Titanacyclobutanes Derived from Strained, Cyclic Olefins: A New Living Polymerization System

Thesis by

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to my husband

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To my parents and to Alan, thank you for your support, your love, and your unfailing optimism.

ABSTRACT

Reaction of precursors of "$Cp_2Ti=CH_2$" ($Cp = \eta^5\text{-}C_5H_5$) with cyclobutene yields polybutadiene. The preparation of the titanacyclobutane **3** by the addition of 3,3-dimethylcyclopropene to "$Cp_2Ti=CH_2$" is described. When phosphines $PMeR_2$ (R = Me, Ph) are added to **3**, phosphine adducts of the isomeric α-substituted titanium-carbene compound are obtained. Reaction with $AlMe_2Cl$ affords a heterobimetallic complex. Poly(dimethylpropenamer) is produced from reaction of **3** with excess olefin. The observed reactivity is consistent with productive cleavage of the metal-containing ring in **3** to "$Cp_2Ti=CHC(CH_3)_2CHCH_2$."

Titanacyclobutanes **7** and **11** have been prepared from the reaction of norbornene with precursors of "$Cp_2Ti=CH_2$" and with metallacycle **3**, respectively. On thermolysis, both **7** and **11** produce products consistent with the intermediacy of α-substituted titanocene-carbene compounds. Thermolysis at 65°C in the presence of excess norbornene affords ring-opened polynorbornene with a cis to trans ratio of 38:62. The polymerizations are highly efficient in catalyst and yield polymers of controlled molecular weight. Polymer prepared from **11** shows polydispersities as low as 1.07 based on gel permeation chromatography versus polystyrene standards. The molecular weight distributions of polymers obtained with **7** are always broader than those obtained with **11**. The kinetics of both polymerizations are zero-order in monomer with $\Delta G^{\ddagger}_{338}$ = 24 kcal/mol, $\Delta H^{\ddagger}$ = 27 kcal/mol, and $\Delta S^{\ddagger}$ = 9 e.u. Polymerization with **7** shows an induction period corresponding to a first-order decay of **7** with $t_{1/2}$ = 80 min at 65°C, whereas the polymerization with **11** is linear throughout. Simultaneous incorporation of d^2-norbornene into the polymer by all active sites confirms that this system is best described as a living polymer. The polymerization mechanism is discussed as an olefin metathesis with rate-limiting cleavage of trisubstituted titanacyclobutanes affording high energy carbene intermediates.

Reaction of endo-dicyclopentadiene with "$Cp_2Ti{=}CH_2$" and **3** affords titanacyclobutanes **15** and **16** with exclusive addition to the bicyclic double bond. The X-ray diffraction study of **15** indicates a puckered metal-containing ring. Polymerization of endo-dicyclopentadiene occurs with cleavage of the bicyclic ring system. Preliminary results demonstrate that cyclopentene can be polymerized with **3** at high monomer concentrations. The polymerization of norbornadiene to a linear ring-opened polymer is described. Reaction of these catalysts with 1,4-epoxy-1,4-dihydronapthalene occurs at the double bond and yields oligomers.

Analysis of the microstructure of polymers prepared from methylnorbornenes indicates that the double bonds in these polymers are predominantly trans. The catalysts exhibit a moderate head-to-tail selectivity. The preferred tacticity of dyads at trans double bonds is racemic while that at cis double bonds is meso.

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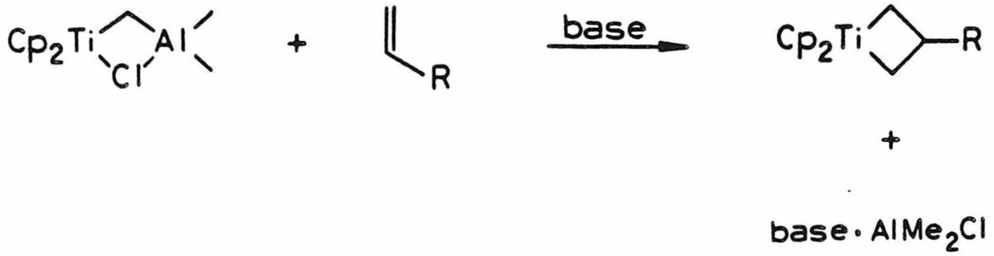
INTRODUCTION

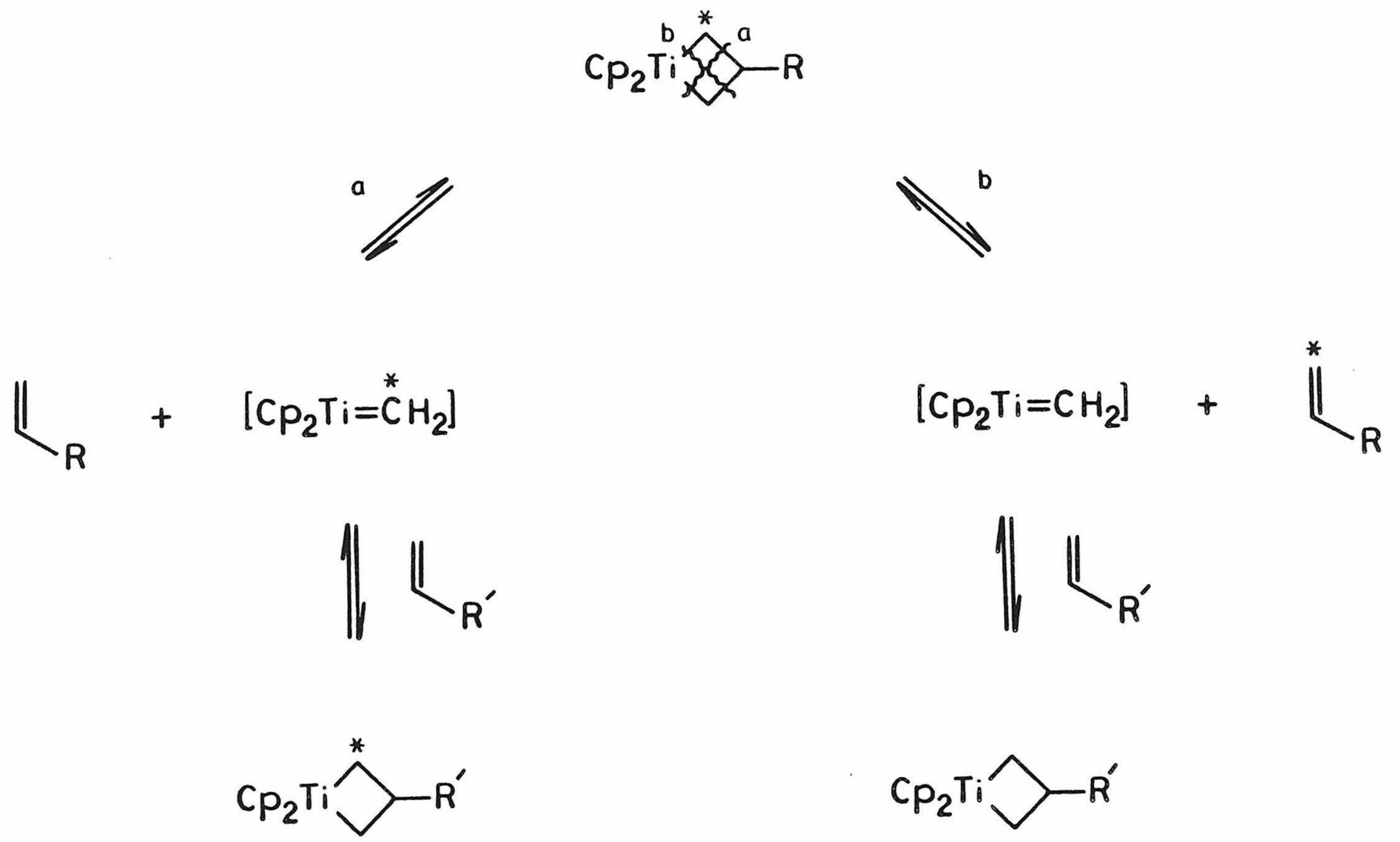
Although metallacyclobutane compounds have been invoked as intermediates in the olefin metathesis reaction[1] for many years,[2] the isolation of metallacycles capable of catalyzing metathesis has only recently been reported. A variety of bis(cyclopentadienyl)titanacyclobutanes were prepared by the reaction of Tebbe reagent[3] with terminal olefins.[4] The



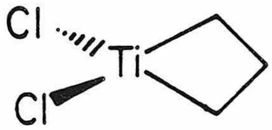
regioselectivity of the addition of "$Cp_2Ti{=}CH_2$" to the olefins placed substituents in the β-position of the product metallacycle ring. An alternate synthesis of β-substituted titanacyclobutanes from titanocene dichloride and 1,3-digrignard reagents has been described.[5] Incorporation of either a carbon-13 or a deuterium label on the α-position of the ring permitted observation of degenerate metathesis reactions as shown in Scheme I.[4b]

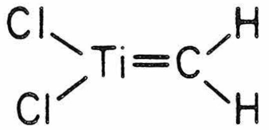
Theoretical studies[6] of degenerate metathesis using the model compound $\overline{Cl_2TiCH_2CH_2CH_2}$ were consistent with the experimental results. The metallacycle was found to be 11.5 kcal/mol more stable than the isomeric titanacarbene-olefin complex with the transition state essentially isoenergetic with the high energy complex. Since an additional 10.4 kcal/mol barrier was found for the dissociation of the ethylene fragment from the carbene

Scheme I. Degenerate metathesis catalyzed by titanacyclobutanes.



complex, the calculated barrier to dissociative metathesis in this system is 21.9 kcal/mol. This value is considerably larger than the 7-14 kcal/mol barrier observed[7] for typical metathesis catalysts. Calculated geometrical features of the titanacycle, which include a flat metal-containing ring that is perpendicular to the plane defined by the two chlorine ligands and the titanium center, agree well with the results of crystallographic studies[8] of

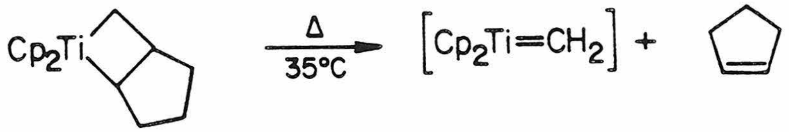


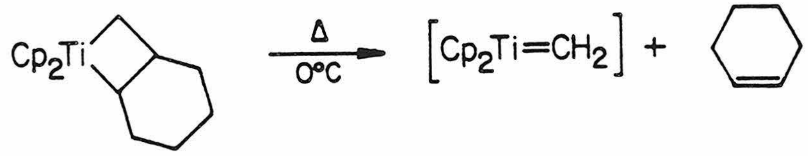


β-substituted bis(cyclopentadienyl)titanacyclobutane compounds. The calculated geometry of dichlorotitanium-methylidene is planar.

While the observation of degenerate metathesis with these systems is a significant advance in the mechanistic study of olefin metathesis, useful metathesis reactions are non-degenerate. Entry into a productive metathesis system requires, first, a synthetic route to titanacyclobutanes with an α-substituent and, secondly, cleavage of the titanacycles to afford α-substituted titanium carbenes. Two approaches to the synthesis of α-substituted titanacycles have been studied. Straus and Grubbs[9] reported that the reaction of acyclic, internal olefins with precursors of "$Cp_2Ti{=}CH_2$" afforded α,β-disubstituted titanacyclobutanes. Work on the simplest such compound $Cp_2\overline{\mathrm{TiCHMeCHMeCH_2}}$ has shown this system to be capable of the non-degenerate metathesis of olefins. Unfortunately, it was highly inefficient due to a low ratio of productive to non-productive cleavage of the metallacycle (1:30) and because of the decomposition of intermediates.

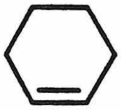
The second approach to the synthesis of α-substituted titanacyclobutane compounds was preparation through the reaction of "$Cp_2Ti=CH_2$" with cyclic olefins. Two such compounds have been made. Unfortunately, both the metallacycle derived from cyclopentene[10] and that derived from cyclohexene[11] quantitatively regenerated the cyclic olefin on thermolysis. No cleavage to α-substituted titanium carbene occurred.[10,11]





The experimental approach to a productive metathesis system described in this thesis is based on the synthesis of titanacyclobutanes from strained, cyclic olefins. Table I lists calculated and experimental strain energies for a number of cyclic olefins. Strain energy values for the analogous alkanes are listed in Table II. Cleavage of a metallacycle derived from a strained, cyclic olefin could occur by two pathways. The inherent

Table I. Strained Energies of Selected Cyclic Olefins.[a]

	Benson[b]	Schleyer[c]	Wiberg[d]
	53.7	54.5	52
	29.8	30.6	29
	--	27.2	24
	5.9	6.8	--
	1.4	2.5	--

[a] Energies in kcal/mol. [b] Reference 12. [c] Reference 13. [d] Reference 14.

Table II. Strain Energies of Selected Cycloalkanes.[a]

	Benson[b]	Schleyer[c]	Wiberg[d]
	27.6	28.1	27
	26.2	27.0	26
	--	17.6	14
	6.3	7.2	--
	0.0	1.4	--

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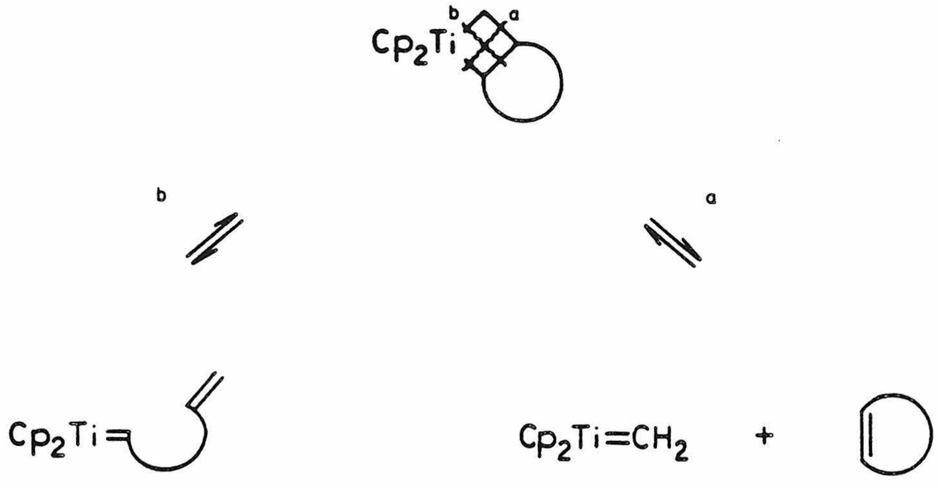
[a] Energies in kcal/mol. [b] Reference 12. [c] Reference 13. [d] Reference 14.



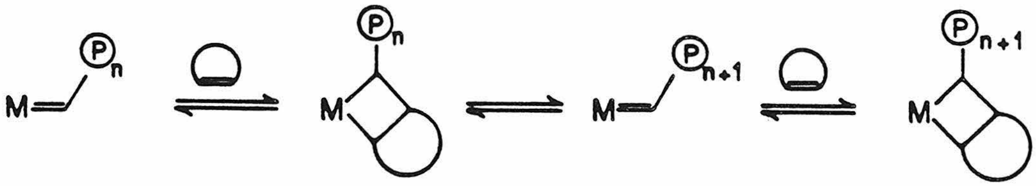
strain of the cyclic olefin relative to its saturated analogue will disfavor reaction along path a (non-productive cleavage). Strain in the saturated cyclic ring system should enhance productive cleavage to α-substituted carbene (path b). Once a route to substituted titanium-carbene is found, an investigation of the activity of such carbenes toward the metathesis of cyclic olefins can be undertaken.

The requisite product of the metathesis of a cyclic olefin is a ring-opened polymer.[15,16] In contrast to 1,2-addition polymerization, the ring-opening polymerization of cyclic olefins is an isodesmic reaction. The number

and type of bonds in the monomer are conserved in the polymer. Thus, the extent to which and ease with which the reaction proceeds in the direction of high polymer is governed primarily by release of ring strain in the monomer. The polymerizations of highly strained ring systems such as cyclopropene, cyclobutene, and norbornene are thermodynamically favorable. Because of its low strain, entropic factors can govern the polymerizability of cyclopentene. Cyclohexene cannot be polymerized by metathesis under any conditions, since ring cleavage is disfavored both entropically and enthalpically.

Regardless of its equilibrium thermodynamics, ring-opening polymerization of cyclic olefins requires net cleavage of bonds with bond strengths greater than 100 kcal/mol. A large number of catalysts effective in the metathesis of acyclic olefins have also been shown to initiate ring-opening polymerization. The common systems consist typically of a Group IVA-VIIIA metal halide in combination with an organometallic co-catalyst such as alkyl lithium, aluminum, tin, and zinc compounds. Several isolable Group VIA carbene complexes, including $(CO)_5W=C(C_6H_5)_2$ and $(CO)_5Cr=C(OCH_3)C_6H_5$, have been reported to initiate ring-opening polymerization without added co-catalysts.[17]

The presumed mechanism of polymer propagation, shown below, was based on the known Chauvin mechanism[2] for metathesis of acyclic olefins. Reaction of an intermediate α-substituted carbene affords an α,β,α'-trisubstituted metallacycle. Productive cleavage of the metallacycle yields an α-substituted carbene identical to the initial one except for an



additional unit in the pendant polymer chain. Non-productive cleavage to regenerate the cyclic monomer may also be possible. Little direct evidence for the proposed intermediates has been obtained. Using X-ray photoelectron spectroscopy, Gassman[18] acquired data consistent with the presence of a polypentylene-attached tungsten carbene. Direct ^1H NMR observation of chain-propagating carbene complexes in the polymerization of several substituted norbornenes with $W(CHCMe_3)(OCH_2CMe_3)_2Br_2/GaBr_3$ has also been reported.[19]

The experiments described in this thesis are based on investigations of titanacyclobutanes as potential initiators for the polymerization of strained, cyclic olefins. Chapter 1 contains studies of the reactivity of three and four-membered ring cycloolefins toward the titanium system. The polymerization of norbornene using these catalysts, described in Chapter 2, proved to be living. The polymerization kinetics and a molecular weight analysis of the product polymers are included. Chapter 3 details studies of the ability of the titanacyclobutanes to polymerize monomers bearing potentially reactive functionalities. Finally, an analysis of the microstructure of selected poly(methylnorbornenes) is included in Chapter 4.

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CHAPTER 1

Reaction of Bis(cyclopentadienyl)titanium-methylidene with Small Ring Olefins

Introduction

The presence of ring strain greatly enhances the thermodynamic driving force in the ring-opening polymerization of cyclic olefins. Although the contribution of ring strain to increasing the rate of polymerization is less clear,[1] highly strained cycloolefins frequently are studied to assess the activity of new catalysts.[1] The study of the reactions of bis(η^5-cyclopentadienyl)titanium-methylidene with small ring alkenes detailed below was initially undertaken to test the viability of these compounds as catalysts for productive metathesis. Two olefins, cyclobutene and 3,3-dimethylcyclopropene, were chosen as model three- and four-membered ring substrates.

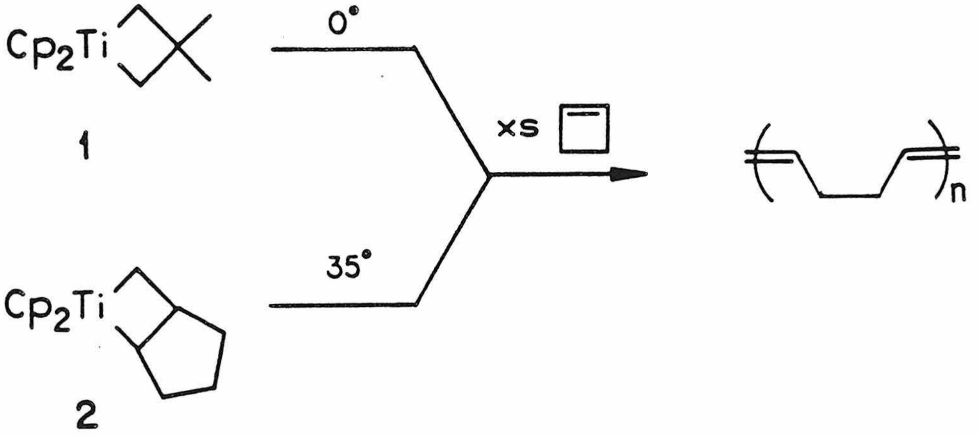
Cyclobutene has previously been ring-opening polymerized to polybutenamer by a variety of metathesis catalysts.[2] A wide range of *cis:trans* ratios have been obtained. These polymerizations have little practical value since the product polymer, also known as polybutadiene, is readily and much less expensively obtained by the anionic polymerization of butadiene.[3] Polymerization of cyclobutene can also occur by 1,2-addition to the double bond with the ratio of vinyl to ring-opening polymerization dependent on the catalyst and conditions used.[2] Titanium-based systems, including typical Ziegler-Natta catalysts such as $TiCl_4/AlEt_3$, predominantly afford ring-opened polymer.[4]

No ring-opening polymerization of any three-membered cycloolefin has been reported. In view of their large strain energies, cyclopropenes are expected to be reactive toward transition metals. Reactions with low-valent transition metals generally result in either 2,3-carbon-carbon single bond cleaving reactions or in cyclooligomerizations at the double bond which preserve the three-membered ring.[5] The only reported example of reaction resulting in cleavage of the double bond involved addition of 3,3-dimethylcyclopropene to a rhodium dimer.[6] The dearth of reports of double bond cleaving reactions could be attributable to limited study of this ring system rather to any inherent lack of reactivity.

Results and Discussion

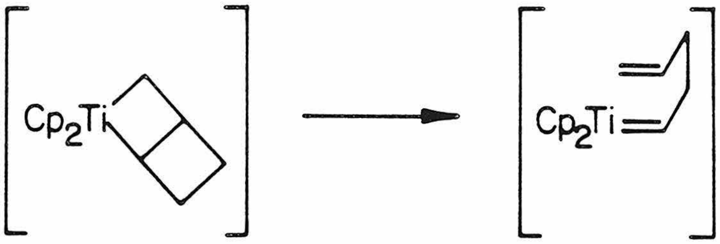
Cyclobutene. Reaction of $\overline{Cp_2TiCH_2C(Me)_2CH_2}$, **1**,[7] with cyclobutene afforded polybutadiene in quantitative yield. The red monomer/catalyst solution rapidly became dark and viscous with substantial heat evolution. The product polymer, identified by comparison of its ^1H and ^{13}C NMR spectra with published data,[8] had a cis:trans ratio of 45:55.

Although the isolation of polybutadiene is suggestive of a metathesis reaction, more data are required before any mechanistic conclusions can be made. Careful observation of the reaction of cyclobutene with 1 by ^1H NMR spectroscopy showed that the polymerization occurs readily at 0°C. When the metallacycle derived from cyclopentene **2**[9] was used as the catalyst,



polymerization occurred only at temperatures greater than 35°C. Since the metallacycles 1 and 2 are known to cleave to carbene-olefin at 0°C and 40°C, respectively,[10] the polymerization appears to be coupled to the generation of "$Cp_2Ti{=}CH_2$."

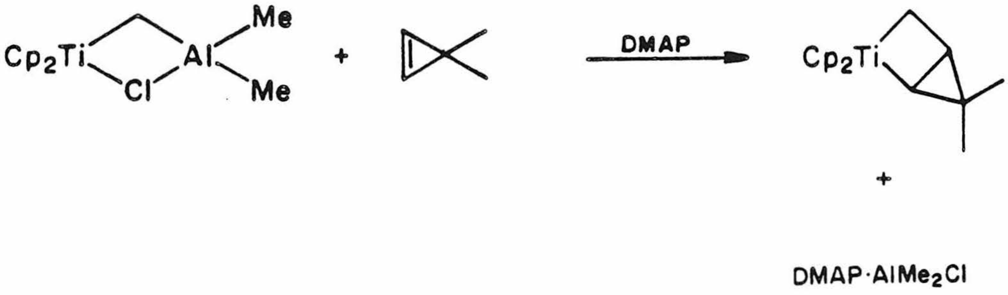
No peaks attributable to metallacycles other than the catalyst were observed. Even the α,β-disubstituted titanacyclobutane expected from the reaction of "$Cp_2Ti{=}CH_2$" with cyclobutene was not present in concentrations sufficient for NMR detection. Since the difference in strain energy of cyclobutene and cyclobutane is only 3 kcal/mol,[11] little of the strain of cyclobutene would be relieved on formation of a metallacycle. Effective



release of strain would occur only on cleavage to carbene plus olefin. Consequently, observation of titanacyclobutanes may have been prevented by rapid reaction to carbene.

If olefin metathesis occurs, the intermediacy of α-substituted titanacarbenes is required. In an effort to provide evidence for such carbenes, the polymerization of cyclobutene with 1 was attempted in the presence of trimethylphosphine. Reaction between the phosphine and any carbenes could yield stable phosphine-carbene adducts. The predominant reaction product by ^{1}H NMR was $Cp_2Ti{=}CH_2(PMe_3)$[12] which presumably results from trapping of "$Cp_2Ti{=}CH_2$" generated by the thermolysis of **1**. Identification of the adduct was based on the presence of a doublet at δ 12.08 assigned as the methylene protons.[12] An additional NMR signal, broad and unresolved, was observed at δ 12.51. This result provides suggestive, but inconclusive, evidence for the presence of α-substituted carbenes in this sytem.

3,3-Dimethylcyclopropene. Reaction of the Tebbe reagent[13] with 3,3-dimethylcyclopropene and N,N-dimethylaminopyridine (DMAP) afforded titanacycle **3** as red needles in 33% isolated yield.[14] Compound **3** was stable at 23°C as a solid but slowly decomposed in solution with a half-life of approximately one week. Proton NMR analysis of **3** showed the α-proton[15] at δ 4.90



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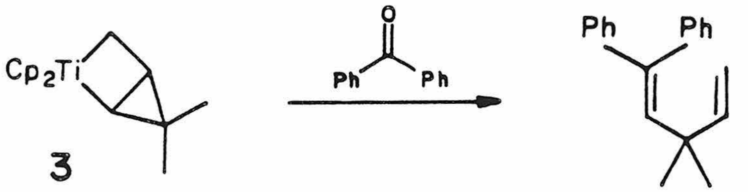
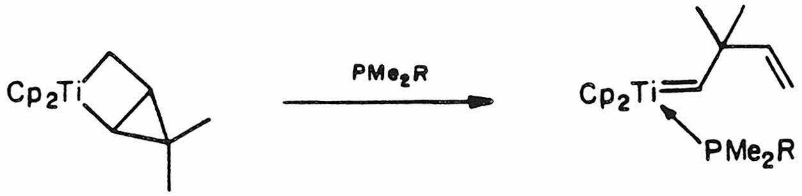
and the β-proton at δ -0.28. The diastereotopic α'-protons occur at δ 2.39 and 2.03 with the expected coupling patterns. A high-field β-proton and low-field α-protons are characteristic of the titanacyclobutane structure.[8,9] Signals assigned as the two inequivalent Cp groups and the two inequivalent methyl groups appear in the appropriate regions of the spectrum. The chemical shift of the α-carbon (δ = 134.82) occurs at low field while that of the β-carbon occurs at δ 18.43. The large C-H coupling observed for the β-carbon, J = 170 Hz, is similar to those generally obtained in cyclopropane ring systems.[16] Interestingly, the J_{CH} for the α-position (149 Hz) is close to that at the α'-position (145 Hz) even though the α-carbon is in a three-membered ring. Additional evidence for the formulation of **3** as shown was provided by the acidolysis of **3**. Reaction with HCl at -50°C yielded 1,1,2-trimethylcyclopropane as the only organic product. No 3,3-dimethyl-1-butene was observed.

When metallacycle **3** was stirred at 23°C with benzophenone, 3,3-dimethyl-1,1-diphenyl-1,4-pentadiene was obtained in high yield. Many of the previously reported titanacyclobutanes have proven to be useful synthetic reagents for the methylenation of ketones.[17] Thermolysis of the metallacycles



generally affords olefin and "$Cp_2Ti{=}CH_2$" which then reacts in a manner analogous to other early transition metal carbenes[18] -- exchanging the methylidene fragment with the carbonyl oxygen of added ketones. In the case of metallacycle **3**, isolation of 3,3-dimethyl-1,1-diphenyl-1,4-pentadiene suggests intermediacy of the α-substituted carbene "$Cp_2Ti{=}CHC(CH_3)_2CHCH_2$." Since no 1,1-diphenylethylene was obtained, the productive cleavage must be greatly favored over the non-productive reaction to give "$Cp_2Ti{=}CH_2$."

Upon reaction of **3** at room temperature with appropriate alkyl-phosphine compounds, the monophosphine adducts of the α-substituted titanium-carbene complex were obtained. Complexes containing trimethylphosphine



3 **4**

(**4a**) and dimethylphenylphosphine (**4b**) were cleanly isolated as tan powders. The ^1H and ^{13}C NMR data of **4a** and **4b** are consistent with the proposed structures. Signals for H_α and C_α are found at low field (see Table I) as reported for other high valent (nucleophilic) carbenes.[19] For example, the signals for the carbene carbons of $Cp_2ClTa{=}CHCMe_3$,[19d] $(^tBuCH_2O)_2$-$Br_2W{=}CHCMe_3$,[19a] and $Cp_2(PPh_3)Zr{=}CHCMe_3$[18c] are found at 273, 299, and 270 ppm, respectively. The observed values of J_{CH} at the α-position of **4** are much smaller than expected for an sp^2-hybridized carbon. Presumably, this is due to a deformation of the β tertiary center to reduce the adverse interaction with the cyclopentadienyl ligand required by the preferred geometry[20] of early transition metal carbene species.[22] The resulting increased Ti-C-C bond angle yields greater p-character in the C_α-H_α bond. The electronic demands of the titanium-carbon double bond may also lower the J_{CH} at the α-position.[23] Both **4a** and **4b** decompose slowly in solution at room temperature. The half-life for **4a** is three to four days while that for **4b** is roughly one day.

Table I. Selected NMR Spectroscopic Data[a]

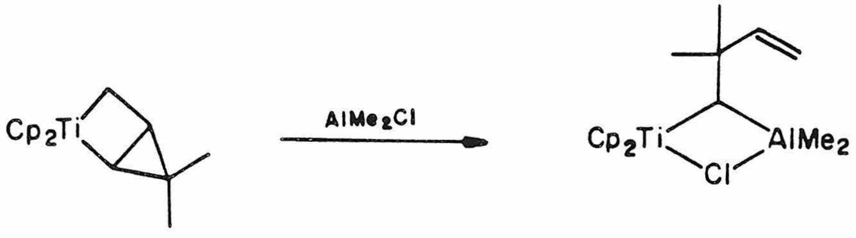
Complex	H [b]	C [b]	J_{HP}[c]	J_{CP}[c]	J_{CH}[c]
3	4.90	134.82	--	--	149
4a	12.06	306.90	7.3	26.6	111
4b	13.23	309.38	6.8	24.9	115
4c	12.32	312.20	5.9	23.5	110
5	9.78	225.83	--	--	116

[a] NMR solvent was C_6D_6. [b] In ppm relative to residual C_6D_5H. [c] In Hz.

In contrast to reaction with PMe_3 and $PPhMe_2$, reaction of **3** with $PMePh_2$ does not go to completion. The $PMePh_2$ complex (**4c**) is formed in equilibrium with metallacycle **3**.[26] The equilibrium constant was measured as $10.5 \pm 0.5\ \ell \cdot M^{-1}$ corresponding to a $\Delta G^{o}_{296} = 1.4(1)$ kcal/mol^{-1}. NMR spectroscopic data for **4c** are similar to that discussed above for the other phosphine adducts. No adduct formation is observed when **3** is stirred with PPh_3 even after heating to 45°C. This trend is attributable to the increased steric demands of the larger phosphines and to their lowered basicity.

Since the strain energy of cyclopropane (27 kcal/mol)[11] can be used as a lower limit of the inherent strain in the ring system of titanacycle **3**, it is perhaps surprising that **3** was stable enough with respect to ring cleavage to permit isolation. The observed stability of previously reported titanacyclobutanes relative to titanium carbene compounds has been discussed in terms of electronic factors.[21] Non-productive cleavage of **3** to "$Cp_2Ti{=}CH_2$" requires loss of the highly strained olefin. The experimental evidence discussed above clearly precludes the pathway. Cleavage of **3** to "$Cp_2Ti{=}CHC(CH_3)_2CHCH_2$" is favored by relief of ring strain; however, this productive cleavage places a tertiary center in the β position of the titanium carbene. Since the preferred geometry of titanium carbene compounds requires an adverse interaction of the α-substituent and a cyclopentadienyl group, the overall energy of the cleavage product is increased. Once the carbene is formed, the absence of β-hydrogens and steric barrier to dimerization may enhance its kinetic stability. Hence, a balance of structural and electronic effects permits isolation of both titanacyclobutane **3** and phosphine adducts of the isomeric α-substituted carbene compound.

A bimetallic alkylidene-bridged complex analogous to the Tebbe reagent was obtained when $AlMe_2Cl$ was added to titanacycle **3**. In contrast



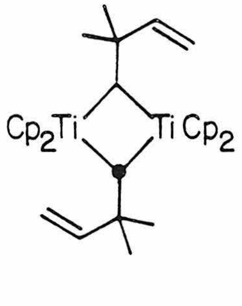
3 **5**

to the reactivity of **3** with phosphines or with benzophenone, this reaction was rapid at -40°C. One explanation is a strong assistance by $AlMe_2Cl$ in the ring-opening reaction.[27] Low-temperature NMR data for **5** are included in Table I and in the Experimental Section. The two cyclopentadienyl groups, the aliphatic methyl groups, and the two aluminum-bonded methyl groups are inequivalent. The chemical shifts of H_α and C_α are similar to reported data for related compounds.[13,28,29] In the case of **5**, the J_{CH} of 116 Hz is a reasonable value for an sp^3-hybridized carbon attached to the electrophilic Ti and Al centers. The purple, crystalline complex **5** is less stable than the phosphine adducts, decomposing in solution at temperatures above 10°C. Metallacycle **3** was not regenerated.

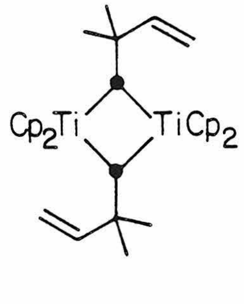
Although synthetic routes to α-alkyl-substituted zirconium-carbene compounds[18c] and to bimetallic bridged alkylidene complexes[28,29] had been described, none of the reported methods had proven useful for the isolation of the analogous titanium compounds.[30] Schwartz and Hartner[28] had observed

^{1}H NMR signals attributable to a propylidene-bridged bimetallic complex on addition of an organoaluminum hydride compound to a titanocene-alkenyl complex; however, paramagnetic impurities prevented full characterization. Yoshida[29] had observed reactivity consistent with the aluminum adduct of a titanocene-carbene complex on addition of alkenyl aluminum compounds to titanocene dichloride. Synthesis of substituted analogs of the Tebbe reagent[13] by the same method used to prepare it had failed, presumably due to the presence of β-hydrogens.[31] The only monometallic carbene complexes of titanium which had been reported are phosphine adducts of the parent methylidene compound.[24,28] This work has provided the first examples of isolable α-substituted titanium-carbenes.

On reaction of metallacycle **3** with pyridine, a color change from red to an intense purple was observed. Observation of the reaction by ^{1}H NMR shows that loss of signals for **3** was accompanied by growth of a pair of singlets at δ 8.18 and 8.12, a pair of singlets at δ 5.81 and 5.77, and another pair at δ 1.18 and 1.17 along with signals attributable to a terminal olefin.



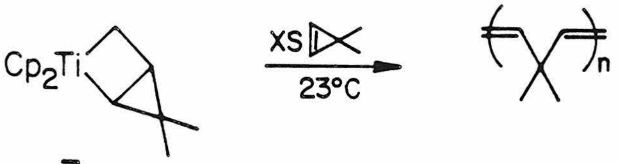
6a



6b

The area ratio within each pair was approximately 2:1. Although the presence of a loosely bound pyridine adduct cannot be ruled out, these data could be attributable to dimers of the substituted carbene (**6**). Ott and Grubbs[32] report that the parent dimer $(Cp_2Ti{=}CH_2)_2$ is purple and that the ^1H NMR signal for the methylene groups is found at δ 8.72. Schwartz and Hartner[18c] have prepared zirconium dimetallacyclobutanes with α-substituents. Attempts to isolate **6** were unsuccessful.

Preliminary experiments in which metallacycle **3** was stirred at 23°C in the presence of excess dimethylcyclopropene showed that a polymeric product was obtained. Analysis of the spectral data indicates the product is a ring-opened polypropenamer. The ^1H NMR spectrum consists of two broad singlets, one in the olefinic region and one in the aliphatic region with relative areas of 1:3. The fact that the ^{13}C NMR spectrum consists of three sharp singlets suggests that only one double bond isomer was obtained. Assignment as the all <u>trans</u> polymer is based on the strong absorbance at 973 cm^{-1} in the infrared spectrum of the polymer and absence of bands between 600 and 800 cm^{-1}. The consistently low number of turnovers -- approximately three monomers per catalyst were consumed -- may result from destructive decomposition of intermediates in the polymerization. Since



3

both chain-carrying titanacycles and carbenes must be substituted at the α-position by a tertiary center, adverse steric interactions with the proximal cyclopentadienyl should lower their overall stability. Further work is needed to optimize reaction conditions and polymer yields.

Conclusions

The results of this study on the reactions of 3,3-dimethylcyclopropene with "$Cp_2Ti{=}CH_2$" demonstrate definitively that metallacycles derived from strained, cyclic olefins can cleave productively to afford α-substituted titanacarbenes. The synthesis of a ring-opened poly(dimethylpropenamer) indicates that inefficient productive metathesis reactions occur with this olefin. The efficient production of polybutadiene from cyclobutene on reaction with "$Cp_2Ti{=}CH_2$" suggests operation of a metathetical polymerization; however, since no intermediates were characterized, conclusions about the mechanism cannot be made.

Experimental Section

All manipulations of air and/or moisture sensitive compounds were carried out with use of standard Schlenk or vacuum line techniques. Argon was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4Å molecular sieves. Solids were transferred in a N_2-filled Vacuum Atmospheres Dri-Lab equipped with an MO-40-1 purification train and a DK-3E Dri-Kool.

Tebbe reagent,[33] metallacycle **1**,[7] metallacycle **2**,[9] and 3,3-dimethylcyclopropene[34] were prepared according to published procedures. The trans-1,2-cyclobutanedicarboxylic acid was purchased from Pfaltz and Bauer. N,N-dimethylaminopyridine (Aldrich) and benzophenone (Aldrich) were recrystallized from hot toluene. The 3,3-dimethyl-1-butene was purchased from Aldrich Chemical Co. The 1,1,2-trimethylcyclopropane was purchased from Chemical Samples Co. Trimethylphosphine (Strem), dimethylphenylphosphine (Aldrich), and methyldiphenylphosphine (Strem) were used without further purification. Dimethylaluminum chloride (Texas Alkyls Co.) was used as a 2.5 M solution in toluene. Dichloromethane was dried over P_2O_5 and degassed on a vacuum line. Pentane was stirred over H_2SO_4, dried over CaH_2, and vacuum-transferred onto sodium-benzophenone ketyl. Benzene was dried over CaH_2, degassed, and vacuum-transferred onto sodium-benzophenone ketyl. Diethyl ether, toluene, benzene-d_6 (Cambridge Isotope Laboratories), and toluene-d_8 (Cambridge Isotope Laboratories) were degassed and stirred over sodium-benzophenone ketyl. The dried and degassed solvents were vacuum-transferred into dry vessels equipped with Teflon valve closures and stored under Ar.

Reagent grade petroleum ether (35-60°C) and methanol were used without further purification.

NMR spectra were recorded on a JEOL FX-90Q (89.60 MHz ^1H; 22.53 MHz ^{13}C; 36.27 MHz ^{31}P) NMR spectrometer or on a JEOL GX-400 (399.65 MHz ^1H; 100.40 MHz ^{13}C) NMR spectrometer. Chemical shifts for ^1H and ^{13}C spectra are reported versus residual solvent signals. Chemical shifts for ^{31}P are reported relative to external 85% H_3PO_4. Temperatures were measured using $\Delta\nu$ (CH_3OH) and were accurate to $^+0.2$°C. Difference NOE spectra were obtained using standard procedures.[35] Analytical gas chromatographic analyses (VPC) were performed on a Shimadzu GC-Mini 2 flame ionization instrument modified for capillary used and equipped with a Hewlett-Packard Model 339A integrator and a 0.33 mm x 40 m SE30 capillary column. Infrared analyses utilized a Shimadzu IR-435 infrared spectrophotometer.

Cyclobutene. Cyclobutene was prepared by the lead tetraacetate decarboxylation of trans-1,2-cyclobutanedicarboxylic acid using a reported procedure.[36]

Polymerization of Cyclobutene with Metallacycle 1. Metallacycle 1 (20 mg, 0.081 mmol) was dissolved in 1.0 mL toluene in a flask with a Teflon valve closure. Cyclobutane (128 mg, 2.4 mmol) was condensed onto the frozen catalyst solution at 77 K. The flask was warmed to -20°C and stirred for 5 min to ensure complete mixture of the reagents. The -20°C bath was removed and the solution allowed to warm to 23°C. After approximately 5 min a rapid reaction occurred as indicated by a color change from red to brown, rapid warming of the solution, and its increased viscosity. The volatiles were removed under vacuum. Yield: 145 mg (111%).

The polymerization was also monitored by ^{1}H NMR spectroscopy. Cyclobutene (0.1 mmol) was condensed at 77 K onto a frozen solution of **1** (10 mg, 0.04 mmol) in 0.5 mL toluene-d_8 in a 5 mm NMR tube. The tube was thawed and placed in the -20°C probe of the JEOL-FX90 NMR spectrometer. Proton spectra were recorded regularly as the probe was warmed to 0°C. Signals at δ 5.93 attributable to the olefinic protons of cyclobutene began to decrease in intensity at 0°C and eventually disappeared. A small (<10%) decrease in signals for **1** was observed.

Polymerization of Cyclobutene with Metallacycle 2. An NMR sample was prepared as described above for **1**, using metallacycle **2** (10 mg, 0.04 mmol) rather than **1**. The tube was thawed and placed in the -20°C probe of the JEOL-FX90 spectrometer. Proton spectra were recorded regularly as the probe was warmed to 40°C. Loss of cyclobutene peaks occurred at 35°C.

Reaction of 1 with Cyclobutene and PMe$_3$. To a 5 mm NMR tube containing metallacycle **1** (30 mg, 0.12 mmol) dissolved in 0.5 mL toluene-d_8 and frozen at 77 K were added small amounts of both cyclobutene and trimethylphosphine. The solution was thawed and placed in the -20°C probe of the JEOL-FX90 spectrometer. Integration of the proton spectrum indicated a ratio of **1**:olefin:phosphine of 1:2:0.5. Spectra were recorded as the sample was warmed to 0°C.

Preparation of Metallacycle 3. Approximately 1.5 g (22.0 mmol) 3,3-

brown, rapid warming of the solution, and its increased viscosity. The volatiles were removed under vacuum. Yield: 145 mg (111%).

The polymerization was also monitored by ^{1}H NMR spectroscopy. Cyclobutene (0.1 mmol) was condensed at 77 K onto a frozen solution of 1 (10 mg, 0.04 mmol) in 0.5 mL toluene-d_8 in a 5 mm NMR tube. The tube was thawed and placed in the -20°C probe of the JEOL-FX90 NMR spectrometer. Proton spectra were recorded regularly as the probe was warmed to 0°C. Signals at δ 5.93 attributable to the olefinic protons of cyclobutene began to decrease in intensity at 0°C and eventually disappeared. A small (<10%) decrease in signals for 1 was observed.

Polymerization of Cyclobutene with Metallacycle 2. An NMR sample was prepared as described above for **1**, using metallacycle **2** (10 mg, 0.04 mmol) rather than **1**. The tube was thawed and placed in the -20°C probe of the JEOL-FX90 spectrometer. Proton spectra were recorded regularly as the probe was warmed to 40°C. Loss of cyclobutene peaks occurred at 35°C.

Reaction of 1 with Cyclobutene and PMe_3. To a 5 mm NMR tube containing metallacycle **1** (30 mg, 0.12 mmol) dissolved in 0.5 mL toluene-d_8 and frozen at 77 K were added small amounts of both cyclobutene and trimethylphosphine. The solution was thawed and placed in the -20°C probe of the JEOL-FX90 spectrometer. Integration of the proton spectrum indicated a ratio of **1**:olefin:phosphine of 1:2:0.5. Spectra were recorded as the sample was warmed to 0°C.

Preparation of Metallacycle 3. Approximately 1.5 g (22.0 mmol) 3,3-

dimethylcyclopropene was vacuum-distilled onto 1.5 g (12.6 mmol) dimethylaminopyridine (DMAP). The mixture was dissolved in CH_2Cl_2 (10 mL) and stirred at -20°C. A -20°C solution of Tebbe reagent (3.0 g, 10.5 mmol) in 5.0 mL CH_2Cl_2 was added. After 30 min, the red solution was added dropwise to 150 mL of vigorously stirred pentane at -30°C. The precipitated DMAP-$AlMe_2Cl$ adduct was removed by rapid filtration and the filtrate was evaporated to dryness under vacuum. The resultant solid was crystallized from diethyl ether by slow cooling to give 0.89 g (33%) of **3** as red needles. ^1H NMR (90 MHz, C_6D_6): δ 5.46 (s, 5H, Cp), 5.26 (s, 5H, Cp), 4.90 (d, 1H, J_{HH} = 10.3 Hz, H_α), 2.39 (dd, 1H, J_{HH} = 10.7, 8.4 Hz, $H_{\alpha'}$), 2.03 (pt, 1H, J_{HH} = 8.4, 8.4 Hz, $H_{\alpha'}$), 1.42 (s, 3H, Me), 1.03 (s, 3H, Me), -0.28 (ddd, 1H, J_{HH} = 10.3, 10.7, 8.4 Hz, H_β). Difference NOE (400 MHz, C_6D_6): Irradiation of the signal at δ 5.46 (Cp) enhances signals at δ 2.03 ($H_{\alpha'}$-cis) and 1.03 (Me). Irradiation of the signal at δ 5.26 enhances signals at δ 4.90 (H_α), 2.39 ($H_{\alpha'}$-trans), -0.28 (H_β). ^{13}C NMR (90 MHz, C_6D_6): δ 134.82 (d, J_{CH} = 149 Hz, C_α), 107.46 (d, Cp), 107.07 (d, Cp), 62.56 (t, J_{CH} = 145 Hz, $C_{\alpha'}$), 61.13 (quaternary), 35.53 (q, Me), 20.19 (q, Me), 18.43 (d, J_{CH} = 170 Hz, C_β). IR: 3090 (w), 3010 (w), 2940 (s), 2850 (w), 1440 (m), 1363 (m), 1290 (w), 1017 (s), 823 (sh), 796 (s), 752 (w) cm^{-1}. Anal. calcd. for $C_{16}H_{20}Ti$: C, 73.85; H, 7.75. Found: C, 73.53; H, 7.59.

Reaction of 3 with Benzophenone. To a solution of **3** (50 mg, 0.19 mmol) in 1.0 mL toluene at 0°C was added benzophenone (39 mg, 0.21 mmol). The reaction mixture was warmed to 23°C, stirred at 23°C for 10 h, and then diluted with 10 mL petroleum ether. The resultant yellow precipitate was removed by rapid filtration through silica gel. Evaporation of the solvent under reduced pressure afforded a colorless oil. Identification of the product as 3,3-dimethyl-1,1-diphenyl-1,4-pentadiene was based on comparison of the ^1H NMR data with published data[37] and on a high-resolution mass spectrum. Yield: 40 mg, 83%.

Acidolysis of 3. HCl was generated by the addition of NaCl (25 mg, 0.43 mmol) to 1.5 mL concentrated H_2SO_4. The evolved gas was vacuum-transferred onto titanacycle 1 (50 mg, 0.19 mmol) in 2.0 mL toluene. The reaction flask was isolated by means of a Teflon needle valve and warmed to -50°C. After 15 min, the volatiles were removed by vacuum distillation. Cyclohexane (10 μL, 0.09 mmol) was added to the volatiles and the products were quantitated by capillary VPC. The single volatile product, 1,1,2-trimethylcyclopropane, was identified by coelution with an authentic sample. Yield: 0.17 mmol, 89%.

Preparation of PMe_3 Adduct 4a. To 3 (100 mg, 0.38 mmol) in 2.0 mL benzene was added 60 μL PMe_3 (0.76 mmol). The solution was stirred at 23°C for 1.5 h. Removal of the volatiles in vacuo afforded a brown oil. The flask was cooled to -78°C and its contents were triturated with 0.5 mL -78°C pentane. The added pentane was removed in vacuo. Phosphine adduct 4a was obtained as a tan powder (63 mg, 50%). ^1H NMR (400 MHz, C_6D_6): δ 12.06 (d, 1H, J_{HP} = 7.3 Hz, H_α), 6.24 (dd, 1H, J_{HH} = 17.5, 10.4 Hz, $C\underline{H}CH_2$), 5.35 (d, 5H, J_{HP} = 2.4 Hz, Cp), 5.33 (d, 5H, J_{HP} = 2.0 Hz, Cp), 5.05 (dd, 1H, J_{HH} = 17.5, 1.8 Hz, $CHC\underline{H}H$), 4.96 (dd, 1H, J_{HH} = 10.4, 1.8 Hz, $CHCH\underline{H}$), 1.27 (s, 3H, Me), 1.18 (s, 3H, Me), 0.80 (d, 9H, J_{HP} = 6.3 Hz, $P\underline{Me}_3$). ^{13}C

NMR (100.4 MHz, C_6D_6): δ 306.90 (J_{CP} = 26.6 Hz, J_{CH} = 111 Hz, C), 151.83 (J_{CP} = 4.5 Hz, $\underline{C}HCH_2$), 106.55 ($CH\underline{C}H_2$), 102.42 (Cp), 99.85 (Cp), 56.28 (quaternary), 31.41 (J_{CP} = 4.4 Hz, Me), 30.42 (J_{CP} = 6.0 Hz, Me), 20.44 (J_{CP} = 17.7 Hz, $P\underline{Me}_3$). IR (C_6D_6): 3070 (w), 2940 (s), 2900 (s), 2850 (m), 1625 (w), 1420 (m), 1365 (w), 1298 (w), 1279 (m), 1020 (sh), 1010 (m), 942 (s), 933 (sh), 892 (m), 818 (w), 790 (vs), 780 (sh), 720 (w), 710 (s), 660 (w) cm^{-1}. ^{31}P NMR (36.27 MHz, C_6D_6): δ +11.91. *Anal.* calcd. for $C_{19}H_{29}TiP$: C, 67.86; H, 8.70. Found: C, 67.83; H, 8.18.

Preparation of PMe_2Ph Adduct 4b. The adduct **4b** was prepared by the same procedure described for **4a** using $PPhMe_2$ (60 μL, 0.42 mmol). Phosphine adduct **4b** was obtained as a tan powder (84 mg, 55%). ^1H NMR (400 MHz, C_6D_6): δ 13.23 (d, 1H, J_{HP} = 6.8 Hz, H_α), 7.22-7.09 (m, 5H, Ph), 6.22 (dd, 1H, J_{HH} = 10.6, 17.6 Hz, $C\underline{H}CH_2$), 5.46 (s, 5H, Cp), 5.37 (d, 5H, J_{HP} = 2.0 Hz, Cp), 5.07 (d, 1H, J_{HH} = 17.6, $CHC\underline{H}H$), 4.96 (d, 1H, J_{HH} = 10.6 Hz, $CHCH\underline{H}$), 1.30 (s, 3H, Me), 1.29 (d, 3H, J_{HP} = 6.8 Hz, $P\underline{Me}MePh$), 1.21 (s, 3H, Me), 1.18 (d, 3H, J_{HP} = 6.4 Hz, $PMe\underline{Me}Ph$). ^{13}C NMR (100.4 MHz, C_6D_6): δ 309.38 (J_{CP} = 24.9 Hz, J_{CH} = 115 Hz, C_α), 151.80 (J_{CP} = 3.0 Hz, $\underline{C}HCH_2$), 140.92 (J_{CP} = 13.2 Hz), 131.52 (J_{CP} = 10.3 Hz), 129.11, 128.34, 106.71 ($CH\underline{C}H_2$), 102.96 (Cp), 100.17 (Cp), 56.67 (J_{CP} = 3.0 Hz, quaternary), 31.68 (J_{CP} = 4.4 Hz, Me), 30.40 (J_{CP} = 5.8 Hz, Me), 21.59 (J_{CP} = 22.1 Hz, $P\underline{Me}MePh$), 20.01 (J_{CP} = 20.5 Hz, $PMe\underline{Me}Ph$). ^{31}P NMR (36.27 MHz, C_6D_6): δ +25.10. IR (C_6D_6): 3015 (w), 2950 (s), 2900 (m), 2860 (w), 1625 (w), 1480 (w), 1465 (w), 1432 (s), 1365 (m), 1285 (w), 1275 (w) 1091 (w), 1065 (w), 1015 (s), 937 (m), 900 (s), 825 (w), 792 (vs), 740 (s), 722 (w), 692 (m) cm^{-1}. *Anal.* calcd.

for $C_{24}H_{31}TiP$: C, 72.35; H, 7.84. Found: C, 72.12; H, 7.59.

Reaction of 3 and PPh_2Me. To a 5 mm NMR tube containing **3** (10 mg, 0.04 mmol) in 0.5 mL benzene-d_6 was added 20 µL PPh_2Me (0.10 mmol). The tube was placed in the probe of the JEOL-GX400 NMR instrument and the reaction was monitored by ^1H NMR spectroscopy. The reaction was observed to reach an equilibrium between **3** and its PPh_2Me adduct **4c**, with an approximate ratio of 1:1, within 1 h. ^1H NMR (400 MHz, C_6D_6) assignment based on exclusion of peaks attributable to **3**: δ 12.32 (d, 1H, J_{HP} = 5.9 Hz, H_α), 7.22-7.02 (m, 10H, Ph), 6.14 (dd, 1H, J_{HH} = 17.6, 10.5 Hz, C$\underline{H}$CH$_2$), 5.49 (d, 5H, J_{HP} = 2.0 Hz, Cp), 5.36 (d, 5H, J_{HP} = 2.0 Hz, Cp), 5.12 (d, 1H, J_{HH} = 17.6 Hz, CHC$\underline{H}$H), 4.97 (d, 1H, J_{HH} = 10.5 Hz, CHCH$\underline{H}$), 1.65 (d, 3H, J_{PH} = 6.0 Hz, P$\underline{Me}$), 1.38 (s, 3H, Me), 1.26 (s, 3H, Me). ^{13}C NMR (100.4 MHz, C_6D_6): δ 312.20 (J_{CP} = 23.5 Hz, J_{CH} = 110 Hz, C_α).

Equilibrium Measurements. To each of three 5 mm NMR tubes was added 400 µL of a 0.096 M solution of **3** in benzene-d_6 (10 mg **3** to each). One, two, and four equivalents (7.2, 14.3, and 28.6 µL) $PMePh_2$ were added to the tubes along with additional benzene-d_6 to bring the volume of the contents of each tube to 450 µL. The samples were stored at -20°C until use. Each tube was placed in the probe of the JEOL-GX400. The reactions were monitored by ^1H NMR spectroscopy until no change was observed for 30 min. All samples required less than 1.5 h to reach equilibrium. The equilibrium ratio was measured by integration of the doublet at δ 4.90 (H_α of **3**) and the doublet at δ 4.97 (CHCH$\underline{H}$ of **4c**). The three derived equilibrium constants were averaged to obtain the reported constant.

Preparation of the $AlMe_2Cl$ Adduct 5. To a -40°C solution of **3** (250 mg, 0.96 mmol) in 2.0 mL toluene was added 400 µL of a 2.5 M $AlMe_2Cl$ solution (1.0 mmol $AlMe_2Cl$). An immediate color change from red to purple was observed. After 30 min at -40°C, the volatiles were removed _in vacuo_ at -10°C yielding a dark purple solid. The solid was redissolved in -10°C pentane. A small amount of insoluble material was discarded. Slow cooling of the pentane solution to -50°C afforded 95 mg (28%) of **5** as a purple powder. Solid **3** was stored at -40°C. In solution, **5** is unstable at temperatures above 10°C. ^1H NMR (90 MHz, C_6D_6, 10°C) δ 9.78 (s, 1H, H_α), 6.63 (dd, 1H, J_{HH} = 16.6, 10.0, $C\underline{H}CH_2$), 5.85 (s, 5H, Cp), 5.61 (s, 5H, Cp), 5.04 (d, 1H, J_{HH} = 16.6, $CHC\underline{H}H$), 5.01 (d, 1H, J_{HH} = 10.0, $CHCH\underline{H}$), 1.20 (s, 3H, Me), 0.96 (s, 3H, Me), -0.13 (s, 3H, $Al\underline{Me}Me$), -0.24 (s, 3H, $AlMe\underline{Me}$). ^{13}C NMR (22.5 MHz, C_6D_6, 10°C) δ 225.83 (d, J_{CH} = 116 Hz, $H\alpha$), 150.51 (d, $\underline{C}HCH_2$), 113.33 (d, Cp), 111.12 (d, Cp), 109.12 (t, $\underline{C}HCH_2$), 59.13 (quaternary), 34.83 (q, Me), 30.99 (q, Me), -4.7 (broad q, J_{CH} = 115 Hz, $Al\underline{Me_2}$). Anal. calcd. for $C_{18}H_{26}TiAlCl$: C, 61.29; H, 7.43. Found: C, 60.96; H, 7.23. A more complete analysis was precluded by the thermal instability of **5**.

Reaction of Metallacycle 3 with Pyridene. To a 5 mm NMR tube containing a solution of **3** (10 mg, 0.04 mmol) in 0.5 mL benzene-d_6 was added pyridene (10 µL, 0.12 mmol). The tube was placed in the probe of the JEOL-FX90. Proton spectra were recorded periodically. The reaction was complete within 1.5 h.

Polymerization of 3,3-Dimethylcyclopropene with 3. Metallacycle **3**

(20 mg, 0.077 mmol) was dissolved in 0.75 mL toluene in a flask equipped with a Teflon valve closure. Dimethylcyclopropene (150 mg, 2.2 mmol) was condensed onto the frozen catalyst solution at 77 K. The solution was thawed and warmed to 23°C. After being stirred for 2.5 h at 23°C, the contents of the flask were slowly added to 20 mL rapidly stirred methanol. The resulting white powder was collected by centrifugation and dried under vacuum. Yield: 17 mg (11% conversion). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.28 (s, 2H, $\underline{H}$C=), 1.05 (s, 6H, Me). ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 135.24 (d, J_{CH} = 156 Hz), 37.67 (s), 28.37 (q, J_{CH} = 126 Hz). IR (KBr): 3000, 2960 (s), 2915, 2870, 1473, 1378, 1360, 1300, 1220, 973 (s), 932 cm^{-1}.

References and Notes

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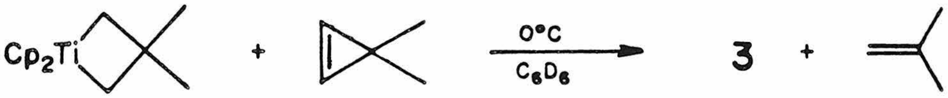
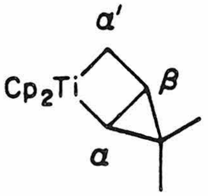


(15) Ring positions on metallacycle **3** are discussed as shown below:



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in 18-electron Ta and Nb carbene complexes.

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(24) The PMe_3, PMe_2Ph, and PEt_3 adducts of titanocene-methylidene have been isolated and an X-ray structural analysis in progress. Meinhart, D.; Grubbs, R. H. Unpublished results.

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CHAPTER 2

The Living Polymerization of Norbornene

Introduction

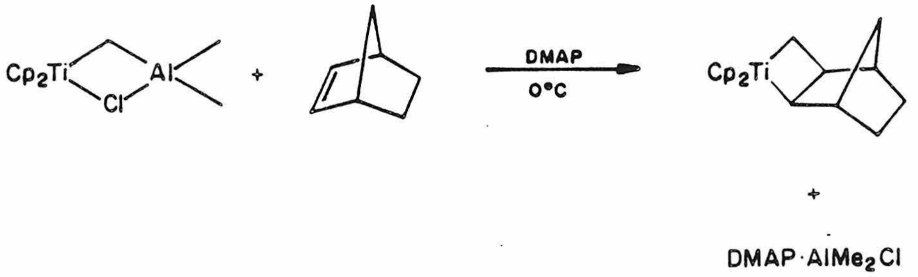
The first cycloolefin to be successfully polymerized by ring-opening was norbornene (bicyclo[2.2.1]hept-2-ene).[1] Since that report, the high reactivity and general availability of this monomer have contributed to the large number of patents and publications based on its polymerization. Commercial production of a ring-opened polynorbornenamer was initiated by CdF Chemie in 1970 and later competition was provided by American Cyanamid and Nippon Zeon.[2] The primary applications of the commercial product include oil absorption, vibration dampening, and use as a speciality rubber.[2]

Catalyst systems for the ring-opening polymerization of norbornene based on Ti, Zr, W, Mo, Cr, Ru, Ir, Os, and Re compounds have been reported.[3,4] The useful titanium systems generally consist of $TiCl_4$, an organometallic cocatalyst, and frequently a third component such as a tertiary amine.[5] A recent patent suggests that one such system is capable of producing polynorbornene of controlled molecular weight.[6]

Based on the promising results described in Chapter 1, a study of the reactions of norbornene with precursors of bis(cyclopentadienyl)titanium-carbenes was undertaken. Preliminary work performed by Drs. A. Marchand[7] and S. Hentges[8] had shown that the reaction of norbornene with Tebbe reagent[9] afforded a titanacyclobutane compound. The present work, detailed below, includes the full characterization of this titanacycle, an examination of the reaction of metallacycle **3** with norbornene, the use of both products as catalysts for the ring-opening polymerization of norbornene, a kinetic study of the polymerization, and analyses of the product polymers.

Results

Preparation and Thermolysis of the Metallacycles. Reaction of the Tebbe reagent[9] with norbornene and N,N-dimethylaminopyridine (DMAP) as previously described for other olefins[10] affords red crystals of metallacyclobutane **7** in 58% yield. The NMR spectral data of **7** are similar to that of



7

reported α,β-disubstituted titanium metallacycles.[11] The characteristic high-field chemical shift for the β-proton of the four-membered ring is at 0.14 ppm, the single α-proton[12] is shifted downfield to 3.51 ppm, and the two α'-protons[10] are at δ 1.91 and δ 3.11. Full assignment, based on homonuclear decoupling, is shown in Figure 1. Difference NOE experiments confirm exo addition of "$Cp_2Ti{=}CH_2$" to norbornene, which is also seen in additions of most electrophiles to norbornene.[13] Irradiation of Cp_1 at δ 5.29 shows enhancement of H_7 at δ 1.08. Metallacycle **7** is the most stable titanacyclobutane reported to date; it can be prepared by olefin exchange from $Cp_2\overline{TiCH_2CH(^iPr)CH_2}$ [14] in spite its more sterically demanding α,β-substitution pattern and bridged ring system.

Previous studies have shown that titanium carbene species are rapidly

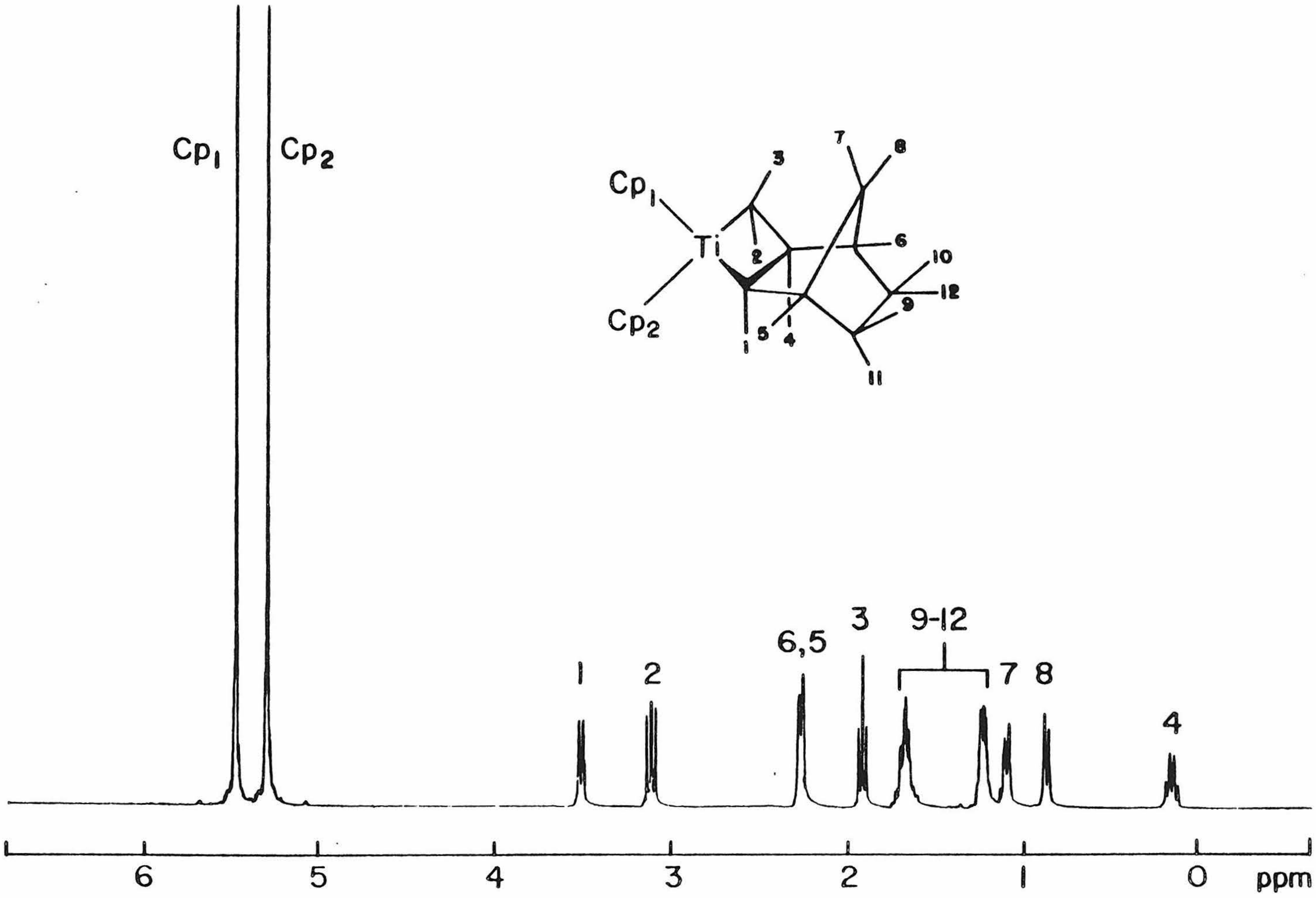
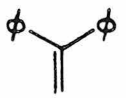
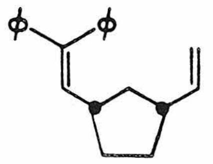


Figure 1. 400 MHz ^{1}H NMR spectrum of metallacycle 7 in C_6D_6.

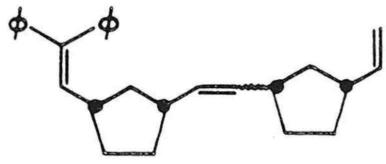
trapped by ketones and aldehydes.[16] They act similarly to Wittig reagents: substituting the alkylidene fragment for the carbonyl oxygen. Heating **1** in the presence of benzophenone yields olefins **8a, 9a** and **10a** as the major isolable organic products.[17] Diphenylethylene was readily identified by comparison with an authentic sample. Olefins **9a** and **10a** were characterized by the usual spectroscopic techniques. Capillary VPC analysis of **10a** coupled with high resolution GC-MS suggested the presence of a mixture of isomers. Further confirmation of these structures was provided by degradative ozonolysis. The same dialdehyde produced from the ozonolysis of norbornene and the appropriate equivalent of benzophenone were obtained.



8a



9a



10a

The product yields for three different trapping reactions are presented in Table I. Addition of free norbornene (reaction 2) to the reaction mixture increases the yield of **10a** and addition of extra benzophenone (reaction 3) reduces the yield of **10a**. Ninety-five percent of the norbornene initially present in metallacycle **7** can be accounted for in the products of reaction 3.

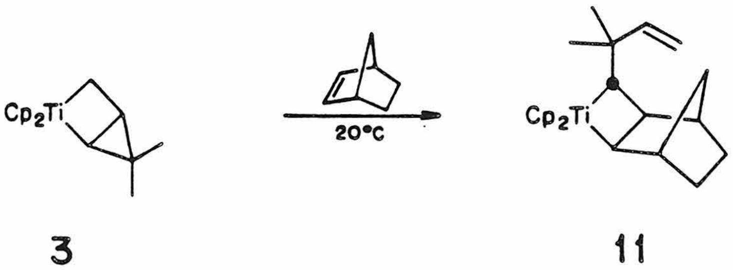
The synthesis and characterization of the titanacycle, **3**, derived from reaction of "$Cp_2Ti{=}CH_2$" and 3,3-dimethylcyclopropene were described in Chapter 1. Upon thermolysis, **3** cleaved to give an α-substituted carbene

Table I. Analysis of Benzophenone Trapping Experiments with **7**.

	Reagents[a]			Products[a]			
Reaction	**7**	B[b]	N[c]	**8a**	**9a**	**10a**	Yields[d]
1	0.17	0.19	0.0	0.040	0.064	0.007	65
2	0.17	0.19	0.22	0.037	0.048	0.014	58
3	0.17	0.38	0.0	0.045	0.107	0.003	91

[a] In mmol. [b] Benzophenone. [c] Norbornene. [d] In %. Based on initial **7**.

which was trapped by a variety of coordinating ligands. Thermolysis of 3 at 20°C in the presence of norbornene affords trisubstituted metallacyclobutane 11 as a deep red oil. Metallacycle 11 could not be cleanly isolated by either crystallization or chromatography. ^{1}H NMR spectroscopy shows that 11 is



the predominant product. Samples of 11 contain approximately 30% of a second species assigned as the product of the addition of two equivalents of norbornene to 3 (see Discussion Section). Spectral assignments for 11, shown in Figure 2 and reported in the Experimental Section, are based on 2-dimensional ^{1}H-^{1}H and ^{1}H-^{13}C NMR experiments. The β-proton, a pseudo-triplet at δ 0.08, is coupled to the doublet at δ 3.72 and to the doublet at δ 2.63, which are assigned as the α and α' protons, respectively. A high-field β-proton and low-field α-proton are characteristic indicators of titanium metallacyclobutane structures. The indicated <u>trans</u> stereochemistry is based on difference NOE experiments. Irradiation of the β-proton signal at δ 0.08 enhances signals at 6.15 ppm and 3.72 ppm, assigned as H_4 and H_1 (see Figure 1b) without substantial enhancement of the signal for H_2.[18]

The peaks in the spectrum of 11 due to the double addition product are indicated with asterisks in Figure 2. Signals at δ 3.67 and δ -0.22 occur at positions characteristic of the α and β protons of titanacyclobutane com-

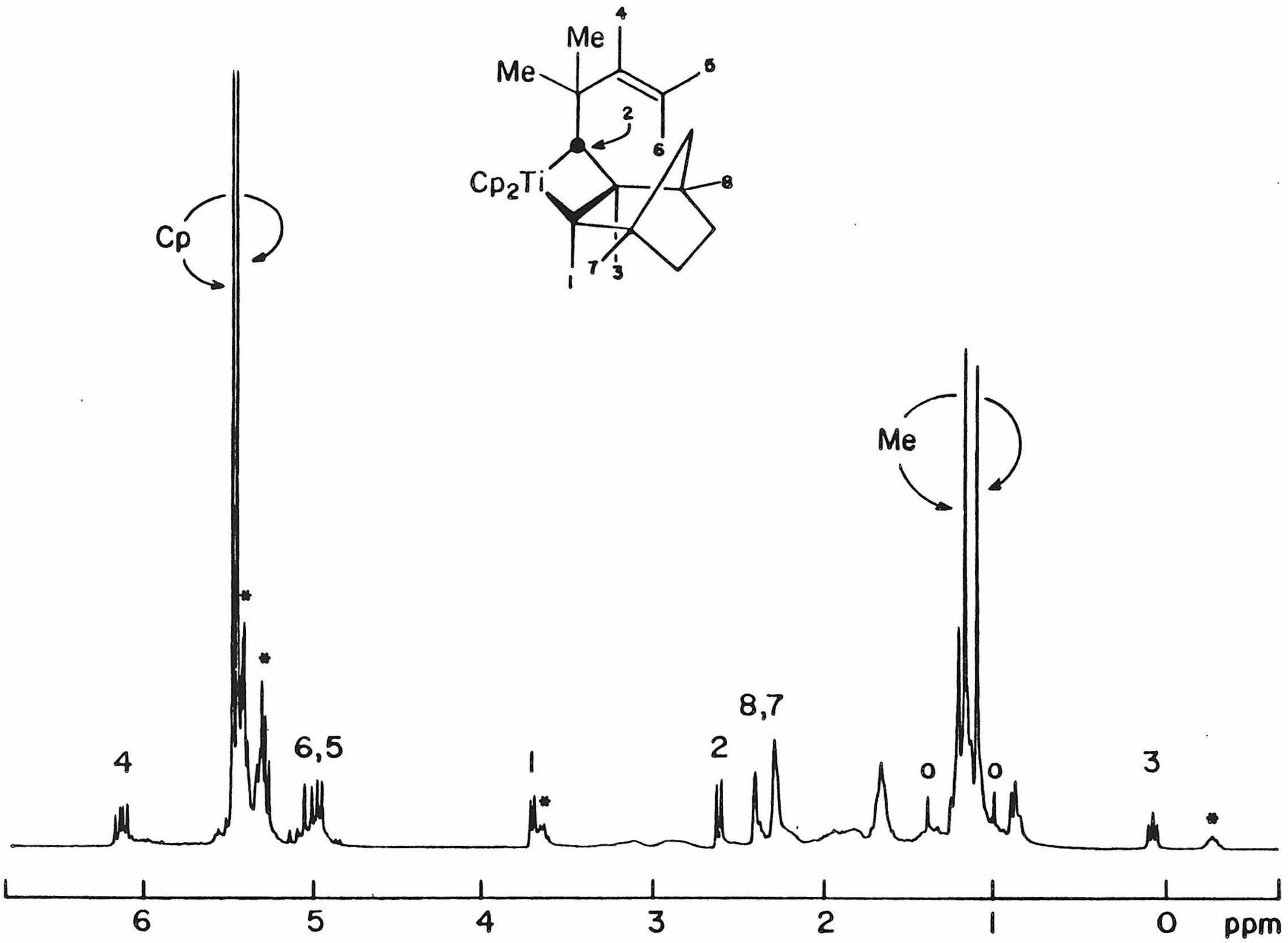
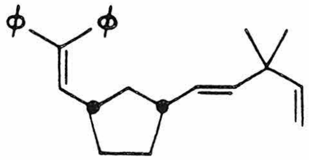


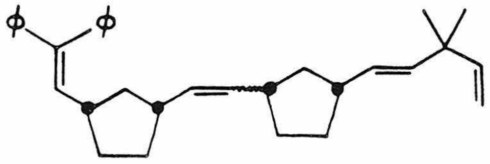
Figure 2. 400 MHz ^{1}H NMR spectrum of metallaycle **11** in C_6D_6. Peaks attributable to residual **3** are marked with a circle(O). Peaks attributable to **14** are marked with an asterisk (*).

pounds. When **11** was stirred with additional norbornene, the signals assigned to **11** diminished while the peaks marked with asterisks grew larger.

When **11** was heated to 65°C in the presence of benzophenone, olefins **12a** and **13a** were obtained.[17] Products **12a** and **13a** were identified on the basis of both spectral data and degradative ozonolysis. High resolution GC/MS



12a



13a

analysis of **13a** indicates that it is a mixture of two isomers, each of which gives the correct parent ion and a fragmentation pattern similar to that obtained for **12a**. When **11** was prepared by stirring **3** with norbornene for 3 h rather than the usual 1.5 h, the amount of **13a** relative to **12a** increased. The reaction conditions and product yields are summarized in Table II.

Due to the difficulty in isolating pure metallacycle, **11** was prepared in situ by reaction of norbornene with a measured amount of **3** for 1.5 h at room temperature and was used immediately in the experiments detailed below.

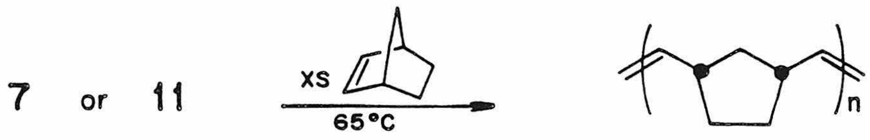
Polymerization of Norbornene. When heated at 65°C in the presence of excess norbornene, metallacycles **7** and **11** each produce polymeric products. Precipitation in excess methanol and drying under vacuum afforded an amorphous polymer in 92% yield based on initial monomer. The product polymers

Table II. Analysis of Benzophenone Trapping Experiments with **11**.

Reaction	t[a]	Reagents[b]		Products[b]		Yield[d]
		3	B[c]	**12a**	**13a**	
1	1.5	0.19	0.44	0.088	0.032	63
2	3.0	0.19	0.44	0.059	0.099	52

[a] Catalyst preparation time. In h. [b] In mmoles. [c] Benzophenone. [d] In %. Based on initial **3**.

retain the deep red color of the reaction mixture. Comparison of the ^{13}C NMR spectra of these polymers (Fig. 3 and Table III) with those in the literature[20] shows that both 7 and 11 yield ring-opened polynorbornene with a trans:cis ratio of 1.5 to 1. Further analysis of the ^{13}C spectrum indicates no cis-trans blockiness.



The polymerizations were monitored by VPC and stopped at 95% conversion of monomer by cooling the reaction mixture to room temperature. The product polymers could be stored indefinitely at room temperature under inert atmosphere. If the reaction mixture was kept at 65°C after complete conversion of monomer, a rapid degradation of the polymer resulted with a color change from red to brown.

Gel permeation chromatographic analysis (GPC)[21] of the polymer produced by reaction of 100 equivalents of norbornene with 7 gives M_n = 21,000 and polydispersity (d = M_w/M_n) of 1.13. The analogous reaction with 11 gives M_n = 21,000 and a d value of 1.07. Table IV summarizes molecular weight results obtained from sampling the polymerizations at intermediate conversions of monomer. Molecular weights for initiation with both 7 and 11 increase linearly with conversion. The molecular weight distributions of

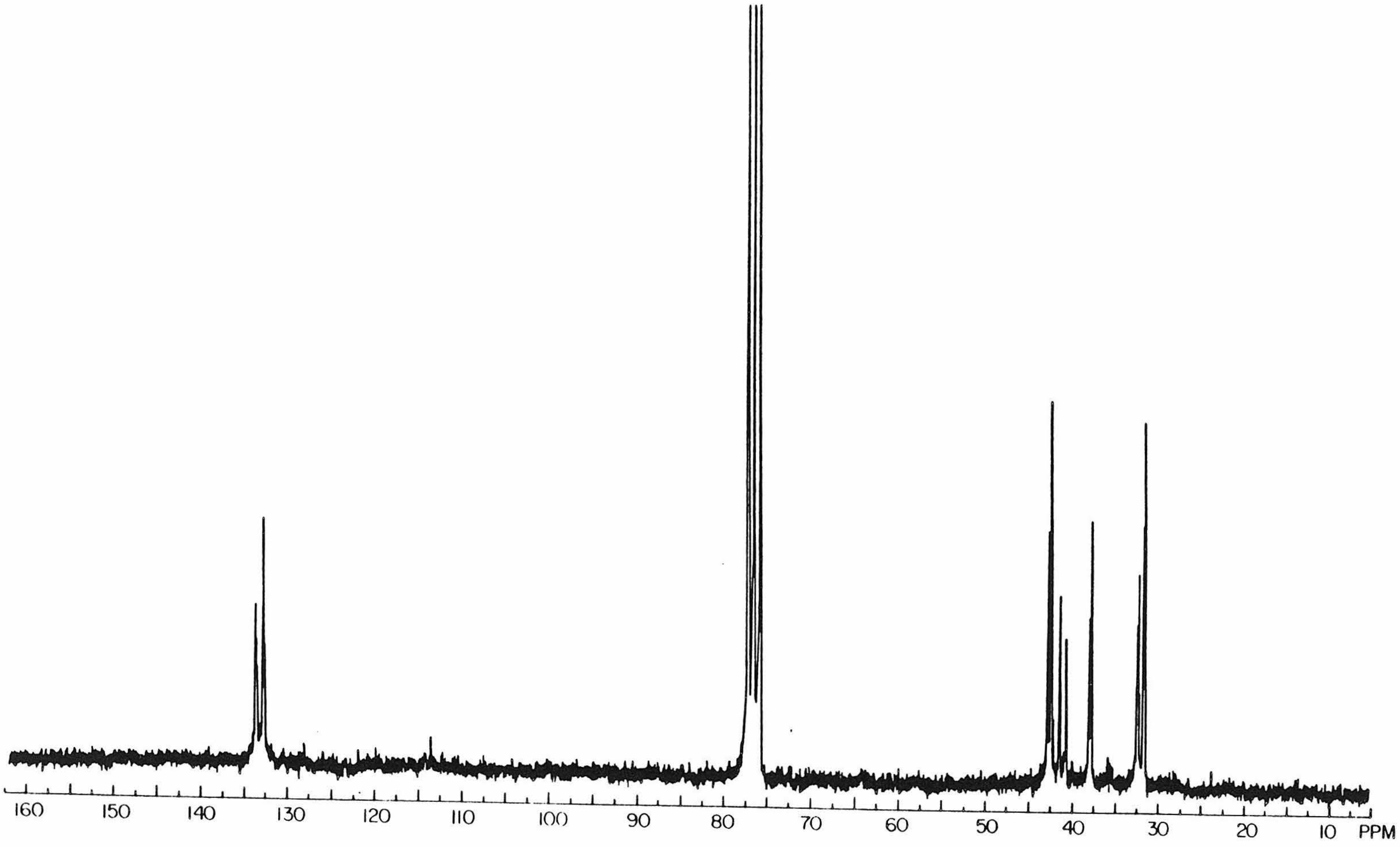
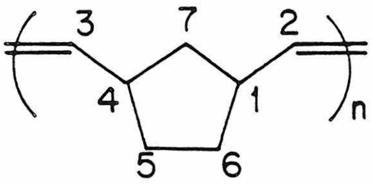


Figure 3. 50.3 MHz ^{13}C NMR spectrum of the polynorbornene obtained from **7** and **11**.

Table III. ^{13}C NMR Data and Assignments for the Polynorbornene Prepared with **7** and **11**.



Chemical[a] Shift	Relative Intensity	Assignment[b] C#	Assignment[b] c,t[c]
133.90	340	$C_{2,3}$	c
133.82	212		c
133.75	214		c
133.13	333	$C_{2,3}$	t
133.01	511		t
132.85	256		t
43.42	508	$C_{1,4}$	tc
43.12	773		tt
42.76	130	C_7	cc
42.10	376		ct,tc
41.35	297		tt
38.66	337	$C_{1,4}$	cc
38.40	537		ct
33.08	326	$C_{5,6}$	cc
32.92	427		ct
32.36	529		tc
32.20	734		tt

[a] In ppm, relative to solvent ($CDCl_3$) signal. [b] Assignments based on Reference 20. [c] c = cis, t = trans.

Table IV. Molecular Weight Analysis of the Polymers.

Catalyst	Time[a]	Conversion	M_n[b]	M_w[b]	d[b,c]	M_n^{corr} [d]	M_n^{theor}	Efficiency
7	6.0	31	8,300	10,400	1.25	--	--	--
	9.5	63	14,600	16,700	1.14			
	13.0	95	20,800	25,600	1.13	10,400	9,000	87%
11	4.0	31	7,200	8,100	1.12	--	--	--
	7.5	63	14,600	15,700	1.08	--	--	--
	11.0	95	20,900	22,700	1.09	10,450	9,100	87%

[a] Polymerization time in h. [b] Based on calibration with polystyrene standards. [c] Polydispersity. [d] $M_n^{corr} = 0.5\ M_n^{expt}$. See Ref. 35 and text.

polymers prepared from **11** are more narrow than those of polymers produced by **7**. Polydispersities for **7** were found to decrease with increasing conversion, whereas the dispersities for initiation with **11** were roughly constant.

Polynorbornene with M_n = 92,000 was prepared by the reaction of **11** with 500 equivalents to norbornene. The observed polydispersity of 1.09 (M_w = 100,000) is well within experimental error of the d values reported above for polymers with M_n = 21,000.

The polymerizations were also monitored by 400 MHz ^{1}H NMR spectroscopy. Upon heating at 65°C, signals attributable to metallacycle **7** gradually diminished. Simultaneously, new signals appeared: singlets in the Cp region, a broad doublet at δ 3.67 and a multiplet at δ -0.22.[22] New signals attributable to ring-opened polynorbornene were also observed in the aliphatic and olefinic regions. The olefinic protons of the polymer eventually obscured the new Cp signals; however, the doublet at 3.67 ppm and multiplet at -0.22 ppm were not obscured and remained undiminished throughout the polymerization. After complete consumption of monomer, these signals gradually decreased in intensity.

In contrast, no signals attributable to **11** were observed after 5 min at 65°C. New signals that are identical to the signals described above -- singlets in the Cp region, a doublet at δ 3.67, and a multiplet at δ -0.22 -- were observed. They also remained unchanged through the course of the polymerization and disappeared when the polymerization was complete.

Figures 4 and 5 show room temperature spectra obtained after polymerization with **7** and **11**, respectively, and removal of volatiles. The doublet at δ 3.67 and multiplet at δ -0.22 are evident in both spectra. Additional peaks at 3.51, 3.11, and 0.14 ppm present in Figure 4 are attributable to residual catalyst **7**.[23]

Kinetics of Polymerization and Initiation. The kinetics of the polymerization of norbornene with **7** and **11** were monitored by ^{1}H NMR spectroscopy. Figures 3 and 4 show the time dependence of the monomer concentration for catalysis by **7** and **11**, respectively. The data for polymerization with **7** at 65°C are shown in Figure 6. After an induction period, during which the rate of consumption of norbornene gradually increases, the plot (Figure 6a) for **7** becomes linear, indicating a zero-order reaction. Halving the norbornene concentration does not affect the rate. Doubling the concentration of **7** doubles the rate. The length of the induction period is not affected by changing concentrations of the reactants. The plot for polymerization by **11** (Figure 7a) is linear throughout the course of the polymerization. The rate and concentration dependences are the same, within experimental error, as those obtained for the zero-order region of polymerization with **7**.

First-order rate constants, k, were calculated as

$$-d[\mathrm{N}]/dt = k_{obs} = k[\mathbf{7}]_o \text{ or } k[\mathbf{3}]_o$$

for the linear portions of the kinetic plots. The rate data obtained at 53°C,

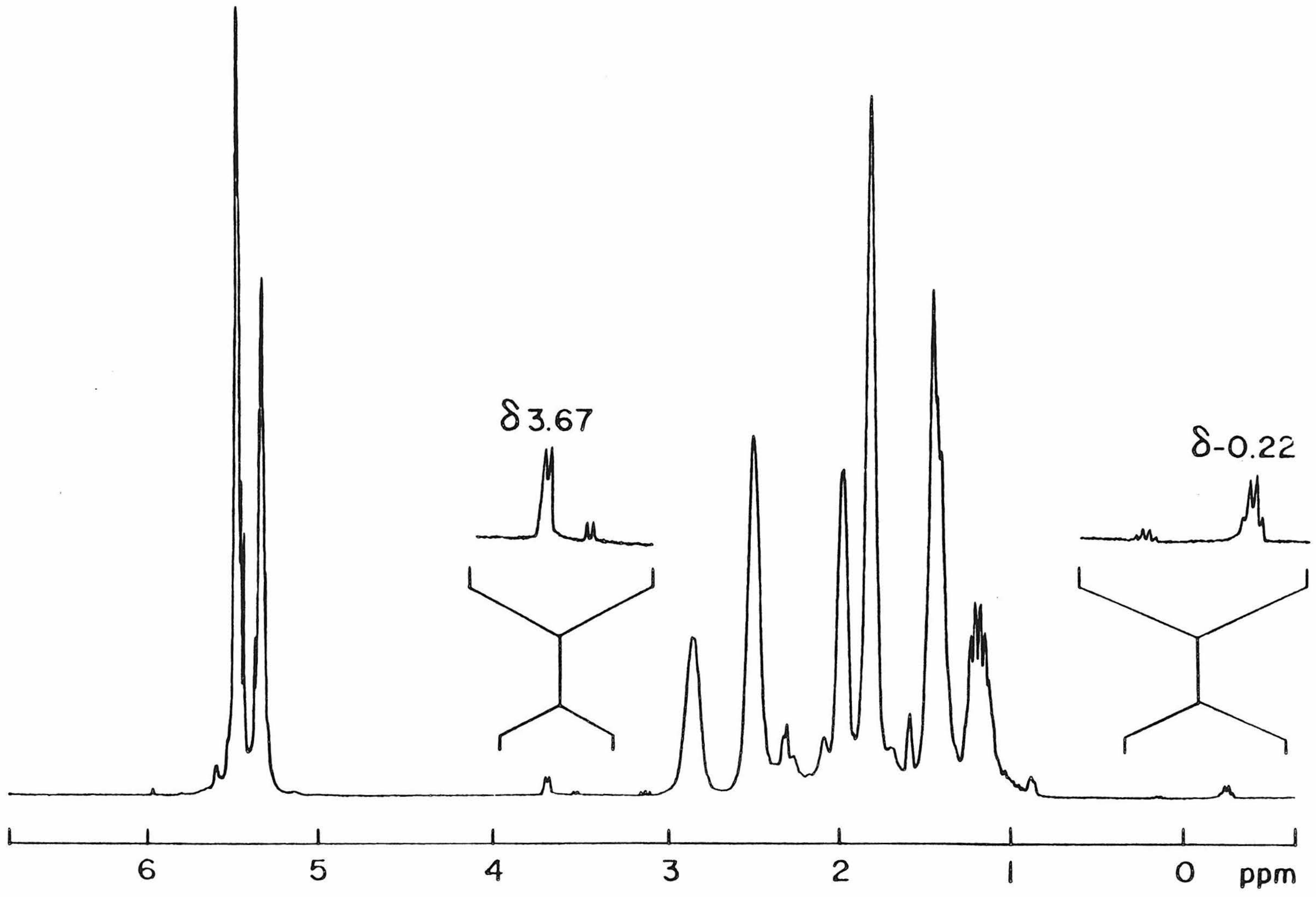


Figure 4. 400 MHz ^{1}H NMR spectrum of the reaction mixture after polymerization with **7** (4.5 h polymerization time at 65°C) and removal of volatiles. The solvent is C_6D_6.

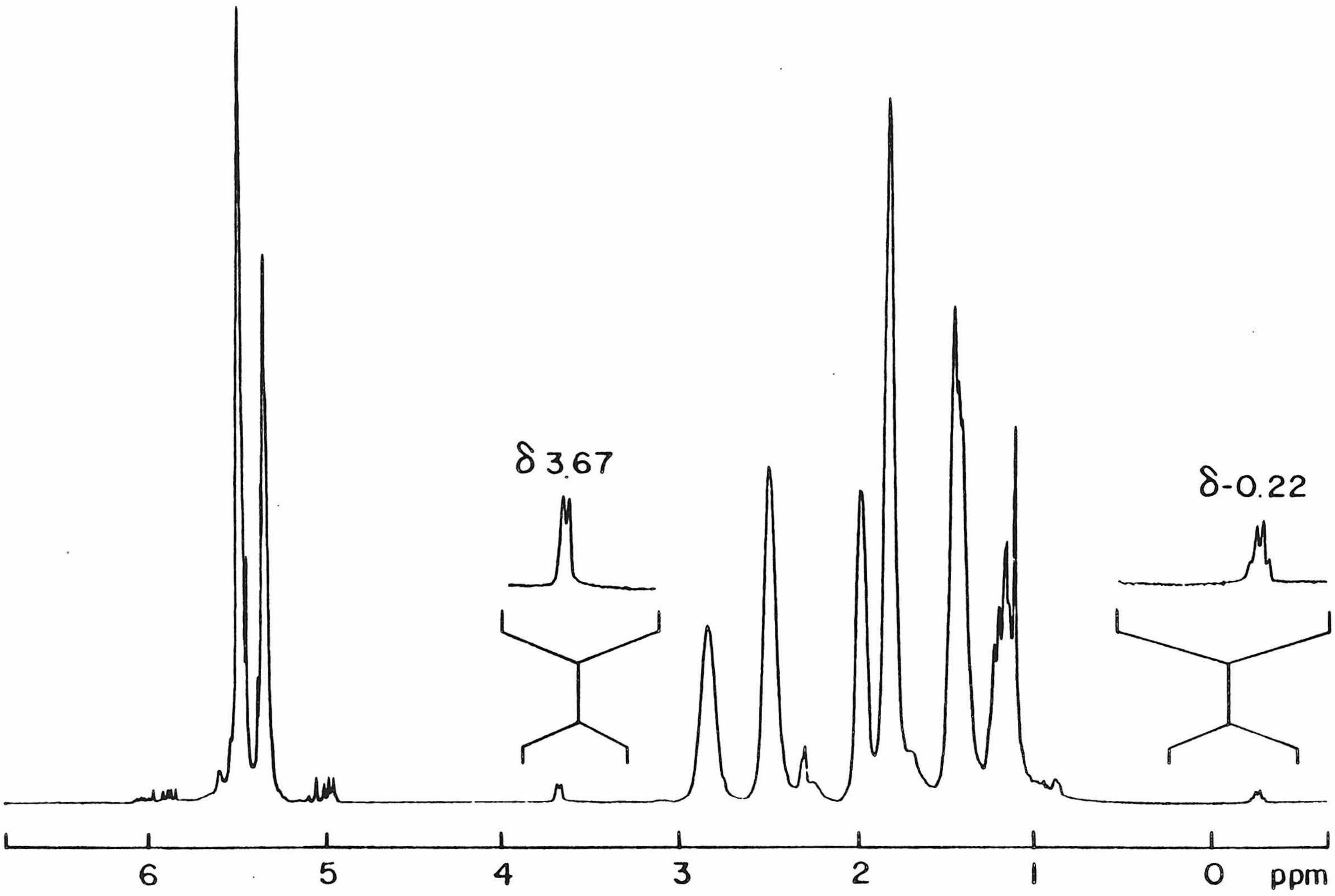


Figure 5. 400 MHz ^{1}H NMR spectrum of the reaction mixture after polymerization with **11** (3.0 h polymerization time at 65°C) and removal of volatiles. The solvent is C_6D_6.

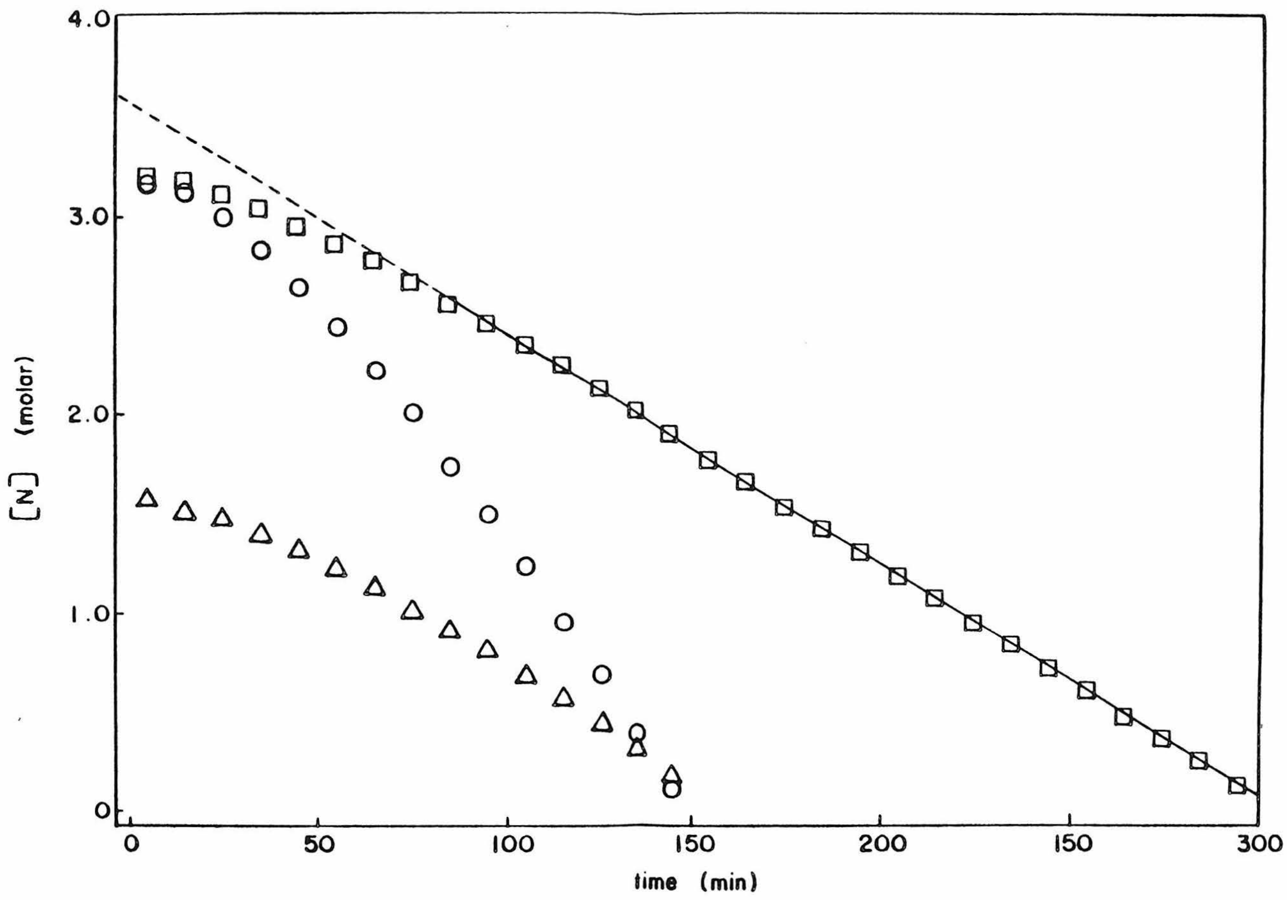


Figure 6. Kinetic data for polymerization of norbornene with 7 at 73°C. (□) $[7]_o = 0.035$ M, $[N]_o = 3.2$ M. (○) $[7]_o = 0.070$ M, $[N]_o = 3.2$ M. (△) $[7]_o = 0.35$ M, $[N]_o = 1.6$ M. The solid line in (a) indicates the points used to obtain the polymerization rate for the zero-order region.

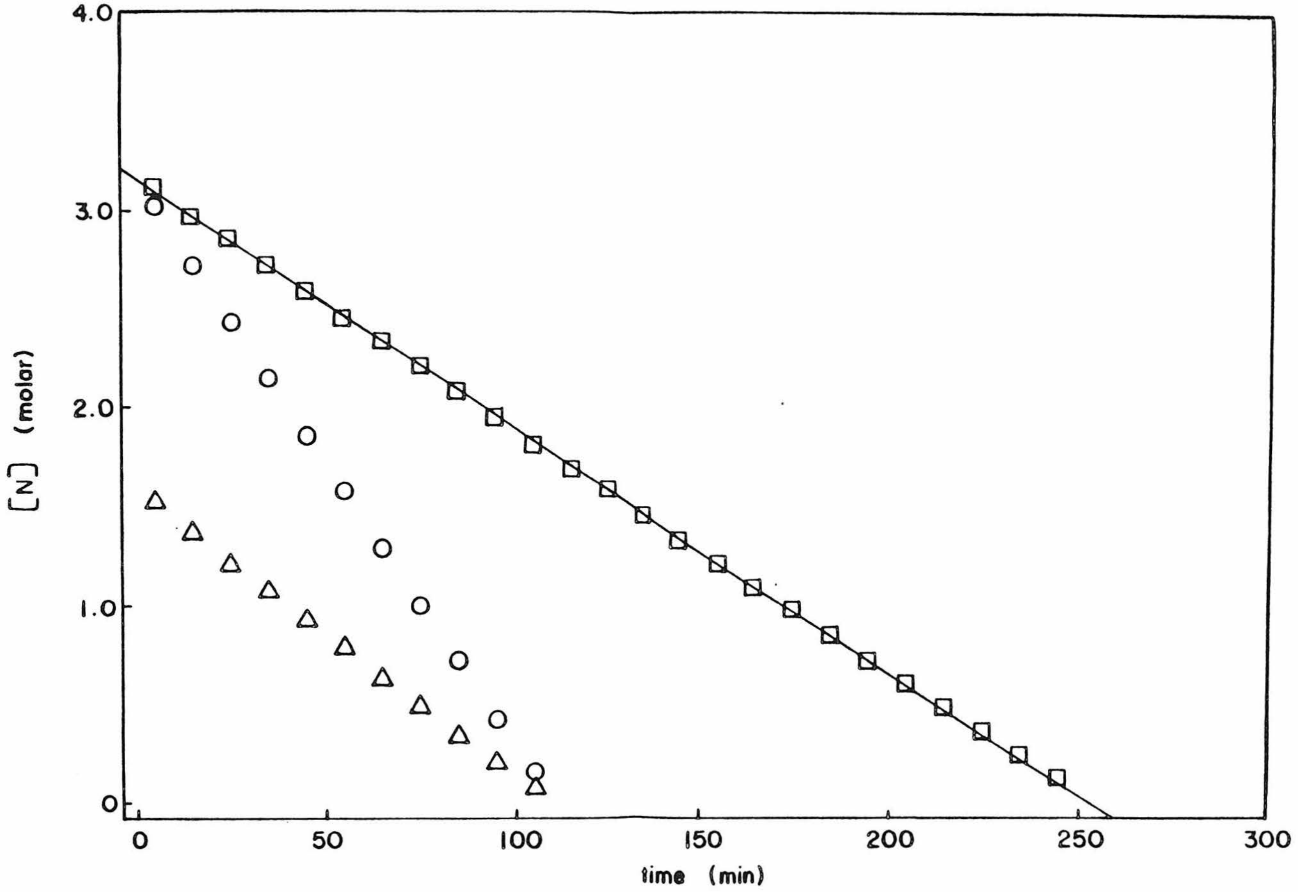


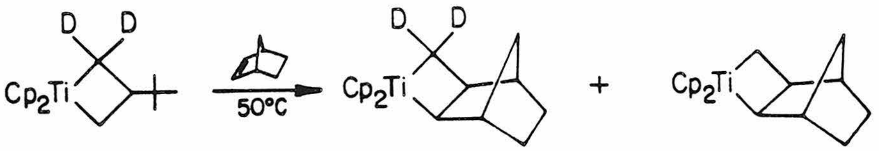
Figure 7. Kinetic data for polymerization of norbornene with **11** at 73°C. (□) $[3]_o = 0.035$ M, $[N]_o = 3.2$ M. (○) $[3]_o = 0.070$ M, $[N]_o = 3.2$ M. (△) $[3]_o = 0.035$ M, $[N]_o = 1.6$ M. The solid line in (a) indicates the points used to obtain the polymerization rate.

63°C, and 73°C are listed in Table V together with derived activation parameters.

The kinetics of the disappearance of **7** under the polymerization conditions were obtained at 65°C. A plot of $-\ln[7]$ versus time was linear for greater than three half-lives. The data fit the rate law

$$-d[7]/dt = k'[7] \qquad k' = 1.5(1) \times 10^{-4}\ s^{-1}.$$

Catalysis by Deuterated Metallacycle. Dideuterated **7** was prepared by olefin exchange from the α,α-dideuterotitanacyclobutane derived from neohexene, as illustrated below. The mixture of labeled and unlabeled **7**



was heated at 65°C in the presence of excess norbornene. A ^2H NMR spectrum of the resultant polymer showed a broad singlet at δ 5.03. This chemical shift is consistent with deuterium substitution of a terminal double bond.

Incorporation of Norbornene-d$_2$. The polymerization of norbornene initiated by **11** was stopped by cooling to room temperature. The remaining norbornene was removed and replaced with three equivalents of norbornene-

Table V. Kinetics Data for Polymerization with **7** and **11**.[a]

T (°C)	k^{b} (**1**), s^{-1}	k^{b} (**3**), s^{-1}
53	5.0×10^{-4}	5.1×10^{-4}
63	1.6×10^{-3}	1.8×10^{-3}
73	5.8×10^{-3}	6.3×10^{-3}

$\Delta H^{\ddagger} = 27.1 \pm 0.5$ kcal/mol, $\Delta S^{\ddagger} = 9 \pm 4$ e.u.,

$\Delta G^{\ddagger}_{338} = 24 \pm 1$ kcal/mol.

---

[a] $(\mathbf{7})_0 = 0.035$ M, $(\mathbf{3})_0 = 0.035$ M, $(\mathrm{N})_0 = 3.2$ M.
[b] $k = k_{obs}/(\text{catalyst})$.

2,3-d_2. After heating to 90% conversion of monomer, the reaction mixture was again cooled, the deuterated norbornene was replaced by perprotio-norbornene, and the solution was heated for an additional 15 min. The entire process was monitored at each step by both ^1H and ^2H NMR spectroscopy.

The ^2H spectra are shown in Figure 8. Figure 8a exhibits two signals due to C_6D_6 added as an internal standard and to unreacted norbornene-d_2 at δ5.94. Upon polymerization of the deuterated monomer, broad signals appeared at 5.45, 3.60, 2.39, and -0.36 ppm. After further polymerization with norbornene-d_0, all the deuterium was found at δ5.45.

Simultaneously, in the ^1H spectra (Fig. 9), signals at 3.57 and -0.35 ppm disappeared upon incorporation of deuterated monomer. When norbornene-d_0 was added and polymerized, these missing signals reappeared.

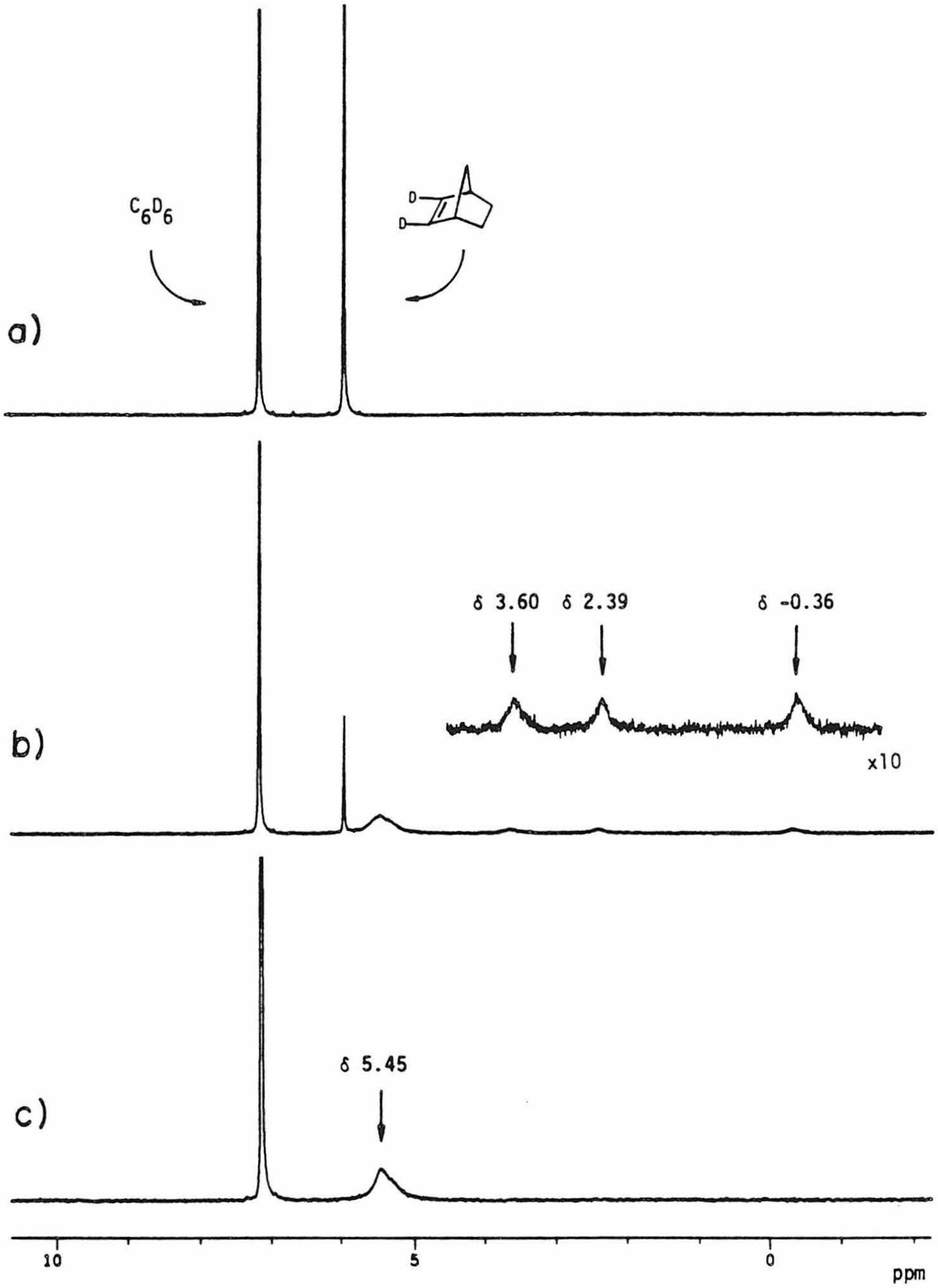


Figure 8. 61.25 MHz {^{1}H} ^{2}H NMR spectra in C_6H_6 showing the incorporation of deuterated norbornene into the polymer. (a) After addition of norbornene-d_2 but prior to heating. (b) After heating at 60°C for 15 min. (c) After addition of norbornene-d_0 and heating at 65°C for 15 min.

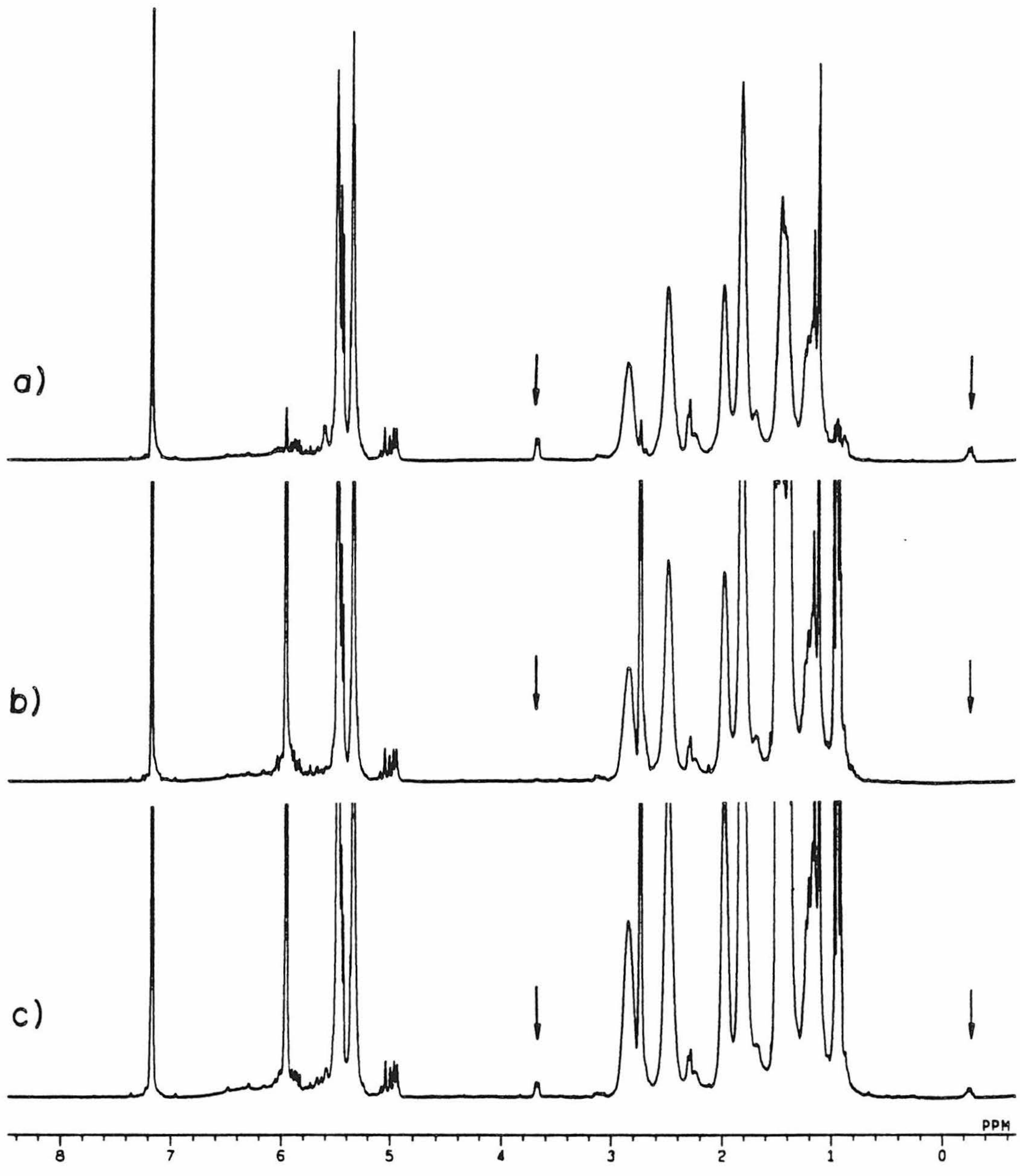


Figure 9. 400^{1}H NMR spectra in C_6D_6 showing the incorporation of deuterated norbornene into the polymer. (a) After polymerization of norbornene-d_0. (b) After polymerization of norbornene-d_2. (c) After polymerization of additional norbornene-d_0.

Discussion

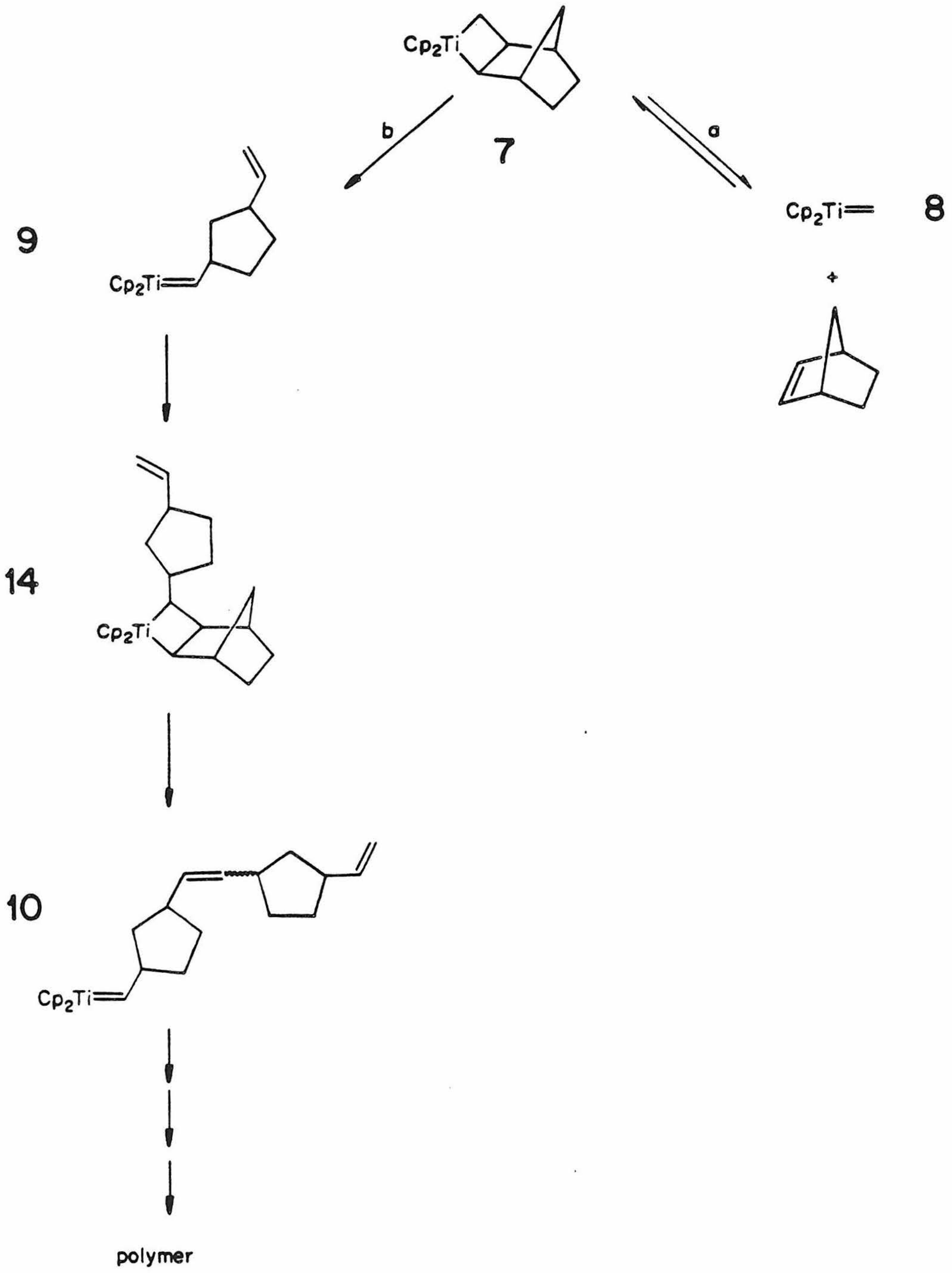
The experimental evidence suggests that polymerizations catalyzed by both **7** and **11** proceed by the same mechanism except for differences in the initiation steps. The product polynorbornenes have identical cis:trans ratios. NMR spectra of both polymerization reactions show identical peaks at δ 3.67 and -0.22, positions consistent with a titanacyclobutane intermediate. The reaction order, rate of disappearance of norbornene, and activation parameters for polymerization with **11** are the same, within experimental error, as those observed for the post-initiation region for **7**.

All the data presented here are consistent with the mechanisms outlined in Schemes I and II.[24] Metallacycle **7** can cleave to a carbene-olefin complex in two possible ways. Path a is non-productive but rapidly reversible. Path b leads to substituted titanacarbene **9**. Titanacarbene **9** is trapped by norbornene, forming an α,β,α'-trisubstituted metallacycle, **14**. Cleavage of **14** affords substituted carbene **10** which when trapped by norbornene, again produces trisubstituted metallacycle. Propagation in this manner yields a growing chain of ring-opened polynorbornene attached to the α' position of a trisubstituted titanacyclobutane analogous to **14**.

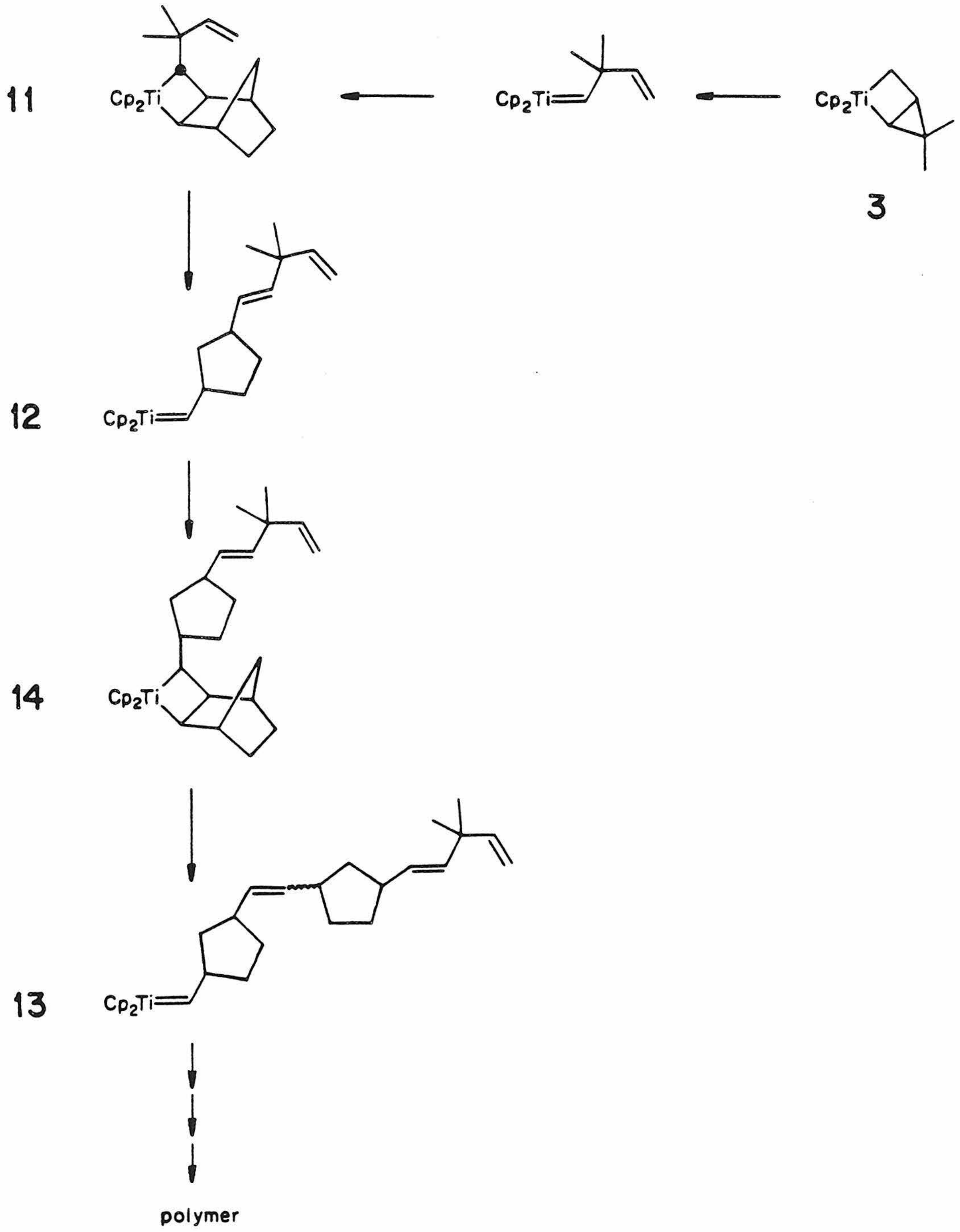
A direct route to the chain propagating metallacycles **14** is afforded by thermolysis of **11** in the presence of excess norbornene as shown in Scheme II. Propagation as discussed above again produces polynorbornene.

Identification of the Intermediates. The existence of most of the organometallic compounds shown in Schemes I and II has been substantiated

Scheme I. Proposed Mechanism for Catalysis by 7.

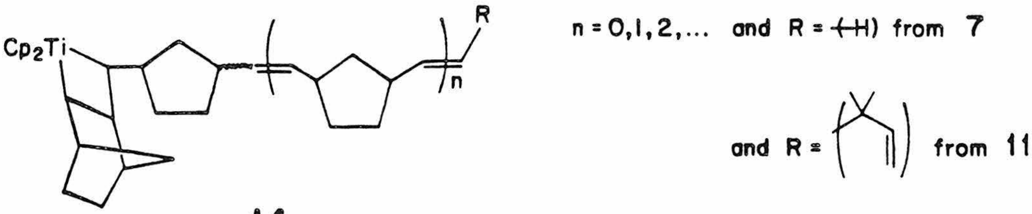


Scheme II. Proposed Mechanism for Catalysis by 11.



by isolation, spectral evidence, and/or trapping studies. Metallacycles **7** and **3** are fully characterized. Trisubstituted metallacycle **11** could not be cleanly isolated; however, ^{1}H and ^{13}C spectra are consistent with the assigned structure. Furthermore, the expected product **12a** was obtained from reaction of **11** with benzophenone.

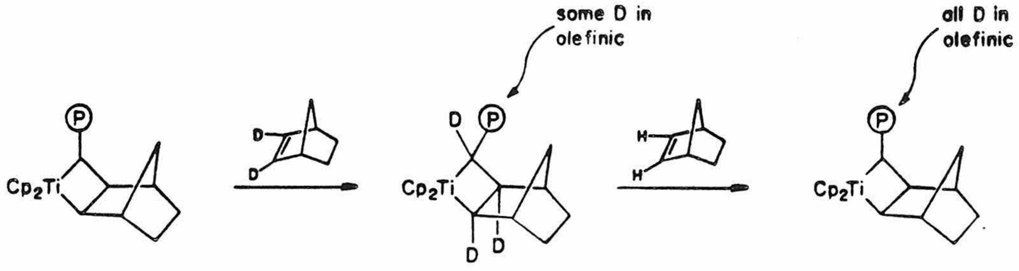
In Schemes I and II all the chain-propagating metallacycles have been labeled **14**. If consideration of cis-trans isomerism on the ring is excluded, they are all structurally identical with respect to the metal-containing ring. The α and β positions are annealed to the norbornene ring and the α' position



14

is attached to a secondary carbon. In contrast, the α' position for **11** is attached to a tertiary center. Since the metallacycles **14** differ only by the length of the growing polymer chain and its end group, the chemical shifts of the metallacycle ring protons should be similar.

The NMR signals at δ 3.67 and -0.22 are observed throughout polymerizations with both catalysts. Since they occur in regions characteristic of α and β protons on titanacyclobutanes, they are attributed to the α and β protons of the chain-propagating metallacycles **14**. Further substantiation of this assignment is provided by the incorporation of deuterium of these positions when



norbornene-d_2 is added to the growing polymer chain. The deuteration experiment also suggests that the α'-proton appears at 2.4 ppm.

None of the proposed carbene intermediates was observed; however, products derived from the alkenylation of benzophenone by the proposed titanacarbenes were obtained. Isolation of hydrocarbons **8a, 9a,** and **10a** from reaction with **7** suggests the presence of titanacarbenes **8, 9,** and **10.** Product **10a** presumably arises by addition of free norbornene, formed by the non-productive cleavage of **7** (Path a), to **9** and subsequent trapping of **10.** The relative yields of the hydrocarbon products shown in Table I can be rationalized in terms of the mechanism outlined in Scheme I. Addition of an equivalent of norbornene (reaction 2) increases the amounts of higher molecular weight products because the norbornene competes with benzophenone in trapping intermediate carbenes. Extra benzophenone (reaction 3) enhances the rate of trapping relative to addition of free norbornene; thus, a substantial increase in the amount of **9a** and decrease in the amount of **10a** is observed. Ninety-five percent of the norbornene initially present in metallacycle **7** can be accounted for in the products of reaction 3. Under these conditions, addition of two equivalents of benzophenone effectively prevents polymerization.

Similarly, the production of hydrocarbons **12a** and **13a** on thermolysis of **11** supports the intermediacy of titanacarbenes **12** and **13**. Since no additional norbornene was added to the reaction, the presence of **12a** suggests that trisubstituted metallacycle **14** (n = 0) is the major impurity in samples of **11**. The fact that an increased amount of **13a** and a decreased amount of **12a** were obtained when **11** was prepared by reaction of **3** and norbornene for 3.0 h rather than the usual 1.5 h confirms the suggestion that the metallacycle impurities obtained with **11** result from a competitive reaction of **11** in the direction of polymerization.

Kinetics of Polymerization. The zero-order dependence of polymerization rates on the concentration of norbornene implies a rate-determining step which does not involve monomer. One previously described explanation of such zero-order dependence is a strong prior coordination of monomer to the catalyst followed by rate-determining reaction of the catalyst-monomer complex.[25] In fact, few such cases have been observed in the kinetics of homogeneous polymerizations.[26] In this case the observed zero-order dependence is consistent with rate-determining unimolecular cleavage of metallacycle **14** followed by rapid trapping of the subsequent carbene with norbornene. Additional evidence for rate-determining metallacycle cleavage is provided by the observed positive entropy of activation.

The fact that no induction period is observed for polymerizations with

11 suggests rapid formation of the chain-carrying metallacycles **14**. Since **11** is substituted on the α'-carbon by a tertiary carbon while **14** has a secondary carbon attached at that position and since the stability of other titanacyclobutanes is sensitive to increased steric bulk on the ring, **11** is expected to be less stable than **14**. Because ring-opening affords structurally analogous carbenes **12** and **13**,[27] the initiation reaction (cleavage of **11**) is arguably faster than propagation (cleavage of **14**). Experimentally, by the time a spectrum could be recorded in the kinetic studies at 73°C, no signals attributable to **11** remained.

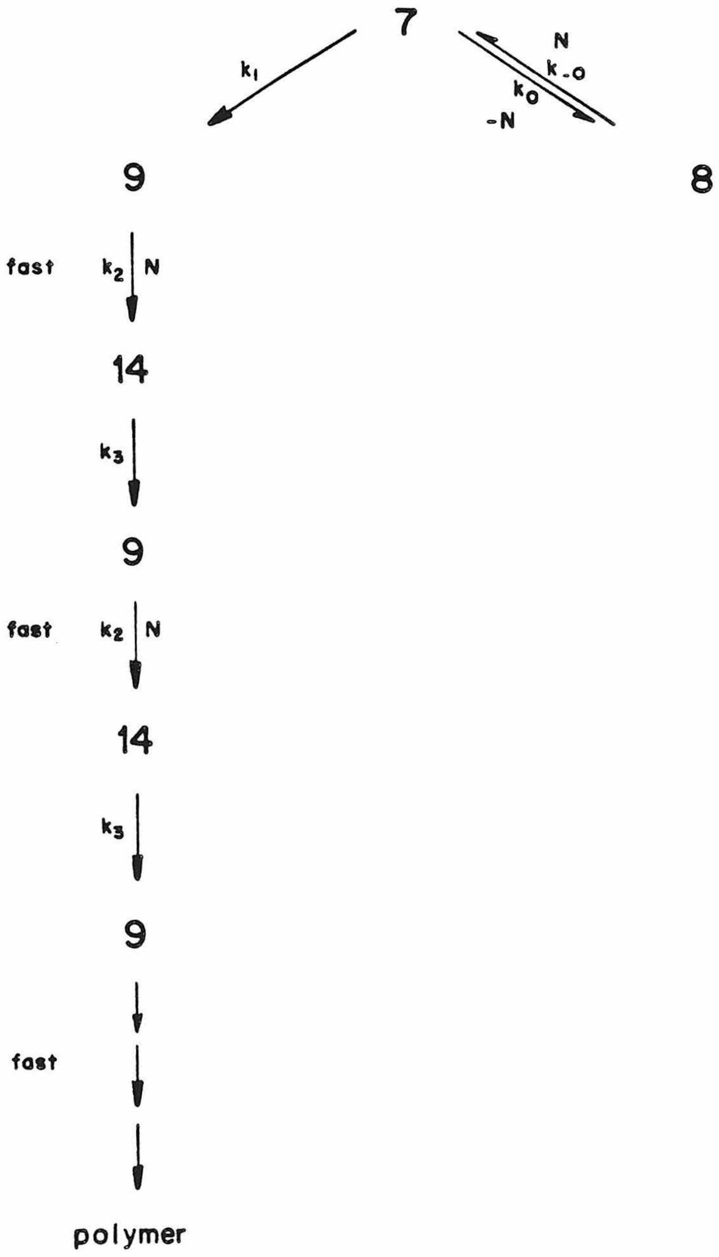
In contrast, polymerizations catalyzed by **7** do show an induction period. The length of this period does not depend on the concentration of either **7** or norbornene. The NMR studies showing the appearance of signals attributed to **14** as **7** disappears suggest that the induction period is due to slow conversion of **7** to **14**. The interaction of the α'-substituent of **14** and the Cp groups on titanium should destabilize **14** relative to the unsubstituted **7**. Consequently, cleavage of **7** (initiation) should be slower than cleavage of **14** (propagation).

Making the assumptions that k_{-1}, k_{-2}, and k_{-3} are all slow compared to the forward reactions[28] and assuming the steady-state approximation for all titanacarbenes (see Scheme III)[29] lead to the prediction that

$$-\frac{d(N)}{dt} = k_1 \cdot (\mathbf{7}) + k_3 \cdot (\mathbf{14}) \qquad (1)$$

where $k_1(\mathbf{7})$ corresponds to the first-order decay of initiator **7** and the $k_3(\mathbf{14})$ term corresponds to the first-order decay of each of the chain-carrying metallacycles **14**. Once the initiation period is over, the overall concentration of **14**

Scheme III. Mechanism used in the Kinetic Analysis.



remains unchanged and the rate of reaction should appear zero-order.

Equation 1 allows prediction of the time dependence of the concentration of norbornene with time for polymerization initiated by **7**. The constant k_1 is set equal to the rate constant obtained from monitoring the first-order disappearance of **7** at 65°C ($k_1 = 1.5 \times 10^{-4}$ s^{-1}). The value for k_3 at 65°C is derived from the Arrhenius parameters found for polymerization with **11** ($k_3 = 2.4 \times 10^{-3}$ s^{-1}). A plot obtained using equation 2 with $[7]_0 = 0.035$ M is shown in Figure 10 along with the experimental data

$$[N]_t - [N]_0 = Ae^{-k_1 t} - Bt - A \qquad (2)$$

where

$$A = \frac{k_1 - k_3}{k_1}[7]_0 \quad \text{and} \quad B = k_3[7]_0$$

obtained by monitoring the polymerization at 65°C. The similarity of the calculated and the observed curves supports the validity of the rate expression in equation 1 and the mechanisms presented in Schemes I and II.

Stereochemistry of the Polymer. The polymerization mechanism shown in Schemes I and II predicts that the stereochemistry of each double bond in the polymer is determined by the irreversible addition of norbornene to the substituted carbenes **9**. Decomposition of the subsequent metallacycle occurs without isomerization, affording a *trans* double bond for *trans* metallacycles **14t** and a *cis* double bond for *cis* metallacycles **14c**. In fact, olefin exchange has been shown to occur with retention of stereochemistry for other titanacyclobutane systems.[10]

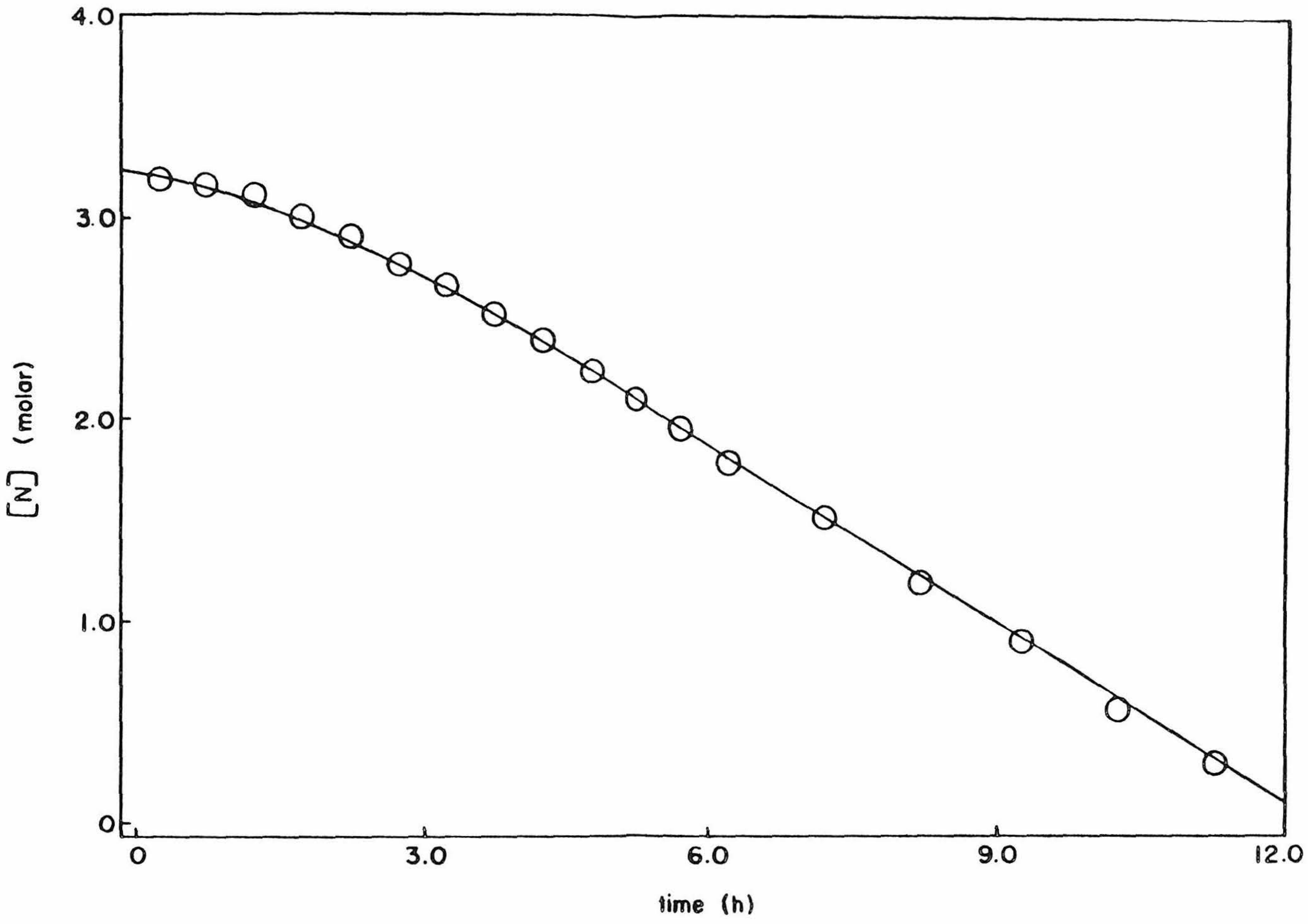
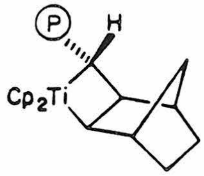
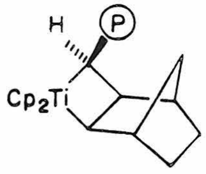


Figure 10. Experimental data and the calculated curve for the kinetics for the polymerization of norbornene with **1** at 65°C. Circles (O) are used to indicate experimental data. The solid line (——) indicates the theoretical curve derived as described in the text.



14t



14c

The experimentally observed *trans* to *cis* ratio of 62:38 suggests some *trans* preference but shows low stereoselectivity. Such a preference for trans addition could be due to an adverse steric interaction between the norbornene ring system and the α-substituent on the carbene which is required by *cis* addition. The early transition state expected for the conversion of the high energy carbenes to more stable metallacycles may lower the *trans* selectivity.

In some ring-opening polymerizations thermodynamic mixtures of stereoisomers have been obtained,[30] presumably due to secondary metathesis[31] and isomerization of the double bonds in the polymer chain. We believe that the *cis:trans* ratio observed in our study reflects the actual stereochemistry of monomer addition and not a subsequent equilibration reactions. A true thermodynamic mixture of double bond isomers on polynorbornene would have a much lower *cis* content.[32] Also, the same *cis* to *trans* ratio is observed at low conversion and throughout the polymerization.

One model for the stereochemistry of olefin metathesis suggests that selectivity is inherently high and that lowered selectivity is due to the presence of co-catalysts.[34] This idea is particularly interesting in view of the high *cis* selectivity observed by Katz[35] in his ring-opening polymerizations using unicomponent tungsten-carbene catalysts. Our present results, however, show that low selectivity can be observed in the absence of co-catalysts.

Several authors have suggested that high stereoselectivity arises from retained coordination of the last formed double bond at the metal center.[36-38] Such chelation in the case of polymerization of norbornene with titanacyclobutane compounds such as **7**, **11**, and **14** is sterically untenable. Chelation in the titanocene-carbene compounds would require a 20-electron intermediate as well as a crowded reaction center. The low selectivity observed here may be attributable to an inability to chelate.

Molecular Weights of the Polymers. The molecular weights reported above are based on calibration with polystyrene standards and therefore are not an accurate measure of the true molecular weight values for the polymer samples. Currently there are no literature values of a correction factor relating the polystyrene numbers to values for ring-opened polynorbornene. In his molecular weight analysis of cis-polynorbornene, Katz suggested that values obtained by polystyrene calibration be halved to obtain corrected molecular weights.[35] The sixth column of Table IV lists corrected molecular weight data for the ring-opened polynorbornenes reported here. Comparison with theoretical values suggests high efficiencies in catalyst for polymerization with **7** and **11**.

Since polymerizations with **7** have a slower rate of initiation than propagation while polymerizations with **11** show no induction period, the molecular weight distributions of polymers obtained form **7** should be broader than those of polymers made with **11**. As stated in the Results section, the polydispersity is always lower for polymers of comparable M_n when **11** is the catalyst. The d values of polymers from **7** rapidly decrease with increased conversion, while those for polymers from **11** remain roughly constant throughout the polymerization. This trend is consistent with slow first-order decay of initiator **7** and rapid initiation with **11**.

The molecular weight distributions obtained for catalysis by both **7** and **11** are narrow. Gold,[39] in his analysis of anionic polymerizations, has shown that narrow distributions can be obtained even when chain propagation is much faster than initiation. Polymers prepared with **11** have polydispersities as low as 1.07. The extremely narrow distributions obtained by some anionic systems[40] are not obtained here. One factor in this system which may broaden the distribution is the presence of the two different propagating species **14c** and **14t** with different stabilities and different rates of propagation.

Conclusion

The narrow and controlled molecular weights of the product polymers, the high efficiencies in catalyst, and the observation of chain-carrying intermediates suggest that the polymerizations of norbornene by titanacyclobutanes **7** and **11** are living polymerization systems. While a number of anionic[41] and cationic[42,43] living polymers are known, there are few examples of coordinative polymerization systems that are living.[44-46] This system is the only living polymerization system for the ring-opening polymerization of cyclic olefins reported to date.[47-50] It differs from the classical living systems only in that the living polymer is unstable in the absence of monomer at the polymerization temperature; however, it can be maintained at lower temperatures indefinitely.

Minimal requirements for a living polymerization system include a stable chain-carrying species, effective initiation, and the absence of chain transfer and termination reactions.[51] Titanacyclobutanes are unique among metathesis systems in that the metallacycles appear to be the principal chain-carrying species rather than metal carbenes.[4b,10] Titanacyclobutanes **7**, **11**, and **14** cleave exclusively to carbene and olefin. Other reaction pathways such as cyclopropanation and β-hydride chemistry that would lead to chain termination must be disfavored. We believe that factors which have been previously discussed for the predominance of metathesis-type reactions in the chemistry of titanacyclobutanes[4b] -- an accessible metal-carbene, the covalent nature of titanium carbon double bonds, a single open coordination site on the metal, and the instability of bare titanocene -- account for the absence of termination and transfer in the ring-opening polymerization of norbornene with **7** and **11**.

Experimental Section

General Procedures. All manipulations of air and/or moisture sensitive compounds were carried out with use of standard Schlenk or vacuum line techniques. Argon was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4Å molecular sieves. Solids were transferred in a N_2-filled Vacuum Atmospheres Dri-Lab equipped with an MO-40-1 purification train and a DK-3E Dri-Kool.

Materials. Tebbe reagent,[9] metallacycle **3**, and the neohexene metallacycle[10] were prepared according to literature procedures. Norbornene was purchased from Aldrich Chemical Co. and was refluxed over sodium and distilled prior to use. The 2,3-d_2-norbornene[53] was kindly provided by Dr. J. K. Stille. N,N-dimethylaminopyridine (Aldrich) and benzophenone (Aldrich) were recrystallized from hot toluene. Dimethylsulfide, 1,1-diphenylethylene, diphenylfulvene, tetraphenylethylene, 2,6-di-tert-butyl-4-methyl phenol (BHT), and Sudan III dye were purchased from Aldrich Chemical Co. Trans-1,2-diphenylethylene was purchased form MCB Reagents. Cyclopentane-1,3-dicarboxaldehyde was prepared according to a literature procedure.[54] Dichloromethane was dried over P_2O_5 and degassed on a vacuum line. Pentane was stirred over H_2SO_4, dried over CaH_2, and vacuum transferred onto sodium-benzophenone ketyl. Benzene was dried over CaH_2 and vacuum-transferred onto sodium-benzophenone ketyl. Diethyl ether, toluene, and benzene-d_6 (Cambridge Isotope Laboratories) were degassed and stirred over sodium-benzophenone ketyl. The dried and degassed solvents were vacuum-transferred into dry vessels equipped with Teflon valve closures and stored under Ar.

Reagent grade petroleum ether (35-60°C) and methanol were used without further purification.

Instrumentation. NMR spectra were recorded on a JEOL FX-90Q (89.60 MHz ^1H; 22.53 MHz ^{13}C), a Varian XL-200 (50.28 MHz ^{13}C), a JEOL GX-400 (399.65 MHz ^1H; 100.40 MHz ^{13}C; 61.25 MHz ^2H), or a Bruker WM-500 (500.13 MHz ^1H). Temperatures were measured using $\Delta\nu(CH_2OH)_2$ and were constant to $\pm0.5^\circ C$. Difference NOE experiments were performed according to published procedures.[55] Analytical gas chromatographic analyses (VPC) were performed on a Shimadzu GC-Mini 2 flame ionization instrument modified for capillary use and equipped with a Hewlett-Packard Model 339A integrator (column: 0.24 mm x 15 m DB1). Preparative gas chromatography was performed on a Varian Aerograph Model Model 920 instrument using a 5' x 1/4" 15% SE-30 on Chromosorb W column (column a) or a 2' x 1/4" 5% SE-30 on Chromosorb W column (column b). Gel permeation chromatographic (GPC) analyses utilized a single Shodex KF-803 column, a Spectroflow 757 absorbance detector with λ = 254 nm, and a Knauer differential refractometer. Low-resolution GC-MS analyses were obtained on a Kratos MS25. High-resolution mass spectroscopy was performed by the mass spectroscopy center at the University of California, Riverside or the Midwest Center for Mass Spectroscopy at the University of Nebraska, Lincoln. Oil bath temperatures for all polymerizations were maintained at $65.0 \pm 0.2^\circ C$ by use of an I^2R Therm-O-Watch. Ozone was obtained using a Welsbach generator.

Two-Dimensional ^1H-^{13}C Correlated NMR Spectra. The data were acquired using a JEOL GX-400 NMR spectrometer operating at 399.65 MHz proton frequency and 100.52 MHz carbon frequency. The pulse sequence was taken from Bax[56] and the phases of the pulses and the receiver were cycled to provide quadrature detection in f_1. The 90° ^{13}C pulse width was 6.5 μs and the 90° ^1H pulse width (decoupler) was 30 μs on the 5 mm $^1H/^{13}C$ probe. The f_2 spectral width was 12000 Hz and the pulse delay (PD) was 3.0 sec. Sixty-four transients of 4 K data points were collected for 256 increments of t_1. The incrementation of t_1 provided an f_1 spectral width of 3200 Hz. The fixed delays were optimized for J_{HC} = 125 Mz. Broad-band proton decoupling was applied during the acquisition time. The data were apodized in both dimensions with a sine-bell window function, Fourier-transformed, and the absolute value spectrum calculated.

Two-Dimensional ^1H-^1H Correlated NMR Spectra. The data were acquired using a JEOL GX-400 NMR spectrometer operating at 399.65 MHz proton frequency. The pulse sequence was 90°-t_1-45°-ACQTM-PD and the phases of the pulses and receiver were cycled to provide quadrature detection in f_1 and selection of "P-type" peaks. The 90° ^1H pulse width on the 5 mm $^1H/^{13}C$ probe was 15.0 μs. The f_2 spectral width was 3201.0 Hz and the pulse delay (PD) was 3.0 sec. Two dummy scans were taken before each slice to eliminate non-equilibrium magnetization. Eight transients of 1 K data points were collected for 512 increments of t_1. The total acquistion time was 4.5 h. The data were apodized with a sine-bell window function and Fourier-transformed in both dimensions. The absolute value spectrum was calculated and the entire data set symmetrized.

Preparation of 7. A solution of norbornene (3.3 g, 35.8 mmol) in

CH_2Cl_2 (7 mL) was degassed by three freeze-pump-thaw cycles. Addition of the norbornene solution to Tebbe reagent (5.0 g, 17.6 mmol) dissolved in 13 mL CH_2Cl_2 was followed by addition of (dimethylamino)pyridine (2.45 g, 20.1 mmol). The resulting red solution was slowly added dropwise to 200 mL of vigorously stirred pentane at -20°C. The precipitated DMAP-$AlMe_2Cl$ adduct was filtered off and the filtrate was evaporated to dryness under vacuum. The resultant solid was crystallized from diethyl ether by slow cooling to give 2.92 g (10.2 mmol, 58%) of **7** as red crystals. ^1H NMR (500 MHz, C_6D_6) assignment as in Figure 1a and shifts versus residual solvent: δ 5.47 (s, 5H, Cp_1), 5.29 (s, 5H, Cp_2), 3.51 (d, J_{14} = 9.0 Hz, 1H, H_1), 3.11 (dd, J_{24} = 10.5 Hz, J_{23} = 8.5 Hz, 1H, H_2), 2.27 (bs, 1H, H_6), 2.25 (bs, 1H, H_5), 1.91 (pt, J_{32} = 8.5 Hz, J_{34} = 8.5 Hz, 1H, H_3), 1.67 (m, 2H, H_9 and H_{10}), 1.22 (m, 2H, H_{11} and H_{12}), 1.08 (d, J_{78} = 9.0 Hz, 1H, H_7), 0.86 (d, J_{87} = 9.0 Hz, 1H, H_8), 0.14 (pq, J_{41} = 9.0 Hz, J_{42} = 10.5 Hz, J_{43} = 8.5 Hz, 1H, H_4). Difference NOE (500 MHz, C_6D_6): Irradiation of the signal at δ 5.74 (Cp_1) strongly enhances signals at δ 2.25 (H_5), 1.91 (H_3), and 1.08 (H_7). Irradiation of the signal at δ 5.29 (Cp_2) strongly enhances signals at δ 3.51 (H_1), 3.11 (H_2), and 0.14 (H_4). Assignment of the ^1H spectrum was aided by a two-dimensional ^1H-^1H correlated spectrum (Fig. 11). ^{13}C NMR (22.53 MHz, C_6D_6) chemical shifts versus C_6D_6: δ 109.22, 108.44, 107.46 (C_α), 76.40 ($C_{\alpha'}$), 47.55, 42.28, 35.13, 34.62, 29.87, 20.77 (C_β). Assignment of the carbon spectrum was aided by a two-dimensional ^1H-^{13}C correlated spectrum (Fig. 12). Anal. calcd. for $C_{18}H_{22}Ti$: C, 75.52; H, 7.75. Found: C, 75.28; H, 7.84.

Preparation of 11. To **3** (0.25 g, 9.6 mmol) was added a solution of

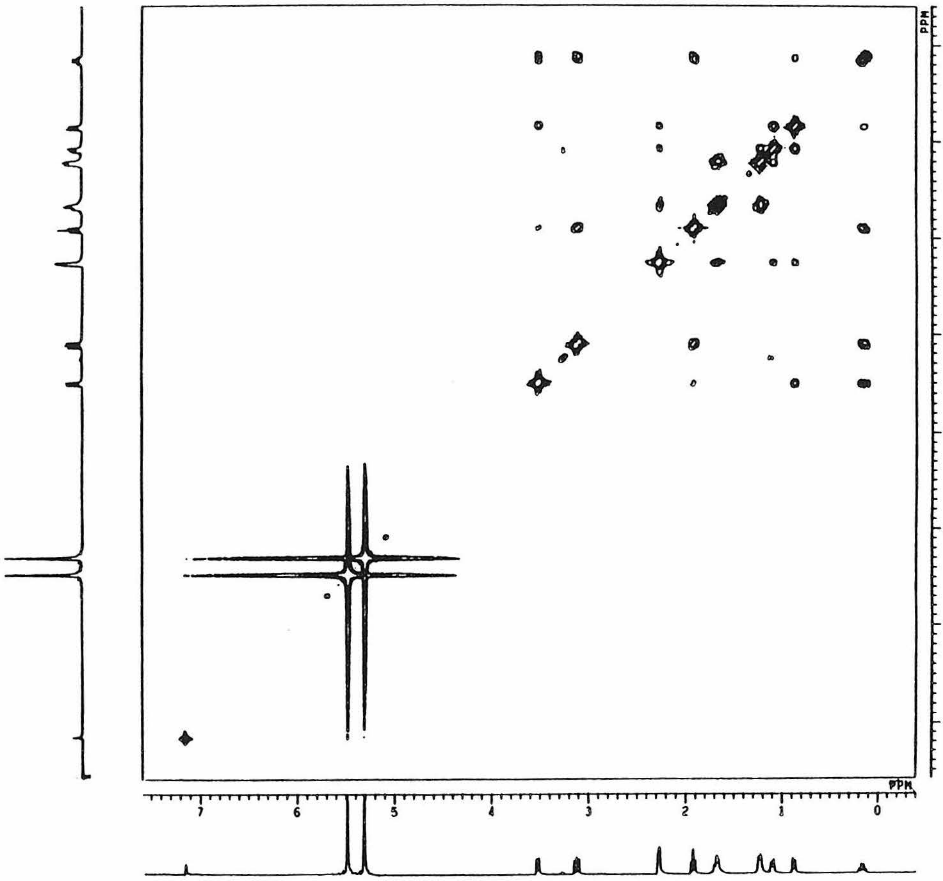


Figure 11. Two-dimensional ^1H-^1H correlated spectrum of 7.

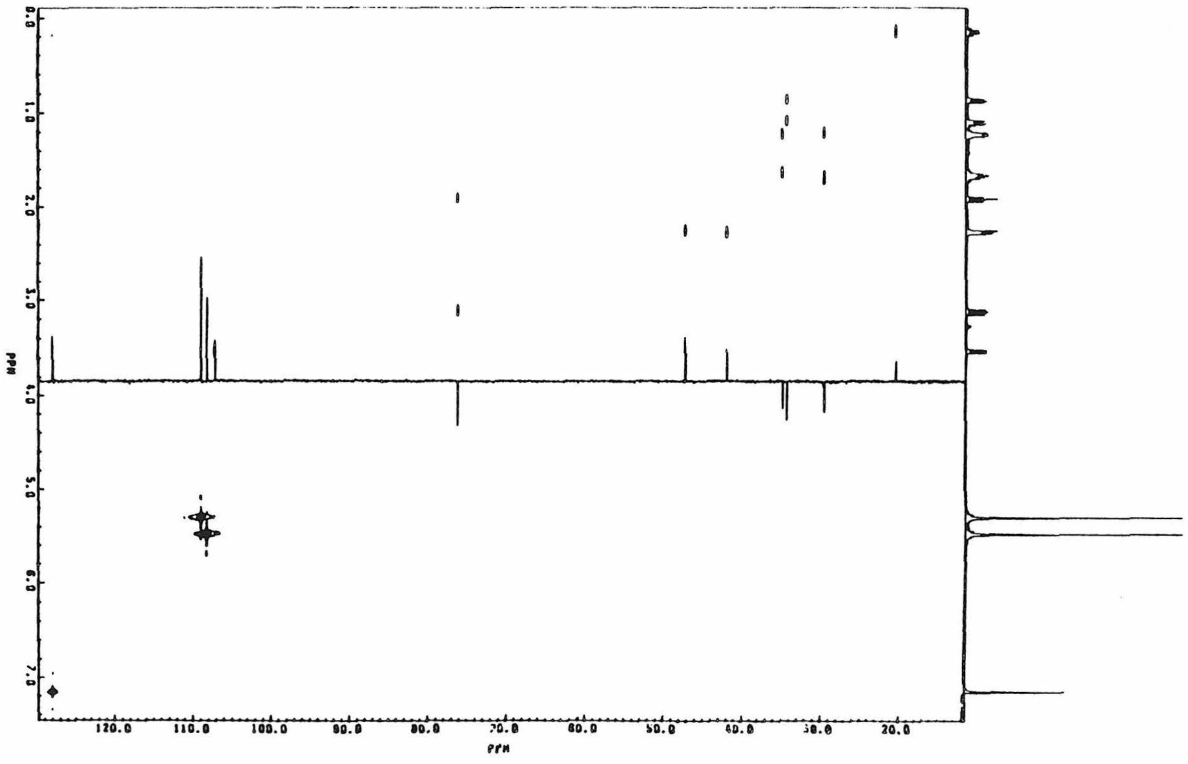


Figure 12. Two-dimensional ^{13}C-^{1}H correlated spectrum of 7.

norbornene (0.15 g, 15.6 mmol) in benzene (3 mL). The reaction mixture was stirred 1.5 h at 20°C. Volatiles were removed under vacuum affording approximately 300-350 mg of a deep red oil. Attempted crystallization from diethyl ether, pentane, toluene, and mixed solvent systems did not yield solid material. ^{1}H NMR analysis of the oil showed product **11** with roughly 30% impurity assigned as **14** (n = 0). The estimate of the relative amount of **14** is based on integration of the ^{1}H NMR signals at δ 0.08 and δ -0.22. Reaction of **3** (30 mg, 0.12 mmol) with norbornene (20 mg, 0.21 mmol) in benzene-d_6 (0.5 mL) for 1.5 h at 20°C afforded **11** with 30% **14**. An identical reaction stirred for 3 h at 20°C shows 50% **14**. ^{1}H NMR (400 MHz, C_6D_6) assignment as in Figure 2a, peaks attributed to **14** indicated by I, and shifts versus residual solvent: δ 6.14 (dd, J_{45} = 17.5 Hz, J_{46} = 10.5 Hz, 1H, H_4), 5.49 (5H, Cp), 5.46 (5H, Cp), 5.43-5.31 (I, singlets, Cp), 5.04 (dd, J_{54} = 17.5 Hz, J_{56} = 1.5 Hz, 1H, H_5), 4.97 (dd, J_{64} = 10.5 Hz, J_{65} = 1.5 Hz, 1H, H_6), 3.72 (bd, J_{13} = 10.0 Hz, 1H, H_1), 3.66 (I, m, H_α), 2.63 (d, J_{23} = 11.0 z, 1H, H_2), 2.41 (bs, 1H, H_8), 2.30 (s, 1H, H_7), 1.67 (m, 2H), 1.21-1.17 (m, 3H), 1.18 (s, 3H, Me), 1.12 (s, 3H, Me), 0.90 (d, 1H, J = 12.0 Hz), 0.08 (pt, J_{31} = 10.5 Hz, J_{32} = 10.5 Hz, 1H, H_3), -0.26 (I, m, H_β). Difference NOE (400 MHz, C_6D_6): Irradiation of the signal at δ 3.72 (H_1) enhances signals at δ 0.08 (strong, H_3) and 2.30 (weak, H_7). Irradiation of the signal at δ 2.63 (H_2) enhances signals at δ 2.41 (strong, H_8), 6.14 (weak, H_4), and 0.08 (weak, H_3). Irradiation of the signal at δ 0.08 (H_3) enhances signals at δ 6.14 (strong, H_4), 3.72 (strong, H_1), 2.41 (strong, H_8), and 2.63 (weak, H_2). The cyclopentadienyl region δ 5.5-5.2 and the methyl region δ 1.3-1.0 were uninterpretable. Assignment of the ^{1}H spectrum was aided by a two-dimensional ^{1}H-^{1}H correlated spectrum (Fig. 13). ^{13}C NMR (400 MHz, C_6D_6) chemical shifts versus C_6D_6: 149.62, 110.88 (C_α), 109.00, 108.77, 104.36 (C_α'), 57.36, 47.79, 41.96, 35.85, 35.10, 33.37, 30.88, 30.11, 24.20 (C_β). Assignment of the carbon spectrum was aided by a two-dimensional ^{1}H-^{13}C correlated spectrum (Fig. 14). Anal. calcd. for 70% $C_{23}H_{30}Ti$ and 30% $C_{30}H_{40}Ti$: C, 78.66; H, 8.66. Found: C, 78.92; H, 8.57.

Reaction of 7 with Benzophenone. To three flasks, each containing **7** (50 mg, 0.17 mmol) in 1.5 mL C_6H_6, were added appropriate amounts of benzophenone and norbornene as indicated in Table I. The solutions were immersed in a 65°C oil bath and stirred for 10 h. After cooling to 23°C, 1.0 mL of a 0.055 M solution of trans-1,2-diphenylethylene was added as an internal standard. The amounts of products **8a**, **9a**, and **10a** were determined by capillary VPC analysis of the solutions. Response factors for **9a** and **10a** were assumed based on carbon number.

Isolation of 8a, 9a, and 10a. To **7** (0.15 g, 0.52 mmol) in 4.0 mL C_6H_6 was added benzophenone (0.10 g, 0.55 mmol). The solution was stirred at 65°C for 10 h. After cooling to 23°C, the solution was diluted with 20 mL petroleum ether. The resultant yellow precipitate was removed by rapid filtration through silica gel. Evaporation of the solvent under reduced pressure afforded 82 mg of a yellow oil. Analysis by capillary VPC indicated three major products. The first two products appear as single, sharp peaks at short and intermediate retention times, respectively. The third product, appearing at long retention time, is a cluster of at least two overlapping

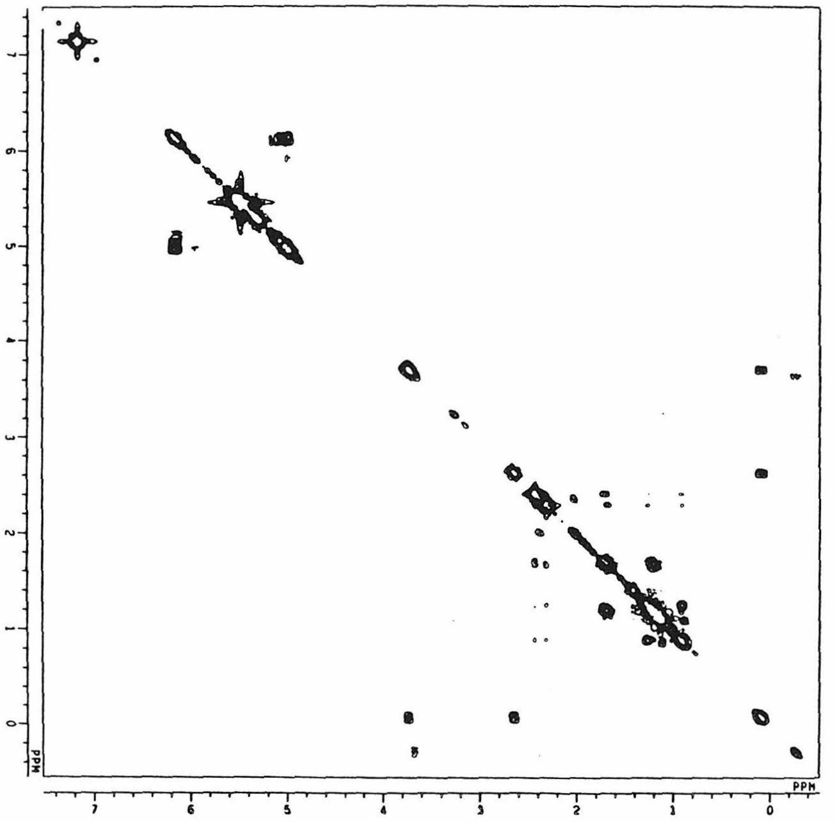


Figure 13. Two-dimensional ^1H-^1H correlated spectrum of 11.

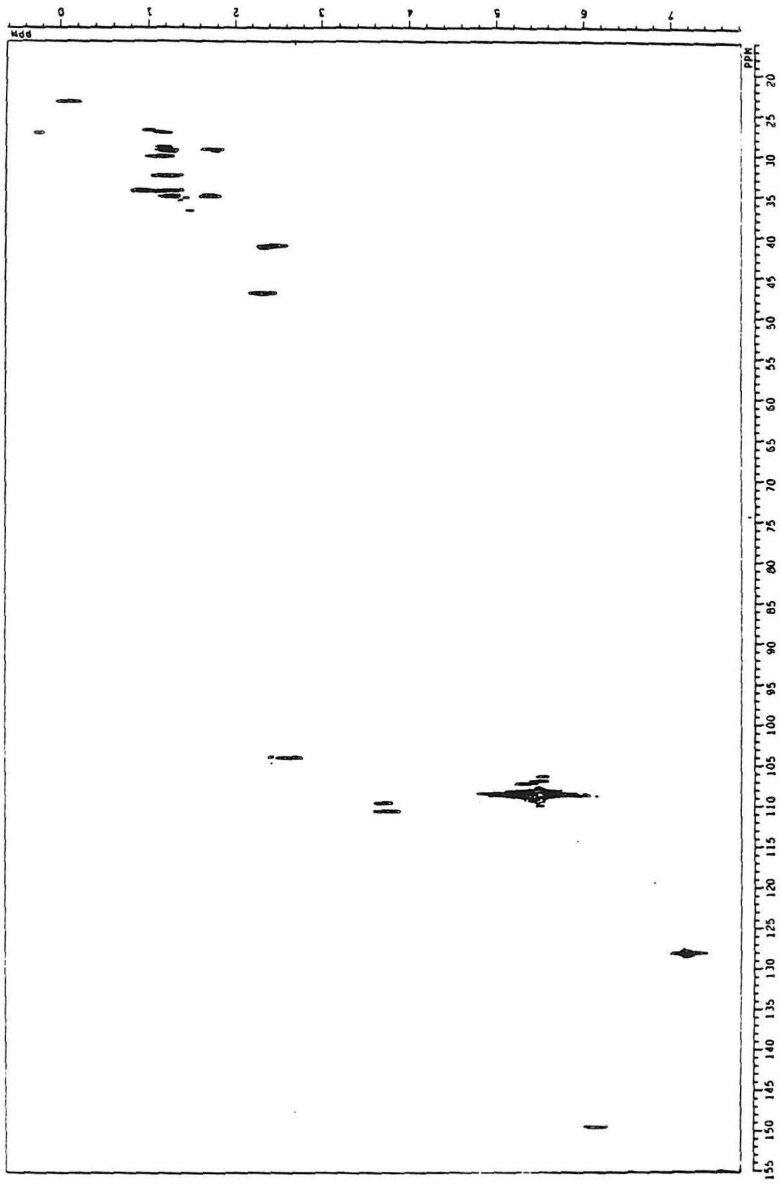


Figure 14. Two-dimensional 13C-1H correlated spectrum of 11.

peaks. Preliminary purification by preparative layer chromatography (silica, hexane) was followed by isolation of the three fractions by preparative VPC on column a.

8a: 6.0 mg. Identification based on comparison of NMR spectral data with data from an authentic sample and by coinjection by capillary VPC.

9a: 13.0 mg. ^{1}H NMR (500 MHz, CDCl$_3$) shifts versus added TMS: δ 7.4-7.1 (m, 10H), 5.97 (d, 1H), 5.80 (ddd, 1H), 4.96 (d, 1H), 4.88 (d, 1H), 2.64 (m, 1H), 2.45 (m, 1H), 1.93 (m, 1H), 1.80 (m, 2H), 1.51 (m, 2H), 1.25 (m, 1H); ^{13}C NMR (22.53 MHz, CDCl$_3$) shifts versus solvent: δ 143.09, 142.70, 140.49, 140.23, 134.97, 129.96, 128.08, 127.74, 126.78, 112.45, 44.51, 41.51, 40.28, 33.00, 31.97; mass spectrum *m/e* 274 (M$^+$), 205, 180 (base), 167, 165, 91. *Exact mass* calcd. for $C_{21}H_{22}$: 274.1722. Found: 274.1737.

10a: 2.0 mg. ^{1}H NMR (500 MHz, CDCl$_3$) shifts versus added TMS: δ 7.4-7.1 (m, 10H), 5.97 (d, 1H), 5.79 (m, 1H), 5.22 (m, 1H), 4.96 (d, 1H), 4.86 (d, 1H), 2.8-2.3 (m, 4H), 1.9-0.9 (m, 12H); mass spectrum *m/e* 368 (M$^+$), 245, 205, 180, 157, 91 (base). *Exact mass* calcd. for $C_{28}H_{32}$: 368.2504. Found: 368.2543. Capillary GC/MS suggests *m/e* of 368 applies to all peaks in the cluster at long retention time.

Ozonolysis of 9a and 10a. To a solution of 4.5 mg **9a** in 1.0 mL MeOH were added two drops of a saturated solution of Sudan III dye in MeOH. The solution was cooled to -78°C and ozonized until color change from pink to clear was observed. Dimethyl sulfide (10 µL) was added and the solution was warmed to 23°C. Capillary VPC analysis indicated three products which coeluted with authentic samples of dimethylsulfoxide, *cis*-1,3-dicarboxycyclopentane, and benzophenone. The molar ratio of benzophenone to dialdehyde was 1.0:0.7. Response factors were measured using authentic samples.

Ozonolysis of **10a** was performed as described above using 0.6 mg **10a** in 0.25 mL MeOH. The molar ratio of benzophenone to dialdehyde was 1.0:1.7.

Reaction of 11 with Benzophenone. To two flasks, each containing **2** (50 mg, 0.19 mmol) in 1.0 mL C_6D_6, was added norbornene (40 mg, 0.42 mmol). The solutions were stirred at 23°C for 1.5 and 3 h, respectively. Volatiles were removed under vacuum and replaced with 1.0 mL benzene containing benzophenone (80 mg, 0.44 mmol). The solutions were warmed to 60°C over 1 h and stirred at 60°C an additional 5 h. After cooling to 23°C, 1.0 mL of a 0.030 M solution of tetraphenylethylene was added to each of the flasks as an internal standard. The amounts of products **12a** and **13a** were determined by capillary VPC analysis of the solutions. Response factors were assumed based on carbon number.

Isolation of 12a and 13a. To **3** (50 mg, 0.19 mmol) in 1.0 mL C_6D_6 was added norbornene (40 mg, 0.42 mmol). The solution was stirred 1.5 h at 23°C. Volatiles were removed under vacuum, 1.0 mL C_6D_6 and 70 mg benzophenone (0.38 mmol) were added, and the solution was stirred at 40°C for 10 h. After cooling to 23°C,10 mL petroleum ether was added. The resultant yellow precipitate was removed by rapid filtration through silica gel. Evaporation of the solvent under reduced pressure afforded 59 mg of a yellow oil. Analysis by capillary VPC revealed three major peaks, one of which occurred at moderate retention time. The other two peaks eluted close together at long retention time. Purification by preparative VPC on column b cleanly afforded **12a**. The two peaks occurring at long retention time were not individually isolated. Purification by preparative VPC (column b) afforded a mixture of the two peaks. Assignment as isomeric forms of **13a** is based primarily on high resolution GC/MS results.

12a: ^{1}H NMR (400 MHz, $CDCl_3$) shift versus added TMS: δ 7.4-7.1 (m, 10H), 5.95 (d, 1H, J = 9.8 Hz), 5.77 (dd, 1H, J = 10.6, 17.4 Hz), 5.35 (d, 1H, J = 15.6 Hz), 5.29 (dd, 1H, J = 6.1, 15.6 Hz), 4.90 (dd, 1H, J = 15, 17.4 Hz), 4.87 (dd, 1H, J = 1.5, 10.6 Hz), 2.58 (m, 1H), 2.37 (m, 1H), 1.86 (m, 1H), 1.75 (m, 2H), 1.51 (m, 1H), 1.42 (m, 1H), 1.22 (m, 1H), 1.05 (s, 6H); ^{13}C NMR (100.40 MHz, $CDCl_3$) shift versus solvent: δ 147.43, 142.44, 140.20, 139.71, 136.67, 134.95, 130.67, 129.70, 127.80, 126.97, 126.56, 126.47, 109.94, 43.71, 42.35, 40.42, 39.00, 33.17, 31.14, 27.39; mass spectrum m/e 342 (M^+), 245, 205, 180, 167, 129, 115, 91, 67. Exact mass calcd. for $C_{26}H_{30}$: 342.2347. Found: 342.2355.

13a: ^{1}H NMR (400 MHz, $CDCl_3$) shift versus added TMS: δ 7.4-7.1 (m), 5.95 (d), 5.95 (dd), 5.97 (dd), 5.4-5.1 (m), 5.0-4.8 (m), 2.94 (m), 2.57 (m), 2.41 (m), 2.35 (m), 1.9-0.8 (m), 1.13 (s), 1.05 (s); Peak 1: mass spectrum m/e 436 (M^+, 49), 273, 245, 205, 167, 129, 115, 91 (base), 67. Exact mass calcd. for $C_{33}H_{40}$: 436.3130. Found: 436.3107. Peak 2: mass spectrum m/e 436 (M^+, 66), 273, 245, 205, 167, 129, 115, 91 (base), 67. Exact mass calcd. for $C_{33}H_{40}$: 436.3130. Found: 436.3147.

Ozonolysis of 12a and 13a. The products **12a** and **13a** were ozonized by the same procedure described above for **9a** and **10a**. Solutions of 1.0 mg **12a**

or **13a** in 0.25 mL MeOH were used. The molar ratio of benzophenone to <u>cis</u>-1,3-dicarboxycyclopentane obtained for **12a** was 1.0:0.5 and that obtained for **13a** was 1.0:1.3

Polymerization of Norbornene.. A standard solution of norbornene was prepared as follows: To 8.15 g (87.6 mmol) of freeze-degassed norbornene were added approximately 30 mL benzene and 0.5 mL octane. The solution was further degassed by two freeze-pump-thaw cycles and then diluted with additional benzene to 50 mL total volume (1.75 M).

To **7** (20 mg, 0.07 mmol) or **3** (18 mg, 0.07 mmol), in a flask equipped with a Teflon valve closure, was added 4.0 mL of the standard norbornene solution (7.0 mmol norbornene). The solutions were stirred at 23°C for 1.5 h and then at 65°C. The relative ratio of norbornene to octane was monitored by capillary VPC. Polymerizations were stopped at 95% conversion by cooling to 23°C. The resulting red solution was added dropwise to 100 mL rapidly stirred methanol containing a small amount of BHT. The precipitated red amorphous polymer was dried under vacuum and stored under inert atmosphere. Isolation of polymer at intermediate conversions was effected by removal of an aliquot of the reaction mixture.

In the preparation of the high molecular weight polynorbornene, 100 µL of a 0.08 M solution of **3** in benzene was placed in a flask equipped with a Teflon valve closure. The solvent was removed under vacuum leaving 0.008 mmol **3** (2.0 mg). After addition of 2.5 mL of the standard norbornene solution, the reaction mixture was stirred at 23°C for 1.5 h and then at 65°C for 54 h. The product polymer was isolated by precipitation in methanol as described above.

GPC Analysis of the Polymers. All analyses were performed on 0.2% w/v solutions of polymer in dichloromethane. An injection volume of 0.1 mL and flow rate of 1.0 mL/min were used. Calibration was based on narrow dispersity polystyrene standards (Polysciences) ranging from MW = 3550 to 110,000 and was repeated with each analysis. The molecular weight averages and distribution were calculated by standard procedures[57] from the refractive index trace and were not corrected for peak broadening.

Kinetics of Polymerization with 7 and 11. Stock 0.09 M and 0.18 M solutions of **7** and **3** in C_6D_6 were prepared. A stock 5.3 M solution of norbornene in C_6D_6 containing 0.4 M added C_6D_6 was prepared. NMR tubes (5 mM) were charged with appropriate aliquots of the stock solutions diluted where necessary with additional C_6D_6 to provide 0.5 M total solution. The tubes were kept at 23°C for 1.5 h to allow for conversion of **3** to **11** and were then stored at -10°C until use. The samples were thawed and placed in the probe of the JEOL FX-90Q maintained at the appropriate temperature. After allowing the samples to reach thermal equilibrium, spectra were recorded at regular intervals. The disappearance of the olefinic protons of norbornene at δ 5.94 was monitored with respect to the C_6D_6 signal. To obtain rate data for polymerization with **7** at different temperatures, samples prepared as described above were heated in an oil bath for 3 h at 73°C to get past the non-linear decay region before NMR kinetic data were obtained. Least-squares analysis of zero-order plots of $[N]$ versus t yielded the k_{obs}. Activation parameters were obtained from least-squares analysis of $\ln k_1/T$ versus $1/T$ plots, where

$k_1 = k_{obs}/[\text{catalyst}]$.

Kinetics of Disappearance of 7. An NMR sample with $[7]_o = 0.035$ M and $[N]_o = 3.2$ M was prepared form stock solutions as described above and stored at -10°C until use. Approximately 2 µL mesitylene was added as an internal standard. The sample was placed in the probe of the JEOL GX-400 maintained at 65°C. After the samples were allowed to reach thermal equilibrium, spectra were obtained at regular intervals. The disappearance of 7 was monitored by integration of the signal for H_α of 7 at δ 3.51 versus the signal for the aromatic protons of the added mesitylene at δ 6.68. The disappearance of the olefinic protons of norbornene at δ 5.94 was monitored simultaneously by comparison with the C_6D_6 signal (see Fig. 6).

Polymerization of Norbornene by 7-d_2. To 5 mg of the α,α-dideutero-titanacyclobutane derived from neohexene (0.02 mmol) dissolved in 0.5 mL benzene was added norbornene (10 mg, 0.1 mmol). The mixture was heated at 50°C for 2 h. The volatiles were removed under vacuum and replaced with 0.5 mL C_6H_6. A ^2H NMR spectrum (13.70 MHz) of the product showed peaks at δ 3.10 and 1.90 attributable to the $D_{\alpha'}$ trans and $D_{\alpha'}$ cis of 7-d_2. The solution was transferred into a flask with a Teflon valve closure. The volatiles were removed under vacuum and replaced with 1.0 mL of a standard 1.75 M solution of norbornene in benzene. The mixture was heated at 65°C for 8 h. The volatiles were removed under vacuum yielding red polymer and replaced with 0.5 mL C_6H_6. A ^2H NMR spectrum of the polymer showed a major peak at δ 5.03 and a minor peak at δ 0.95 (10:1 ratio).

Incorporation of d_2-Norbornene into the Polymer. To 3 (10 mg, 0.04

mmol) was added 0.5 mL of a 1.2 M solution of norbornene in C_6D_6 (1.2 mmol). The solution was stirred at 23°C for 1.5 h then at 65°C for 1 h. The volatiles were removed under vacuum and replaced with 0.5 mL C_6D_6. A ^1H NMR spectrum was recorded. The C_6D_6 was removed under vacuum and replaced with 0.5 mL C_6D_6 containing 12 mg (0.12 mmol) d_2-norbornene. A ^2H NMR spectrum was recorded. The NMR tube was heated at 60°C in the probe of the JEOL GX-400 for 30 min allowing polymerization of 90% of the d_2-norbornene. The sample was cooled and a ^2H spectrum was recorded. The volatiles were removed under vacuum and replaced with 0.5 mL C_6D_6 containing 20 mg (0.21 mmol) norbornene. A ^1H NMR spectrum was recorded. The NMR tube was heated at 65°C in the probe of the NMR spectrometer for 15 min. The sample was cooled and a ^1H spectrum was recorded. The volatiles were removed under vacuum and replaced with 0.5 mL C_6D_6. A ^2H spectrum was recorded. All spectra were recorded at 23°C.

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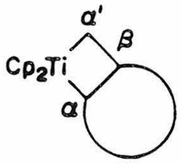
(12) The ring positions of the titanacyclobutane ring for metallacycles derived from cyclic olefins are discussed as shown:



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(14) $Cp_2\overline{TiCH_2CH(^{i}Pr)C}H_2$ is the most stable of the previously reported titanacyclobutanes.[15]

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(17) An additional organic product, diphenylfulvene, was also observed in these trapping reactions in variable yield. Identification was based on comparison of the ^{1}H NMR spectrum with that of an authentic sample and on adequate high-resolution mass spectral data.

(18) Further evidence for the formulation of **11** as shown: Compounds analogous to **11** have been prepared from the reaction of **3** with endo-dicyclopentadiene (Chapter 3 of this thesis) and with endo,endo-bicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid dialkyl esters.[19] They are isolable as crystalline solids, give adequate elemental analyses, and are fully characterized spectroscopically.

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(21) Molecular weights and polydispersities obtained by GPC are based on calibration with polystyrene standards.

(22) Homonuclear decoupling experiments show that the signals at 3.67 and -0.22 ppm are coupled with J = 10.2 Hz.

(23) Signals characteristic of a monosubstituted terminal olefin are present in Figure 5, but are not observed in Figure 4. We do not understand why such signals are absent in Figure 4. Observation of the polymerization by NMR spectroscopy shows that signals at δ 4.85, 4.95, and 5.37 are initially present, but disappear during the

polymerizations. Isomerization or hydrogenation of the terminal double bond may account for these observations.

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(28) The assumption that k_{-1} and k_{-3} are negligible compared to k_2 is required to explain the observed zero-order dependence in monomer. The rate $k_{-2}(\mathbf{14})$ is expected to be slower than $k_{-3}(\mathbf{14})$ since productive cleavage (ring-opening) relieves the strain of the bicyclic system while non-productive cleavage (loss of norbornene) requires

generation of a strained olefin. Both pathways afford structurally similar carbenes **9** from the metallacycles **14**.

(29) The kinetic indistinguishability of all chain-propagating metallacycles **14** and the kinetic indistinguishability of all α-substituted carbenes (labeled **9** in Scheme III) is assumed.

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(32) The ΔH for isomerization of trans-2,5-dimethyl-3-hexene to the cis isomer has been measured at 25°C as 1.9 kcal/mol.[33] Using this as a reasonable approximation to the free energy difference between the isomers affords an equilibrium ratio, trans to cis, of 96:4. Extrapolation to 65°C lowers the ratio to 94:6. As the steric requirements for the C_8 isomers should be similar to those for the double bond substituents in polynorbornene, this ratio may serve as an estimate of the thermodynamic trans:cis ratio in the polymer.

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CHAPTER 3

Selectivity in the Polymerization of Norbornene Derivatives

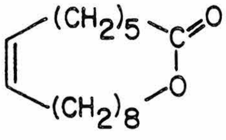
Introduction

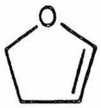
In recent years, much research in studies of ring-opening polymerization has focused on efforts to polymerize monomers bearing a second, potentially reactive functional group.[1] One of the reasons for this interest is that the presence of such substituents can dramatically alter the material properties of the product polymers. While ring-opened polynorbornene can be processed as a rubber,[2] polymers of 5-cyanonorbornene[3] show promise as thermoplastic materials.[4] The high thermal stability of the polymer derived from 5,6-bis-(trifluoromethyl)norbornene enhances its potential utility.[5] An additional source of interest in the polymerization of functionalized monomers is the possibility of using secondary reactions at that functional group as a means of further modification of the product polymers or as a site for controlled cross-linking.

The many difficulties encountered in attempted metatheses of functionalized olefins have been discussed.[6] Reaction with the functional group can poison the catalyst. Even when no destructive reaction occurs, the functional group may compete effectively for open coordination sites on the catalyst. When a second double bond is present, metathesis may occur at both positions. The result, for cyclic monomers, would be an intractable, highly cross-linked polymer. Finally, the presence of substituents on the substrate can slow or prevent metathesis for purely steric reasons.

When metathesis of strained cycloolefins bearing a second functional group is attempted, the probability of competing reaction of the functional group is lowered.[7] The strain in the cyclic double bond enhances its reactivity. Derivatives of norbornene containing pendant groups -- carboxylic acid, amide, amine, anhydride, ester, ether, halogen, hydroxide, nitrile, and additional olefinic groups[8] -- have been successfully polymerized by metathesis catalysts.

If, however, the second group is in the strained ring, its reactivity toward ring-cleaving reactions is also enhanced. There are no examples of the polymerization of highly strained heterocycles by olefin metathesis. Examples of less strained heterocycles which have been successfully polymerized are shown below. Lammens et al.[9] have reported the ring-opening polymerization of 1,1-dimethyl-1-silacyclopent-3-ene to a highly cis polymer of MW = 4800. Unsaturated polyesters were obtained by Ast's[10] polymerization of ambrettolide, a naturally occurring lactone, using $WCl_6/SnMe_4$ catalyst. Höcker and coworkers[11] recently described the synthesis of an unsaturated polyether from metathesis polymerization of 2,3-dihydrofuran. Ring-cleavage is presumed to occur at the carbon-carbon double bond in all these reactions.

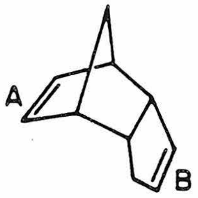




Because of the interest in the ring-opening polymerization of functionalized cycloolefins and our success in the polymerization of norbornene with titanacyclobutanes, we have examined the polymerizations of several norbornene derivatives using these catalysts.

Endo-Dicyclopentadiene

As a result of the low cost and ready availability[12] of dicyclopentadiene (2,4,7,7a-tetrahydro-4,7-methano-1H-indene), considerable effort has been applied to finding uses for this diolefin.[13] The 1,2-addition polymerization is readily effected thermally and by a variety of catalyst systems. Product polymers have been utilized in a number of specialty applications as rubbers and tackifiers.[13] Successful polymerization of endo-dicyclopentadiene to a linear ring-opened polymer requires a catalyst system sensitive to differences in ring strain. The monomer has two polymerizable double bonds contained in two distinct rings. The challenge is to effect ring-opening metathesis at the double bond in the norbornene-like ring system (bond A) without any reaction of the double bond in the less strained cyclopentene-like ring (bond B). Concomitant polymerization at B would lead to a cross-linked, intractable material.



Early work[14] on the ring-opening polymerization of dicyclopentadiene using Mo, W, and Re catalysts suggested that it could be polymerized at A; however, the yields of soluble polymer were low. More recent reports[15] in the patent literature claim that high yields of linear ring-opened polymer were produced using specific catalyst systems which generally included W or

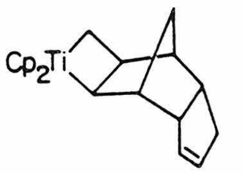
Mo salts and alkylaluminum halides.

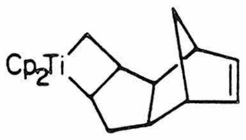
In view of the facile polymerization of norbornene by titanacyclobutane compounds[16] and their apparent inability to initiate cyclopentene polymerization,[17] study of the polymerization of endo-dicyclopentadiene by these catalysts was appropriate.

Results and Discussion

Preparation of Titanacyclobutanes Derived from endo-Dicyclopentadiene. Reaction of Tebbe reagent[18] with endo-dicyclopentadiene in the presence of dimethylaminopyridine afforded titanacyclobutane products. Although endo addition of "Cp_2TiCH_2" to the dicyclopentadiene is sterically untenable, exo addition may occur to either of the two double bonds and could result in four possible regioisomers. Addition of two equivalents of titanium-carbene to each molecule of dicyclopentadiene could also occur.

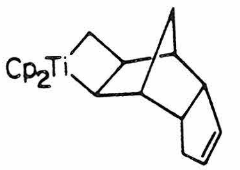
15a

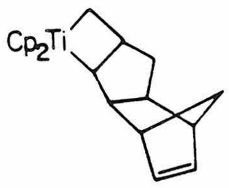




15c

15b

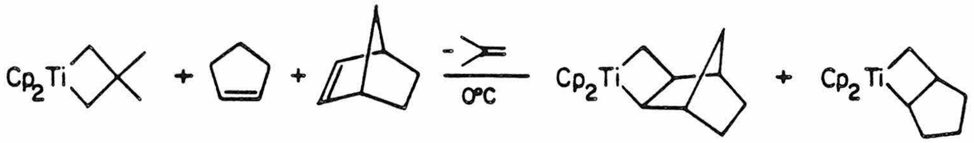




15d

Elemental analysis proved that the product metallacyclobutanes are monometallic. Determination of the actual structures, however, required consideration of the NMR spectral data of the products. The ^1H NMR spectrum of **15** is shown in Figure 1. The presence of two isomers in a ratio of 55:45 is indicated by observation of two sets of diastereotopic cyclopentadienyl groups, two doublets in the α-region, and two quartets in the β-region. The similarity of this spectrum to that of the norbornene metallacycle **7**[19] suggests that the two product isomers are **15a** and **15b**. Signals for both the α- and the β-protons in the ^1H NMR spectrum of the cyclopentene metallacycle **2** show much more complex coupling patterns. Tentative NMR assignments for **15** are included in Figure 1.

The absence of signals assignable to **15c** or **15d** shows that addition of "$Cp_2Ti{=}CH_2$" to <u>endo</u>-dicyclopentadiene occurs exclusively at bond A. In an effort to understand the origin of this preference, "$Cp_2Ti{=}CH_2$" was generated by decomposition of the isobutylene metallacycle **1** in the presence of five equivalents each of norbornene and cyclopentene. The fact that product



1 7 2

metallacycles from the addition of both olefins were obtained in an approximate ratio of 1:1 indicates no inherent kinetic preference for addition to the bicyclic ring system. When the solution of **2** and **7** were heated to 40°C in the presence of the excess olefins, signals assigned to **2** disappeared

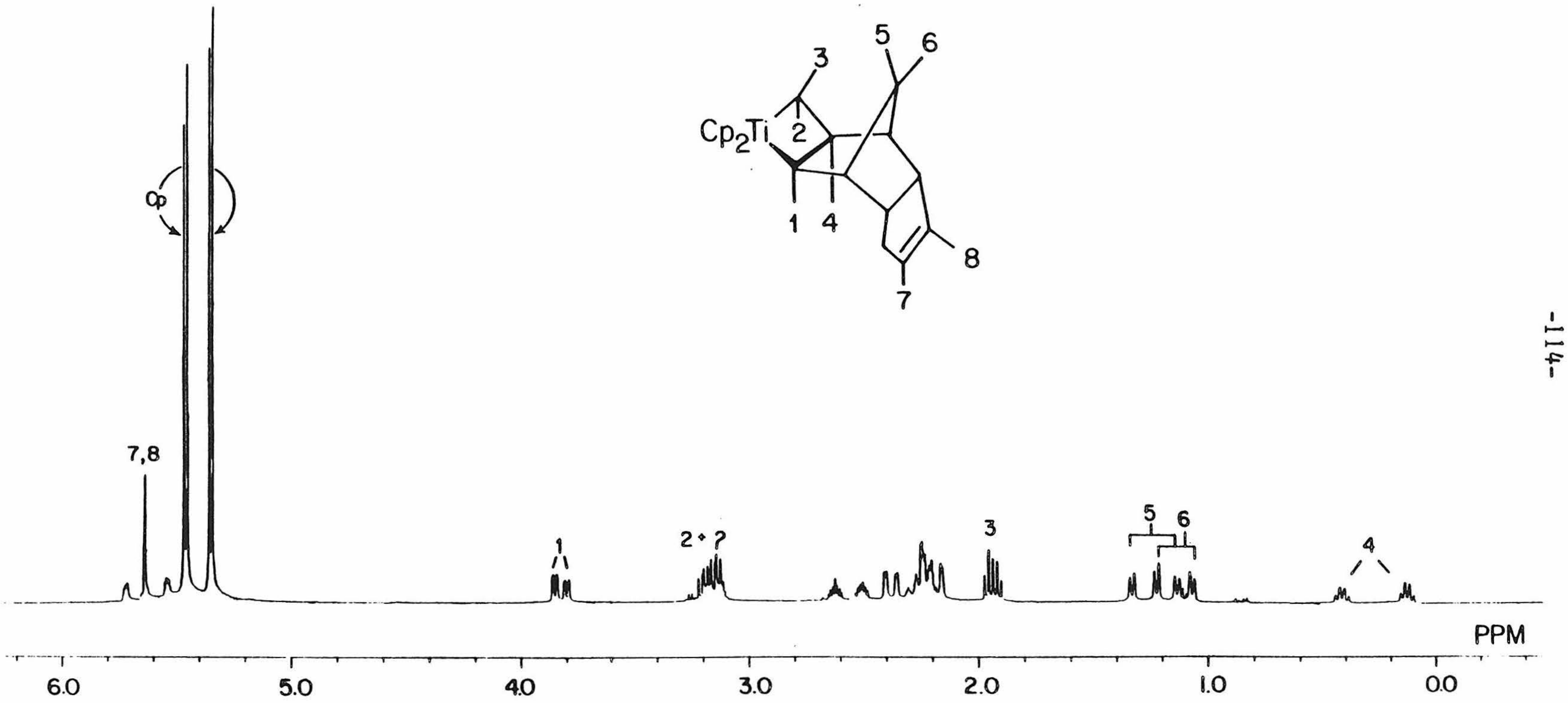
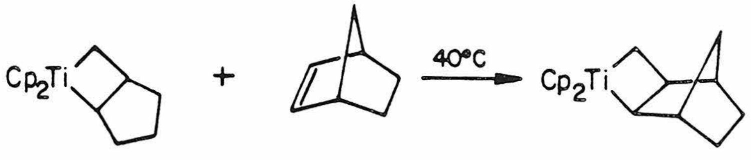


Figure 1. The 500 MHz ^1H NMR spectrum of **15** in C_6D_6.

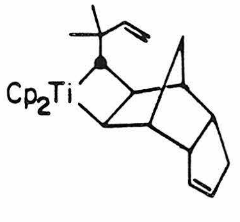
while those of **7** increased as the less stable metallacycle cleaved to cyclopentene and "$Cp_2Ti{=}CH_2$" which was then trapped by norbornene. One



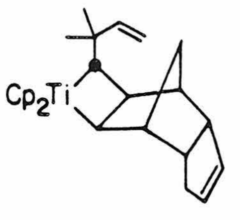
2 **7**

possible explanation for the absence of products from addition to bond B in the reaction of *endo*-dicyclopentadiene with "$Cp_2Ti{=}CH_2$" is that isomerization to bond A occurs at low temperatures. Alternatively, the 3,4-disubstitution of the cyclopentene ring may prevent any reaction at bond B.

Reaction of the dimethylcyclopropene metallacycle **3**[20] with *endo*-dicyclopentadiene afforded the two trisubstituted titanacyclobutanes **16** in a



16a



16b

60:40 ratio. Two diastereotopic sets of cyclopentadienyl groups and two sets of methyl groups are apparent in the ^1H NMR spectrum of **16** (see Fig. 2). The β-proton appears as well separated pseudo-triplets while the doublets due to the α-proton are partially superimposed. Since the signal assigned to the α'-proton is a single doublet, the α'-proton must be far from the cyclic

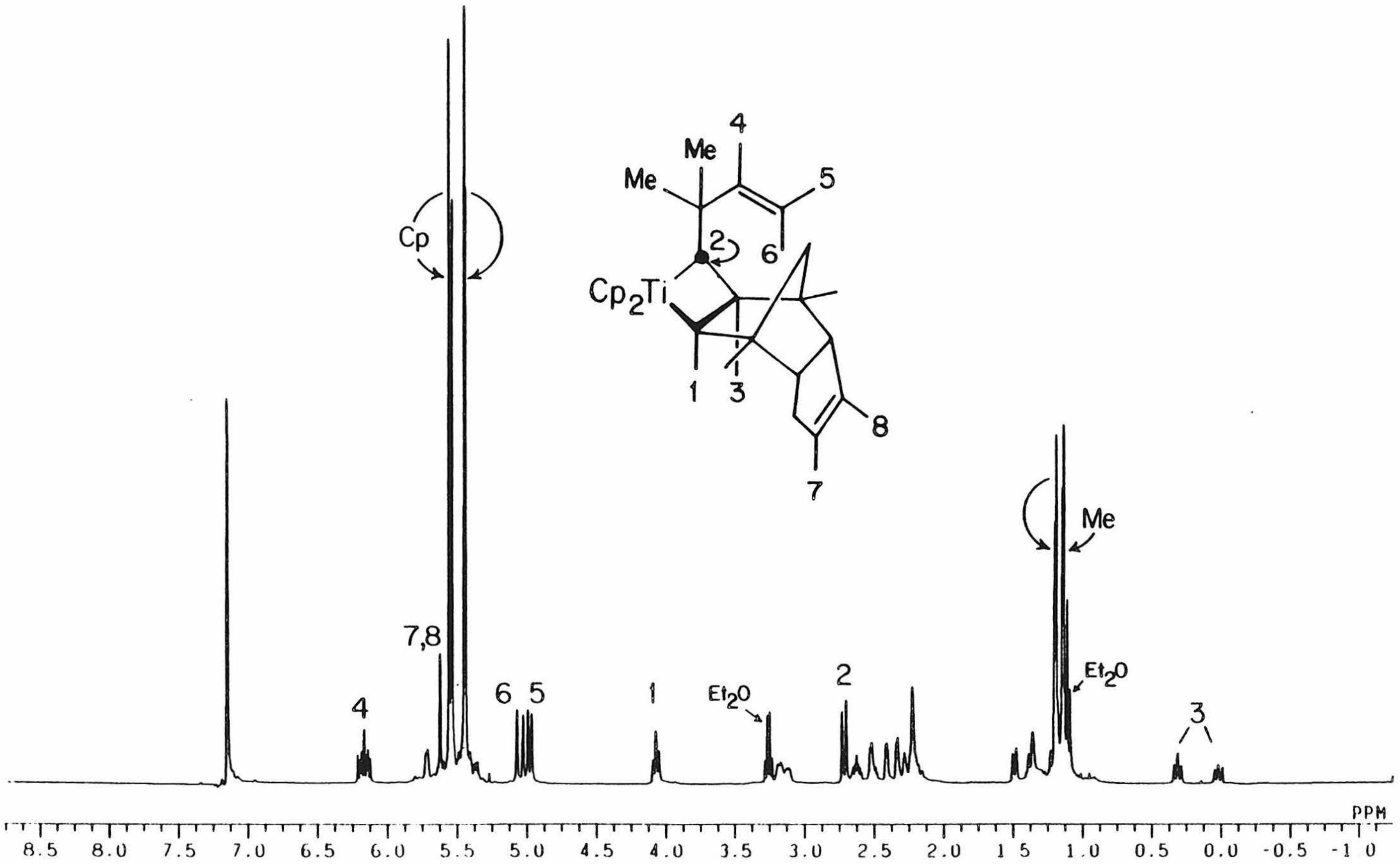


Figure 2. The 400 MHz ^1H NMR spectrum of **16** in C_6D_6.

double bond. This fact and an analogy with the trisubstituted metallacycle derived from norbornene suggest a trans stereochemistry with respect to the α'-substituent and the dicyclopentadienyl ring system.

Trisubstituted metallacyclobutane compounds have been postulated as intermediates or transition states in olefin metathesis for many years.[1] Although products consistent with the presence of such metallacycles were observed in one titanacyclobutane-catalyzed metathesis system,[21] no direct observation of these compounds was made. The reaction of **3** with internal olefins is the only route to α,β,α'-substituted titanacyclobutanes reported to date.[22] Observation of the metallacycle **11** derived from norbornene and isolation of **16** provide some of the first examples of this class of compounds.[24]

Crystal Structure of Metallacycle 15. Crystals of the α,β-disubstituted metallacycle **15** were obtained by the slow cooling of a solution of **15** in diethylether. The X-ray crystal structure was solved by Dr. Robert Coots. Refinement of the structure led to a final R value of 0.042. The molecular structure of **15** is shown in Figures 3 and 4. Table I contains selected structural data for **15** and for previously reported titanacyclobutane compounds.[26]

The bond lengths in the metallacycle ring of **15**, with the exception of the C_α-C_β bond, are similar to those found for the structurally characterized titanacyclobutane compounds[26] derived from the addition of "$Cp_2Ti=CH_2$" to neohexene, styrene, and isobutylene, respectively. The C_α-C_β bond length of 1.61 Å is substantially longer than the 1.55-1.58 Å found experimentally[27] for the C_2-C_3 bond of norbornene. Presumably this is a result of the cis-

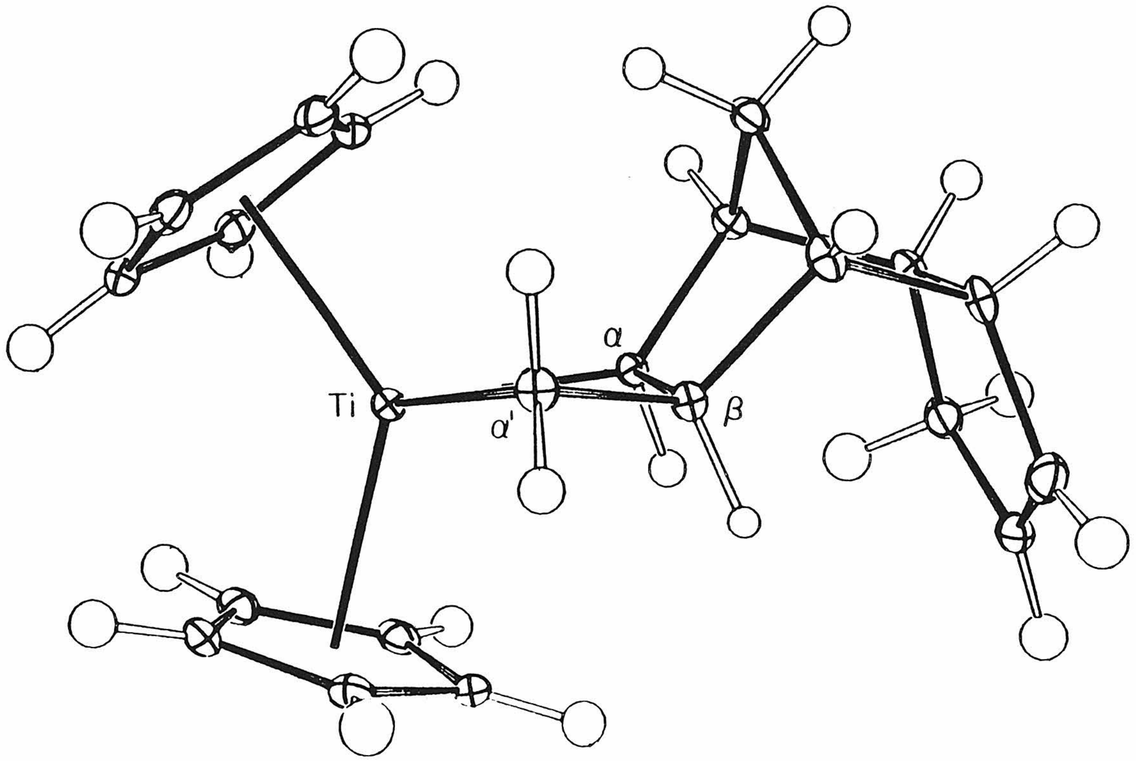


Figure 3. Structure of 15.

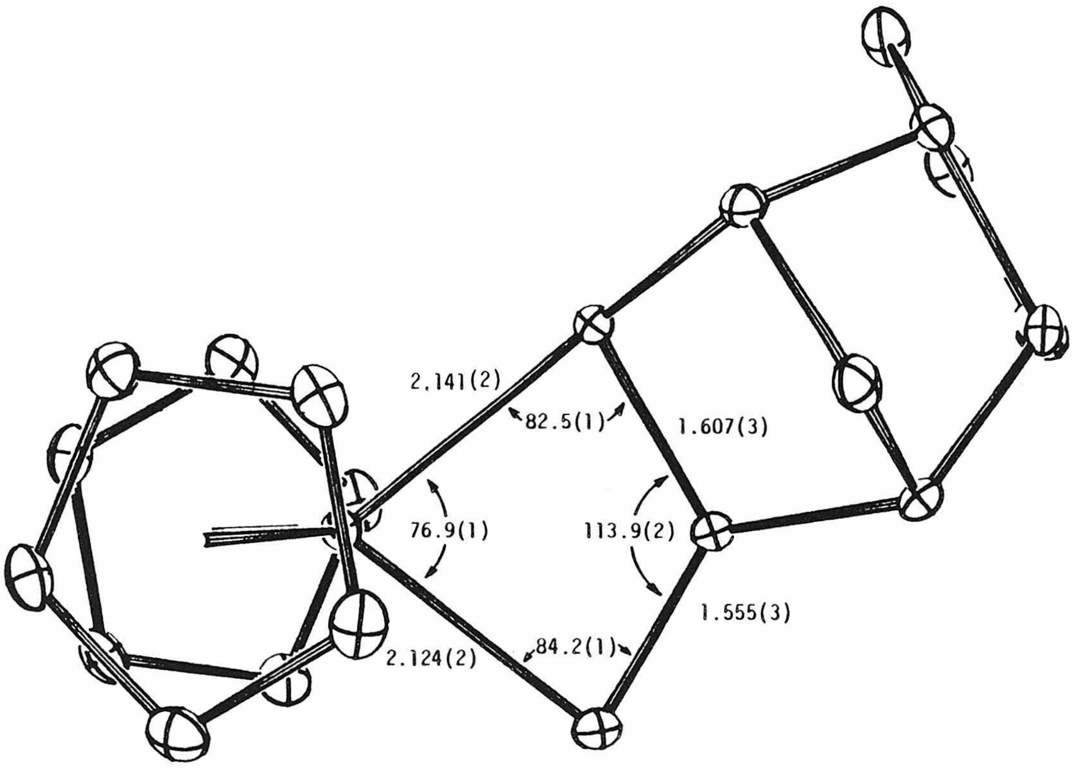
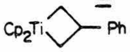


Figure 4. Selected bond lengths and angles of **15**.

Table I. Selected Structural Parameters.

Metallacycle	**15**	 [a]	 [a]	**1**[a]
Bond Lengths				
Ti-C$_\alpha$	2.141(2)	2.14	2.113(4)	2.152(7)
Ti-C$_{\alpha'}$	2.124(2)	2.16	2.127(3)	2.138(8)
C$_\alpha$-C$_\beta$	1.607(3)	1.53	1.579(5)	1.58(1)
C$_{\alpha'}$-C$_\beta$	1.555(3)	1.55	1.546(5)	1.59(1)
Bond Angles				
C$_\alpha$-Ti-C$_{\alpha'}$	76.9(1)	75	75.3(1)	74.8(3)
C$_\alpha$-C$_\beta$-C$_{\alpha'}$	113.9(2)	116	112.0(3)	110.9(6)
Ti-C$_\alpha$-C$_\beta$	82.5(1)	85	85.7(2)	87.0(4)
Ti-C$_{\alpha'}$-C$_\beta$	84.2(1)	84	86.0(2)	87.2(4)
Pucker Angle[d]	18	6	3	0.5
Displacement[e]	0.27	0.09	0.05	<0.01

[a] Reference 26.

[b] In Å.

[c] In degrees (°).

[d] The angle between the plane containing C$_\alpha$-Ti-C$_{\alpha'}$ and the plane containing C$_\alpha$-C$_\beta$-C$_{\alpha'}$. In degrees (°).

[e] In Å. The displacement of C$_\beta$ from the plane defined by C$_\alpha$-Ti-C$_{\alpha'}$.

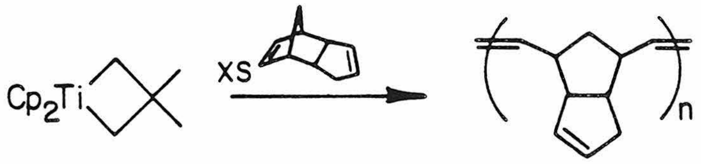
disubstitution present on the norbornane ring in **15** rather than any distortion toward substituted-carbene and olefin. None of the other structural parameters indicate such distortion. Bond angles in **15** are comparable to those seen for the other titanacycles. The acute C_{α}-Ti-$C_{\alpha'}$ bond angle in these compounds (75° ± 2) has been explained in terms of the electronic structure of titanium.[28]

In contrast to the other structurally characterized titanacyclobutanes, the metal-containing ring in **15** is puckered rather than essentially planar. Since one theory for the origin of stereoselectivity in the metathesis of acyclic olefins is based on the assumption of strongly puckered metallacycles,[29] the observation of puckering in a titanacyclobutane could be significant. Unfortunately, **15** is not a good model for puckering in other α,β-disubstituted titanacyclobutane compounds because the bicyclic norbornane ring system has steric requirements which would not occur in metallacycles of acyclic internal olefins. A planar ring would require an unfavorable interaction between the bridging methylene group and a cyclopentadienyl group. Distortion of the titanium-containing ring from planarity may have occurred to relieve this interaction. Even with the ring slightly puckered, the distance between the hydrogens at those positions of 2.2 Å is within the sum of their van der Waals radii.

It must be noted, however, that the rigidity of the bicyclic ring system will itself disfavor any puckering. A large value for the torsion angle $C_{\alpha'}$-C_{β}-C_{α}-Ti would require distortions at C_{α} and C_{β} since the torsion angle in the norbornane ring containing these atoms cannot be large. In view of these competing constraints -- the rigidity of the norbornane ring (favoring planarity) and the repulsive steric interactions between the cyclopentadienyl group and the bridging methylene (favoring puckering) -- conclusions about the inherent preference for puckering in a α,β-disubstituted titanacyclobutanes cannot be made based on the structure of **15**.

Repeated attempts to grow crystals of **16** suitable for an X-ray crystallographic study were unsuccessful.

Polymerization of endo-Dicyclopentadiene. As discussed above, reaction of **1** with endo-dicyclopentadiene initially affords titanacycle **15**. If the solution is then heated at 70°C in the presence of excess diolefin (1.4 M), polymer is obtained in yields varying from 30-60% based on initial monomer.



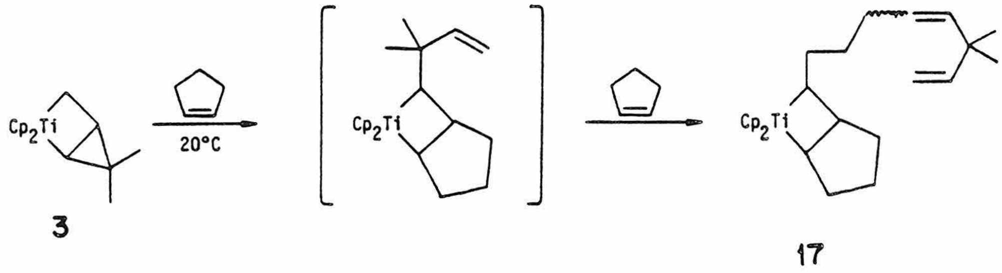
1

Assignment of the product as the ring-opened polymer obtained by cleavage of bond A is based on the ^{1}H NMR data and on comparison of its infrared spectrum with published spectra.[14b] Vibrational bands at 973 cm^{-1} and 755 cm^{-1} indicate the presence of both cis and trans acyclic double bonds. The cis:trans ratio was not obtained due to the complexity of the NMR spectra and the lack of literature assignments. The product polymers were moderately air-sensitive. When handled under inert atmosphere, they were soluble in benzene and chloroform at room temperature.

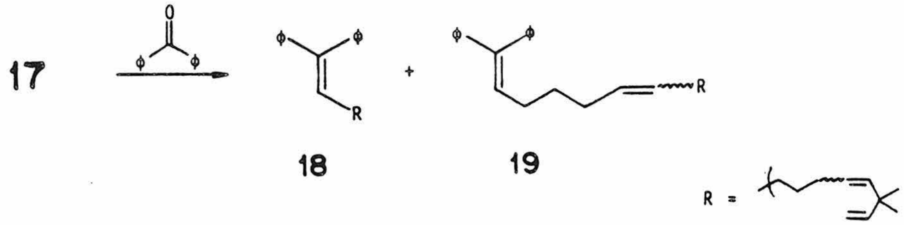
When polymerizations, initiated by both **1** and **3**, were attempted using a 2.0 M solution of endo-dicyclopentadiene, an intractable gel was obtained. VPC analysis of the residue indicated that a substantial amount of the monomer had not reacted. Although incidental differences in experimental conditions and/or reagent purity between these experiments and those producing soluble polymer cannot be ruled out, the formation of a gel suggests cross-linking involving reaction at bond B of the monomeric units in the polymer. These results prompted a reexamination of the polymerizability of cyclopentene with titanacyclobutane catalysts.

Reaction of Cyclopentene with 3. The metallacycle **2** derived from addition of cyclopentene to "$Cp_2Ti{=}CH_2$" does not polymerize cyclopentene. The fact that quantitative loss of the olefin occurs on reaction of **2** with benzophenone shows that its cleavage does not yield any α-substituted carbene compound. No route to the chain-carrying trisubstituted metallacycles exists from **2**. The question of whether chain propagation requires high ring strain in the monomer was not addressed in studies with **2**.

Initiation with **3**, however, would permit direct access to an α-substituted carbene and should circumvent the problems of initiation with **2**. The reaction of **3** with cyclopentene at 23°C was monitored by ^1H NMR spectroscopy. Exactly two equivalents of the olefin were consumed. This and the peaks characteristic of titanacyclobutanes observed in the cyclopentadienyl region (δ 5.36 and 5.30), the α-region (δ 4.77 and 2.77), and the β-region (δ 0.44 and -0.21) suggest formation of metallacycle **17** as shown below. Detailed NMR assignment and stereochemical analysis were not performed.



Benzophenone reacted with **17** producing two major organic products. Although these products were not isolated, analogy with trapping experiments on the norbornene metallacycle 7[30] and high resolution mass spectra support their formulation as olefins **18** and **19**. The formation of both metallacycle cleavage products in a ratio of 3:1 indicates that, although the non-productive cleavage pathway predominates, reaction in the direction of polymerization does occur.



Nevertheless, when **17** was heated to 45°C in the presence of three equivalents of cyclopentene, the metallacycle decomposed without consuming any of the olefin. Subsequent polymerization of norbornene in the presence of the cyclopentene showed that **17** is active toward polymerization in the presence of strained olefins. No consumption of the cyclopentene occurred. These results are consistent with observations made in attempted cyclopentene polymerizations with a variety of other metathesis catalysts.[31] The large ΔH_0 for polymerization of strained olefin drives the reaction. Cyclopentene has a relatively low strain energy. At low monomer concentrations, the unfavorable ΔS_0 term overwhelms gains in enthalpy and polymerization is impossible.

Preliminary results indicate cyclopentene can be polymerized by titanacyclobutane **17** at high concentrations of monomer. Reaction of **17** with a 3.2 M solution of the olefin in benzene-d_6 was monitored by ^{1}H NMR spectroscopy at 40°C. Peaks attributable to ring-opened polymer[32] were observed. The cis:trans ratio of 86:14 found for the isolated polymer is equal, within experimental error, to the expected thermodynamic cis:trans ratio of[33] poly(1-pentylene). GPC analysis of the product polymer shows that its molecular weight is less than 2000 g/mol.

Although the conversion of monomer was low, the fact that this titanium system can polymerize cyclopentene is a significant and somewhat surprising result. The most common metathesis systems have low activation barriers.[34] The activation barrier of 24 kcal/mol for the polymerization of norbornene with titanacycles **3** and **7** is high in comparison despite the relief of ring strain in the rate-limiting step. One factor which may contribute to the polymerizability of cyclopentene is the lowered energy of the intermediate α-substituted carbenes resulting from monosubstitution on the β-carbon rather than the disubstitution required in the polymerization of norbornene.

In contrast to the results of polymerizations with norbornene,[35] the thermodynamic ratio of double bond isomers was obtained rather than a kinetic ratio. The reversibility of metallacycle formation as observed in the reaction with benzophenone and the probable reversibility of ring-cleavage may account for the observed cis:trans ratio. Formation of macrocyclic rings by reaction with double bonds in the polymer chain is also possible.[36]

In summary, the polymerization of endo-dicyclopentadiene can give a moderate yield of soluble ring-opened polymer under certain conditions. The synthesis of **15** and of **16** permitted the first structural characterization of an α,β-disubstituted titanacyclobutane and the isolation of a α,β,α'-trisubstituted titanacyclobutane. The polymerization of cyclopentene, effected by catalyst **3**, appears to be thermodynamically controlled. More detailed studies of the effects of monomer concentration on the polymerization of cyclopentene and on selectivity in the polymerization of endo-dicyclopentadiene are needed. In view of these preliminary results, studies of other less strained cyclic monomers such as cycloheptene and cyclooctene may prove useful.

Norbornadiene

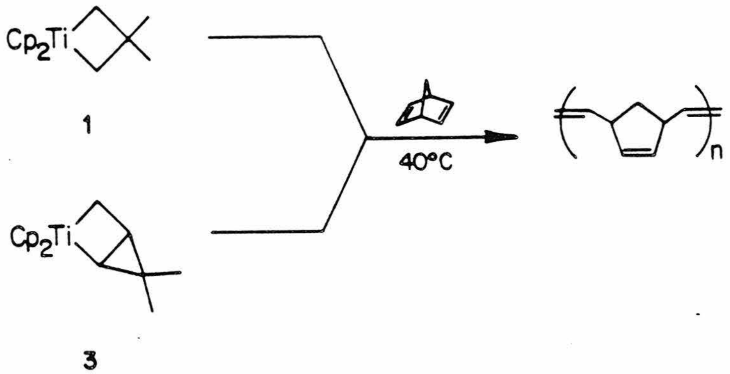
Norbornadiene (bicyclo[2.2.1]hepta-2,5-diene), like endo-dicyclopentadiene, has two double bonds. In this case, however, the double bonds are part of the same six-membered ring rather than isolated in two different rings. Since the strain energy of norbornadiene is greater than 30 kcal/mol,[37] it may be expected to be reactive toward polymerization catalysts. The majority of the reported polymers of norbornadiene are the result of 1,2-vinyl additions which preserve the bicyclic ring system or of 1,4-additions resulting in 3,5-disubstituted nortricylene units.[38,39] Frequently, the polymers are highly cross-linked and, consequently, intractable.

Metathesis at one of the double bonds would relieve most of the strain in the monomer. The remaining bond, in a single five-membered ring, should be much less reactive; however, any subsequent reaction on the second olefin would produce cross-linked material. There are only two reports of the ring-opening polymerization of norbornadiene to a linear polymer in the literature. Ivin et al.,[40] used a $MoCl_5/EtAlCl_2$ catalyst system to produce polynorbornadiene with a cis to trans ratio of 57:43. With a $WCl_5/Sn(Me)_4$ catalyst, Reif and Höcker[41] first produced the linear ring-opened polymer and then, in a subsequent reaction, showed that it could be reversibly cross-linked by the same catalyst.

In view of their low reactivity toward cyclopentyl double bonds and their ability to polymerize norbornene, the bis(cyclopentadienyl)titanacyclobutanes should be effective catalysts for the polymerization of norbornadiene.

Results and Discussion

When a solution of norbornadiene in benzene was stirred with metallacyclobutane **1** for 10 h at 40°C, the norbornadiene was polymerized to 53% conversion of monomer. The same reaction with titanacycle **3** resulted in 64% conversion. Doubling the amount of monomer solution did not affect the yield of polymer. The appearance of the reaction mixture when **1** was the catalyst was markedly different than when **3** was used. While polymerizations initiated with **3** remained orange-red throughout, those initiated by **1** had a purple hue which gradually became orange-red after several hours.



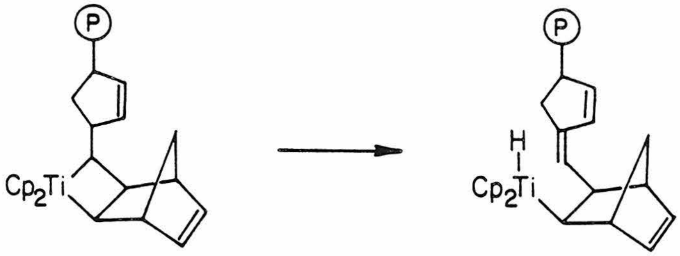
Comparison of the ^{13}C NMR spectral data of the product polynorbornadiene with Ivin's reported spectrum^{40} shows that it is the linear ring-opened polymer and has nearly the same cis:trans ratio (57% cis) that he observed using the molybdenum catalyst. The complete solubility of the polymer in organic solvents such as benzene and chloroform confirms the absence of cross-linking. GPC analysis of the product polymers showed that the molecular weights are low (<3000) and distributions are quite broad (d > 2). No substantial differences in the elution curves were observed for the polymers prepared with either **1** or **3**.

Preliminary work on the initial reaction of titanacyclobutanes with norbornadiene performed by Marchand and Grubbs[42] was confirmed by the following experiments. Solutions of **1**, which were initially red, turned purple on addition of the diene. Observation of the reaction by ^1H NMR spectroscopy at 20°C indicated the formation of new metallacycles. Peaks in the α region (at δ 3.2 to 3.7), a multiplet in the β-region (at δ 0.20), and at least four new peaks in the cyclopentadienyl region (δ 5.51, 5.49, 5.38, and 5.37) were observed. Examination of the reaction of **1** with one equivalent of norbornadiene clearly indicated that less than one equivalent of the diene was consumed. This suggests probable formation of dimetallic species **20** resulting from the addition of "$Cp_2Ti{=}CH_2$" to each of the double bonds of a single norbornadiene. Assuming exo addition to the ring system, two possible regio isomers could have been formed. Presumably, the purple hue observed in polymerizations with **1** is attributable to the presence of these dimetallic species which would only slowly disappear as polymerization is initiated by productive cleavage of one of the titanacycle rings. If analogous bimetallic compounds are formed at all in reactions with **3**, the expected rapid cleavage

20

of the trisubstituted metallacycles would prevent any substantial concentration.

As discussed above, polymerizations with either **1** or **3** did not go to completion. Nevertheless, the solutions (and the isolated polymers) retained the red color characteristic of titanacyclobutanes even after VPC analysis indicated no further consumption of monomer had occurred. In contrast, polymerizations quenched by the presence of an oxygen-containing impurity such as air or water acquire a characteristic yellow color. One explanation for the premature termination of these polymerizations of norbornadiene is reaction to form a metallacycle which is stable at 40°C. Norbornene potentially could be produced by the reduction of norbornadiene by adventitious titanium-hydride species.[43] Based on studies on the polymerizations of norbornene (Chapter 2), its trisubstituted metallacycles are stable at 40°C. In fact, VPC analysis of one of the polymerizations of norbornadiene indicated the presence of norbornene. Reaction of a living chain end with norbornene would be expected to stop further reaction of that chain. Alternatively, elimination of allylic hydrogen β to the metal could

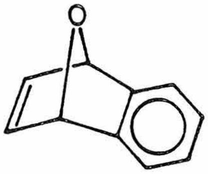


occur in this system. Although similar reactivity is not observed in polymerizations of norbornene, favorable overlap could enhance this decomposition pathway. The observed broad molecular weight distributions also suggest a random termination reaction has occurred.

To summarize, norbornadiene has been polymerized by titanacyclobutane compounds **1** and **3** to form a linear ring-opened polymer. No cross-linking was observed.

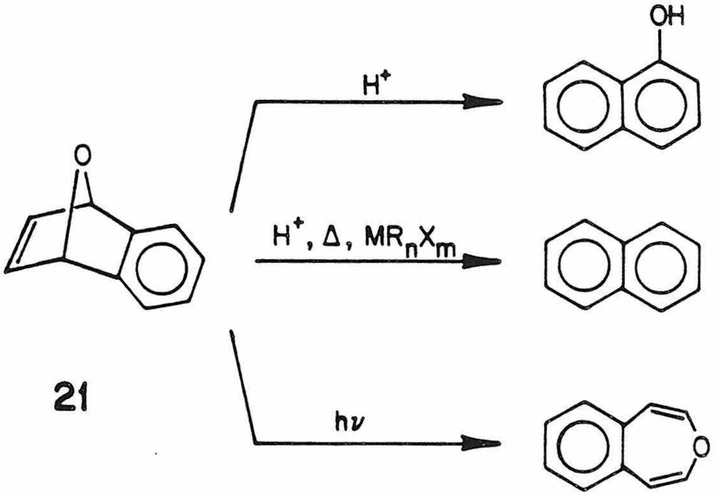
1,4-Epoxy-1,4-dihydronapthalene

Since the heterocycle 1,4-epoxy-1,4-dihydronapthalene (**21**) has both a double bond and an oxygen atom in the strained bicyclic ring system, two types of polymerizations are available. A metathetical cleavage of the double bond could afford ring-opened polymer similar to that obtained in polymerizations of norbornene. Alternatively, one of the carbon-oxygen single bonds may be broken as observed in polymerization of cyclic ethers such as tetrahydrofuran.[44] Wittbecker et al.[45] has reported that the cationic polymerizations of the saturated analogue of **21**, 1,4-epoxy-1,2,3,4-tetrahydronapthalene, and of a variety of other bridged bicyclic ethers occur readily. Since both reaction pathways open the bicyclic ring, both types of reactivity are expected to be enhanced by the inherent ring strain of **21**.



21

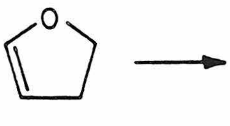
There are no reported attempts to polymerize **21** to date. Other reactions have been observed for **21** and related compounds. Isomerization to α-napthols occurs by acid catalysis.[46] Photochemical isomerization to benzoxepin has been observed.[47] Extrusion of the oxygen atom to afford napthalenes is effected by a variety of reagents[48] including some early transition metal alkyl compounds[48] and has been developed as a synthetic route to poly-aromatic compounds. Competition by any of these alternate



21

modes of reactivity with polymerization could lead to chain termination or could prevent polymerization entirely.

The only reported example of the ring-opening polymerization of a monomer containing both a double bond and an ether linkage is the polymerization of 2,3-dihydrofuran.[11] Höcker and coworkers[11] found that reaction of the vinyl ether with chromium carbenes readily affords poly(oxy-1-buten-1,4-ylene). The mechanism was discussed as a metathetical cleavage



$+\!CH-O-CH_2-CH_2-CH\!+_n$

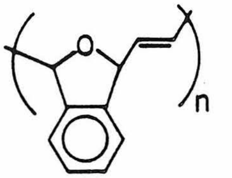
of the double bond. Attempted polymerizations of 2,5-dihydrofuran, an allyl ether, were unsuccessful.

Results and Discussion

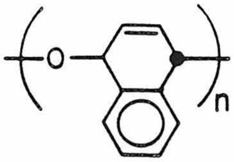
When titanacycle **1** was heated at 65°C in the presence of 25 equivalents of olefin **21**, polymeric product was obtained in low to moderate yield based on initial monomer. Most of the yellow polymer is soluble in benzene and chloroform. The analogous reaction using **3** as the catalyst affords the identical polymer in a lower yield. Although reasons for the diminished conversion of monomer with **3** are not apparent, this trend is reproducible. In both cases, overall conversions correspond to the consumption of six to eight monomer units per catalyst molecule. GPC analysis of the product polymer indicates that it is a low molecular weight oligomer with a peak molecular weight of approximately 1000. This result indicates that a sevenmer is the major oligomer.

The low conversion of monomer and low molecular weight of the product oligomers suggest that a chain-terminating reaction competes with polymerization. Although no specific evidence for any one such pathway was obtained, reaction of the electrophilic titanium-carbenes with the oxygen in the monomer to afford a favorable titanium-oxygen bond may have occurred.

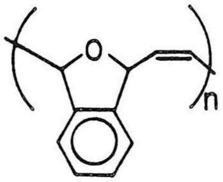
The fact that polymeric product was obtained does not prove that an olefin metathesis reaction has occurred. The titanacyclobutanes could potentially have served as initiators of ether-type polymerizations. Four possible structures of the product polymer **22** are shown below. Olefin metathesis would yield polymer with <u>trans</u> (**22a**) and/or <u>cis</u> (**22b**) double bonds. Two stereoisomers (**22c** and **22d**) could also result from polymerization by C-O single bond cleavage. Polymers obtained from this ether-type polymerization



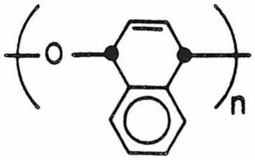
22a



22c



22b



22d

would be expected to have low molecular weight, since isomerization of the living chain end to a napthol would terminate the reaction.

The ^{1}H NMR spectrum of the product polymer is shown in Figure 5. The four broad peaks in the olefinic region are presumably attributable to two different olefinic protons and two different benzylic protons. No coupling whatsoever is observed. The absence of substantial peaks upfield of 5.0 ppm confirms the fact that ring-opening has occurred rather than 1,2-vinyl polymerization. The presence of two different aliphatic carbons is confirmed by the ^{13}C NMR spectrum (Fig. 6). Signals in the spectrum between δ 140.0 and 120.0, attributable to olefinic and aromatic carbons, show substructure possibly resulting from different tacticities in polymer subunits. These results suggest the presence of two isomeric monomer units in the polymer; however, assignment as **22a** and **22b** or as **22c** and **22d** cannot be made. The data are consistent with either of the two sets of structures. Similarly, no

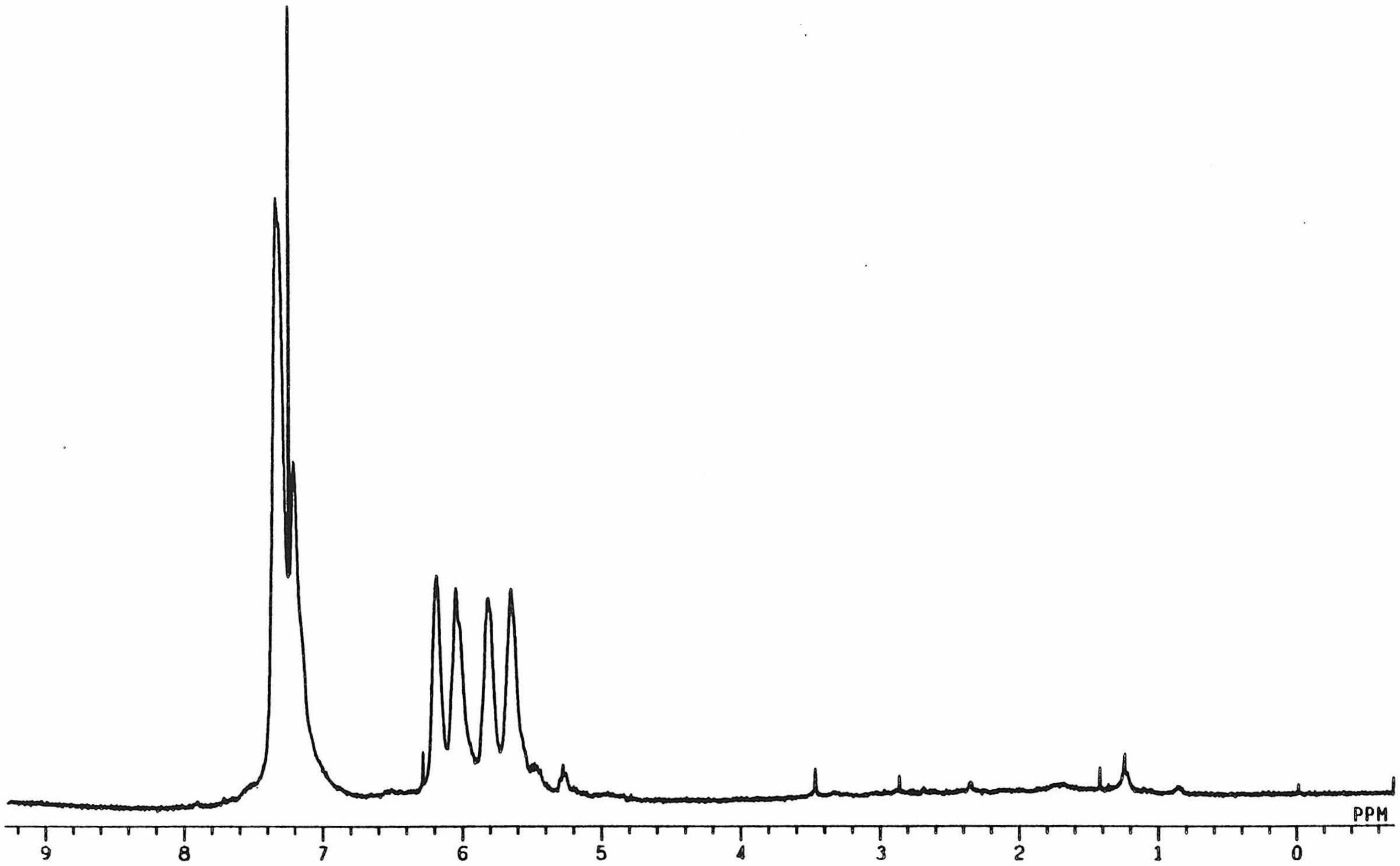


Figure 5. The 400 MHz ^1H NMR spectrum of polymer **22** in $CDCl_3$.

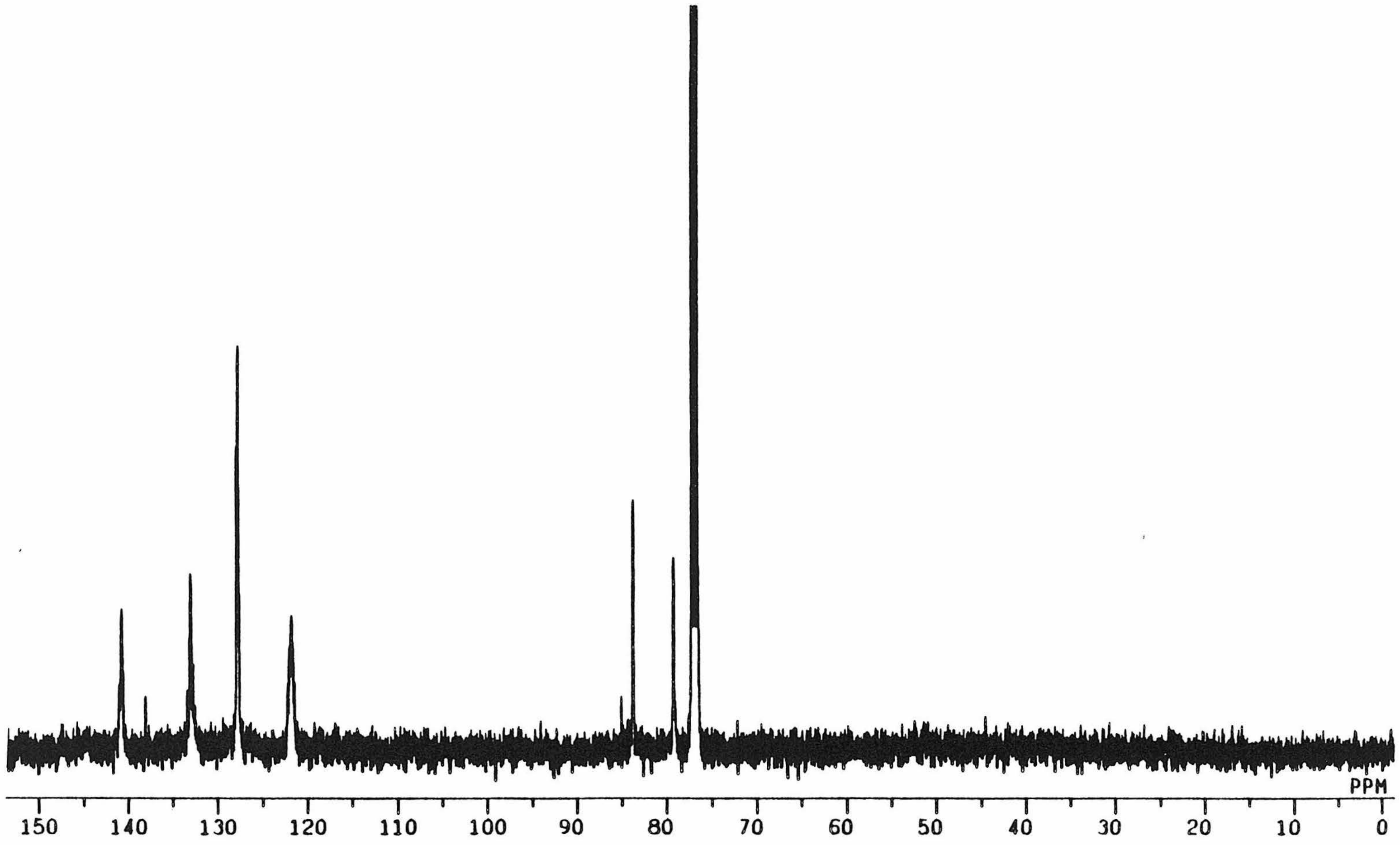
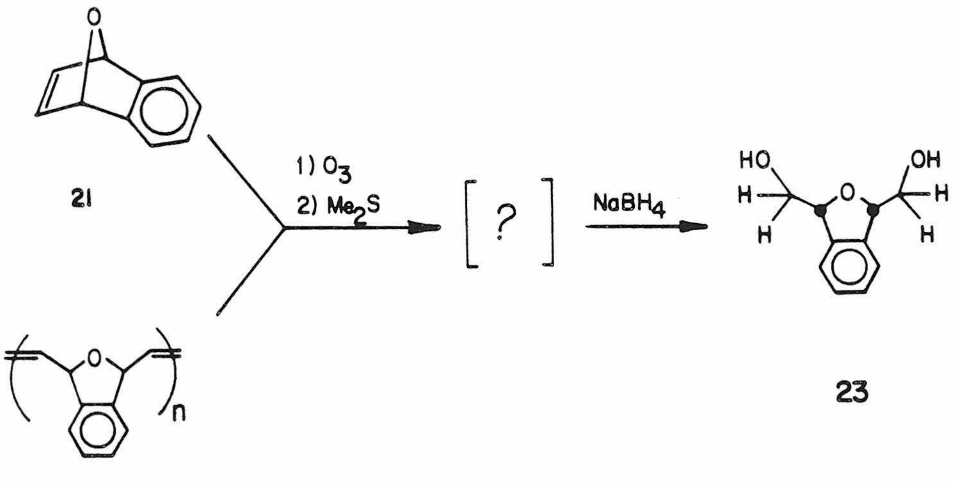


Figure 6. The 100.64 MHz ^{13}C NMR spectrum of polymer **22** in $CDCl_3$.

distinction can be made on the basis of infrared spectroscopy. The absorbance at 742 cm^{-1} may be assigned to a cis double bond. The out-of-plane bend for trans double bonds is generally observed at 960-900 cm^{-1}. In the IR spectrum of **22** (Fig. 7) this region is fairly complex and an unambiguous assignment cannot be made.

An attempt was made to prepare polymer of **21** by standard Lewis acid catalysis. Any such polymerization could occur only by C-O bond cleavage.[44] Hence, spectral comparison with **22** would establish the structure of **22**. Unfortunately, reaction of **21** with BF$_3$·Et$_2$O afforded α-napthol as the only organic product.

Compelling evidence for the formulation of the product polymer as **22a** and **22b** -- the result of double bond cleavage -- is provided by degradative ozonolysis. Ozonolysis of the polymer followed by a reductive workup with dimethylsulfide afforded the same monomeric product obtained



21

22

23

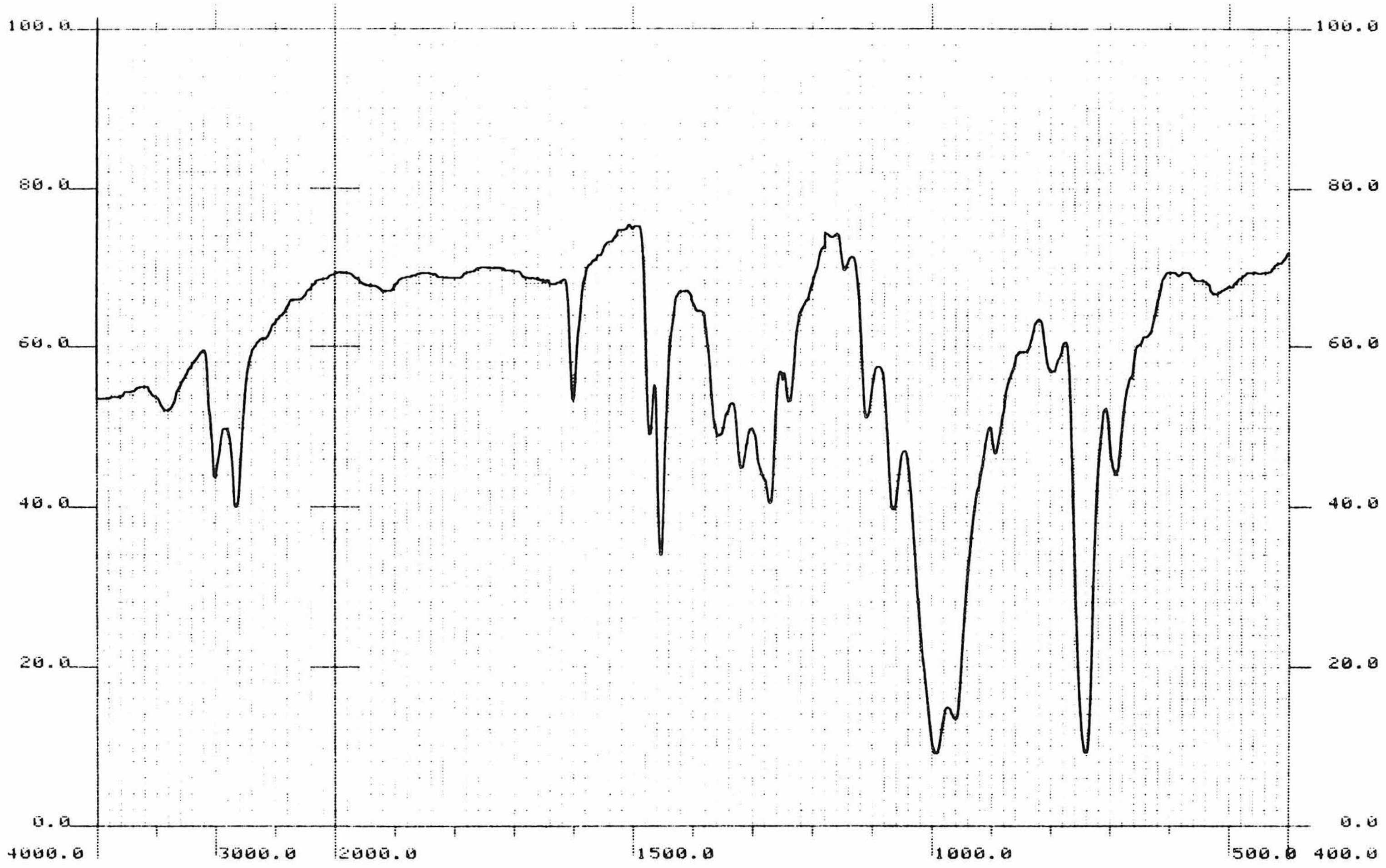


Figure 7. The IR spectrum of polymer 22.

by the identical reaction of **21**. Although this product could not be cleanly isolated, observation of a signal at δ 9.76 in the ^{1}H NMR spectrum suggested the presence of an aldehyde. Further reaction of the intermediate product with $NaBH_4$ yielded the readily isolable and characterizable 1,3-bis(hydroxymethyl)-1,3-dihydroisobenzofuran (**23**). The overall yields of **23** starting from either the monomer **21** or the polymer **22** were comparable. Identification of **23** was based on spectral evidence, elemental analysis, and high-resolution GC/MS.

In summary, polymerization of 1,4-epoxy-1,4-dihydronapthalene initiated by titanacycles **1** and **3** occurs by metathesis of the double bond. Competition of a chain-terminating reaction is suggested by the low molecular weights of the product polymers. The oligomeric products themselves may be of interest, since they are open chain equivalents of hard-to-prepare crown ethers.[49] Many naturally occurring antibiotics are also open-chain polyethers.[49] In view of this successful preparation of oligomers from **21**, research into similar bicyclic ethers such as 1,4-epoxycyclohexene may be fruitful.

Other Functional Groups

In view of the known reactivity of titanium carbene species with ketones, aldehydes, esters, anhydrides, acid chlorides, amides, and nitriles,[50] the probability of successful ring-opening polymerization of monomers containing these groups is low. Surprisingly, Stille and Grubbs were able to prepare titanacyclobutane compounds from a variety of norbornene *endo*-esters and diesters.[25] Presumably the carbonyl functionality is protected from reaction by its *endo* position and reaction of the carbene with the norbornene double bond occurs preferentially. Heating the carbonyl-containing titanacycle in the presence of excess *endo*-ester does not afford polymer. Instead, a "Wittig-like" reaction with the carbonyl functionality occurs since, after ring cleavage, it is no longer sterically protected.[25] Stille and Grubbs have developed this intramolecular trapping reaction for organic synthesis.[25]

Experimental Section

General Procedures. All manipulations of air and/or moisture sensitive compounds were carried out with use of standard Schlenk or vacuum line techniques. Argon was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4 Å molecular sieves. Solids were transferred in a N_2-filled Vacuum Atmospheres Dri-Lab equipped with a MO-40-1 purification train and a DK-3E Dri-Kool.

Materials. Tebbe reagent[51] and metallacycles **1**[52] and **3**[53] were prepared as previously described. Endo-dicyclopentadiene (99%, Wiley) and 1,4-epoxy-1,4-dihydronapthalene (Aldrich) were used without further purification. Norbornene (Aldrich) and norbornadiene (99.9%, Wiley) were refluxed over sodium and distilled prior to use. Cyclopentene (Wiley) was dried over 4 Å molecular sieves. Dimethylaminopyridine (Aldrich) was recrystallized from hot toluene. Sudan III dye, boron trifluoride etherate, and dimethylsulfide were purchased from Aldrich Chemical Co. Sodium borohydride was purchased from Alfa. Dichloromethane was dried over P_2O_5 and degassed on a vacuum line. Pentane was stirred over H_2SO_4, dried over CaH_2, and vacuum-transferred onto sodium-benzophenone ketyl. Benzene was dried over CaH_2 and vacuum-transferred onto sodium-benzophenone ketyl. Diethyl ether and benzene-d_6 (Cambridge Isotope Laboratories) were degassed and stirred over sodium-benzophenone ketyl. The dried and degassed solvents were vacuum-transferred into dry vessels equipped with Teflon valve closures and stored under Ar. Chloroform-d_1 was dried over 4 Å molecular sieves. Reagent grade methanol, ethanol, and chloroform were used without further purification

Instrumentation. NMR spectra were recorded on a JEOL FX-90Q (89.60 MHz ^{1}H; 22.53 MHz ^{13}C), a Varian XL-200 (200.15 MHz ^{1}H; 50.28 MHz ^{13}C), a JEOL GX-400 (399.65 MHz ^{1}H; 100.40 MHz ^{13}C), or a Bruker WM-500 (500.13 MHz ^{1}H). Infrared analyses utilized either a Shimadzu IR-435 or a Beckman 4240 spectrophotometer. Analytical gas chromatographic analyses (VPC) were performed on a Shimadzu GC-Mini 2 flame ionization instrument modified for capillary use and equipped with a Hewlett-Packard Model 339A integrator (columns: 0.24 mm x 15 m DB1 or 0.33 mm x 40 m SE30). Gel permeation chromatographic (GPC) analyses utilized Shodex KF-803 and KF-804 columns, a spectroflow 757 absorbance detector with λ = 254 nm, and a Knauer differential refractometer. Mass spectroscopy was performed by the mass spectroscopy center at the University of California, Riverside. Melting points were taken on a Hoover melting point apparatus. Ozone was obtained using a Welsbach generator.

Preparation of Metallacycle 15. To Tebbe reagent (1.0 g, 3.5 mmol) was added a freeze-degassed solution of endo-dicyclopentadiene (0.93 g, 7.0 mmol) in 7.0 mL CH_2Cl_2. The mixture was cooled to 0°C and 0.5 g dimethylaminopyridine (4.1 mmol) was added. The resulting red solution was added dropwise to 50 mL of rapidly stirred pentane at -20°C. Removal of the precipitated DMAP-$AlMe_2Cl$ adduct by filtration followed by removal of volatiles under vacuum yielded a red solid. This solid was crystallized from diethyl ether by slow cooling to give 0.12 g (0.37 mmol, 11%)[54] of **15** as red crystals suitable for X-ray structure determination. ^{1}H NMR (500 MHz,

C_6D_6) assignment in Figure 1 and shifts versus residual solvent: δ 5.72 (m), 5.64 (s), 5.53 (m), 5.47 (s, Cp), 5.46 (s, Cp), 5.36 (s, Cp), 5.35 (s, Cp), 3.86 (d, H_α), 3.80 (d, H_α), 3.2-3.1 (m), 2.63 (m), 2.53 (m), 2.41-2.16 (m), 1.96 (t), 1.94 (t), 1.33 (d), 1.22 (d), 1.15 (d), 1.06 (d), 0.42 (pq, H_β), 0.13 (pq, H_β). ^{13}C NMR (22.53 MHz, C_6D_6) shifts versus C_6D_6: δ 133.20, 132.87, 131.51, 130.99, 109.35 (Cp), 108.50 (Cp), 101.94, 98.17, 77.12, 76.66, 58.53, 53.72, 51.90, 50.67, 46.83, 46.18, 45.53, 42.61, 38.64, 37.61, 32.93, 16.16, 13.30. IR ($CDCl_3$): 3105 (w), 3078 (w), 3042 (w), 3028 (w), 2950 (m), 2911 (s), 2903 (s), 2856 (m), 1635 (w), 1444 (m), 1298 (w), 1287 (w), 1024 (m), 1019 (m), 809 (vs), 741 (m), 720 (m), 690 (w), 599 (w) cm^{-1}.

Anal. calcd. for $C_{21}H_{24}Ti$: C, 77.78; H, 7.46. Found: C, 77.54; H, 7.35.

Competitive Reaction of 1 with Cyclopentene and Norbornene. To metallacycle **1** (30 mg, 0.12 mmol) in a 5 mm NMR tube was added a -40°C solution of cyclopentene (39 μL, 0.44 mmol) and norbornene (40 mg, 0.43 mmol) in 0.5 mL toluene-d_8. After a preliminary ^1H NMR spectrum was recorded at -20°C, the sample was warmed to 20°C in the probe of the JEOL-FX90 spectrometer. The reaction was monitored until consumption of **1** was completed. The ratio of product metallacycles **2** and **7**, determined by integration of the cyclopentadienyl signals, was 1:1 (±5%). The sample was then warmed to 40°C. Peaks attributable to **7** increased in direct proportion to decreases in peaks attributable to **2** until no **2** remained. An increase in the cyclopentene olefinic signal and decrease in the norbonene signal were also observed.

Preparation of Metallacycle 16. To titanacycle 3 (250 mg, 1.0 mmol) was added 140 mg endo-dicyclopentadiene (1.1 mmol) in 5 mL benzene. The mixture was stirred for 2 h at 23°C. Removal of volatiles under vacuum yielded a red oil. Crystallization from diethyl ether by slow cooling from 0°C to -50°C afforded 45 mg (0.12 mmol, 13%)[54] of **16** as small red crystals. ^1H NMR (400 MHz, C_6D_6) assignment in Figure 2 and shifts versus residual solvent: δ 6.17 (m), 5.71 (m), 5.62 (s), 5.56 (s, Cp), 5.54 (s, Cp), 5.45 (s, Cp), 5.44 (s, Cp), 5.05 (d), 5.98 (d), 4.08 (d, H_α), 4.06 (d, H_α), 3.18 (m), 3.11 (m), 2.71 (d, $H_{\alpha'}$), 2.62 (m), 2.52-2.20 (m), 1.48 (d), 1.37 (d), 1.20 (s, Me), 1.19 (s, Me), 1.14 (s, Me), 1.13 (s, Me), 0.32 (pt, H_β), 0.02 (pt, H_β). ^{13}C NMR (90 MHz, C_6D_6) shifts versus C_6D_6: δ 150.03, 132.87, 132.74, 131.57, 131.12, 130.08, 125.86, 108.89, 108.63, 108.11, 105.97, 105.45, 104.80, 101.76, 58.53, 53.59, 51.84, 50.60, 46.12, 44.69, 42.61, 38.58, 37.47, 32.93, 32.73, 32.35, 30.65, 30.10, 27.47, 18.95, 15.96, 15.51.

Anal. calcd. for $C_{26}H_{32}Ti$: C, 79.58; H, 8.22. Found: C, 78.67; H, 8.47.

Polymerization of endo-Dicyclopentadiene. To 30 mg (0.12 mmol) of compound 1 was added 2 mL of a 1.4 M solution of endo-dicyclopentadiene in benzene. The mixture was stirred at 23°C for 15 min with occasional venting to vacuum to remove isobutylene produced. The catalyst solution was heated to 65°C over 2 h and maintained at 65°C for an additional 10 h. After cooling to 23°C, the solution was added dropwise to excess rapidly stirred deoxygenated methanol. The resulting precipitated powder was collected by centrifugation. Yields varied form 30-60% based on initial monomer. ^1H

NMR (90 MHz, $CDCl_3$) shifts versus residual solvent: δ 5.64, 5.54, 5.41, 5.36, 3.20, 2.85, 2.27, 1.55, 1.23. All peaks were broad. ^{13}C NMR (22.53 MHz, $CDCl_3$) shifts versus $CDCl_3$: δ 132.30, 131.39, 130.81, 55.16, 47.04, 46.00, 45.16, 44.83, 44.12, 42.23, 41.39, 38.85, 37.88, 36.71, 34.89, 34.63. All peaks were broad. IR (film): 3052 (m), 3008 (m), 2932 (vs), 2900 (sh), 2856 (s), 1710 (w), 1622 (w), 1453 (s), 1410 (w), 1360 (m), 1312 (m), 1286 (m), 1178 (m), 974 (s), 944 (m), 798 (m), 753 (s), 731 (s) cm^{-1}.

A second set of conditions producing cross-linked product was as follows: To **1** (20 mg, 0.08 mmol) or **3** (20 mg, 0.08 mmol) was added 1.0 mL of a 1.8 M solution of endo-dicyclopentadiene in benzene. The solutions were stirred at 23°C for 1.5 h with occasional venting to vacuum and then at 65°C for 10 h. Both reaction mixtures solidified. The product gels were insoluble in benzene and CH_2Cl_2. VPC analysis indicated the presence of monomeric endo-cyclopentadiene.

Preparation of Metallacycle 17. Cyclopentene (50 µL, 0.6 mmol) was added to a 5 mm NMR tube containing **3** (50 mg, 0.2 mmol) and benzene-d_6 at 10°C. The tube was placed in the probe of the JEOL GX-400, a spectrum was recorded at 10°C, and the sample was warmed to 25°C. Consumption of cyclopentene was monitored by integration of spectra recorded at regular intervals. After 1.25 h, no peaks attributable to **3** remained and two equivalents of cyclopentene had reacted. Metallacycle **16** was obtained as a red oil by removal of volatiles under vacuum. It was redissolved in benzene-d_6 and a ^1H NMR spectrum was recorded. ^1H NMR (400 MHz, C_6D_6) shifts versus residual solvent: δ 5.91 (dd), 5.59 (s), 5.37 (s, Cp), 5.36 (s, Cp), 5.31 (s, Cp), 5.30 (s, Cp), 5.05 (d), 4.97 (d), 4.76 (m), 2.76 (m), 2.29 (m), 2.21-1.32 (m), 1.15 (s, Me), 1.09 (s), 1.03 (s), 0.43 (m), -0.21 (m). The ratio of the olefinic region (δ 6.0 to 4.0) to the aliphatic region (δ 3.0 to -1.0) by NMR integration was approximately 2:3.

Thermolysis of 17 in the Presence of Cyclopentene. A sample of **17** was prepared as described above. Prior to removal of excess cyclopentene under vacuum, the sample was heated to 45°C. Decomposition of **17** was indicated by disappearance of its cyclopentadienyl signals. The excess cyclopentene was not affected.

Reaction of 17 with Benzophenone. A sample of **17** (0.2 mmol) prepared as described above from 50 mg **3** was stirred with benzophenone (75 mg, 0.4 mmol) in 1 mL benzene for 5 h at 60°C. After cooling to 23°C, the solution was diluted with 10 mL petroleum ether. The resultant yellow precipitate was removed by rapid filtration through silica gel. Evaporation of the solvent under vacuum yielded a 48 mg of a yellow oil. Analysis by capillary VPC indicated two major products eluting at moderate (peak 1) and long (peak 2) retention time, respectively.

Peak 1 (**18**): Mass spectrum m/e 316 (M^+), 246, 233, 206, 193, 167, 129, 115, 91 (base). Exact mass calcd. for $C_{24}H_{28}$: 316.2191. Found: 316.2195.

Peak 2 (**19**): Mass spectrum m/e 384 (M^+), 245, 206, 193, 167, 115, 91 (base), 44. Exact mass calcd. for $C_{29}H_{36}$: 384.2817. Found: 384.2818.

A small amount of material coeluted with each peak having m/e of 318 and 386, respectively. Presumably these producs arise from secondary hydrogenation of **18** and **19**.

Polymerization of Norbornene with 17. To metallacycle **3** (20 mg, 0.08 mmol) dissolved in 0.5 mL benzene-d_6 in a 5 mm NMR tube was added cyclopentene (20 μL, 0.23 mmol). The reaction of **3** to give **17** was monitored by ^1H NMR spectroscopy. After conversion was complete, norbornene (25 mg, 0.27 mmol) in 0.1 mL benzene-d_6 was added. The tube was heated in the probe to 50°C. Polymerization of norbornene was indicated by reduction in signals assigned to the monomer and by the appearance of signals attributable to ring-opened polynorbornene. No consumption of cyclopentene was observed. In fact, 0.7 equivalents of additional cyclopentene was released by the reaction of **17** with norbornene.

Polymerization of Cyclopentene with 17. Cyclopentene (150 μL, 1.7 mmol) was added to a 5 mm NMR rube containing **3** (20 mg, 0.08 mmol) in 450 μL benzene-d_6. After 1.5 h at 23°C to allow reaction of **3** to **17**, the tube was placed in the probe of the JEOL-GX400 spectrometer and was heated to 40°C. The appearance of broad peaks at δ 5.31, 1.95, and 1.37 indicated possible polymerization of cyclopentene. The tube was removed from the probe and heated in a 40°C oil bath for 6 h. A ^1H NMR spectrum indicated that a moderate amount of polymer had formed. The polymer was isolated by dropwise addition of the reaction mixture to 10 mL rapidly stirred methanol. Yield 15 mg (13% conversion). Identification of the product of poly-1-pentylene with *cis:trans* ratio of 15:85 was based on comparison of ^{13}C NMR data with published data.[32] Preliminary GPC analysis suggested M_n = 2200 and d = 1.3.

Polymerization of Norbornadiene. A standard solution of norbornadiene was prepared as follows: A mixture of norbornadiene (2.0 mL, 18.5 mmol) and octane (50 μL) was degassed by three freeze-pump-thaw cycles. Sufficient benzene was added to dilute the mixture to 10 mL total volume (1.85 M).

To **1** (20 mg, 0.081 mmol) in a flask equipped with a Teflon valve closure, was added 0.25 mL of the standard norbornadiene solution. After 15 min at 23°C the volatiles, including isobutylene produced by cleavage of **1** and excess norbornadiene, were removed in vacuo. Following addition of 1.0 mL of the standard solution (1.85 mmol norbornadiene), the mixture was stirred at 23°C for 2 h. Similarly, to **3** (20 mg, 0.077 mmol) in a flask equipped with a Teflon valve closure, was added 1.0 mL of the standard solution (1.85 mmol norbornadiene) and the mixture was stirred at 23°C for 2 h. Both flasks were placed in an oil bath and stirred at 40°C for an additional 10 h. The polymerizations were monitored by VPC using the added octane as an internal standard. The rate of consumption of monomer diminished with time. Final conversions: **1**, 53%; **3**, 64%. The procedure described above was repeated using 2.0 mL standard solution (3.7 mmol norbornadiene). Final conversions: **1**, 28%; **3**, 34%. Isolation of the product polynorbornadiene was achieved by dropwise addition of the solutions to 50 mL rapidly stirred methanol containing BHT and vacuum drying. The polymers were stored under inert atmosphere.

Reaction of Metallacycle 1 with Norbornadiene. A 5 mm NMR tube was loaded with **1** (30 mg, 0.12 mmol) and 0.5 mL toluene-d_8. The tube was cooled to -10°C and 14 μL norbornadiene (0.13 mmol) was added. The sample was placed in the probe of the JEOL FX-90Q at -10°C. Integration of the ^{1}H

NMR spectrum confirmed an equimolar mixture of reagents. The probe was slowly warmed to 20°C and the reaction monitored by ^{1}H NMR. After complete consumption of **1**, integration of the spectrum suggested that approximately 25% of the initial norbornene was still present.

Polymerization of the Bicyclic Ether 21. To **1** (20 mg, 0.081 mmol) and to **3** (20 mg, 0.077 mmol) was added 0.5 mL of a 1.39 M solution of 1,4-epoxy-1,4-dihydronapthalene **21** in benzene. The solutions were stirred at 20°C for 1.5 h. After removal of volatiles under vacuum, an additional 1.0 mL of the monomer solution was added to each reaction mixture. The solutions were heated for 10 h at 65°C. Product polymers were collected by slow addition of the cooled reaction mixtures to rapidly stirred methanol and centrifugation of the resulting slurries. The polymers were washed three times with additional methanol and dried under vacuum. Yield: 95.5 mg (33% conversion) from **1**; 72.5 mg (24% conversion) from **3**. ^{1}H NMR (400 MHz, $CDCl_3$) shifts versus residual solvent: δ 7.4-7.0 (m, aromatic), 6.18 (br s), 6.04 (br s), 5.83 (br s), 5.66 (br s). ^{13}C NMR (22.53 MHz, $CDCl_3$) proton decoupled, shifts versus solvent: δ 141.01 (br m), 133.34 (br m), 128.18 (s), 128.01 (s), 122.10 (br m), 83.89 (s), 79.27 (s). IR (KBr): 3100 (m), 2920 (m), 1600 (m), 1492 (m), 1452 (s), 1355 (w), 1319 (w), 1271 (m), 1239 (w), 1150 (w), 1110 (m), 1065 (m), 993 (vs), 960 (sh), 893 (w), 800 (w), 742 (vs), 688 (m) cm^{-1}.

Reaction of 21 with $BF_3{\cdot}Et_2O$. To a solution of **21** (200 mg, 1.4 mmol) in 2.0 mL dichloromethane at -20°C was added three drops of $BF_3{\cdot}Et_2O$. A color change from clear to light purple was observed within 15 min along with precipitation of a solid. The volatiles were removed under reduced pressure.

Identification of the product as α -napthol was made by its comparison of ^1H NMR spectrum with that of an authentic sample.

Ozonolysis of the Monomer 21. To **21** (20 mg, 0.14 mmol) dissolved in 2.0 mL chloroform was added six drops of a saturated methanol solution of Sudan III dye. The mixture was cooled to -50°C and ozonized until a color change from pink to colorless was observed. After flushing with argon to remove excess ozone, dimethylsulfide (100 μ L, 1.37 mmol) was added and the solution was warmed to room temperature and stirred for 4 h. A solution of $NaBH_4$ (20 mg, 0.53 mmol) in 0.5 mL ethanol and 0.5 mL water was added. The slurry was stirred first for 0.5 h at 23°C and then warmed to 50°C for 0.5 h. Acidification with 10% H_2SO_4 was followed by removal of all volatiles under reduced pressure. The solid residue was taken up in 1.0 mL H_2O and basified with dilute NaOH solution. The organic product was collected by extraction with chloroform and removal of the chloroform under reduced pressure. The sample was dissolved in C_6D_6 containing 5 μ L toluene as an internal standard. Quantitation by ^1H NMR spectroscopy shows 0.044 mmol (31% yield) of the product diol **23**. Alternatively, recrystallization from ether-pentane afforded **23** as colorless needles: ^1H NMR (200 MHz, $CDCl_3$) shifts versus residual solvent: δ 7.4-7.2 (m, 4H), 5.33 (br s, 2H), 4.07 (dd, J = 12.0, 2.2 Hz, 2H), 3.87 (dd, J = 12.0, 2.4 Hz, 2H), 3.16 (br s, 2H). ^{13}C NMR (50.3 MHz, $CDCl_3$) shifts versus $CDCl_3$: δ 139.07, 128.37, 121.37, 84.27, 65.26. IR (KBr): 3330 (s), 3280 (vs), 2840 (m), 1457 (m), 1440 (s), 1079 (vs), 1069 (s), 1030 (m), 972 (s), 900 (s), 835 (s), 745 (vs), 707 (m), 570 (m) cm^{-1}. Mass spectrum m/e 180 (M^+), 149 ($-CH_3O$, base), 131, 121, 103, 91,

77. Exact mass calcd. for $C_{10}H_{12}O_3$: 180.0786. Found: 180.0789.

Anal. calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.27; H, 6.46; Melting point: 124.0-124.5°C.

Ozonolysis of the Polymer 22. Ozonolysis was performed as described above for the monomer **21** using 20.0 mg of the polymer **22**. The same product (**23**) was obtained. Quantitation by ^1H NMR spectroscopy shows 0.047 mmol (34% yield).

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CHAPTER 4

Microstructure in Polymers of Methylnorbornene

Introduction

While direct observation of intermediates and study of the reaction kinetics for the polymerization of norbornene with **1** and **3** permitted development of the mechanism outlined in Chapter 2, a more complete understanding of the individual steps was not obtained. Indirect insight into the details of the reaction can be obtained from analysis of the microstructure of product polymers.

Specific aspects of the microstructure of polynorbornene and its derivatives which are of interest include:[1]

(1) Double bond isomerism. The substituents on the individual carbon-carbon double bonds may have a cis or a trans orientation. The distribution of double bonds throughout the polymer may be random or non-random.

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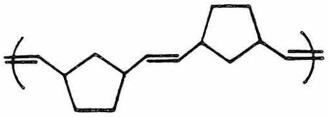

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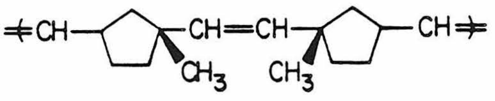
(2) Regiochemistry of monomer addition. Substituted derivatives of norbornene having C_1 symmetry can add to form head-to-tail (HT), head-to-head (HH), or tail-to-tail (TT) sequences in the polymer.



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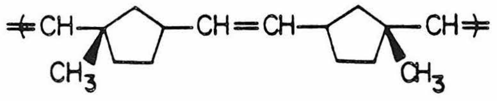
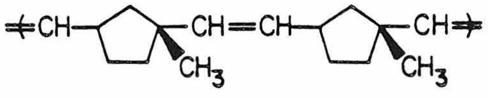
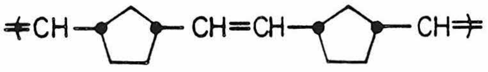


TT



HT

(3) Tacticity. Dyads within the polymer may be meso (m) or racemic (r). Polymers consisting entirely of m dyads would be isotactic while those containing only r dyads would be syndiotactic. A random distribution of monomer tacticity would lead to atactic polymer.



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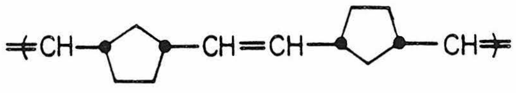

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Ivin, Rooney, and coworkers[2] have pioneered study of the microstructure of polymers of norbornene and its derivatives. A number of reviews[2] tabulate their results which were obtained by studying polymerizations of a variety of monomers initiated by a number of different metathesis catalysts. Their research has provided detailed NMR assignments from which the microstructure of polymers prepared from these norbornene derivatives can be readily deduced by consideration of their ^{13}C NMR spectra. Included below is a brief discussion of their results and interpretations.

The *cis* to *trans* ratios were found to vary from completely *cis* through completely *trans* depending on the specific catalyst used. In polymers containing both double bond isomers, *cis*-*trans* blockiness was observed for some catalysts while polymers prepared from other catalysts were random. The regiochemistry of addition was selective toward HT dyads for some catalysts and non-selective for other. The only real trend observed was in the study of the polymer tacticities. Although some catalysts afforded completely atactic polymers, in the tactic polymers dyads containing *cis* double bonds were *r* while those containing *trans* double bonds tended to be *m*.

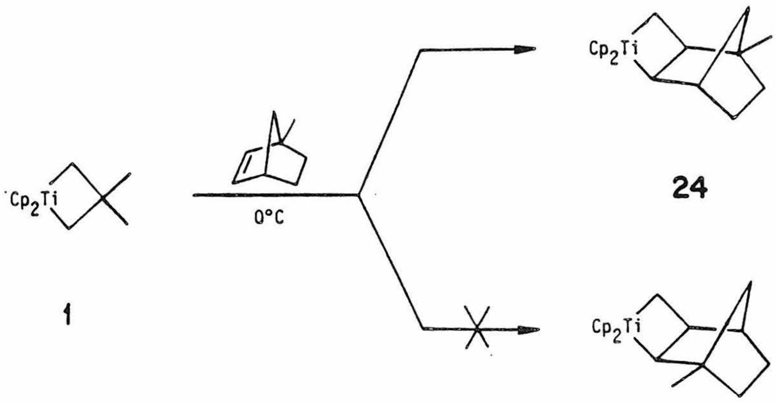
The interpretation for these results offered by Ivin, Rooney, and coworkers is based on the assumption that the chain-carrying species for all of the catalysts used is a metal-carbene compound. The metal is presumed to have an octrahedral coordination sphere with two different potential carbene sites *cis* to one another. The positions of the carbene and of the empty coordination site alternate between the two sites with successive monomer additions. Using this model, all *cis* polymers are expected to be syndiotactic while an all *trans* polymer would be isotactic. A further refinement of their interpretation suggests that *cis* double bonds can be retained in the coordination sphere of the metal while *trans* bonds are not retained.

Polymerizations using bis(cyclopentadienyl)titanacyclobutane compounds as catalysis differ from the catalysts used by Ivin, Rooney, and coworkers[2] in that trisubstituted titanacyclobutane compounds are the chain-carrying intermediates.[3,4] Also, as a result of the two strongly coordinated cyclopentadienyl ligands and the preferred mode of bonding in titanium-carbene complexes,[5] only one coordination site is available for the carbene ligand. The cyclopentadienyl ligands impose greater steric constraints than do the ligands in more common metathesis catalysts. Due to these unique features, the microstructure of polymers prepared from titanacyclobutane catalysts could differ from those of the previously reported studies.

The cis:trans ratio and distribution for the polymerization of norbornene initiated by **1** and **3** were readily obtained directly from the ^{13}C NMR spectrum of the product polymer. These results and a discussion of these results were included in Chapter 2. A study of the stereoselectivity and regioselectivity of these catalysts using methyl-substituted norbornenes is detailed below.

Results and Discussion

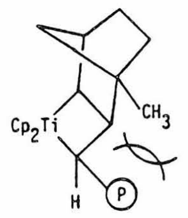
1-Methylnorbornene. Reaction of titanacyclobutane **1** with 1-methylnorbornene afforded metallacycle **24** quantitatively by ^1H NMR integration. Assignment of the product as **24** was based on the similarity of its ^1H and ^{13}C NMR spectra (see Experimental Section) with those obtained for

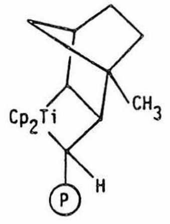


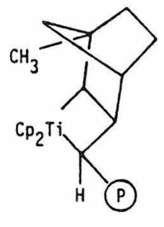
the norbornene metallacycle **7**.[4] A difference NOE experiment permitted assignment of the regiochemistry of addition. Irradiation of the $H_{\alpha'}$ cis to the norbornene fragment produced enhanced signals for $H_{\alpha'}$ (trans) at δ 2.79, the syn proton of the bridging methylene at δ 1.02, and the methyl group at δ 1.32. Thus, only the regioisomer with the methyl group near the β-carbon was observed. An adverse interaction between the methyl group and the proximal cyclopentadienyl group must disfavor the other regioisomer.

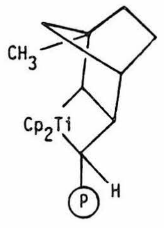
In contrast to the polymerization of norbornene with **7**, which occurs readily at 65°C, polymerization of 1-methylnorbornene requires temperatures of approximately 90°C. The microstructure of the product polymer was derived by comparison of its ^{13}C NMR spectral data (see Figure 1 and Table I)with published data.[6] The olefinic linkages in the polymer are primarily trans, although 5-10% cis bonds are present. The regiochemistry of addition favors head-to-tail (HT) dyads. A substantial amount of HH and TT dyads were also present with (HT+TH)/(HH+TT) ≃ 2.6. No information about polymer tacticity can be obtained from polymers of 1-methylnorbornene.

The trans:cis ratio observed for this polymer is significantly greater than the 64:36 ratio observed for polynorbornene prepared with 7.[4] The fact that HH and TT addition occurs in the polymerization while only one regioisomer results from the addition of 1-methylnorbornene to "Cp$_2$TiCH$_2$" shows that









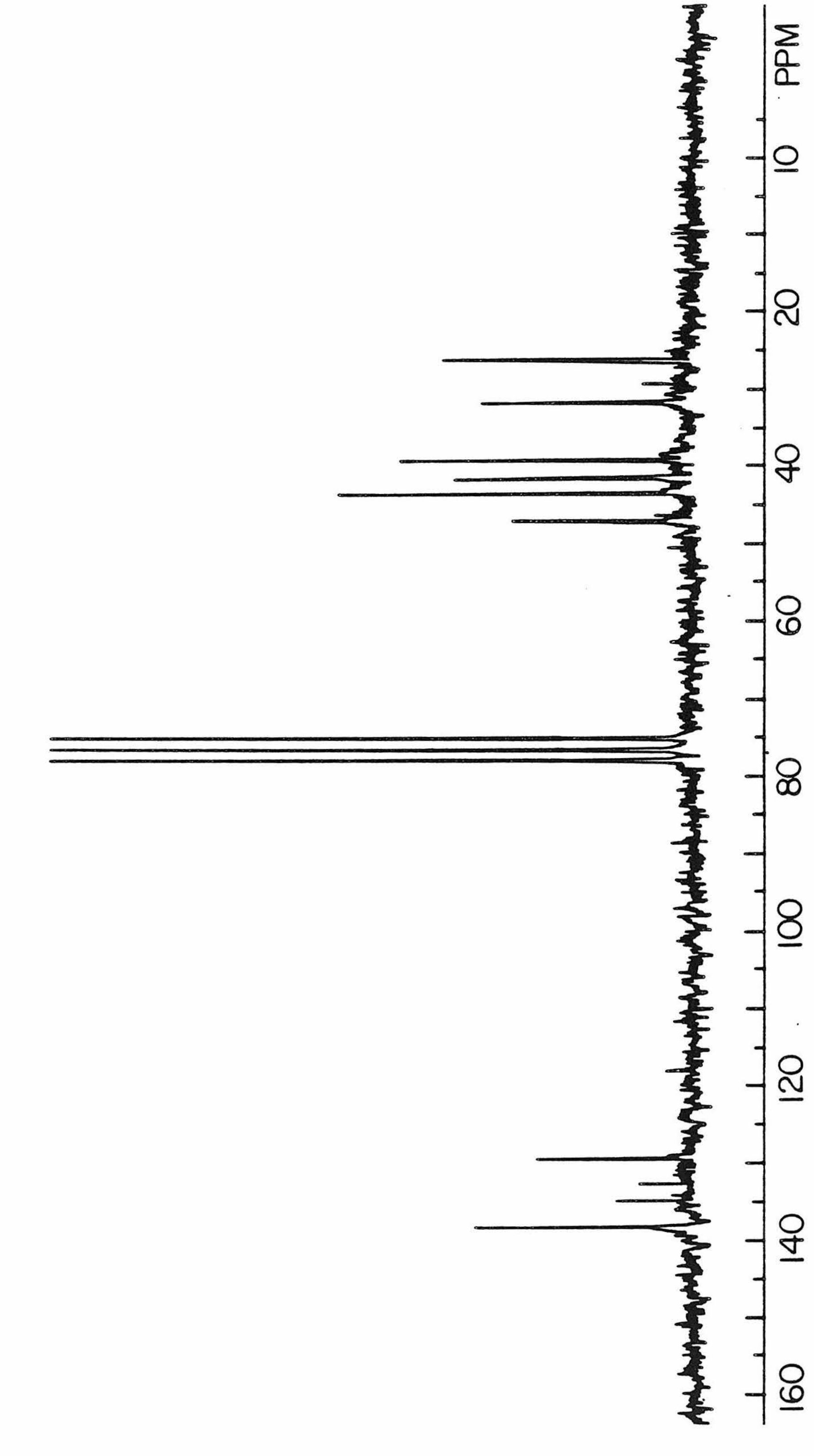
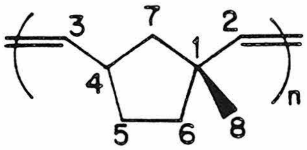


Figure 1. ^{13}C NMR spectrum of the poly(1-methylnorbornene) obtained from 1.

Table I. ^{13}C NMR Data and Assignments for the Poly(1-methylnorbornene) Obtained from 1.

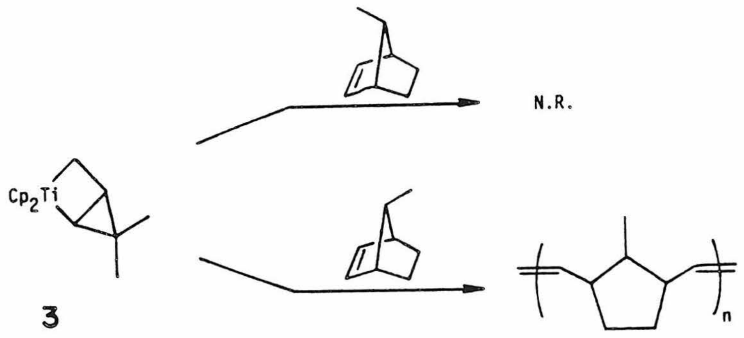


Chemical[a] Shift	Relative Intensity	Assignment[b]		
		C#	c,t[c]	HT, HH, TT[d]
138.87	44.5	C_2	t	HT
135.49	16.4		t	HH
133.21	12.2	C_3	t	TT
129.96	32.2		t	TH
118.72	3.1		terminal	$CH{=}\underline{C}H_2$
47.50	36.8	C_7	t	--
44.05	70.4	C_1	t	--
41.97	48.0	C_4	t	--
39.63	58.9	C_6	t	--
32.22	42.8	C_5	t	--
29.69	10.2	C_8	c	--
26.70	50.2		t	--

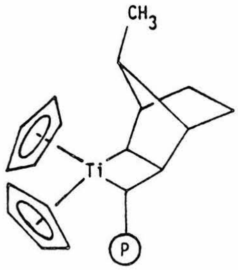
[a] In ppm, relative to solvent ($CDCl_3$) signal. [b] Assignments based on Reference 6. [c] c = cis. t = trans. [d] HT = head-to-tail. HH = head-to-head. TT = tail-to-tail.

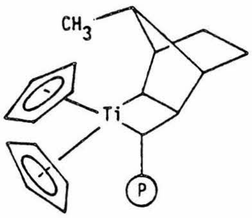
chain propagation is less selective than initial metallacycle formation. These observations can be rationalized by consideration of the four regioisomeric trisubstituted titanacyclobutanes **25** which are the chain-carrying species in this polymerization system. Isomer **25a**, which on cleavage would produce a *cis* juncture, is strongly disfavored by an adverse steric interaction between the methyl group and the pendant polymer chain. Isomers **25b** and **25c** have an unfavorable interaction between the methyl group and a cyclopentadienyl group. The most favored regioisomer on steric grounds is **25c**, although some interaction between the polymer chain and methyl group remains. Polymerization favoring intermediate **25c** would lead to predominantly *trans*, head-to-tail polymer as was observed.

7-Methylnorbornene. The polymerization of a 53:47 mixture of *syn* and *anti* 7-methylnorbornene using metallacycle **3** occurred readily at 50°C. Only the *anti* isomer was consumed. This reluctance in polymerizing the *syn*



isomer has been previously noted for a number of catalysts which successfully polymerize *anti*-7-methylnorbornene.[7] The explanation for this selectivity was based on purely steric grounds -- the *syn* methyl group effectively protects the double bond from attack. In the case of polymerization with **3**, a steric explanation is readily apparent. *Exo* attack on the *syn* monomer would





require a prohibitive interaction between the methyl group and one of the cyclopentadienyl groups. It is interesting that polymerization of *anti*-7-methylnorbornene goes at a lower temperature than the 65°C required for norbornene polymerizations with **3**. We believe that the lowered activation barrier is due to a destabilization of the chain-carrying metallacycles rather than any substitution effects or the carbenes. The proximity of the bridging ethano group (C_5-C_6) to the methyl group forces the C_7-H bond into a cyclopentadienyl group. Cleavage to carbene-olefin would relieve this additional steric interaction.

Assignment of the ^{13}C NMR spectrum of the poly(7-methylnorbornene), shown in Figure 2 and Table 2, was based on the work of Hamilton, Ivin, and Rooney.[7] Complete assignment was difficult, since the polymer prepared

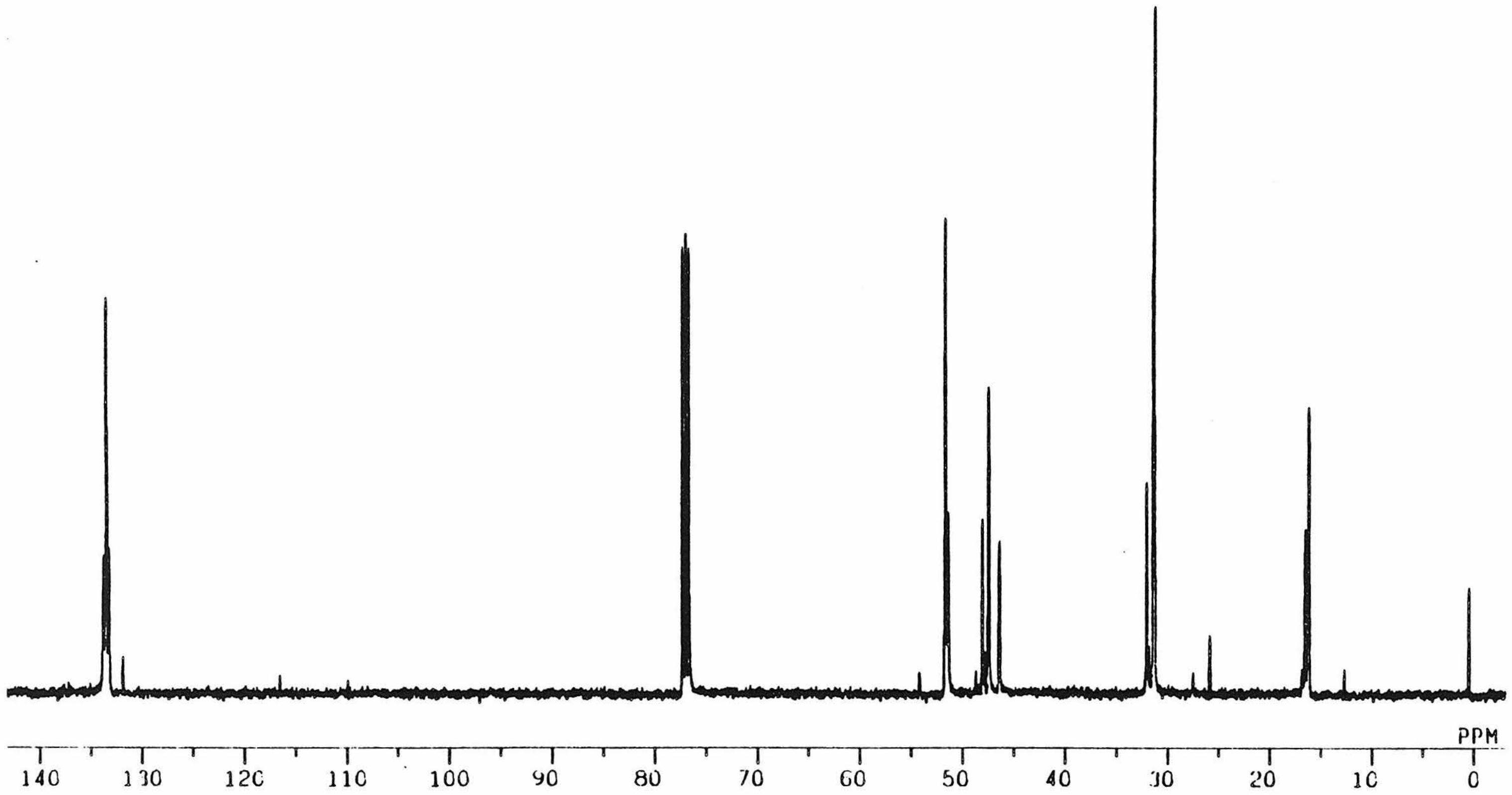
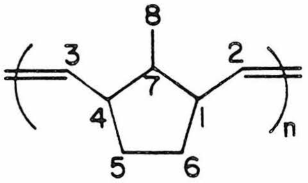


Figure 2. ^{13}C NMR spectrum of the poly(7-methylnorbornene) obtained from 3.

Table 2. ^{13}C NMR Data and Assignments for the Poly(7-methylnorbornene) Obtained from **3**.

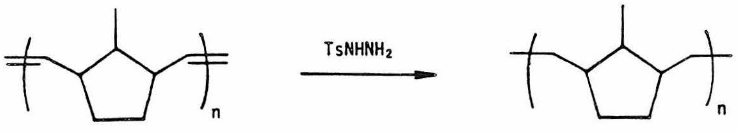


Chemical[a] Shift	Relative Intensity	Assignment[b]		
		C#	c,t[c]	r,m[d]
133.80	20.2	$C_{2,3}$	c	--
133.50	57.7		t	r
133.26	21.3		t	m
51.67	69.3	$C_{1,4}$	t	r
51.44	26.4		t	m
48.73	3.2	C_7	cc	--
48.10	25.5		ct	--
47.43	44.7		tt	--
46.42	22.3	$C_{1,4}$	c	--
32.07	30.9	$C_{5,6}$	c	--
31.81	6.8		c	--
31.42	39.9		t	m
31.32	100.0		t	r
16.53	24.1	C_8	--	--
16.27	38.3		--	--
16.19	41.9		--	--

[a] In ppm, relative to the solvent ($CDCl_3$) signal. [b] Assignments based on Reference 7. [c] c = *cis*. t = *trans*. [d] Dyad tacticity. r = racemic. m = meso.

with **3** differed substantially from those reported previously. The observed trans to cis ratio of 80:20 was based on the relative intensities of peaks for the allylic carbons $C_{1,4}$ at δ 51.4-51.7 for the trans isomer and δ 46.4 for the cis isomer. This ratio was confirmed by analysis of the fine structure of peaks assigned to the olefinic carbons and to $C_{5,6}$. Since C_8 is symmetrically situated between double bonds, its fine structure allows assessment of cis-trans blockiness. The observed data indicate a statistical distribution of isomers in the polymer. Assignments were also made for the dyad tacticity. A three-to-one ratio of r:m junctions at the trans double bonds is shown by examination of the fine structure of $C_{2,3}$, $C_{1,4}$, and $C_{5,6}$. The lower intensity peak of the m dyad is upfield of that of the r dyad for the olefinic and allylic carbons while the opposite order is observed for $C_{5,6}$.

Unfortunately, due to the lower cis content in the polymer and to the fact that the observed chemical shifts of peaks assigned to the cis isomer do not coincide with the published data, no direct assignment of the tacticity of the cis dyads could be made. Hydrogenation of the polymer and examination of the ^{13}C NMR spectrum of the saturated product simplifies assignment of



the tacticity since fine structure due to the double bond isomers is eliminated. Reaction of the poly(7-methylnorbornene) prepared using **3** with *para*-tosylhydrazide at 120°C cleanly afforded hydrogenated polymer with the ^{13}C NMR spectrum displayed in Figure 3. Assignment of all the peaks was readily made by comparison with published spectra.[7] Both the NMR assignments and an analysis of the tacticity in the hydrogenated polymer are included in Table 3. The derived overall *m:r* ratio of 64:36 requires that the *cis* dyads in poly(7-methylnorbornene) be predominantly, if not completely, *m* since the *trans* dyads had a *r:m* ratio of 3:1. Thus, in the polymer produced by reaction of *anti*-7-methylnorbornene and **3**, *trans* double bonds primarily are associated with *r* dyads while *cis* double bonds are associated with *m* dyads.

This relationship of double bond isomerism with tacticity is opposite to that observed by Hamilton, Ivin, and Rooney[7] for a number of common metathesis catalysts. We believe that the trend described above results form the fact that bis(cyclopentadienyl)titanium systems are quite electrophilic and have only one carbene coordination site. The analysis shown in Scheme II is based on the assumption that the electrophilic titanium carbenes retain coordination of the last formed double bond. Attack by the incoming monomer must come from the opposite side. Thus, *trans* attack gives all *r* dyads and *cis* attack gives all *m* dyads. If the double bond dissociates from the titanium center, attack from both sides would be possible. This could explain the moderate amount of *trans m* dyads which was observed.

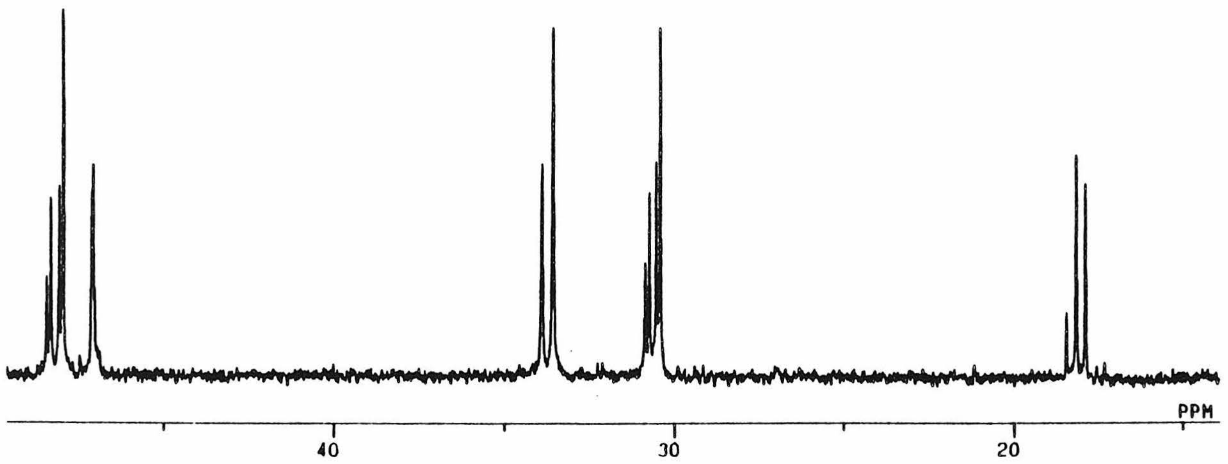
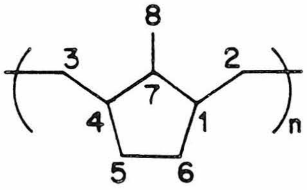


Figure 3. ^{13}C NMR spectrum of the hydrogenated polymer.

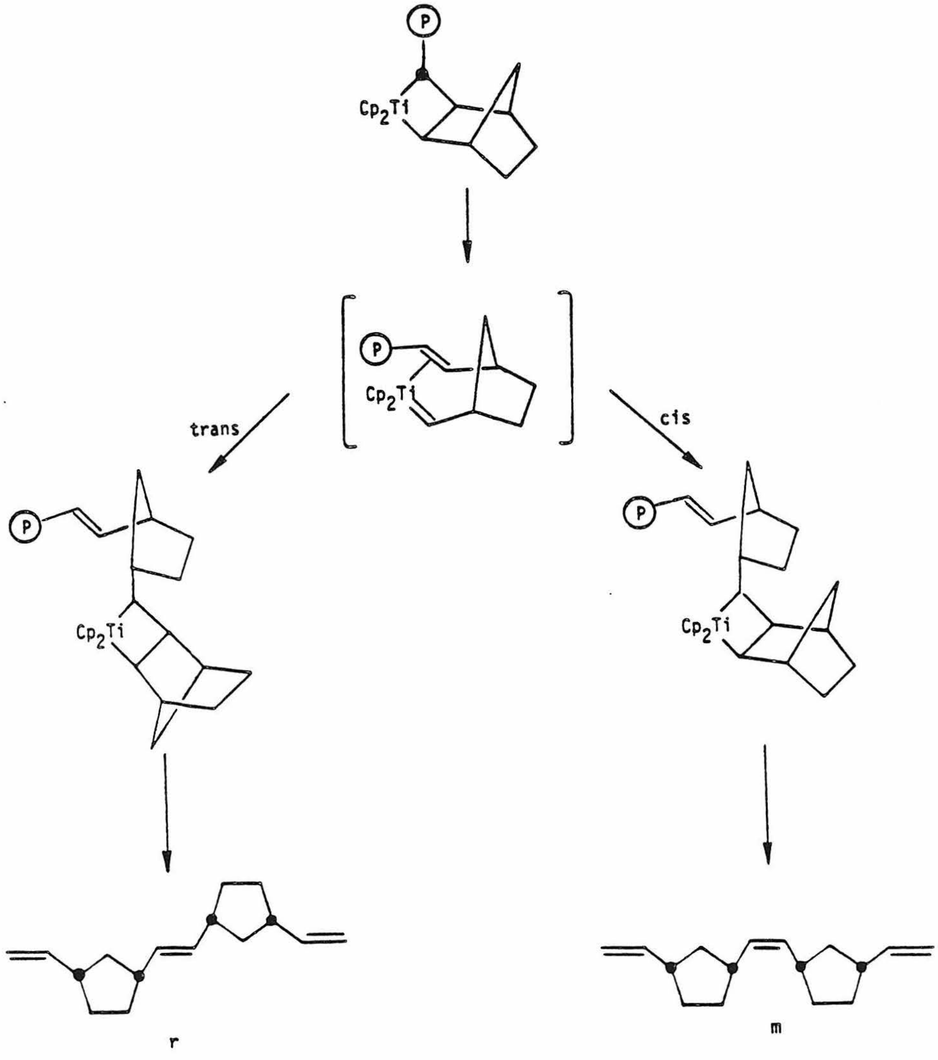
Table 3. ^{13}C NMR Data and Assignments for the Hydrogenated Polymer.



Chemical Shift[d]	Relative Intensity	Assignment[b]		Ratio r:m[c]
		C#	Tacticity[c]	
48.46	3.6	$C_{1,4}$	mm	66:34
48.35	6.4		mr	
48.10	6.8		rm	
47.99	13.0		rr	
47.14	6.6	C_7	--	--
47.09	7.5		--	
47.05	3.2		--	
33.90	7.6	$C_{2,3}$	m	62:38
33.57	12.5		r	
30.86	4.1	$C_{5,6}$	mm	64:36
30.73	6.5		mr	
30.53	7.7		rm	
30.41	12.4		rr	
18.43	2.3	C_8	mm	64:36
18.15	7.9		mr,rm	
17.88	6.9		rr	

[a]In ppm, relative to the solvent ($CDCl_3$) signal. [b]Assignments based on reference 7. [c]Dyad tacticity. r = racemic. m = meso.

Scheme I. Proposed Explanation for the Observed Tacticity.



Conclusion

This study of the polymerization of methylnorbornenes permits formulation of a number of generalizations about the microstructure of norbornene polymers prepared with titanacyclobutanes. These catalysts exhibit moderate *trans* selectivity. The *trans* preference increased in the order of norbornene < 7-methylnorbornene < 1-methylnorborne. This trend presumably arises from increased steric crowding in the transition state yielding *cis* monomer. Some HT preference was observed in the polymerization of 1-methylnorbornene with titanacycle **1**, although a substantial number of HH and TT dyads were present. One possible means of increasing the selectivity of addition in monomers lacking a mirror plane is to lower the temperature of polymerization. Use of catalyst **3** should allow polymerizations to be run at reduced temperatures. S. Lee is currently studying these polymerizations. In the analysis of polymer tacticity, a preference for *r* dyads at *trans* double bonds and *m* dyads at *cis* double bonds was noted. The titanacyclobutanes are the only catalysts reported to date which exhibit this selectivity. With careful design, utilization of these trends may allow preparation of polymers with interesting and useful microstructure.

Experimental Section

All manipulations of air and/or moisture sensitive compounds were carried out with use of standard Schlenk or vacuum line techniques. Argon was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4 Å molecular sieves. Solids were transferred in a N_2-filled Vacuum Atmospheres Dri-Lab equipped with an MO-40-1 purification train and a DK-3E Dri-Kool.

Metallacycles 1[8] and 3[9] were prepared by previously reported procedures. The 1-methylnorbornene and the 7-methylnorbornene (*syn* and *anti* mixture) were kindly provided by Drs. J. J. Rooney and K. Ivin and were stored over Linde 4 Å molecular sieves. Benzophenone (Aldrich) was recrystallized form hot toluene. The *p*-tosylhydrazide (Aldrich) was used without purification. Benzene-d_6 (Cambridge Isotope Laboratories) and toluene-d_8 (Cambridge Isotope Laboratories) were degassed and stirred over sodium-benzophenone ketyl. Benzene was dried over CaH_2, degassed, and vacuum transferred onto sodium-benzophenone ketyl. The *p*-xylene dried over Linde 4 Å molecular sieves. Reagent grade methanol was used without further purification.

NMR spectra were recorded on a JEOL FX-90Q (89.60 MHz ^1H; 22.53 MHz ^{13}C), a JEOL GX-400 (399.65 MHz ^1H; 100.40 MHz ^{13}C), or on a Brucker WM-500 (500.13 MHz ^1H). Difference NOE experiments were performed according to published procedures. Analytical gas chromatographic analyses (VPC) were performed on a Shimadzu GC-Mini 2 flame ionization instrument modified for capillary use and equipped with a Hewlett-Packard Model 339A integrator and a 0.33 mm x 40 m SE-30 capillary column.

Reaction of 1-Methylnorbornene with 1. To 1 (30 mg, 0.12 mmol) dissolved in 0.5 mL benzene-d_6 at 10°C was added 1-methylnorbornene (20 µL, 0.17 mmol). After stirring for 30 min at 23°C, the volatiles were removed under vacuum. The red oil produced was dissolved in benzene-d_6 for NMR analysis. ^{1}H NMR (500 MHz, C_6D_6) shifts versus residual solvent: δ 5.49 (s, 5H, Cp), 5.32 (s, 5H, Cp), 3.54 (d, 1H, J = 9 Hz, H_α), 2.79 (dd, 1H, J = 9 Hz, 11 Hz, $H_{\alpha'}$), 2.20 (br s, 1H), 1.90 (pt, 1H, J = 9 Hz, 9 Hz, $H_{\alpha'}$), 1.77 (m, 1H), 1.57 (m, 1H), 1.32 (s, 3H, Me), 1.30 (m, 2H), 1.02 (d, 1H, J = 10 Hz), 0.74 (d, 1H, J = 10 Hz), 0.06 (pq, 1H, J = 9 Hz, 9 Hz, 11 Hz, H_β). ^{13}C NMR (22.53 MHz, C_6D) shifts versus solvent: δ 109.48, 108.76, 106.94, 72.11, 48.72, 46.38, 40.70, 38.71, 36.70, 25.52, 21.49.

Polymerization of 1-Methylnorbornene with 1. To 1 (15 mg, 0.06 mmol) dissolved in 0.5 mL toluene-d_8 was added 50 µL 1-methylnorbornene (0.42 mmol). The solution was stirred for 15 min at 23°C with occasional venting to vacuum in order to remove isobutylene produced. The solution was transferred to a 5 mm NMR tube and placed in the probe of the JEOL-FX90Q and heated to 90°C. The polymerization was monitored by ^{1}H NMR spectroscopy until 95% consumption of monomer. After cooling to 23°C, the product polymer was isolated by addition of the contents of the NMR tube to 5 mL rapidly stirred methanol. The red gum was dried under vacuum and then dissolved in chloroform-d_1 for NMR analysis.

Polymerization of 7-Methylnorbornene with 3. To 3 (10 mg, 0.04 mmol) was added a solution of 2 mL benzene and 450 µL (3.6 mmol) of a 53:47 mixture of syn and anti 7-methylnorbornene. The mixture was stirred first at 23°C for 1.5 h and then at 50°C for 20 h. The reaction was monitored by VPC using the syn isomer as an internal standard. After 92% conversion of monomer, benzophenone (10 mg, 0.05 mmol) was added and the mixture was stirred at 50°C for 1.5 h. A color change from red to orange was observed. After cooling to 23°C, the solution was added to 50 mL rapidly stirred methanol. The precipitated white powder was collected by centrifugation, washed three times with methanol, dried under vacuum.

The polymerization was also monitored by ^1H NMR spectroscopy. To a 5 mm NMR tube containing a solution of **3** (5 mg, 0.02 mmol) in benzene-d_6 was added 20 μL (0.2 mmol) of a 53:47 mixture of syn and anti 7-methylnorbornene. The tube was placed in the probe of the JEOL-GX400 and was slowly heated while being monitored by ^1H NMR spectroscopy. At 50°C peaks attributable to the anti isomer diminished while peaks assigned as ring-opened polymer appeared. No change in the concentration of the syn isomer was observed.

Hydrogenation of Poly(7-methylnorbornene). An adaptation of the procedure described in Reference 6 was used here. To 100 mg poly(7-methylnorbornene) dissolved in 10 mL p-xylene was added 2.0 g (11 mmol) para-tosylhydrazide. The solution was degassed under vacuum and placed under an argon atmosphere. It was then warmed in an oil bath to 120°C over 30 min and stirred for an additional 30 min. After cooling to 23°C, the solution was added to 250 mL rapidly stirred methanol. The resultant white polymer was collected by centrifugation and dried under inert atmosphere.

References and Notes

(1) This discussion is abstracted from the work of Ivin, Rooney, and coworkers.[2]

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