13
7	3	5	739	744	10
8	3	5	99	-52	-37
9	3	5	124	98	33
10	3	5	314	344	16
11	3	5	690	-681	13
12	3	5	256	-231	19
13	3	5	516	543	16
-14	4	5	140	-125	34
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-11	4	5	153	169	26
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-7	4	5	652	638	10
-6	4	5	782	809	9
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6	4	5	293	-306	13
7	4	5	292	309	16
8	4	5	452	463	13
9	4	5	138	43	32
10	4	5	339	-368	16
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12	4	5	72	66	-58
-14	5	5	465	-444	17
-13	5	5	691	-702	13
-12	5	5	913	916	12
-11	5	5	1057	1066	12
-10	5	5	364	349	16
-9	5	5	65	6	-50
-8	5	5	116	166	36
-7	5	5	528	532	11
-6	5	5	230	-178	14
-5	5	5	587	579	10
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-1	5	5	794	823	8
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2	5	5	1215	1240	8
3	5	5	1108	1108	9
4	5	5	257	-301	12
5	5	5	730	-717	10
7	5	5	823	845	11
9	5	5	312	336	17
10	5	5	565	-567	14
11	5	5	669	-624	14
12	5	5	274	271	21
-14	6	5	56	15	-67
-11	6	5	406	404	15
-10	6	5	390	388	14
-9	6	5	343	-345	14
-8	6	5	253	-253	17
-7	6	5	1114	1120	10
-6	6	5	98	18	31
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-4	6	5	271	-279	11
-3	6	5	808	843	8
-2	6	5	411	373	10
-1	6	5	298	-307	11
0	6	5	532	502	7
1	6	5	116	110	28

Observed and Calculated Structure Factors for $(PPh_3)_2(Cl)_2Ru(C(CH_2)_3)$ (8)

h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
2	6	5	1333	-1302	9	2	10	5	761	767	11	1	16	5	133	-108	34	9	3	6	306	305	16	-4	7	6	173	151	15
3	6	5	837	822	9	3	10	5	177	184	20	-14	0	6	131	165	36	10	3	6	532	-513	13	-3	7	6	958	997	9
4	6	5	519	526	11	4	10	5	716	-726	12	-12	0	6	951	-975	12	11	3	6	341	-342	18	-2	7	6	433	438	10
5	6	5	414	-441	12	5	10	5	132	-57	31	-10	0	6	833	845	11	12	3	6	666	702	15	-1	7	6	1279	-1269	9
6	6	5	297	271	15	6	10	5	87	100	-67	-8	0	6	618	-632	10	-14	4	6	70	-53	-57	0	7	6	551	545	7
7	6	5	423	431	15	7	10	5	300	322	15	-6	0	6	1339	1384	8	-13	4	6	143	-125	35	1	7	6	400	417	11
8	6	5	370	384	14	8	10	5	513	-506	15	-4	0	6	2056	-2064	7	-11	4	6	615	610	13	2	7	6	153	153	21
9	6	5	768	-777	13	9	10	5	118	-180	-66	-2	0	6	1444	-1404	7	-10	4	6	166	-143	26	3	7	6	171	-176	19
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-9	7	5	440	-435	14	-7	11	5	193	220	21	10	0	6	925	-933	12	-4	4	6	246	254	11	10	7	6	184	-174	24
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Observed and Calculated Structure Factors for $(PPh_3)_2(Cl)_2Ru(C(CH_2)_3)$ (8)

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8	11	6	161	151	29
9	11	6	273	272	21
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-8	12	6	191	-203	22
-7	12	6	668	-658	14
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-5	12	6	170	186	23
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5	13	6	133	55	35
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Observed and Calculated Structure Factors for $(PPh_3)_2(Cl)_2Ru(C(CH_2)_3)$ (8)

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1	3	8	152	-170	17
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Observed and Calculated Structure Factors for $(PPh_3)_2(Cl)_2Ru(C(CH_2)_3)$ (8)

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Observed and Calculated Structure Factors for $(PPh_3)_2(Cl)_2Ru(C(CH_2)_3)$ (8)

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Observed and Calculated Structure Factors for $(PPh_3)_2(Cl)_2Ru(C(CH_2)_3)$ (8)

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2	7	15	661	661	15
3	7	15	107	-148	-41
-8	8	15	211	189	24
-7	8	15	452	448	16
-6	8	15	561	567	14
-3	8	15	426	444	16
-2	8	15	212	-227	21
-1	8	15	385	-375	16
1	8	15	170	-171	22
2	8	15	114	112	-42
-6	9	15	90	66	-64
-5	9	15	43	-133	-66
-4	9	15	358	-347	16
-3	9	15	177	195	21
-2	9	15	381	366	15
-1	9	15	544	-578	15
0	9	15	744	-728	16
1	9	15	658	650	15
-4	10	15	321	342	21
-2	10	15	505	-541	15
-1	10	15	47	118	-69
-10	0	16	19	-8	-76
-8	0	16	600	-605	14
-6	0	16	1153	1131	12
-4	0	16	311	310	15
-2	0	16	119	105	33
0	0	16	172	-139	28
2	0	16	254	-234	20
4	0	16	537	557	16
-10	1	16	91	-46	-44
-9	1	16	424	-411	17
-7	1	16	625	-617	13
-6	1	16	263	245	17
-5	1	16	215	249	18
-4	1	16	344	-292	15
-3	1	16	522	-481	13
-2	1	16	320	357	17
-1	1	16	648	639	14
0	1	16	135	92	20
1	1	16	888	-881	13
2	1	16	267	242	18
3	1	16	616	589	15
4	1	16	295	-274	18
-10	2	16	205	180	33
-9	2	16	645	-643	16
-8	2	16	426	-420	15
-7	2	16	816	803	13
-6	2	16	512	471	14
-5	2	16	561	-559	13
-4	2	16	128	-112	32
-3	2	16	301	289	18
-1	2	16	542	-539	13
0	2	16	220	206	13
1	2	16	312	-262	16
2	2	16	261	-268	20
3	2	16	560	566	15
4	2	16	230	-250	21
-10	3	16	487	-497	16
-9	3	16	103	111	-41
-8	3	16	77	-12	-65
-7	3	16	103	-76	-39
-6	3	16	164	174	21
-4	3	16	417	-439	15
-3	3	16	82	-31	-44
-2	3	16	246	245	18
-1	3	16	285	214	22
0	3	16	350	-326	11
1	3	16	514	509	15
2	3	16	522	498	15
3	3	16	133	131	33
4	3	16	486	-476	17
-9	4	16	872	879	13
-8	4	16	120	96	38
-7	4	16	1046	1008	12
-6	4	16	292	277	17
-5	4	16	717	702	13
-3	4	16	285	295	17
-1	4	16	279	282	17
0	4	16	327	318	31
1	4	16	716	713	14
3	4	16	663	[illegible]	15
4	4	16	288	284	18
-9	5	16	294	308	18
-8	5	16	349	330	18
-7	5	16	120	166	38
-6	5	16	331	320	21
-5	5	16	115	91	36
-4	5	16	82	17	-60
-3	5	16	357	378	16
-2	5	16	132	60	30
-1	5	16	381	-38	15
0	5	16	529	527	17
1	5	16	611	587	14
2	5	16	120	[illegible]	37
3	5	16	343	346	17
-8	6	16	580	601	17

Observed and Calculated Structure Factors for $(PPh_3)_2(Cl)_2Ru(C(CH_2)_3)$ (8)

h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
-7	6	16	606	622	14	-7	0	17	1214	1218	13	-2	2	17	472	-431	15	-7	5	17	335	351	17	-4	1	18	207	-204	19
-6	6	16	596	-611	14	-5	0	17	63	98	-54	-1	2	17	130	97	27	-6	5	17	437	-448	16	-3	1	18	213	238	17
-5	6	16	611	-619	13	-3	0	17	405	417	15	0	2	17	248	-243	31	-4	5	17	295	306	18	-2	1	18	201	-173	18
-4	6	16	395	401	15	-1	0	17	240	-263	17	1	2	17	570	-575	15	-3	5	17	339	352	17	-1	1	18	639	-624	14
-3	6	16	312	313	16	1	0	17	537	-518	15	2	2	17	622	607	14	-2	5	17	255	-261	18	0	1	18	406	390	19
-2	6	16	386	-402	15	3	0	17	564	587	15	3	2	17	273	302	21	-1	5	17	222	-223	24	1	1	18	794	756	15
-1	6	16	134	-56	30	-9	1	17	268	266	17	-7	3	17	384	381	16	0	5	17	409	402	16	-7	2	18	310	-342	18
0	6	16	147	-142	18	-8	1	17	76	104	-52	-6	3	17	261	240	19	1	5	17	135	-80	32	-6	2	18	210	-172	22
1	6	16	562	-577	16	-7	1	17	213	171	24	-5	3	17	462	-438	14	-6	6	17	579	-529	14	-5	2	18	204	196	20
2	6	16	443	424	16	-6	1	17	821	813	13	-4	3	17	222	-212	20	-5	6	17	286	327	19	-4	2	18	172	206	21
-7	7	16	256	278	25	-5	1	17	684	-678	14	-3	3	17	168	166	20	-4	6	17	467	471	15	-3	2	18	140	-106	34
-5	7	16	192	184	22	-4	1	17	555	-541	14	-2	3	17	403	369	18	-3	6	17	365	-361	16	-2	2	18	40	-97	-65
-4	7	16	60	-16	-50	-2	1	17	440	474	15	-1	3	17	288	-263	19	-2	6	17	98	-101	-44	0	2	18	98	-91	-42
-3	7	16	290	294	17	-1	1	17	172	-154	24	0	3	17	81	-70	-36	-1	6	17	55	11	-55	-6	3	18	844	-828	14
-2	7	16	389	-400	16	0	1	17	757	-736	10	1	3	17	658	676	15	0	6	17	393	-384	13	-5	3	18	121	-141	37
-1	7	16	760	-730	13	1	1	17	424	403	16	2	3	17	53	109	-65	-4	7	17	491	508	16	-4	3	18	477	475	15
1	7	16	833	842	14	2	1	17	836	802	15	-8	4	17	833	806	13	-3	7	17	290	-283	18	-3	3	18	424	437	17
-6	8	16	671	-668	14	3	1	17	56	-59	-63	-7	4	17	294	-261	18	-2	7	17	487	-513	16	-2	3	18	55	-48	-59
-5	8	16	172	166	22	-9	2	17	162	-174	27	-6	4	17	966	-937	13	-6	0	18	251	-250	20	0	3	18	525	513	11
-4	8	16	233	203	19	-8	2	17	906	862	13	-5	4	17	215	-181	23	-4	0	18	91	12	-44	-5	4	18	431	419	16
-3	8	16	179	-174	22	-7	2	17	434	438	17	-4	4	17	333	340	16	-2	0	18	373	-390	16	-4	4	18	120	-9	35
-2	8	16	216	-237	21	-6	2	17	760	-735	13	-2	4	17	350	-364	15	0	0	18	364	-359	12	-3	4	18	128	-143	35
-1	8	16	102	169	-46	-5	2	17	322	-316	17	0	4	17	361	-370	19	-7	1	18	680	698	15	-2	4	18	100	194	-46
0	8	16	185	-160	25	-4	2	17	159	-138	31	1	4	17	19	12	-76	-6	1	18	406	-399	15	-1	4	18	129	162	26
-9	0	17	174	-197	28	-3	2	17	223	177	19	2	4	17	700	675	14	-5	1	18	1016	-972	13	-3	5	18	97	-169	-46

Chapter 4

Ring-Opening Metathesis Polymerization of Strained Cyclic Olefins Using Molybdenum, Tungsten Alkylidenes and a Ruthenium Carbene Complex

This chapter focuses on the application of early transition metal alkylidenes and a late-transition metal carbene complex to the synthesis of new materials and developing new living polymerization systems.

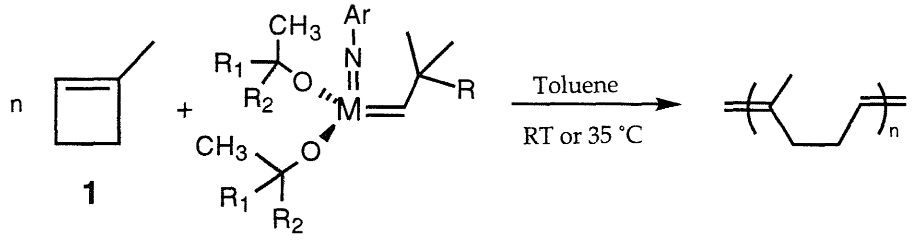
This chapter consists of three sections. In section one, the ring-opening metathesis polymerization (ROMP) of 1-methylcyclobutene using well-defined molybdenum and tungsten alkylidene complexes will be discussed. In section two, a ruthenium carbene complex has been used to catalyze the living ROMP of bicyclo[3.2.0]heptene and bicyclo[4.2.0]octene. In section three, the ROMPs of cyclobutene derivatives for the synthesis of alternating copolymers have been explored.

The Synthesis of Perfect Rubber Using Ring-Opening Metathesis Polymerization of 1-Methylcyclobutene

Introduction

Polyisoprene (natural rubber) is a commercially important material used in the manufacture of many elastomers.[1a] Oligomeric polyisoprenes are also useful precursors in the synthesis of terpenes and a number of natural products.[1b,c] Because of the non-stereospecific nature of the anionic and Ziegler-Nata polymerization of isoprene,[2] it has not been possible to prepare polyisoprene having exclusively *cis* and head-to-tail structure. Although attempted ROMPs of substituted cyclic olefins are often unsuccessful because of unfavorable steric interactions,[3] we decided to investigate the ROMP of 1-methylcyclobutene in an attempt to generate stereoregular polyisoprene.

In this section, we describe the first synthesis of polyisoprene that has an exclusively *cis* and head-to-tail structure. The synthesis uses well-defined molybdenum and tungsten alkylidene complexes to catalyze the ring-opening metathesis polymerization (ROMP)[4] of 1-methylcyclobutene **1**[5] (eq 1).



(1)

M = W, Mo

R = Ph, CH_3

R_1, R_2 = CH_3 or CF_3

Ar = 2,6 - diisopropylphenyl

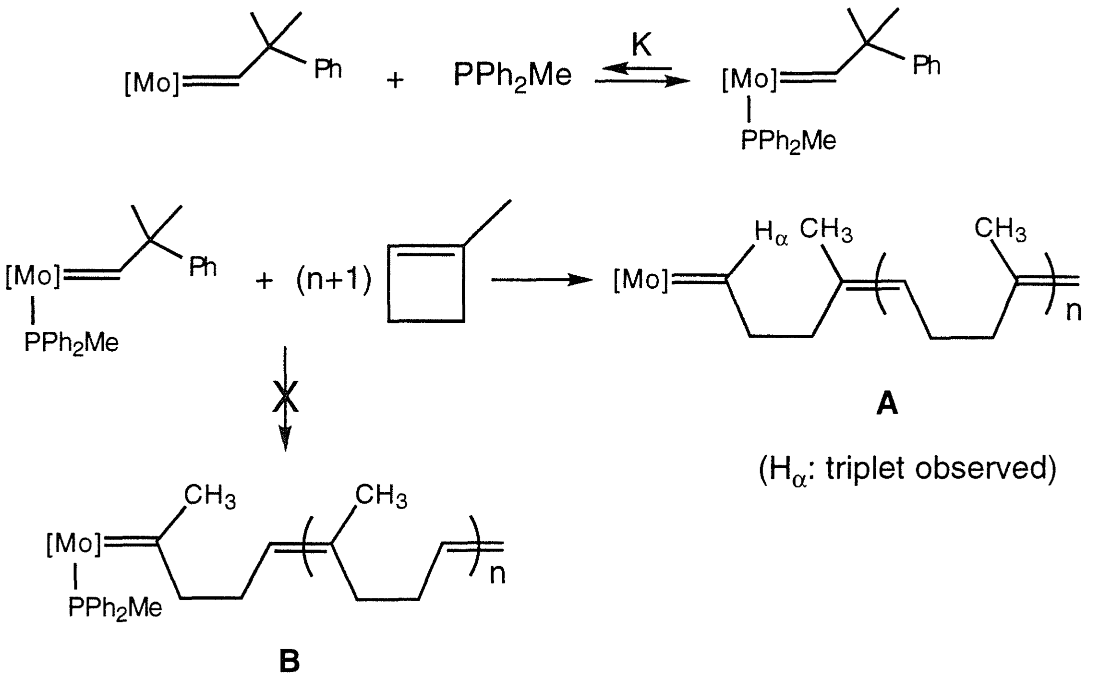
Results and Discussion

The use of $Mo(CHC(CH_3)_2Ph)(NAr)(OC(CH_3)_2CF_3)_2$[6] **2** as catalyst generates a completely stereoregular polymer. The reaction between 174 equiv of **1** and a 0.01 M of **2** in a toluene solution is complete in five minutes at room temperature. No propagating alkylidene can be observed by ^1H NMR spectroscopy during the reaction, indicating that the rate of propagation is much faster than that of initiation. The polymer can be isolated in 78% yield with a molecular weight of 20,000 and a polydispersity of 2.5. Analysis by ^1H and ^{13}C NMR spectroscopy indicates that the polymer backbone has an exclusively *cis* configuration with complete head-to-tail structure. We observe the following resonances by ^1H NMR: δ = 1.67 ppm (CH_3), 2.04 ppm (CH_2), 5.13 ppm (olefinic); ^{13}C NMR: δ = 23.6 ppm (CH_3), 26.8 ppm (CH_2), 32.5 ppm (CH_2 adjacent to quaternary carbon), 125.3 ppm (olefinic CH), 135.5 ppm (olefinic C). Additional support for the assigned structure can be found by hydrogenating the polyisoprene using *p*-tosylhydrazide in xylene at 120 °C for two hours.[7] The ^{13}C NMR spectrum of the hydrogenated polymer shows only four resonances at δ = 20.0 ppm (CH_3 triads), 25.0 ppm (CH_2), 33.3 ppm (CH), 38.0 ppm (CH_2), which is consistent with a perfectly alternating copolymer of ethylene and propylene.[8]

In the polymerization of **1** by **2**, the polydispersity can be lowered by decreasing the rate of propagation relative to the rate of initiation.[9] We obtained a polydispersity of 1.46 by polymerizing **1** in a toluene solution containing **2** in the presence of 50 equiv $P(OMe)_3$. We believe that $P(OMe)_3$ slows the rate of propagation relative to that of initiation.

The high regioselectivity in the polymerization of **1** by **2** probably results from steric repulsion between the methyl group of the approaching olefin and the bulky alkoxide on the catalyst; as a consequence of this interaction, the methyl group points away from the bulky alkoxide upon coordination.[10] This hypothesis is supported by the observation that addition of 10 equiv of PPh_2Me to **2** in a toluene solution containing 17 equiv of **1** results in the initiation of 50% of the starting alkylidene (a new alkylidene resonance at $\delta = 13.2$ ppm corresponding to a triplet with $J_{H\text{-}H} = 6.34$ Hz can be observed by ^1H NMR spectroscopy throughout the reaction),[11] as shown in Scheme 1.

Scheme 1



We have also found that **1** can be polymerized by other well-defined tungsten and molybdenum catalysts. For example, if we employ $W(CHC(CH_3)_3)(NAr)(OC(CH_3)_3)_2$[12] **3** as catalyst, we can generate polymers with perfect regioselectivity. Heating, however, is required for reaction to occur. For example, a toluene solution containing 200 equiv of **1** and 0.01 M of **3** is heated to 30~35 °C for two hours and then precipitated into methanol. The polymer obtained has a molecular weight of 9500 and PDI of 2.0. Analysis of the ^{13}C

NMR spectrum reveals that the structure of the backbone is 80% cis and completely head-to-tail. The yield of polymer is, however, only 43% .

If we employ the more active $W(CHC(CH_3)_3)(NAr)(OCCH_3(CF_3)_2)$[13] **4** as catalyst, the polymerization of **1** occurs rapidly at room temperature to give a polymer whose ^1H and ^{13}C NMR spectra are similar to those of polyisoprene. The polymer has a 95% *cis* configuration but is composed of approximately 20% butadiene (^{13}C NMR: $\delta = 129.4, 129.7, 130.0, 130.2$ ppm) and dimethylbutadiene (^{13}C NMR: $\delta = 128.1, 128.3$ ppm).[14] The reaction typically gives a low yield of polymer (<30%) having a low molecular weight ($M_n = 2000$; PDI = 1.7)[15] even with prolonged reaction time.

The irregular head-to-head and tail-to-tail structures found in the polymerization when using the more reactive catalyst **4** probably results from the great electrophilicity of **4** (steric interactions consequently have a limited influence upon the coordination of **1** to **4**). In contrast, polymerization of **1** using the less electrophilic catalysts **2** and **3** are greatly influenced by steric effects; coordination of **1** to these catalysts thus exhibits large selectivity. We believe that the high *cis* configurations obtained in all the polymerizations of **1** reported here results from the steric interaction between the methyl group of **1** and the growing polymer chain.[10]

Conclusion

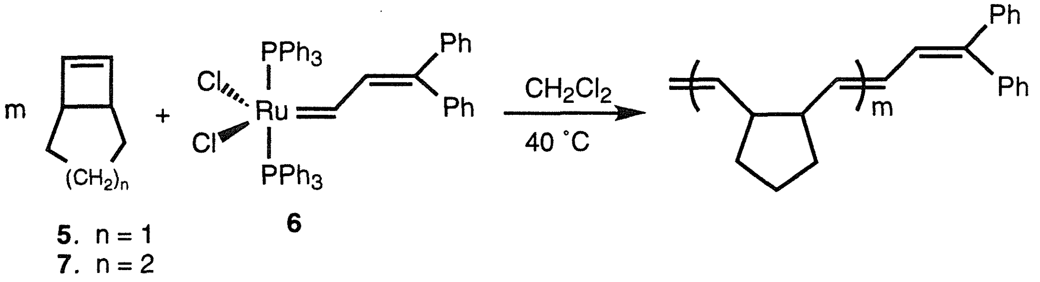
For the first time, perfectly alternating *cis*-1,4- polyisoprene has been prepared using the method presented here. We are currently investigating the synthesis of oligomeric polyisoprene and terpenes using chain transfer techniques.[16] We are also investigating the ROMP of other trisubstituted olefins in order to generate related stereoregular polymers. Future direction will also involve the asymmetric hydrogenation of polyisoprene to prepare optically active polymer, and asymmetric dihydroxylation of polyisoprene to synthesize optically active water soluble polymer.[17]

The Living Ring-Opening Metathesis Polymerization of Bicyclo[3.2.0]heptene and Bicyclo[4.2.0]octene Catalyzed by a Ruthenium Carbene Complex

Introduction

Living polymerizations using ring-opening metathesis catalysts (ROMP) have allowed the synthesis of polymers with controlled structure and properties.[4,18] In the past few years, efforts have been focused on developing novel transition metal alkylidene complexes that catalyze this reaction and provide either access to new product or easier synthesis.[4] All of the catalysts developed to date are high oxidation state organometallic complexes, which exhibit limited tolerance to polar functional groups, and only catalyze the living polymerization of norbornene and its derivatives.[10,13,19] Recently, a ruthenium carbene complex was synthesized, which exhibits exceptional tolerance to a variety of polar functional groups and catalyzes the living ROMP of norbornene.[20] Because we were interested in elucidating the details of this living polymerization,[9,21] we investigated the ROMP of highly reactive monomer bicyclo[3.2.0]heptene **5**,[22] catalyzed by the late transition metal complex $(PPh_3)_2(Cl)_2Ru(=CH-CH=CPh_2)$ **6** (eq 2). We hope that an investigation of this system will provide us with a better understanding of the mechanism of polymerization by late transition metal alkylidene complexes[23] and eventually allow us to control molecular weight in the preparation of functionalized polymers with potential uses in biological applications.[24] In this section, the living ROMP of **5** and **7**[22] will be discussed. The ROMP of *trans*-cyclooctene by **6** will also be examined.

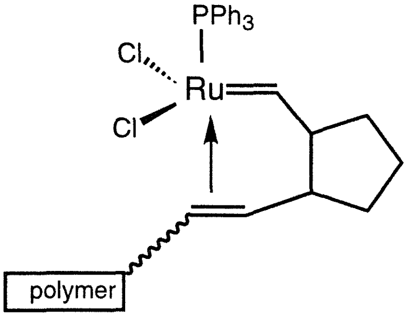
Results and Discussion



(2)

Initial investigations of the polymerization of **5** by several well-defined tungsten and molybdenum alkylidene complexes showed that the rate of polymerization is much greater than that of initiation,[25] which is probably due to the fact that the propagating alkylidene is less hindered than the bulky starting alkylidene. The highly strained monomer[26] thus reacts more rapidly with the propagating alkylidene than with the starting alkylidene. Given these considerations, we thought that monomer **5** might react more rapidly with the starting alkylidene based on **6**, and thus catalyze the polymerization of **5** in a living fashion. Indeed, **6** catalyzes the polymerization of **5** in a controlled manner. The addition of 20 equiv of monomer **5** to a solution of **6** in methylene chloride at 40 °C results in complete initiation of the starting alkylidene. Throughout the polymerization, three new propagating species are observed by ^{1}H NMR spectroscopy at $\delta = 18.06$ (multiplet), 17.38 (doublet) and 16.90 ppm (doublet) in a ratio of 2.0:1.9:1.0 with coupling constants $J_{H\text{-}P} = 14.60$, 14.25, and 6.83 Hz, respectively. Variable temperature analysis by ^{1}H NMR spectroscopy at low temperatures indicates that the three propagating species are in equilibrium. For example, as the temperature was lowered to -40 °C, the ratio of the three propagating species changed to 8.0:1.6:1.0. When 8 equiv of triphenylphosphine was added to the reaction mixture at room temperature, the intensities of two upfield resonances ($\delta = 16.9$ and 17.38 ppm) decreased and the intensity of downfield resonance (δ 18.06 ppm) increased. Furthermore, when the polymerization is carried out in the presence of 10 equiv of deuterium labeled PPh_3, only one propagating resonance (δ 18.06 ppm.) was observed by ^1H NMR spectroscopy. Due to the above observations and observed coupling patterns, we believe that the downfield resonance corresponds to a diphosphine adduct and two upfield resonances correspond to monophosphine adducts. The intensities of these propagating species remain constant during the polymerization (as measured by integration relative to a dichloroethane internal standard). Examination of the reaction mixture by ^{31}P NMR spectroscopy reveals resonances at 41.7 and 29.17 ppm, as well as the presence of free triphenylphosphine at -4.9 ppm.[27] In contrast, the polymerization of norbornene exhibits only one resonance at 17.6 ppm by ^1H NMR spectroscopy and 30.06 ppm by ^{31}P NMR spectroscopy for the propagating species.

In the polymerization of **5** by **6**, dissociation of the phosphine is probably aided by the chelation of the double bond on the growing polymer chain adjacent to the metal carbene bond. Chelation of this type is favored because it leads to the formation of a stable five-member ring.[28] Consistent with this hypothesis is the observation by ^1H NMR spectroscopy that the propagating alkylidene is stable at room temperature for several hours without decomposition. We believe that possible bimetallic decomposition pathways are inhibited by the bulky cyclopentyl substituent on the carbene.[29]



The kinetics of the polymerization of **5** was followed by ^{1}H NMR spectroscopy at 40 °C (Figure 1). The rate of polymerization is first order with respect to both monomer and catalyst concentrations with $k_p = 0.183$ min/M^{-1} and $k_p/k_i = 6.5$[30] (where k_p and k_i are the rate constants for propagation and initiation, respectively). The polymerization of **5** in the presence of 10 equiv of deuterium-labeled PPh_3 was also followed by ^{1}H NMR spectroscopy and the observed rate constant for the polymerization ($k_p' = 0.011$ min/M^{-1}) was determined.[31]

In a typical bulk polymerization, 170 equiv of **5** was allowed to react with 0.007 M of **6** in methylene chloride for approximately one hour at 40 °C, and then with 30 equiv of ethyl vinyl ether,[32] followed by stirring for another 20 minutes. The resulting mixture was then diluted with benzene and passed through a short column of silica gel to give polymer in essentially quantitative yield having a molecular weight of 16500 and polydispersity (M_w/M_n) of 1.2. Analysis by ^{13}C NMR spectroscopy indicated that this polymer had a 58% *cis* configuration of double bonds in the backbone, while the polynorbornene obtained using **6** has a 13% *cis* configuration of double bonds in the backbone. The high *cis* content in the former polymer can be interpreted using Ivin's model[33(a),(b)], but the polymer exhibits only a small degree of blockiness ($\gamma_c\gamma_t = 1.2$)[33(c)]. The polymer is atactic, which was confirmed by hydrogenation with *p*-tosylhydrazide in xylene at 120 °C.[34] Although no melting point was observed, a glass transition temperature T_g of 34 °C (Figure 2) was observed by differential scanning calorimetry (DSC). These observations are consistent with the polymer of having an amorphous structure.

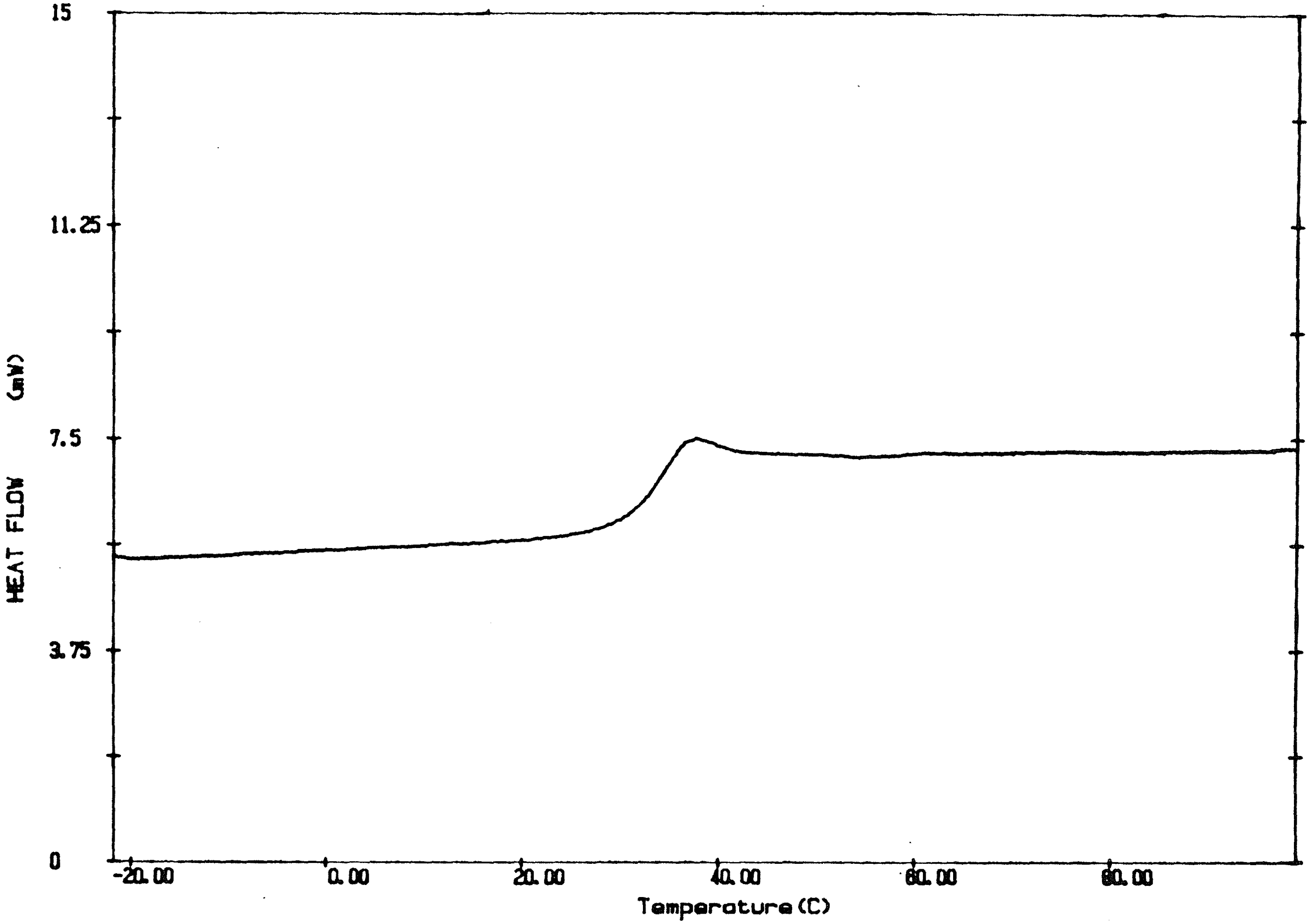


Figure 2. DSC profile of poly-5.

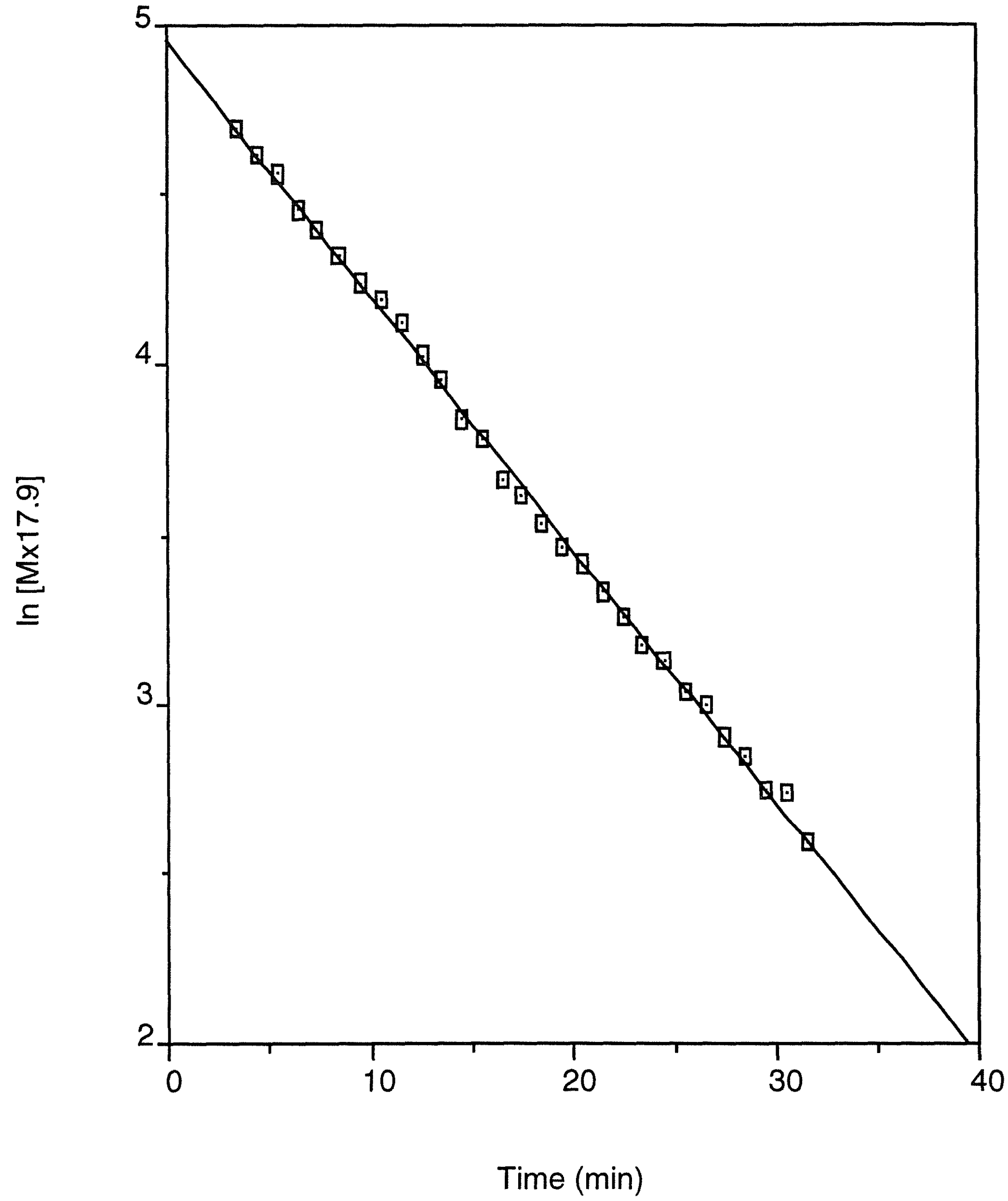
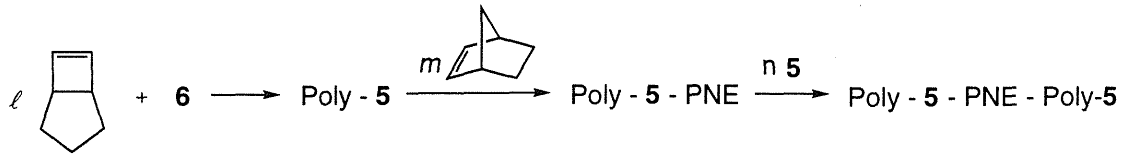


Figure 1. Kinetic data for the polymerization of **5** catalyzed by **6** at 40 °C.

of 34 °C (Figure 2) was observed by differential scanning calorimetry (DSC). These observations are consistent with the polymer of having an amorphous structure.

We have found that the molecular weights obtained from these polymerizations are proportional to the ratio of monomer-to-catalysts as shown in Figure 3. This observation is consistent with a living polymerization. Further evidence for the living polymerization of **5** is the facile preparation of block copolymers. Diblock or triblock copolymers of norbornene and **5** can be synthesized by sequential addition of either **5** or norbornene to catalyst **6** (eq 3). For example, 27.8 equiv of **5** was added to a solution of methylene chloride containing 0.007 M of **6** at 40 °C, and the polymerization followed by ^{1}H NMR spectroscopy. When the polymerization of **5** was complete, 41.7 equiv of norbornene was added to the reaction mixture. The propagating alkylidene resonances of poly-**5** (vide supra) completely disappeared and the resonance corresponding to the propagating species of polynorbornene ($\delta = 17.6$ ppm) grew in. After the norbornene polymerization was complete, another 27.8 equiv of **5** was added to the reaction mixture. As expected, the NMR signal corresponding to the ruthenium alkylidene end group based on ring-opened norbornene vanished, and the resonances corresponding to the propagating species derived from **5** reappeared. (Integration relative to the resonance of triphenylphosphine showed that this process was quantitative.) The tri-block copolymer thus obtained had a molecular weight of 41500 and a polydispersity of 1.2.



5

(3)

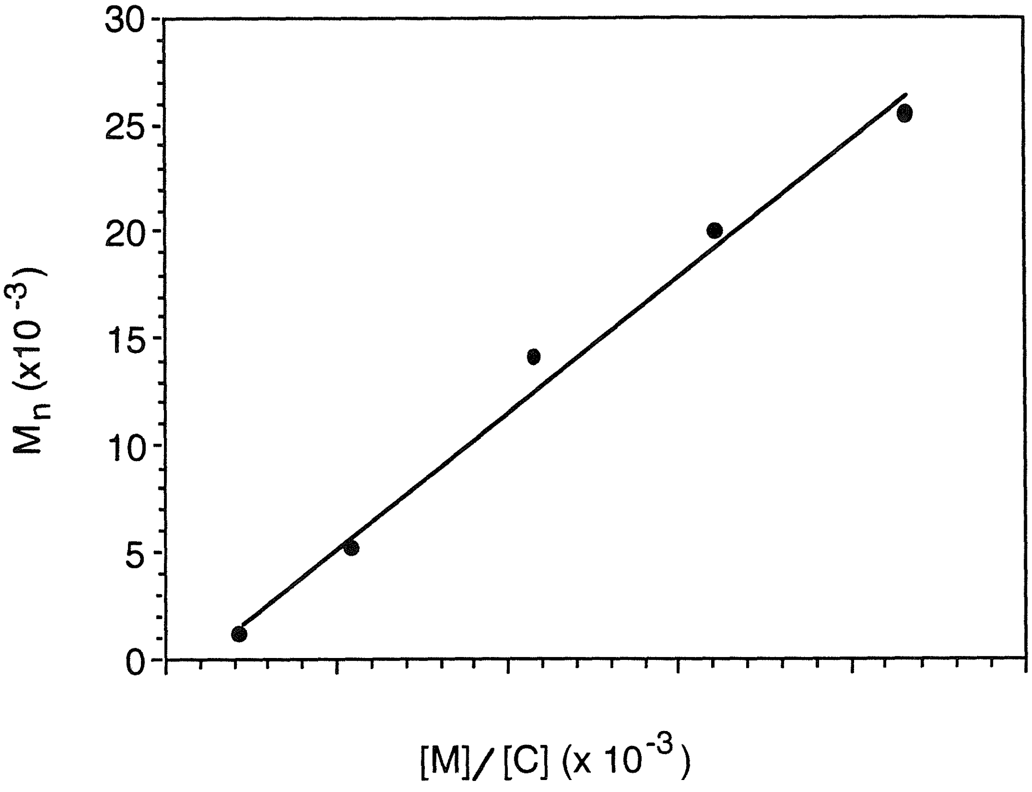
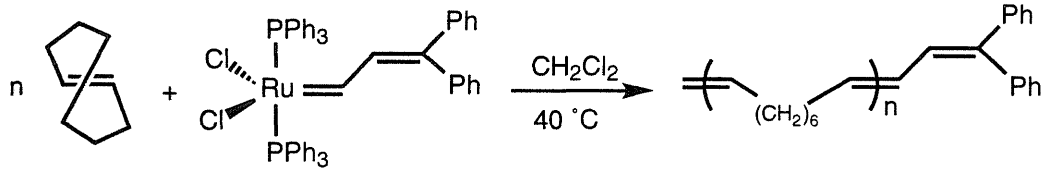


Figure 3. A plot of molecular weight versus the ratio of monomer/catalyst in the polymerization of **5** by **6**. The line through the points was determined by linear least squares with $\rho = 0.995$.

In a similar manner, bicyclo[4.2.0]octene **7** can also be polymerized in a living fashion (eq 1) to give polymer having a PDI of 1.2 and 61% *cis* double bond configuration in the backbone. *Trans*-cyclooctene was also polymerized rapidly by **6** as shown in eq 4. The reaction exhibits certain features of a living polymerization. For example, the H_α and H_β of the propagating species of ring-opened polycyclooctene were observed at 18.22 (septet, $J_{H\text{-}P} = 10.03$ Hz; $J_{H\text{-}H} = 6.98$ Hz) and 3.01 (quartet) ppm by ^1H NMR spectroscopy. The polymer obtained has a PDI of 2.74 and a molecular weight much higher than the value calculated from the ratio of monomer versus catalyst, indicating that the rate of propagation is much faster than that of the initiation.



6

(4)

We have also found that when a 50/50 mixture of **5** and norbornene is added to a solution containing catalyst **6** in methylene chloride, polymerization of norbornene does not initiate until the polymerization of **5** is complete. This observation suggests that the reactivity ratios[35] of chain propagation have the following constraints: $\gamma_{cc} = k_{cc}/k_{cn} \gg 1$ or $\gamma_{nn} = k_{nn}/k_{nc} \ll 1$ (where k_{cn} is the rate constant of poly-**5** reacting with norbornene; k_{cc} is the rate constant for the polymerization of **5**; k_{nc} is the rate constant for the propagating ruthenium-carbene based on polynorbornene reacting with **5**; k_{nn} is the rate constant for the polymerization of norbornene). This can be explained by the fact that the double bond in **5** is less hindered than the double bond in norbornene, thus **5** approaches the propagating alkylidene at a faster rate than norbornene. We have found by homo polymerization studies that the rate constants k_{cc} and k_{nn} are comparable. Based on these observations, it can be concluded that the rate constant k_{nc} is substantially larger than k_{cn} ($k_{nc} \gg k_{cn}$).

Conclusion

Bicyclo[3.2.0]heptene **5** and bicyclo[4.2.0]octene **7** can be polymerized in a living fashion by a ruthenium carbene complex, which demonstrates that this functional group-tolerant carbene complex shows all the desirable features of the early transition metal complexes studied earlier.[4,19,21] The polymerization of **5** fits the criteria for a living polymerization.[36] The ROMP of *trans*-cyclooctene exhibits certain features of a living polymerization. We are currently investigating the use of these systems and other related systems for the preparation of functionalized polymers and new block copolymers.

Preparation of Alternating Copolymers from the Ring-Opening Metathesis Polymerization of 3-Methylcyclobutene and 3,3-dimethylcyclobutene

Introduction

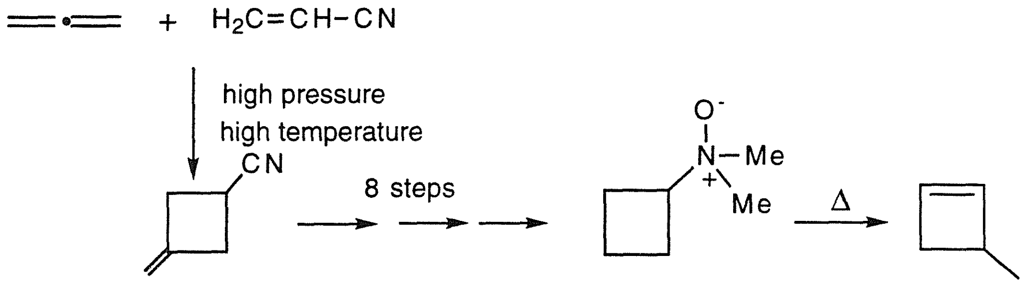
Ring-opening metathesis polymerization (ROMP) of strained cyclic olefins is an extremely useful technique for the synthesis of new materials,[4,37] especially the recent development of living ROMP methods have allowed the preparation of several novel block copolymers.[38] Alternating copolymers, such as poly(ethylene-propylene) and poly(ethylene-styrene), represent important classes of copolymers, which were usually synthesized by Ziegler-Natta polymerization of a mixture of the two monomers.[39] Although some successful examples of synthesizing perfect alternating CO and styrene copolymer were reported recently,[40] it is, however, rather difficult to insert two similar monomers in an alternating fashion to yield polymers with high regioselectivities. In general, the synthesis of perfect alternating copolymer remains a synthetic challenge.

We are interested in using ROMP to tackle this problem. ROMP offers the advantage of producing polymers with low polydispersity, well-defined structure and allow the incorporation of a wide range of functionalities into the polymer compared to other types of polymerization.[23,41] Our approach involves the ROMP of substituted cyclobutenes, such as 3-methylcyclobutene **8**[42] and 3,3-dimethylcyclobutene **9** using high oxidation state molybdenum and tungsten alkylidene complexes.[43] The structures of poly-**8** and poly-**9** upon hydrogenation are equivalent to alternating copolymers of ethylene/propylene and ethylene/isobutylene, respectively. The strain-energy in the monomer should drive the polymerization to proceed irreversibly, which offers the possibility of developing living polymerization systems for these monomers by controlling the rates of the reactions.[44]

Since the microstructures of ring-opened polymers of cyclobutene derivatives are still unknown,[45] this investigation should also provide us some insights to the microstructures of the new polymers and allow us to have a better understanding of the substituent effects of the monomer to such important questions as regioselectivity and stability of the propagating species during the ROMP of strained cyclic olefins. Through this investigation, we will also be able to learn more about controlling the rate of the propagation relative to that of the initiation in ROMP and to synthesize copolymers with low polydispersities.

In this section, synthesis and ROMP of 3-methylcyclobutene **8** and 3,3-dimethylcyclobutene **9** using high oxidation state molybdenum and tungsten alkylidene complexes will be discussed.

Scheme 2



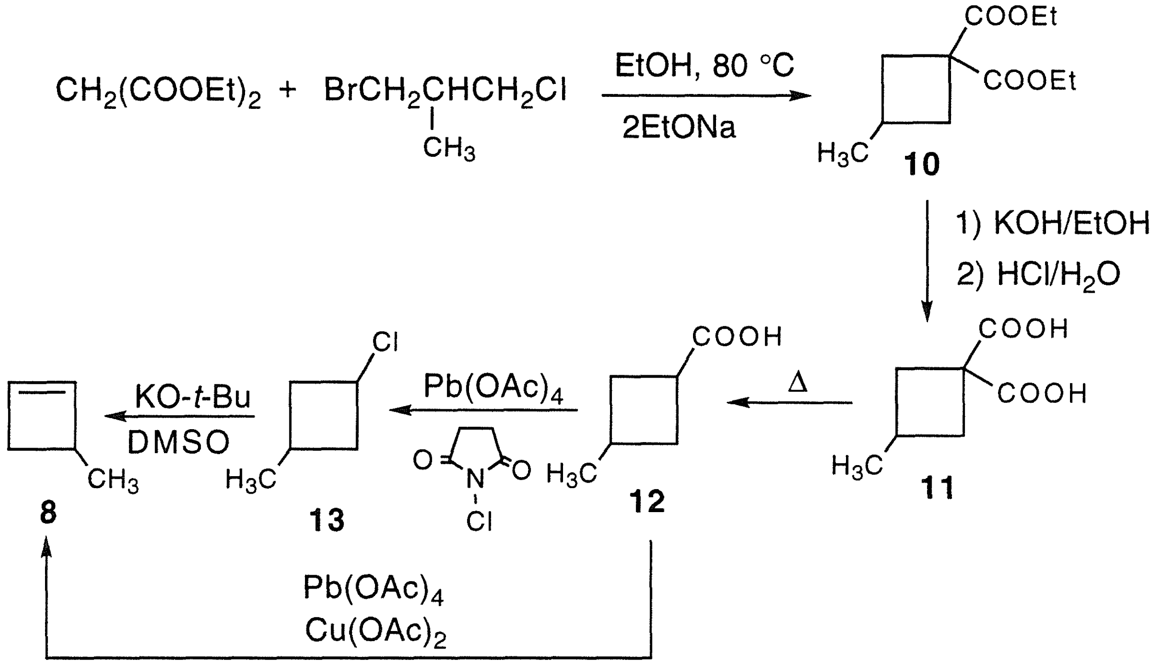
8

Results and Discussion

(I) Monomer Synthesis.

(A) Synthesis of 3-methylcyclobutene **8**.

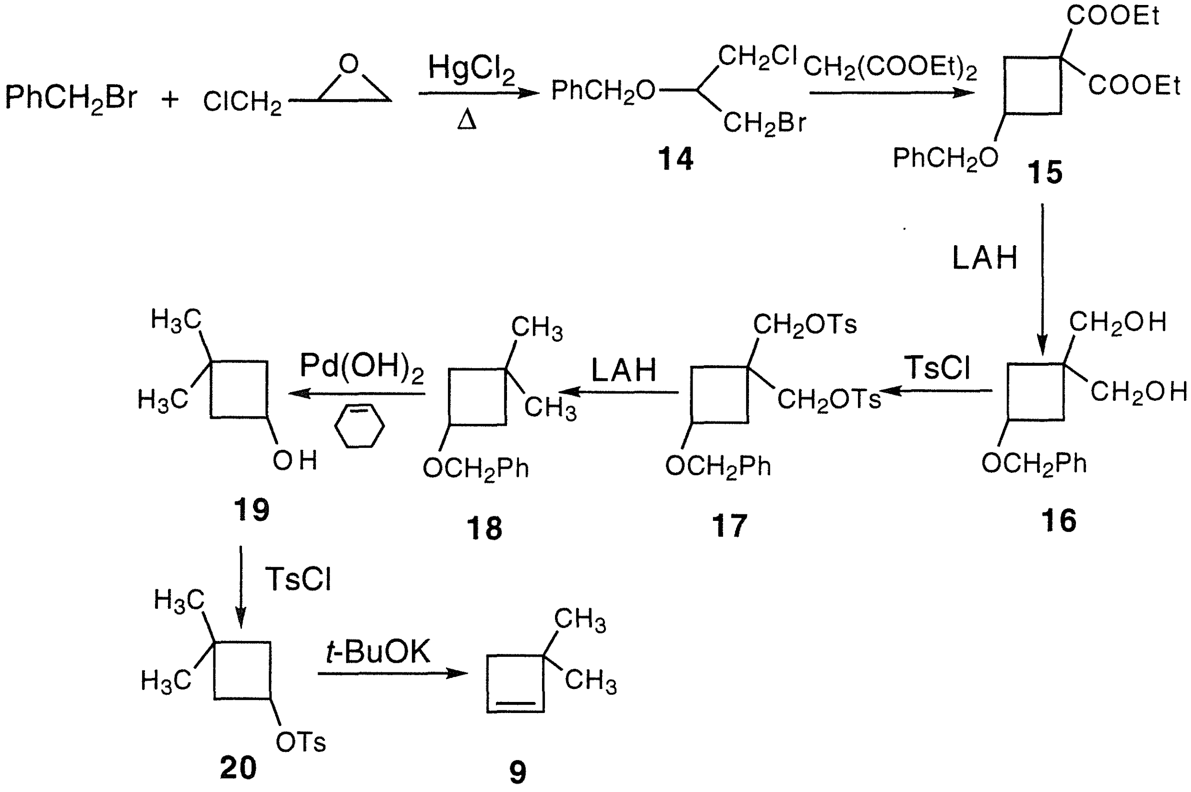
In the literature, **8** was synthesized in 10 steps as shown in Scheme **2**, starting from allene and acrylonitrile.[46] We repeated the procedures and encountered some difficulties in scaling up the reactions and especially in purifying the final product, since **8** decomposes above 135 °C, which is around the reaction temperature of the final step. Also, in the first step, the reaction was carried out at high pressure and temperature, which required special apparatus and precautions. Therefore, we developed a modified procedure as shown in Scheme **3**. The four-member ring was easily constructed by a [1+3] nucleophilic addition reaction. Dimethyl malonate was first reacted with 1-bromo-2-methyl-3-chloropropane to form diethyl 3-methylcyclobutane-1,1-dicarboxylate **10** in 55.4% yield. Compound **10** was readily hydrolyzed to its diacid analog **11** in 97% yield. **11** lost one carboxyl group upon heating to give **12** in 96% yield.[47] Although **12** might be directly decarboxylated in the presence of $Pb(OAc)_4$ and $Cu(OAc)_2$ to yield **8**, a very low yield of **8** resulted.[48] Technical problems also prevented the reaction from being carried out in a large scale. As an alternative route, **12** was first converted to 1-chloro-3-methylcyclobutene **13** followed by decarboxylation.[49] Compound **13** can readily undergo elimination by treating with *t*-BuOK to form the desired product **8** in good yield.[50]



Scheme 3. Synthesis of Monomer **8**.

(B) Synthesis of 3,3-dimethylcyclobutene **9**

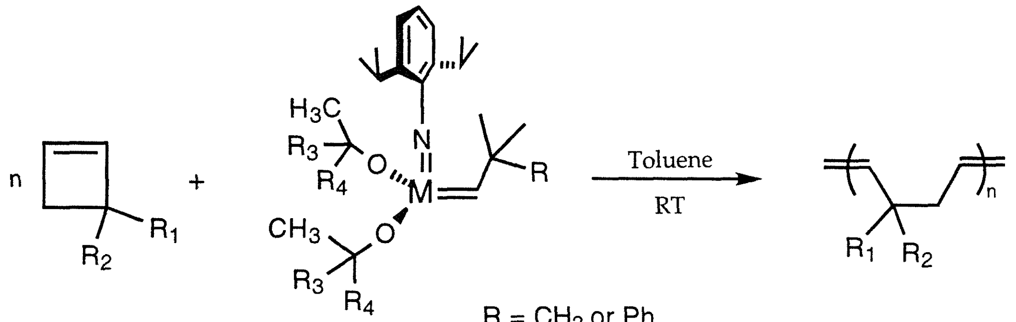
The synthesis used here (Scheme **4**) is based on a modified literature procedure.[51] 1-bromo-2-benzyloxy-3-chloropropane **14** was synthesized in 73% yield. Diethyl 3-benzyloxycyclobutane-1,1-dicarboxylate **15** was obtained in 43% yield by reacting **14** with diethylmalonate in dioxane for several days. Compound **15** was readily reduced to 1,1-di(hydroxymethylene)-3-benzyloxycyclobutane **16** in 87% yield using LAH in THF. **16** was further converted to ditosylate **17** in high yield by reacting with tosyl chloride. **17** was reduced by LAH in THF to yield 3,3-dimethylbenzyloxycyclobutane **18** in 83.3% yield. The attempt to cleave the benzyl protecting group in **18** via hydrogenation using Pd/C as catalyst was not successful,[51] which might partly be attributed to the poisoning effect caused by trace amount of sulfur in **18**. However, the deprotection of **18** was accomplished by hydrogen transfer reaction from cyclohexene employing more functional group tolerant $Pd(OH)_2$ as catalyst and **19** was obtained in 63% yield.[52] Reaction of **19** with tosylchloride to give **20** in high yield, which readily eliminated a tosylate in the presence of *t*-BuOK to yield **9**.



Scheme 4. Synthesis of Monomer **9**.

(II) Polymerization

3-methylcyclobutene **8** can be rapidly polymerized by well-defined molybdenum and tungsten alkylidene complexes at room temperature as shown in eq 5. Low temperature NMR studies revealed that the polymerization initiated at -60 °C in toluene, which was similar to the onset polymerization temperature of cyclobutene[53] suggesting that the methyl substituent on the 3-position of cyclobutene does not decrease the reactivity of the monomer with **3** or **21** to undergo the ring-opening polymerization. When 10 equiv of **8** is added into a toluene solution containing 0.011 M of catalyst $Mo(CHC(CH_3)_3)(NAr)(OC(CH_3)_3)_2$ (Ar = 2,6-diisopropylphenyl) **21** at room temperature, two doublets at 11.95 ppm ($J_{H\text{-}H}$ = 6.6 Hz) and 11.50 ppm ($J_{H\text{-}H}$ = 9.5 Hz) are observed by ^1H NMR spectroscopy.[54] These resonances are attributed to the two rotamers (anti and syn) of the propagating alkylidenes where anti and syn refer to whether the polymer chain attached to the metal-alkylidene double bond is on the opposite or the same side as the imido group.[55] The methyl substituent on the cyclobutene is now on the β-carbon of the propagating species of the ring-opened polymers and apparently stabilizes the propagating alkylidene to a certain degree.



(5)

8: R_1 = H, R_2 = CH_3

9: R_1 = R_2 = CH_3

R = CH_3 or Ph

2: M = Mo
R_3 = CH_3, R_4 = CF_3.

3: M = W
R_3 = R_4 = CH_3

21: M = Mo
R_3 = R_4 = CH_3

In a preparation scale, 207 equiv of **8** was polymerized by **21** and the polymer obtained has a PDI = 2.46 and 84% *cis* double bond configuration in the polymer backbone. 212 equiv of **8** was also polymerized by

$W(CHC(CH_3)_3)(NAr)(OC(CH_3)_3)_2$ (Ar = 2,6-diisopropylphenyl) **3** to yield a polymer having a PDI of 1.38 and 79% *cis* double bond configuration in the back bone. Analysis of ^{13}C NMR data of both poly-**8** and its hydrogenated analog revealed that the polymer was atactic and had no HT bias. For example, in the olefinic region of poly-**8**, four *cis* olefinic resonances at δ (ppm) = 136.81, 134.65, 129.10, 127.01 were observed corresponding to four different structures in poly-**8** (Figure 4). Figure 5 shows four types of configurations in the back bone of the hydrogenated poly-**8**. The head-head and tail-tail irregularity are assigned in the hydrogenated polymer. For example, the peaks at δ 34.9 and δ 25.03 ppm in the ^{13}C NMR spectrum of the hydrogenated polymer correspond to the resonances of CH_2 carbons in the irregular head-head (HH) and tail-tail (TT) structures, respectively, by a comparison of the literature data of EP rubber[56] and the completely head-to-tail hydrogenated poly(1-methylcyclobutene).[56(f)] The ratio of the regular structures (HT + TH) versus the irregular structures (HH+TT) is calculated to be 1:1 from the area under the corresponding peaks (CH_2 carbon) in ^{13}C NMR spectrum. The random regiochemistry indicate that the methyl group is not bulky enough to interact with the bulky alkoxide and imido ligand and to favor the formation of only one type of metallacyclobutane intermediate during the reaction.[57]

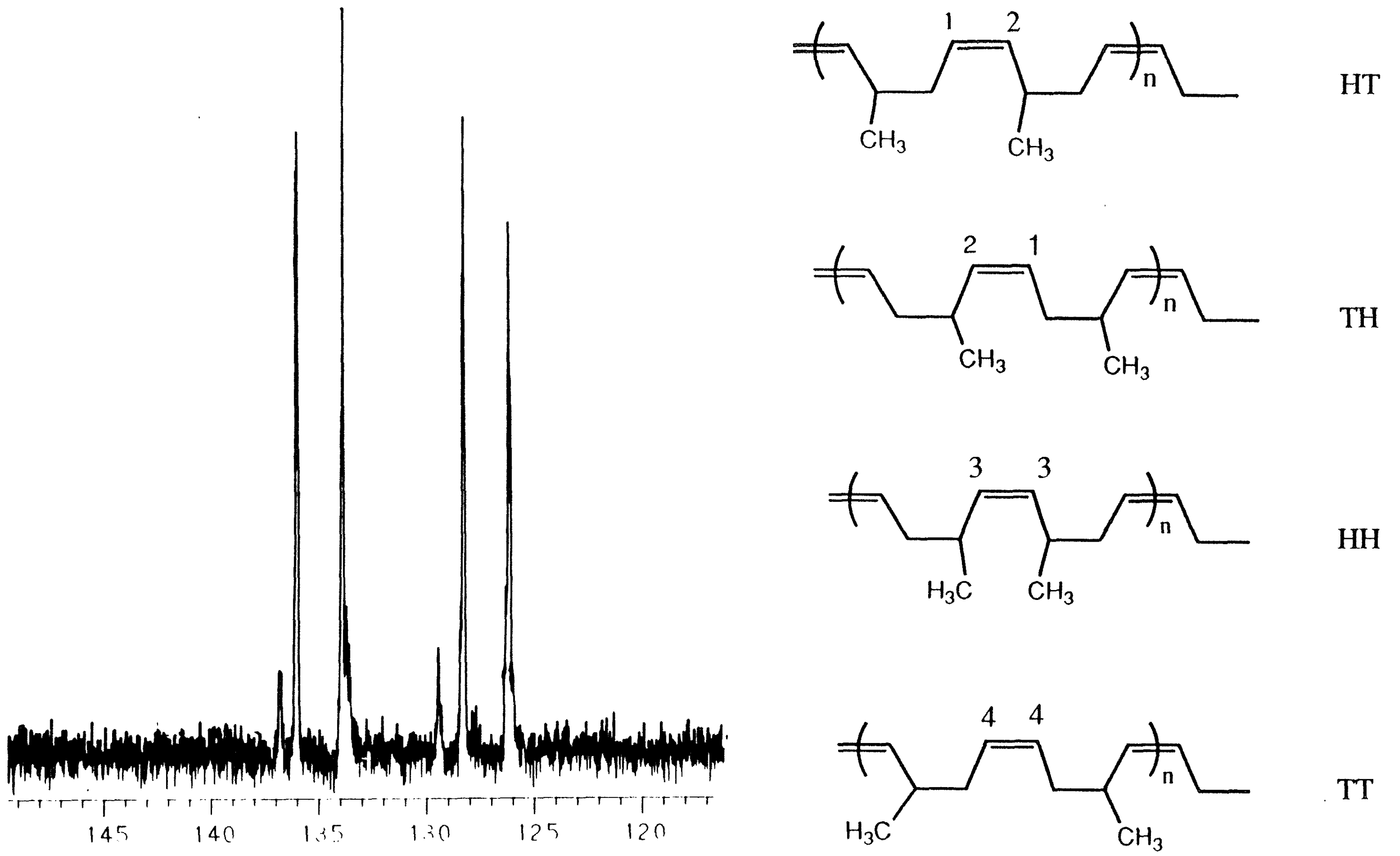


Figure 4 The olefinic region of the ^{13}C NMR spectrum of poly-**8** and the possible dyad structures in the polymer

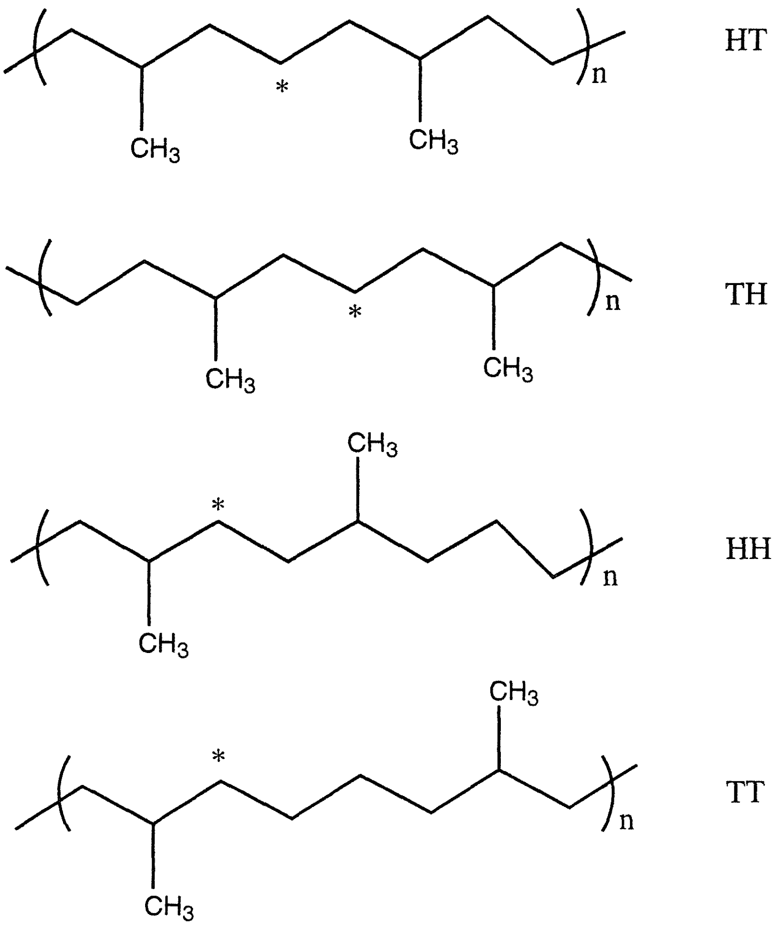
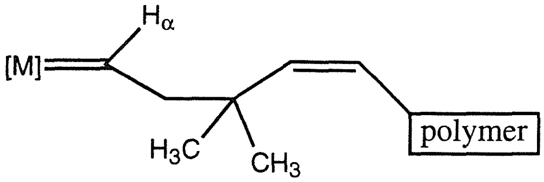


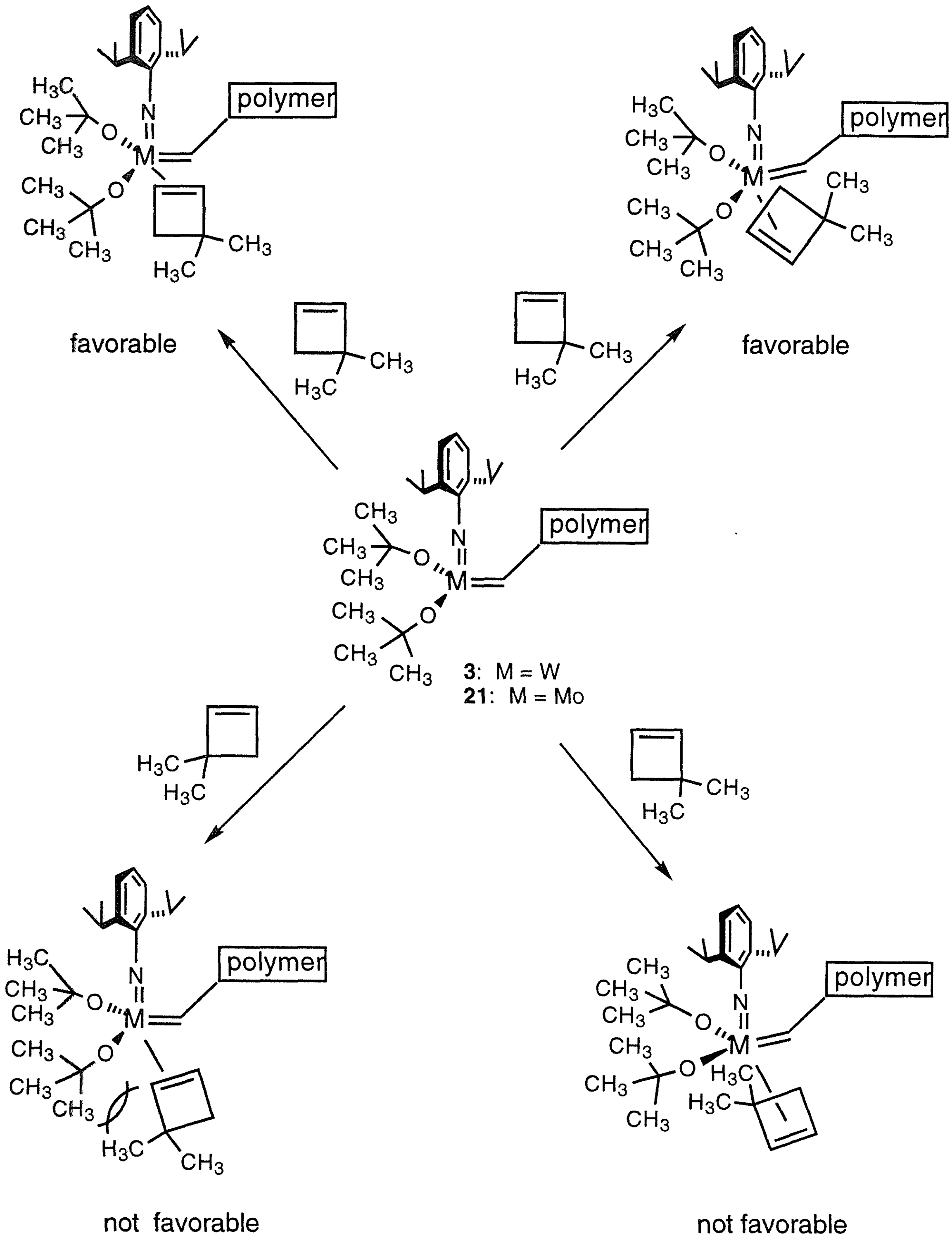
Figure 5. Backbone configurations of hydrogenated poly-**8**.
* represent the carbons that were used for calculating the ratio of HT versus HH and TT.

To increase the steric effect of the substituent of cyclobutene on the polymer microstructure, we looked into the polymerization of **9** (eq 5). **9** can be rapidly polymerized at room temperature by **3** and **21**. When 14 equiv of **9** was added to a 0.013 M toluene solution of **3**, a triplet resonance was observed at 8.53 ppm ($J_{H\text{-}H}$ = 5.93 Hz) corresponding to the H_α of the propagating alkylidenes.[58] Similarly, when **21** was used, a triplet resonance (H_α) was also observed at 11.80 ppm ($J_{H\text{-}H}$ = 6.35 Hz).[59]



M = Mo or W

These observations indicated that the monomer approached the metal center in a regioselective fashion, with the bulky dimethyl groups pointing away from the alkoxide and imido ligand as shown in Figure 6.



3: M = W
21: M = Mo

Figure 6. The possible modes of interaction of **9** with the metal center during the polymerization by attacking the C/N/O face of **3** or **21**.[55]

We can easily infer that other 3-substituted cyclobutenes with even bulkier substituents should also undergo polymerization in a highly stereoselective fashion.

As a consequence, the polymers obtained by ROMP of **9** using **3** and **21** as catalysts are high *cis* (>99%) and regioselective (HT > 98%). For example, in the ^{13}C NMR spectrum of the polymer obtained, only five peaks are observed at δ (ppm) = 142.93 (CH), 122.95 (CH), 46.75 (CH_2), 36.4 (C) and 27.4 (CH_3) (Figure 7). The structure of the polymer upon hydrogenation is consistent with the assigned stereochemistry. Proton NMR spectrum of the hydrogenated polymer shows only three resonances at δ (ppm) = 1.32 (CH_2), 1.31 (CH_2) and 0.994 (CH_3), respectively. In the ^{13}C NMR spectrum of the hydrogenated polymer (Figure 8), only four resonances are observed at δ (ppm) = 43.68 (CH_2), 33.18 (C), 27.58 (CH_3) and 18.90 (CH_2), which confirms a highly regioselective polymer.[60] A totally random hydrogenated poly-**9** will be expected to have at least twelve resonances at the dyad level.[3(c)] The high *cis* content of the polymer is probably a result of the facile ring-opening of the *cis* metallacyclobutane intermediate compared to *trans* one.[61] As a specific example, when 102 equiv of **9** is polymerized by **21**, the polymer obtained has a molecular weight of 11700 and a PDI of 1.6.[62] When 200 equiv of **9** is polymerized by **3**, the polymer obtained has a molecular weight 27600 and PDI of 1.5.[63]

(III) Polymerization of 3-methylcyclobutene in the Presence of Phosphine.

Since 3-methylcyclobutene has similar reactivity as cyclobutene in terms of reactions with **3** and **21** suggested by the low temperature NMR studies (vide infra), phosphines should be able to regulate the rate of the polymerization and to allow the formation of narrow dispersed polymer based on the previous studies.[9] Indeed, we found that $PPhMe_2$ bound reversibly to

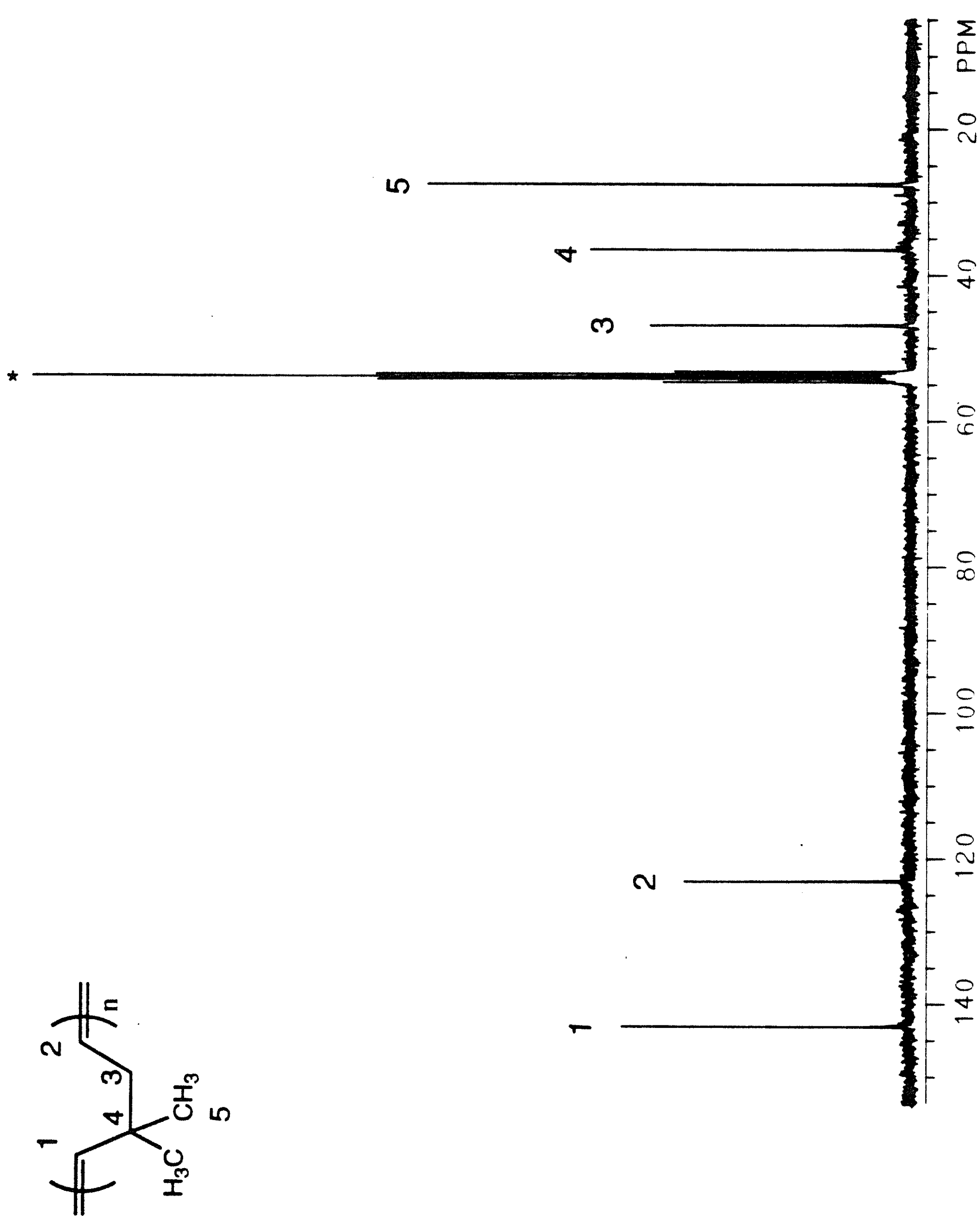


Figure 7. ^{13}C NMR spectrum of poly-9. * is the resonance of solvent (CD2Cl2).

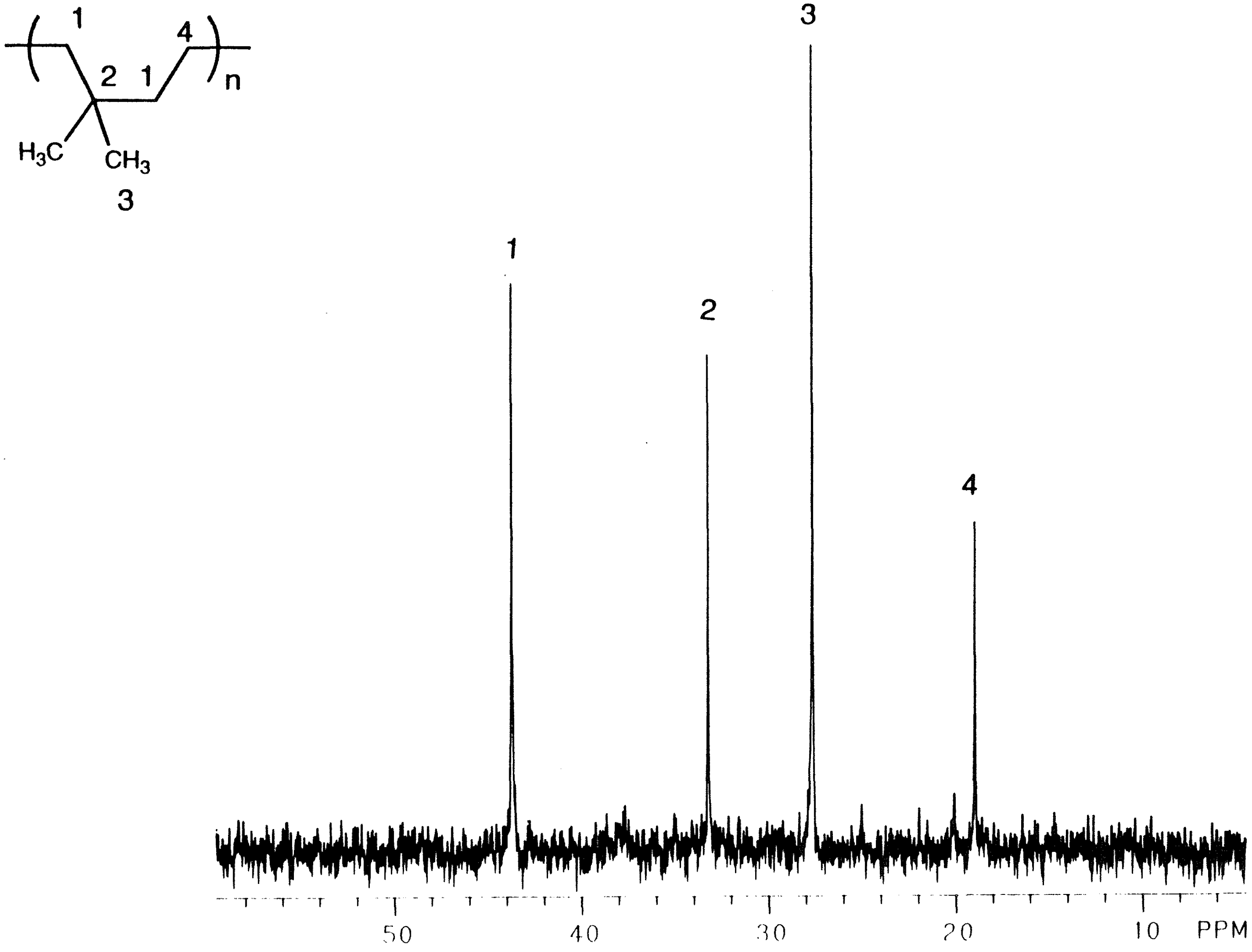
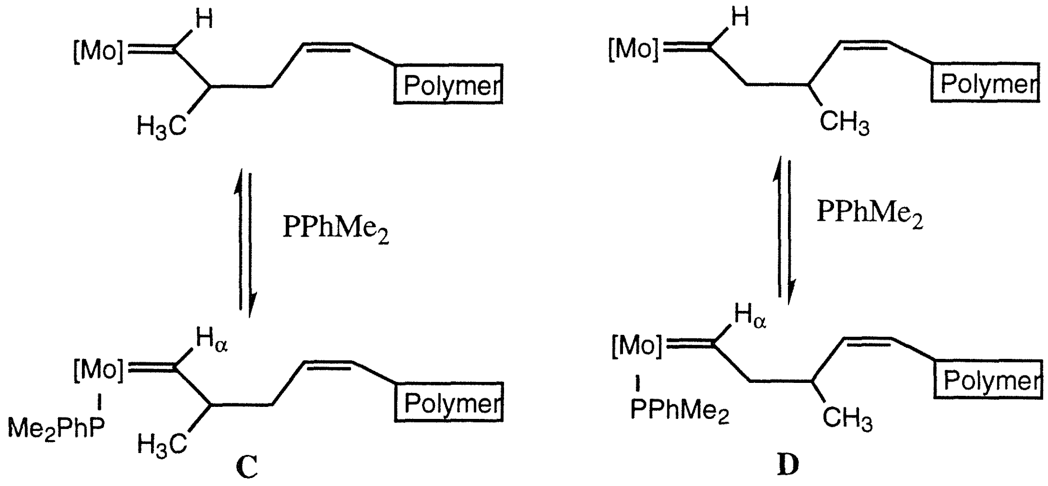


Figure 8. ^{13}C NMR spectrum of hydrogenated poly-9.

$[Mo(CHC(CH_3)_2Ph)(NAr)(OC(CH_3)_2CF_3)_2$ (Ar = 2,6-diisopropylphenyl)] **2** in toluene and the phosphine-bound species were observed at 13.30 ppm ($J_{H\text{-}P}$ = 7.8 Hz). When 12 equiv of **8** was added to a 0.015 M solution of **2** in toluene, two broad resonances were observed at 12.76 and 12.96 ppm corresponding to the H_α of the propagating species **C** and **D** (Scheme 5). The polymer obtained by reacting 62 equiv of **8** with **2** in the presence of 50 equiv of $PPhMe_2$ showed two narrow GPC traces (M_n = 9800, PDI = 1.08; and M_n = 4500, PDI = 1.06). Analysis of ^{13}C NMR data indicated that the polymer had 88% *cis* double bond configuration and no HT bias (vide infra). The molecular weight data indicated that the polymerization was living and suggested further that there were two different types of propagating species, such as **C** and **D** that react with monomers at different rates during the polymerization causing a bimodal distribution. Moreover, it also indicated that one of the species, for example **C**, reacted faster with **8** than **D** does, which was attributed to the steric bulk difference of **C** and **D**, which would further result the binding difference of $PPhMe_2$.

Scheme 5



Conclusion

In summary, these studies demonstrate for the first time that a perfectly alternating isobutylene-ethylene copolymer and narrow dispersed ethylene-propylene (EP) copolymer can be synthesized through ROMP. ROMP of 3-methylcyclobutene catalyzed by **3** or **21** gives polymers that have no HT bias and the microstructures of the polymer are determined using ^{13}C NMR spectroscopy. Narrow dispersed EP polymer has significant theoretical interest for the investigation of rubber elasticity. The successful preparation of perfect alternating copolymer of ethylene-isobutylene has provided a good example for studying the stereo control in ROMP and to synthesize polymers with novel properties. These studies also reveal that the steric bulk on the 3-position of the cyclobutene ring is crucial in regulating the regioselectivity of the polymerization of substituted cyclobutene catalyzed by Mo or W alkylidene complexes. The propagating alkylidenes are slightly stabilized by methyl substituent on the β-carbon. Future directions will involve the ROMP of cyclobutene derivatives with other bulkier substituents on the 3-position to synthesize stereoselective polymers with novel properties.

Experiment

General Procedures. All manipulations of air and/or moisture-sensitive compounds were carried out using standard Schlenk or vacuum-line techniques or in an N_2-filled drybox. Argon was purified by passage through a column of BASF RS-11 (Chemlog) and Linde 4Å molecular sieves. ^1H NMR spectra were recorded on a JEOL GX-400 MHz (399.65 MHz ^1H; 100.5 MHz ^{13}C) or on a QE Plus-300 MHz (300.1 MHz ^1H; 75.49 MHz ^{13}C; 161.85 MHz ^{31}P) spectrometer. The chemical shifts of the phosphorus were determined relative to the phosphoric acid resonances. Gel permeation chromatography (GPC) utilized Shodex KF-803, KF-804, and KF-805 columns and a Knauer differential refractometer. All GPC analyses were performed on a 0.5% W/V solution of polymer in dichloromethane. An injection volume of 0.1 ml and a flow rate of 1.0 ml/min. were used. Calibration was based on narrow dispersity polystyrene standards (Polyscience) ranging from M_n=3,550 to 600,000. Infrared spectra were recorded using a Perkin-Elmer 1600 series FT-IR spectrometer. Gas chromatography was performed using a Hewlett-Packard HP 5890 Series II Gas Chromatography equipped with 30 mm SE-30 (OV-1) capillary column and an HP 3396 Series II integrator. Differential scanning calorimetry (DSC) and thermal gravimetric analyses (TGA) were performed on a Perkin-Elmer PC Series DSC7 and TGA 7, respectively. Photolysis was performed with a 450 watt medium pressure mercury Hanovia lamp. Quartz immersion well was used.

Materials. Catalysts **2**, **3** and **21** were synthesized according to the published procedure.[12,13,64] $Pb(OAC)_4$ and N-chloro succinimide were crystallized from acetic acid before use. $HgCl_2$ was purified by sublimation under high vacuum at 150 °C. Tosyl chloride was purified by recrystallization from pentane. CH_2Cl_2, DMSO and DMF were distilled from CaH_2. Dioxane and pyridine were dried over 3Å molecular sieves. *Trans*-cyclooctene was synthesized according to literature procedure.[65] All the other common solvents used were distilled from Na-benzylphenone ketyl. All the other material were either dried, distilled or degassed before use. Deuterated compounds were purchased from Cambridge Isotope Lab. All the other commercially available compounds were purchased from Aldrich or Lancaster chemical companies.

Synthesis of Methyl Cyclopropyl Tosylhydrazone. Tosylhydrazide (110g, 0.59 mol) was dissolved with 450 ml of methanol in a one-liter round bottom flask and a milky mixture was obtained. Cyclopropyl methyl ketone (60 ml, 0.605 mol) was added slowly via a syringe and the addition rate was controlled so that the temperature was below 30 °C. After the addition, a white precipitate formed suddenly. The mixture was stirred at 40 °C for 2 hours and cooled down to -50 °C. The white solid was filtered and washed with methanol and was further purified by recrystallization from methanol: yield, (133 g, 89%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.78 (d, 2H, Ph), 7.38 (b, 1H, NH), 7.33 (d, 2H, Ph), 2.44 (s, 3H, CH_3), 1.65 (s, 3H, CH_3), 0.6 - 1.7 (m, 5H).

Synthesis of 1-Methylcyclobutene 1. Tosylhydrazone (40 g, 0.1585 mol) was dissolved with 200 ml of diglyme (HPLC grade) in a 500 ml round bottom flask and transferred into a 500 ml dropping funnel. Inside the drybox, NaOMe (18 g, 0.33 mol) was weighed into a 500 ml 3-neck flask and dissolved with 50 ml diglyme. The flask was brought out of the box and assembled onto an Ar line. The outlet of the flask was connected to two dry ice-acetone cold traps. The mixture was then heated to 165 °C and the tosylhydrazone solution was added dropwise at this temperature in an hour. The yellow solution collected was diluted with heptane, washed with H_2O twice and dried by Na_2SO_4. The heptane solution was distilled through a 30 cm long helices-packed column to yield a colorless liquid (2.5 g, 23%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 5.65 (s, 1H, CH), 2.35 (s, 4H, CH_2), 1.54 (s, 3H, CH_3).

Synthesis of Bicyclo[3.2.0]heptene 5.[22(a)] 1,3-cycloheptadiene (10 g, 97%, 0.103 mol) was dissolved in 200 ml ether, degassed twice by a freeze-pump-thaw cycle, and then cannulated into an Ar-filled 250 ml photolysis vessel. The mixture was photolyzed using an unfiltered medium pressure Hg lamp for 7 days. The conversion was greater than 99% as monitored by GC. Ether was distilled off through a vigreux column at atmospheric pressure and the residue was distilled at 100 °C under Ar to yield a colorless liquid (7.5 g, 75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.87 (s, 2H, CH), 3.16 (d, 2H, CH, $J_{H\text{-}H}$ = 6.85 Hz), 1.15 - 1.78 (m, 6H, CH_2).

Synthesis of Bicyclo[4.2.0]octene 7.[22(b)] 1,3-cyclooctadiene (90 ml, 0.723 mol) and acetophenone (3 g, 0.025 mol) were dissolved in 150 ml heptane in a 500 ml round bottom flask. The solution was degassed and cannulated into an Ar-filled 250 ml photochemical reaction vessel. The photolysis vessel was immersed into a 90 °C oil bath and the mixture was photolyzed using an unfiltered medium pressure UV-lamp for 108 hours. Some polymer formed during the reaction. The mixture was cooled down to room temperature and fractionally distilled through a helices-packed column. Heptane was distilled at 45 °C/130 torr and the product was collected (69 °C/100 torr) as a colorless liquid (20.5 g, 26%). ^{1}H NMR (399.45 MHz, $CDCl_3$) δ 6.10 (s, 2H), 2.82 (t, 2H, $J_{H\text{-}H}$ = 4.1 Hz), 1.26 - 1.66 (m, 8H).

Polymerization of Bicyclo[4.2.0]octene 7. In a typical experiment, inside a N_2-filled drybox, catalyst **6** (0.0055 g) and monomer **7** (150 equiv) were dissolved in 1.0 ml CH_2Cl_2 in a flask equipped with a Teflon valve. The flask was brought out of the drybox and the mixture was stirred at 40 °C for 4 hours; and 30 μl ethyl vinyl ether was added and the mixture was again stirred for 2 hours at room temperature. The solution was then evaporated off solvent and the residue was dissolved in minimal amount of benzene and passing through a short column of silica gel. The filtrate was precipitated into methanol and dried in vacuo (70 mg, 71%). GPC, M_n = 18600, PDI = 1.2. The polymer has 61% *cis* double bond configuration in the back bone.

Polymerization of Bicyclo[3.2.0]heptene 5. Similar procedure was used except the reaction was carried out at 40 °C for an hour. The polymer (PDI = 1.2) has 58% *cis* double bond configuration in the back bone.

Polymerization of *Trans*-Cyclooctene. Similar procedure for the polymerization of **5** was employed except the reaction was carried out at room temperature for 0.5 hour. **6** (0.0047 g), *trans*-cyclooctene (70 µl, 102 equiv), CH_2Cl_2 (1.0 ml). Yield, 48 mg (84%). GPC, M_n = 297500, PDI = 2.74. ^1H NMR (300 MHz, CD_2Cl_2) δ 5.35 (t, 2H), 2.02 (d, 4H), 1.31 (br, 8H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 130.69 (CH, trans), 130.17 (CH, cis), 32.98 (CH_2, trans), 27.56 (CH_2, cis). The polymer has 86% *cis* double bond configuration in the back bone.

Synthesis of Diethyl 3-methylcyclobutane-1,1-dicarboxylate 10. Inside the nitrogen-filled drybox, NaOEt (204 g, 3 mol) was weighed into a 2-liter round bottom flask and the solid was dissolved into 1200 ml absolute methanol outside drybox. The solution was then transferred into a dropping funnel. In another 3-liter 3-neck round bottom flask, diethyl malonate (228 ml, 1.5 mol) and 1-bromo-3-chloro-2-methylpropane (175 ml, 1.5 ml) were mixed together, and heated to 80 °C. At this temperature, NaOEt solution was added dropwise over a period of 3 hours. The mixture was refluxed overnight and cooled down to room temperature. The solution was concentrated by evaporating off methanol and water, and then was neutralized by addition of dilute HCl. The organic layer was separated and the aqueous phase was extracted with ether. The etherate was washed with H_2O, saturated Na_2CO_3 and dried with Na_2SO_4. Evaporation of ether yielded a reddish viscous solution, which was distilled (78 ~ 82 °C/2 torr) to afford a colorless liquid (181 g, 55.4%). ^1H NMR (300 MHz, $CDCl_3$) δ 4.17

(quartet, 4H, CH_2), 2.64 (m, 2H, CH_2), 2.42 (m, 1H, CH), 2.1 (m, 2H, CH_2), 1.08 (d, 3H, CH_3), 1.03 (t, 6H, CH_3).

Synthesis of 3-Methylcyclobutane-1,1-dicarboxylic Acid 11. KOH (185 g, 3.3 mol) was dissolved in 500 ml ethanol in a 2-liter round bottom flask. The solution was cooled down to room temperature and a mechanical stir was assembled. **10** (181 g, 0.83 mol) was added dropwise into the flask. After the addition, the mixture was refluxed for 6 hours and then filtered through a frit funnel. The salt collected was dissolved in hot water and calculated amount of 37% HCl was added to neutralize the solution. The organic layer was separated and the solid was filtered off and washed with ether. The aqueous solution was extracted several times with ether. All the organics were combined and evaporated off solvent to yield an off-white powder (730 g, 97%).

Synthesis of 3-Methylcyclobutylcarboxylic Acid 12. Diacid **11** (129 g) was added to a 300 ml round bottom flask equipped with a reflux condenser, and the flask was heated to 200 °C in an oil bath under Ar. Vigorous evolution of gas was observed, and the heating was maintained at 175 °C for 1.5 hour until the gas bubble stopped. The brown solution obtained was distilled at 75 ~ 85 °C/6 torr to yield a colorless liquid (89 g, 96%) with a distinguish smell. ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.07 (s, 1H, COOH), 4.11 (quartet, 1H), 1.8 - 3.2 (m, 5H), 1.11 (d, 1.5H, CH_3), 1.04 (d, 1.5H, CH_3).

Synthesis of 1-Chloro-3-methylcyclobutane 13. Inside the dry box, N-chlorosuccinimide (547 g, 4.09 mol) was weighed into a 3-liter-3-neck round bottom flask and dissolved in 340 ml DMF. The flask was brought out of the dry box and was added with **12** (81.4 g, 0.714 mol) and 67.8 ml acetic acid. $Pb(OAc)_4$ (333 g, 0.714 mol) was then added to the flask and the exothermic reaction started. After the generation of CO_2 bubble ceased, the solid was filtered off and washed with pentane. The filtrate was washed with H_2O, diluted $HClO_4$ and saturated Na_2CO_3 solution. The pentane solution was dried over Na_2SO_4 and distilled off through a helices-packed column to yield a yellow residue, which was vacuum-transferred to give a colorless liquid (26 g, 35%). ^1H NMR (300 MHz, $CDCl_3$) δ 4.1 - 4.6 (m, 1H), 1.2 - 2.8 (m, 5H), 1.13 (d, 3H).

Synthesis of 3-Methylcyclobutene 8. Inside the drybox, *t*-BuOK (65.4 g, 0.584 mol) was weighed into a 3-neck round bottom flask. The flask was brought out of the drybox and added with 250 ml dry DMSO. **13** (23 g, 0.22 mol) was dissolved in 30 ml DMSO and transferred into an Ar-filled 125 ml dropping funnel. The condenser and dropping funnel were assembled to the flask under Ar, and two cold traps were connected via a manifold from the top of the condenser. Ar inlet was connected to the top of the dropping funnel. The flask was heated to 80 °C and at this temperature, **13** was added dropwise in 0.5 hour. After addition, the temperature was increased to 95 °C and the mixture was stirred for 3 hours. The liquid collected in the traps was vacuum-transferred into a thick wall flask containing NaH and capped with a Teflon valve. The content of the flask was vacuum-transferred again to yield a pure liquid (7.0 g, 50 %) by NMR. ^1H NMR (300 MHz, $CDCl_3$) δ 5.86 (d, 1H, 2.68 Hz, CH), 5.8 (d, 1H, J_{H-H} = 2.23 Hz, CH), 2.70 (m, 1H, CH), 2.49 (dd, 1H, J_{H-H} = 3.96 and 4.13 Hz, CH_2), 1.80 (d, J_{H-H} = 13.41 Hz, CH_2), 0.94 (d, 3H, J_{H-H} = 7.0 Hz, CH_3).

Preparation of 1-Bromo-2-benzyloxy-3-chloropropane 14. Benzyl bromide (500 g, 2.92 mol), epichlorohydrin (228.6 ml, 2.92 mol) and $HgCl_2$ (0.5 g, 0.0018 mol) were added into a 2-liter 3-neck round bottom flask. The mixture was then slowly heated to 160 °C in a period of 2 hours. As the temperature increased, the solution became viscous and more (10 ml) epichlorohydrin was added. The heating was maintained at 160 °C for 6 hours. The resulting brown solution was distilled under high vacuum (120 °C/ 0.03 ~ 0.06 torr) to yield **14**

(556 g, 73%) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (m, 5H), 4.7 (s, 2H), 3.5 - 3.9 (m, 4H). GC/MS: $M^+ = 264$.

Synthesis of Diethyl 3-benzyloxycyclobutane-1,1-dicarboxylate 15. In the drybox, NaH (41 g, 1.71 mol) was weighed into a 3-neck round bottom flask and 500 ml of dioxane was added to make a suspension. The flask was brought out of the dry box and assembled with a mechanical stir and a reflux condenser, then cooled down to 0 °C. To the above solution, diethyl malonate (250 ml, 165 mol) was added dropwise in an hour. As the addition continued, the solution turned muddy and the stirring became difficult. After the addition, **14** (308 ml, 1.65 mol) was added to the flask in 20 minutes and the mixture was refluxed for 2 days. More NaH (51 g) in 500 ml dioxane was added and the mixture was refluxed for 8 more days. The solvent was removed under vacuum and H_2O was added to quench the reaction. The aqueous phase was extracted with ether several times and the etherate was dried by $MgSO_4$ and evaporated. The residue was fractionally distilled to yield a colorless oil. The forun from the distillation was repurified by flash chromatography on silica gel (10% ethyl acetate-petroleum ether). Combination of all the product gave **15** (218 g, 43 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (m, 5H), 4.43 (s, 2H), 4.17 (quartet, 4H, CH_2), 4.13 (m, 1H), 2.8 (m, 2H), 2.56 (m, 2H), 1.27 (t, 3H, CH_3).

Synthesis of 1,1-Di(hydroxymethylene)-3-benzyloxycyclobutane 16. In the dry box, LAH (54 g, 1.35 mol) was weighed into a 2-liter-3-neck round bottom flask. The flask was brought out of the dry box and freshly distilled THF (400 ~ 500 ml) was added. To the above flask, diester **15** (218 g, 0.712 mol) dissolved in 200 ml THF was added dropwise over a period of 2 hours at 0 °C. The mixture was refluxed at 60 °C for 48 hours. The flask was cooled down to 0 °C and saturated Na_2SO_4 solution was added to quench the reaction mixture. The solid was filtered off and the filtrate was concentrated and redissolved in dilute HCl. The aqueous phase was extracted with $CHCl_3$ several times. The organic phase was washed with H_2O, saturated NaCl solution and dried by Na_2SO_4. Evaporation of the solvent yielded an off-white solid **16** (138 g, 87%) pure by NMR. ^1H NMR (300 MHz, $CDCl_3$) δ 7.35 (m, 5H, Ph), 4.42 (s, 2H, CH_2), 4.08 (m, 1H, CH), 3.71 (m, 4H), 2.89 (d, 2H, $J_{H\text{-}H}$ = 6 Hz), 1.6-2.4 (m, 4H).

Synthesis of 1,1-Di(tosyloxymethylene)-3-benzyoxycyclobutane 17. A one-liter round bottom flask containing **16** (137 g, 0.617 mol) and 500 ml pyridine was cooled down to 0 °C. TsCl (237 g, 1.24 mol) was added into the flask in small portions over an hour. After the addition, the mixture was warmed to room temperature and stirred overnight. The content of the flask was then poured into 3 liter of ice water containing 500 ml HCl. The organic layer was separated and the aqueous phase was extracted with ether. The etherate was washed with HCl, saturated Na_2CO_3, H_2O and dried by $MgSO_4$. Evaporation of solvent and recrystallization in ether yielded a white solid **17** (286 g, 87.4%). ^1H NMR (300 MHz, CD_2Cl_2) δ 7.2 - 7.8 (m, 8 H, Ph), 4.30 (s, 2H, CH_2), 4.0 (m, 1H), 3.95 (s, 2H, CH_2), 3.92 (s, 2H, CH_2), 2.45 (d, 6H, $J_{H\text{-}H}$ = 6.8 Hz), 1.7 - 2.2 (m, 4H, CH_2).

Synthesis of 1-Benzyloxy-3,3-dimethylcyclobutane 18. Inside the drybox, LAH (44 g, 1.1 mol) was weighed in to a 3-liter round bottom flask and dissolved in 500 ml THF. Outside the drybox, to the above flask, a 1000 ml THF solution of **17** (286 g, 0.54 mol) was added dropwise at 0 °C in an hour. After addition, the mixture was heated to 60 °C and refluxed overnight. The solution was quenched with 15% NaOH solution and the solid was redissolved in dilute HCl. The aqueous phase was extracted with ether and the etherate was washed with saturated Na_2CO_3, H_2O and dried by $MgSO_4$. An orange solution was obtained after evaporation of solvent. Fractional distillation (75 °C/1.5 torr) gave 82.5 g of colorless liquid. The residue and forun from the distillation were repurified by flash chromatography on silica gel (5% Et_2O-hexanes) to yield another 3.2 g. Combination of all the product gave **18** in 83.3% total yield. ^{1}NMR (300 MHz, $CDCl_3$) δ 7.31 (m, 5H, Ph), 4.38 (s, 2H, CH_2), 4.05 (quintet, 1H, CH), 1.7 - 2.2 (m, 4H, CH_2), 1.15 (s, 3H, CH_3), 1.11 (s, 3H, CH_3).

Synthesis of 3,3-Dimethylcyclobutanol 19. To a 3-liter round bottom flask was added 1200 ml EtOH, **18** (30 g, 0.158 mol), cyclohexene (600 ml, 5.92 mol) and 7.5 g of 20 % $Pd(OH)_2$ on carbon. The mixture was refluxed for two days and then filtered through a fine frit funnel. The solvent was distilled off at atmospheric pressure and the residue was distilled at 55 °C/15 torr to give a colorless liquid **19** (10 g, 63 %). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 4.23 (quintet, 1H, $J_{H\text{-}H}$ = 7.3 Hz), 1.6 - 2.2 (m, 4H, CH_2), 1.11 (s, 3H, CH_3), 1.07 (s, 3H, CH_3).

Synthesis of 3,3-Dimethylcyclobutyl Tosylate 20. In a 100 ml round bottom flask, **19** (9.3 g, 0.093 mol) was dissolved in 50 ml dry pyridine and cooled to 0 °C. TsCl (20 g, 0.105 mol) was added in small portions to the flask and the rate of the addition was controlled so that the temperature was not higher than 5 °C. After the addition, the reaction mixture was allowed to stir at room temperature overnight. On the second day, the content was poured into a large beaker containing ice/H_2O and dilute HCl. The aqueous phase was extracted several times with ether and the etherate was washed with saturated Na_2CO_3, H_2O and dried with MgSO4. The solvent was evaporated and the residue was recrystallized in pentane at -50 °C to give **20** (22 g, 93 %) as a white solid. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.76 (d, 2H, $J_{H\text{-}H}$ = 8.3 Hz), 7.37 (d, 2H, $J_{H\text{-}H}$ = 8.1 Hz), 4.80 (quintet, 1H, $J_{H\text{-}H}$ = 7.36 Hz), 2.45 (s, 3H, CH_3), 1.8 - 2.2 (m, 4H, CH_2), 1.10 (s, 3H, CH_3), 1.05 (s, 3H, CH_3).

Synthesis of 3,3-Dimethylcyclobutene 21. In the drybox, *t*-BuOK (31 g, 0.276 mol) was weighed into a 500 ml 3-neck round bottom flask. The flask was brought out of the dry box and charged with 100 ml dry DMSO and heated to 90 °C in an oil bath. Tosylate **20** (22 g, 0.0866 mol) dissolved in 30 ml DMSO was added dropwise to the flask at this temperature in 20 minutes and the mixture was stirred at 85 °C for two hours. The volatiles generated was collected in two consecutive cold traps at -78 °C, which was vacuum-transferred into a flask capped with a Teflon valve to yield **20** (4.0 g, 57%). ^{1}H NMR (300 MHz, C_6D_6) δ 6.03 (d, 1H, $J_{H\text{-}H}$ = 2.81 Hz, CH), 5.96 (d, 1H, $J_{H\text{-}H}$ = 2.84 Hz, CH), 2.21 (s, 2H, CH_2), 1.15 (s, 3H, CH_3).

General NMR Tube Reactions. Inside the dry box, 3~5 mg of catalyst was weighed into an NMR tube and dissolved in toluene-d_8. Calculated amount of monomer was added via a gas-tight syringe. The tube was capped with a septum and brought out of the dry box and shaken vigorously. NMR spectra were recorded at desired time.

General Procedure for the Polymerization. In the dry box, catalysts were weighed and dissolved into a flask equipped with a Teflon valve. The flask was capped, brought out of the dry box and put into a -78 °C dry ice/acetone bath. Calculated amount of monomer was either added via a gas-tight syringe at -78 °C under rapid stirring or by vacuum-transfer from another tared flask at 77 K. The flask was then warmed up to room temperature and stirred for 0.5 ~ 1.0 hour. Several drops of degassed methanol or benzaldehyde were added to terminate the reaction, and the content of the flask was added dropwise into a rapidly stirring methanol. Polymers collected were dried in vacuo.

General Procedures for Hydrogenation of the Polymers. In a small schlenk flask, unsaturated polymer was dissolved in calculated amount of *p*-xylene to make a solution of 0.3 ~ 0.4 M (concentration of the repeating units), and a small amount of BHT was added. 6 equiv (relative to the repeating units) of tosylhydrazide was added to the flask and the mixture was degassed twice using a freeze-pump-thaw cycle. A reflux condenser was assembled under Ar and the mixture was heated to 120 °C under Ar for 3 hours until the generation of gas bubble stopped. The flask was cooled down to room temperature and its content was added into methanol. The polymer was purified by reprecipitation into methanol. The material was dried in vacuo and the isolated yields in all runs are greater than 60%.

Polymerization of 8 in the Presence of PPhMe$_2$. In the dry box, **2** (14.6 mg, 0.0222 mmol) and PPhMe$_2$ (150 µl, 50 equiv) were weighed into a small flask equipped with a Teflon valve and dissolved in 2 ml toluene. The flask was capped and brought out of the dry box. 3-methylcyclobutene **8** (0.1135 g, 1.38 mmol) was vacuum transferred into the flask at 77 K and the mixture was thawed at -78 °C, then stirred at room temperature for an hour. Several drops of methanol were added to quench the reaction and the solution was added into a rapidly stirring methanol. The polymer (62%) obtained was dried under high vacuum. $M_n = 9800$, PDI = 1.08; $M_n = 4500$, PDI = 1.06.

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