The structure determination and subsequent refinement were carried out by using the SDP series of crystallographic programs[22] running interactively on a PDP 11/34a computer. The positions of the heavy atoms were determined by direct methods, and the remaining atoms, including the hydrogen atoms, were located in succeeding difference Fourier syntheses. The hydrogen atoms were assigned an arbitrary isotropic thermal parameter of $B = 5.0$ Å^2 and included as fixed contributors in the final structure factor calculations. Neutral atomic scattering factors were taken from Cromer and Waber.[23a] The effect of the real and imaginary components of anomalous dispersion for the molybdenum and sulfur atoms were included in the structure factor calculations using the tabulated values of Cromer.[23b] Only the 1681 reflections having $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. The final cycles of refinement included 199 variable parameters and converged with $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.028$ and $R_w = [\sum w(|F_o| - |F_c|)^2/(\sum wF_o^2)]^{1/2} = 0.034$ where $w = 4F_o^2/[\sigma^2(F_o^2)+(pF_o^2)^2]$ and p, the factor to prevent overweighting of the strong reflections, was set equal to 0.03. The highest peak in the final difference electron density map had a height of 0.28 e Å^{-3}. Plots of $w(|F_o| - |F_c|)^2$ vs. $|F_o|$, reflection order in data collection, sin θ/λ, and various classes of indicies showed no unusual trends.

Molecular Orbital Calculations. Orbital eigenvalues were calculated by the Fenske–Hall self-consistent-field (SCF) method.[16,17] Atomic basis functions of Richardson[24] were used for molybdenum (with a 5s exponent of 2.0 and a 5p exponent of 1.8) and Clementi[25] for carbon, nitrogen, oxygen (all with double-ζ functions with 1s and 2s reduced to single-ζ form), and sulfur (with double-ζ functions with the 1s, 2s, 2p, and 3s reduced to single-ζ form). An exponent of 1.2 was used for the hydrogen atom. Optimized bond lengths and angles were obtained from the X-ray crystal structure determination of **1** ($R = C_6H_5$). To simplify the calculations, the aryl rings were replaced with hydrogen atoms. A S–H bond length of 1.5 Å, a Mo–S–H bond angle of 120°, and a S–Mo–S bond angle of 90° were used. Furthermore, the cyclopentadienyl ring was constrained to D_{5h} symmetry with a C–C distance of 1.43 Å and a C–H distance of 1.09 Å. The coordinate system oriented the two thiolate ligands along the x and y axes and the nitrosyl ligand along the z axis. The calculations were carried out for conformers A and B. In A the R groups lie in the xz and yz planes and in B the R groups lie in the xy plane. For B, one anti and two syn conformers are possible. One of the syn conformers was chosen for the calculations in order to simplify the energy level diagram. The crystal structure is of the less sterically demanding anti isomer.[26]

Acknowledgment. We thank Dr. R. B. Ortega for assistance with the crystallographic analysis in the Molecular Structure Laboratory of the Department of Chemistry and Prof. D. L. Lichtenberger for helpful discussion and the use of computer programs. Support for portions of this work by the National Institute of Environmental Health Sciences (Grant ES 00966) is also gratefully acknowledged.

Supplementary Material Available: A listing of the anisotropic thermal parameters, hydrogen atom fractional coordinates, and structure factors for $(\eta^5\text{-}C_5H_5)Mo(NO)(SC_6H_5)_2$ (13 pages). Ordering information is given on any current masthead page.

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[22] Frenz, B. A. In "Computing in Crystallography"; Schenk, H., Olthof-Hazelkamp, R., vanKonigsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64-71.

[23] (a) Cromer, D. T.; Waber, J. T. In "International Tables for X-ray Crystallography"; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2a, p 149. (b) Cromer, D. T. *Ibid.* Table 2.3.1, p 72.

[24] Richardson, J. W.; Niewpoort, W. C.; Powell, R. R.; Edgell, W. E. *J. Chem. Phys.* **1962**, *36*, 1057.

[25] Clementi, E. *J. Chem. Phys.* **1964**, *40*, 1944.

[26] In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Titanacyclobutanes Derived from Strained Cyclic Olefins: The Living Polymerization of Norbornene

Laura R. Gilliom and Robert H. Grubbs*

Contribution No. 7220 from the Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91125. *Received June 27, 1985*

Abstract: Bis(cyclopentadienyl)titanacyclobutanes **1** and **3** have been prepared from the reaction of norbornene (bicyclo[2.2.1]hept-2-ene) with precursors of "$Cp_2Ti{=}CH_2$" and "$Cp_2Ti{=}CHC(CH_3)_2CHCH_2$", respectively. On thermolysis, both **1** and **3** 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 **3** shows polydispersities as low as 1.08 based on gel permeation chromatography vs. polystyrene standards. The molecular weight distributions of polymers obtained with **1** are always broader than those obtained with **3**. 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 $\Delta S^{\ddagger} = 9$ eu. Polymerization with **1** shows an induction period corresponding to a first-order decay of **1** with $t_{1/2} = 80$ min at 65 °C, whereas the polymerization with **3** is linear throughout. Simultaneous incorporation of norbornene-d_2 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.

The ring-opening polymerization of cyclic olefins[1] is an important application of the olefin metathesis reaction.[2] Several ring-opened polymers, including *trans*-polyoctenamer[3] and polynorbornene,[4] currently are produced industrially. While a variety of metal systems catalyze ring-opening polymerization, the details of their initiation and propagation have not been firmly established.

The work in this group has dealt with the chemistry of bis(η^5-cyclopentadienyl)titanacyclobutane compounds.[5] These sys-

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[1] Reviews of ring-opening polymerization: (a) Calderon, N. *J. Macromol. Sci. Revs.* **1972**, *C7(1)*, 105. (b) Katz, T. J.; Lee, S. J.; Shippey, M. A. *J. Mol. Catal.* **1980**, *8*, 219. (c) Reference 2.

[2] Recent reviews of the olefin metathesis reaction: (a) Ivin, K. J. "Olefin Metathesis"; Academic Press: London, 1983. (b) Grubbs, R. H. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Ed.; Pergamon Press, Ltd.: Oxford, 1982; Vol. 8, pp 499-551. (c) Banks, R. L. *Catalysis (London)* **1981**, *4*, 100. (d) Basset, J. M.; Leconte, M. *CHEMTECH* **1980**, *10*, 762.

[3] Streck, R. *CHEMTECH* **1983**, *13*, 758 and ref 2a, p 331.

[4] Ohm, R.; Stein, C. In "Encyclopedia of Chemical Technology", 3rd ed.; Grayson, M., Ed.; Wiley-Interscience: New York, 1982; Vol. 18, pp 436-442.

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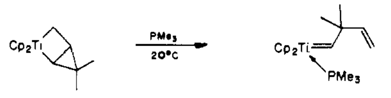
Table I. Analysis of Benzophenone Trapping Experiments with **1**

reaction	reagents[a]			products[a]			yields[d]
	1	B[b]	N[c]	**5a**	**6a**	**7a**	
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 **1**.

tems have been shown to effect the degenerate metathesis of terminal olefins.[5,6] Our approach to the design of catalysts for

nondegenerate metathesis has been to prepare metallacycles by the addition of "$Cp_2Ti{=}CH_2$" (Cp = η^5-C_5H_5) to strained cyclic olefins. We have recently reported that the titanacyclobutane **2** derived from 3,3-dimethylcyclopropene cleanly produces α-substituted carbene compounds.[7] The ability to produce these



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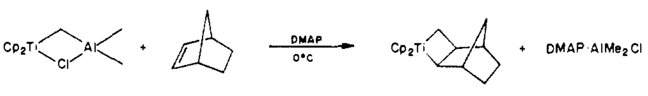
carbenes, however, does not guarantee effective productive metathesis.[8] The present work demonstrates that titanacyclobutanes derived from strained cyclic olefins are useful catalysts for the metathetical polymerization of norbornene. As a class of catalysts they exhibit characteristics not seen in previous ring-opening polymerization systems. Coincidentally, they permit a detailed mechanistic study of ring-opening polymerization.

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[5c] affords red crystals of metallacyclobutane **1** in 58% yield. The NMR spectral data of **1** are similar to that of reported α,β-di-



1

substituted titanium metallacycles.[6] The characteristic high-field chemical shift for the β-proton of the four-membered ring is at 0.14 ppm, the single α-proton[10] is shifted downfield to 3.51 ppm, and the two α'-protons[10] are at δ 1.91 and 3.11. Full assignment, based on homonuclear decoupling, is shown in Figure 1a. Difference NOE experiments confirm exo addition of "$Cp_2Ti{=}CH_2$" to norbornene, which is also seen in additions of most electrophiles to norbornene.[11] Irradiation of Cp_1 of δ 5.29 shows enhancement

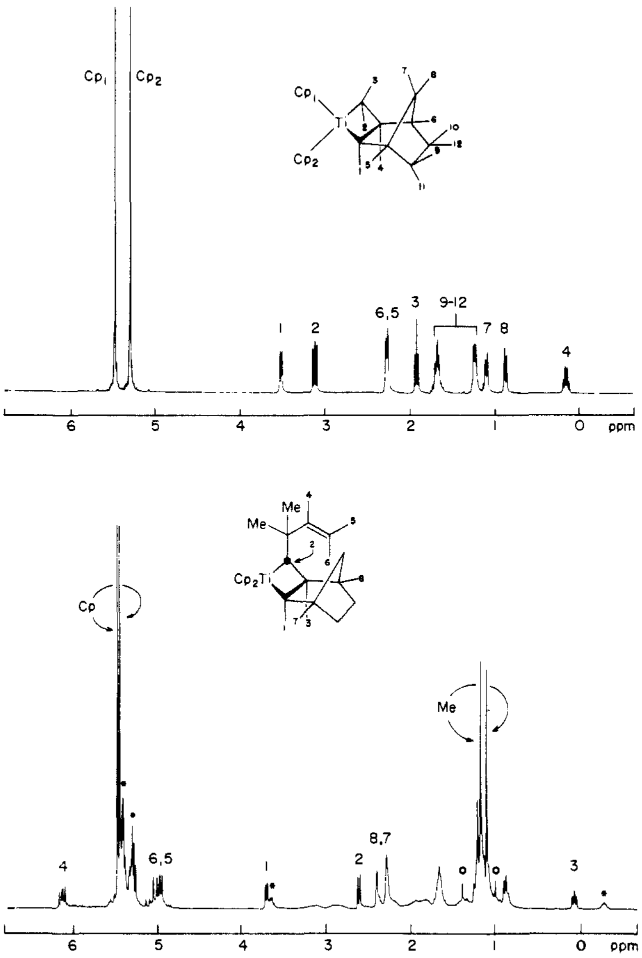


Figure 1. 400-MHz ^1H NMR spectra of the catalyst in C_6D_6: (a) metallacycle **1**; (b) metallacycle **3**. Peaks attributable to residual **2** are marked with an open circle (○). Peaks attributable to **4** are marked with an asterisk (*).

of H_7 at δ 1.08. Metallacycle **1** is the most stable titanacyclobutane reported to date; it can be prepared by olefin exchange from $\overline{Cp_2TiCH_2CH(i\text{-}Pr)CH_2}$[12] in spite its more sterically demanding α,β-substitution pattern and bridged ring system.[13]

Previous studies have shown that titanium carbene species are rapidly trapped by ketones and aldehydes.[14] They act similarly to Wittig reagents: substituting the alkylidene fragment for the carbonyl oxygen. Heating **1** in the presence of benzophenone yields olefins **5a**, **6a**, and **7a** as the major isolable organic products. Diphenylethylene was readily identified by comparison with an authentic sample. Olefins **6a** and **7a** were characterized by the usual spectroscopic techniques. Capillary VPC analysis of **7a**

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(5) (a) Howard, T. R.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 6876. (b) Lee, J. B.; Gajda, G. J.; Schaefer, W. P.; Howard, T. R.; Ikariya, T.; Straus, D. A.; Grubbs, R. H. *Ibid.* **1981**, *103*, 7358. (c) Lee, J. B.; Ott, K. C.; Grubbs, R. H. *Ibid.* **1982**, *104*, 7491.

(6) These systems are also capable of inefficient metathesis of some acyclic internal olefins. Straus, D. A.; Grubbs, R. H. *J. Mol. Catal.* **1985**, *28*, 9.

(7) Gilliom, L. R.; Grubbs, R. H. *Organometallics*, in press.

(8) Reference 2b, p 544.

(9) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. The modified preparation described in ref 5c was used here.

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

(11) March, J. "Advanced Organic Chemistry", 2nd ed.; McGraw-Mill, Inc.: New York, 1977; p 690.

(12) $\overline{Cp_2TiCH_2CH(^iPr)CH_2}$ is the most stable of the previously reported titanacyclobutanes.[13]

(13) Straus, D. A.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1658.

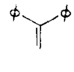
(14) (a) Brown-Wensley, K. A.; Buchwald, S. L.; Cannizzo, L.; Clawson, L.; Ho, S.; Meinhardt, D.; Stille, J. R.; Straus, D.; Grubbs, R. H. *Pure Appl. Chem.* **1983**, *55*, 1733. (b) Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3270. (c) Reference 9.

Table II. Analysis of Benzophenone Trapping Experiments with **3**

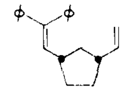
		reagents[b]		products[b]		
reaction	t^a	**2**	B[c]	**8a**	**9a**	yield[d]
1	1.5	0.19	0.44	0.088	0.032	63
2	3.0	0.19	0.44	0.059	0.099	52

[a] Catalyst preparation time. In h. [b] In mmol. [c] Benzophenone. [d] In %. Based on initial **2**.

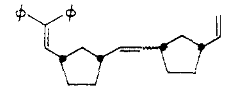
coupled with high-resolution GC–MS suggested the presence of a mixture of isomers. Further confirmation of these structures was provided by degradative ozonolysis. The same dialdehyde produced from the ozonolysis of norbornene and the appropriate equivalent of benzophenone were obtained.



5a



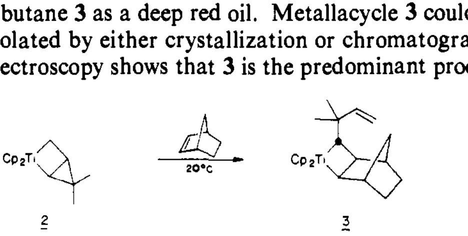
6a



7a

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 **7a** and addition of extra benzophenone (reaction 3) reduces the yield of **7a**. Ninety-five percent of the norbornene initially present in metallacycle **1** can be accounted for in the products of reaction 3.

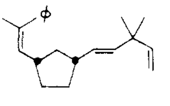
As mentioned above, we have previously reported the synthesis and characterization of the titanacycle, **2**, derived from reaction of "$Cp_2Ti{=}CH_2$" and 3,3-dimethylcyclopropene.[7] Upon thermolysis, **2** cleaves to give an α-substituted carbene which can be trapped by a variety of coordinating ligands.[7] Thermolysis of **2** at 20 °C in the presence of norbornene afforded trisubstituted metallacyclobutane **3** as a deep red oil. Metallacycle **3** could not be cleanly isolated by either crystallization or chromatography. ^{1}H NMR spectroscopy shows that **3** is the predominant product.



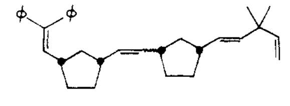
Samples of **3** contain approximately 30% of a second species assigned as the product of the addition of 2 equiv of norbornene to **2** (see Discussion section). Spectral assignments for **3**, shown in Figure 1b and reported in the Experimental Section, are based on 2-dimensional ^{1}H–^{1}H and ^{1}H–^{13}C NMR experiments. The β-proton, a pseudotriplet 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 trans stereochemistry is based on difference NOE experiments. Irradiation of the β-proton signal at δ 0.08 enhances signals at 6.15 and 3.72 ppm, assigned as H_4 and H_1 (see Figure 1b) without substantial enhancement of the signal for H_2.[15]

The peaks in the spectrum of **3** due to the double addition product are indicated with asterisks in Figure 1b. Signals at δ 3.67 and −0.22 occur at positions characteristic of the α and β protons of titanacyclobutane compounds. When **3** was stirred with additional norbornene, the signals assigned to **3** diminished while the peaks marked with asterisks grew larger.

When **3** was heated to 65 °C in the presence of benzophenone, olefins **8a** and **9a** were obtained. Products **8a** and **9a** were identified on the basis of both spectral data and degradative ozonolysis. High-resolution GC/MS analysis of **9a** indicates that it is a mixture of two isomers, each of which gives the correct



8a



9a

parent ion and a fragmentation pattern similar to that obtained for **8a**. When **3** was prepared by stirring **2** with norbornene for 3 h rather than the usual 1.5 h, the amount of **9a** relative to **8a** increased. The reaction conditions and product yields are summarized in Table II.

Due to the difficulty in isolating pure metallacycle, **3** was prepared in situ by reaction of norbornene with a measured amount of **2** 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 **1** and **3** 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 retain the deep red color of the reaction mixture. Comparison of the ^{13}C NMR spectra of these polymers with those in the literature[18] shows that both **1** and **3** 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)[19] of the polymer produced by reaction of 100 equiv of norbornene with **1** gives M_n = 21 000 and polydispersity ($d = M_w/M_n$) of 1.13. The analogous reaction with **3** gives M_n = 21 000 and a d value of 1.08. Table III summarizes molecular weight results obtained from sampling the polymerizations at intermediate conversions of monomer. Molecular weights for initiation with both **1** and **3** increase linearly with conversion. The molecular weight distributions of polymers prepared from **3** are more narrow than those of polymers produced by **1**. Polydispersities for **1** were found to decrease with increasing conversion, whereas the dispersities for initiation with **3** were roughly constant.

Polynorbornene with M_n = 92 000[18] was prepared by the reaction of **3** with 500 equiv of 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 **1** 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.[20] 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 the 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 **3** were observed after 5 min at 65 °C. New signals that are identical with the signals

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[15] Further evidence for the formulation of **3** as shown: Compounds analogous to **3** have been prepared from the reaction of **2** with *endo*-dicyclopentadiene[16] and with *endo,endo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dialkyl esters.[17] They are isolable as crystalline solids, give adequate elemental analyses, and are fully characterized spectroscopically.

[16] Gilliom, L. R.; Grubbs, R. H., unpublished work.

[17] Stille, J. R.; Grubbs, R. H. *J. Am. Chem. Soc.*, in press.

[18] Ivin, K. J.; Laverty, D. T.; Rooney, J. J. *Makromol. Chem.* **1977**, *178*, 1545. Ivin, K. J.; Laverty, D. T.; Rooney, J. J. *Ibid.* **1978**, *179*, 253.

[19] Molecular weights and polydispersities obtained by GPC are based on calibration with polystyrene standards.

[20] Homonuclear decoupling experiments show that the signals at 3.67 and −0.22 ppm are coupled with J = 10.2 Hz.

Table III. 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, %
1	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	9000	87
3	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	9100	87

[a] Polymerization time in h. [b] Based on calibration with polystyrene standards. [c] Polydispersity. [d] $M_n^{corr} = 0.5\ M_n^{exptl}$ See ref 36 and text.

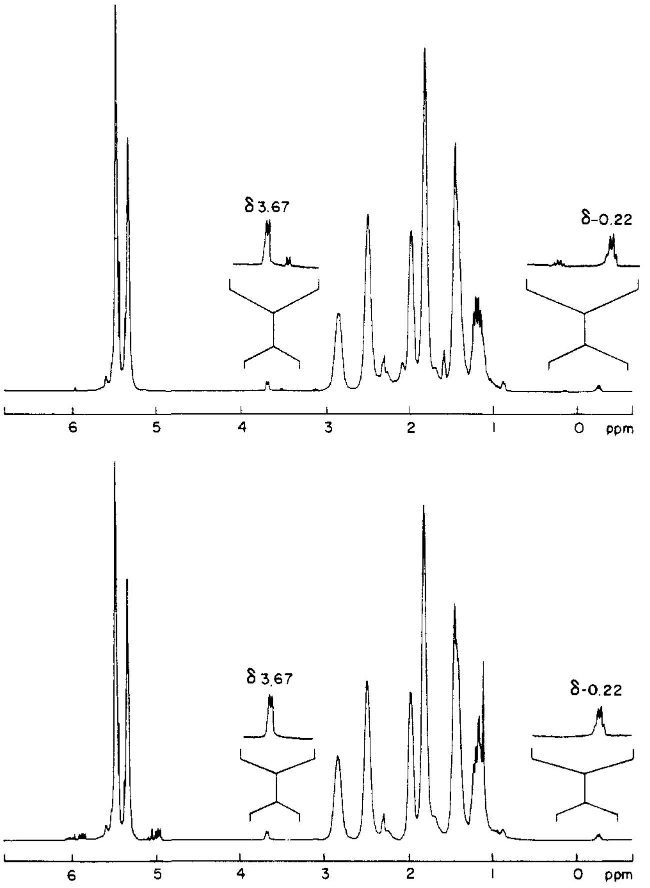

Figure 2. Room-temperature 400-MHz ^{1}H NMR spectra in C_6D_6 of the reaction mixtures after polymerization at 65 °C and removal of volatiles: (a) catalyzed by **1** and 4.5 h of polymerization time; (b) catalyzed by **3** and 3.0 h of polymerization time.

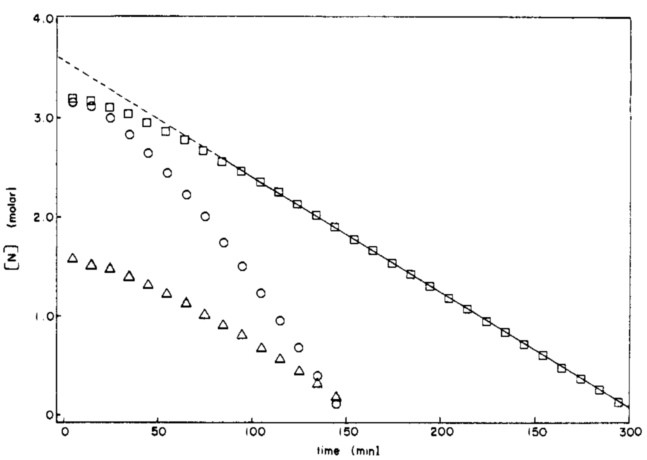

Figure 3. Kinetic data for polymerization of norbornene with **1** at 73 °C. (○) $[\mathbf{1}]_0$ = 0.035 M, $[N]_0$ = 3.2 M. (□) $[\mathbf{1}]_0$ = 0.070 M, $[N]_0$ = 3.2 M. (△) $[\mathbf{1}]_0$ = 0.035 M, $[N]_0$ = 1.6 M. The solid line indicates the points used to obtain the polymerization rate for the zero-order region.

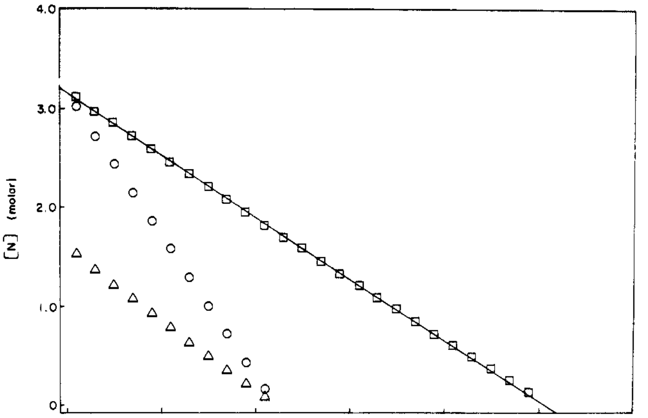

Figure 4. Kinetic data for polymerization of norbornene with **3** at 73 °C. (○) $[\mathbf{2}]_0$ = 0.035 M, $[N]_0$ = 3.2 M. (□) $[\mathbf{2}]_0$ = 0.070 M, $[N]_0$ = 3.2 M. (△) $[\mathbf{2}]_0$ = 0.035 M, $[N]_0$ = 1.6 M. The solid line indicates the points used to obtain the polymerization rate.

Table IV. Kinetics Data for Polymerization with **1** and **3**[a]

T, °C	$k^b(\mathbf{1})$, s^{-1}	$k^b(\mathbf{3})$, 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 ± 0.5 kcal/mol, $\Delta S^\ddagger$ = 9 ± 4 eu,
$\Delta G^\ddagger_{338}$ = 24 ± 1 kcal/mol

[a] $[\mathbf{1}]_0$ = 0.035 M, $[\mathbf{2}]_0$ = 0.035 M, $[N]_0$ = 3.2 M. [b] $k = k_{obsd}/[\text{catalyst}]$.

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.

Spectra a and b in Figure 2 show room-temperature spectra obtained after polymerization with **1** and **3**, 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 2a are attributable to residual catalyst **1**.[21]

Kinetics of Polymerization and Initiation. The kinetics of the polymerization of norbornene with **1** and **3** were monitored by ^{1}H NMR spectroscopy. Figures 3 and 4 show the time dependence of the monomer concentration for catalysis by **1** and **3**, respectively. After an induction period, during which the rate of consumption of norbornene gradually increases, the plot (Figure 3) for **1** becomes linear, indicating a zero-order reaction. Halving the norbornene concentration does not affect the rate. Doubling the concentration of **1** doubles the rate. The length of the induction period is not affected by changing concentrations of the reactants. The plot for polymerization by **3** (Figure 4) is linear throughout the course of the polymerization. The rate and concentration

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(21) Signals characteristic of a monosubstituted terminal olefin are present in Figure 2b but are not observed in Figure 2a. We do not understand why such signals are absent in Figure 2a. 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. We exclude the possibility of substantial secondary metathesis of the terminal double bond because of the narrow polydispersities obtained.

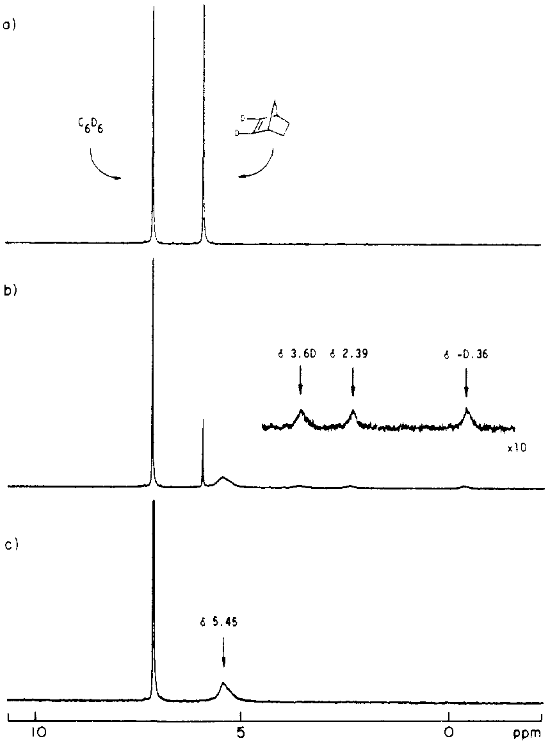


Figure 5. 61.25-MHz [^{1}H] ^{2}H NMR spectra in C_6H_6 showing the incorporation of deuterated norbornene into the polymer: (a) after addition of norbornene-d_2 but prior to heating; (b) after heating at 60 °C for 15 min; (c) after addition of norbornene-d_0 and heating at 65 °C for 15 min.

dependences are the same, within experimental error, as those obtained for the zero-order region of polymerization with **1**.

First-order rate constants, k, were calculated as

$$-\mathrm{d}[\mathrm{N}]/\mathrm{d}t = k_{\mathrm{obsd}} = k[\mathbf{1}]_0 \text{ or } k[\mathbf{2}]_0$$

for the linear portions of the kinetic plots. The rate data obtained at 53, 63, and 73 °C are listed in Table IV together with derived activation parameters.

The kinetics of the disappearance of **1** under the polymerization conditions were obtained at 65 °C. A plot of -ln [**1**] vs. time was linear for greater than 3 half-lives. The data fit the rate law

$$-\mathrm{d}[\mathbf{1}]/\mathrm{d}t = k'[\mathbf{1}] \qquad k' = 1.5\ (1) \times 10^{-4}\ \mathrm{s}^{-1}$$

Incorporation of Norbornene-d_2. The polymerization of norbornene initiated by **3** was stopped by cooling the reaction to room temperature. The remaining norbornene was removed and replaced with 3 equiv of norbornene-*2,3*-d_2. After being heated to 90% conversion of monomer, the reaction mixture was again cooled, the deuterated norbornene was replaced by perprotionorbornene, and the solution was heated for an additional 15 min. The entire process was monitored at each step by both ^{1}H and ^{2}H NMR spectroscopy.

The ^{2}H spectra are shown in Figure 5. Figure 5a exhibits two signals due to C_6D_6 added as an internal standard and to unreacted norbornene-d_2 at δ 5.94. Upon polymerization of the deuterated monomer, broad signals appeared at 5.45, 3.60, 2.3., and -0.36 ppm. After further polymerization with norbornene-d_0, all the deuterium was found at δ 5.45.

Simultaneously, in the ^{1}H spectra which are shown in Figure 6, signals at 3.67 and -0.22 ppm disappeared upon incorporation of deuterated monomer. When norbornene-d_0 was added and polymerized, these missing signals reappeared.

Discussion

The experimental evidence suggests that polymerizations catalyzed by both **1** and **3** 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 **3** are the same, within experimental error, as those observed for the post-initiation region for **1**.

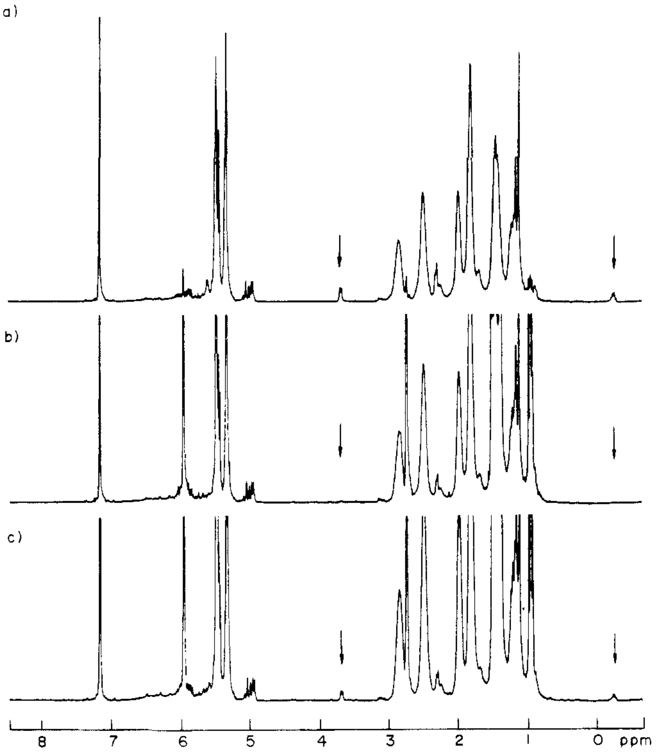
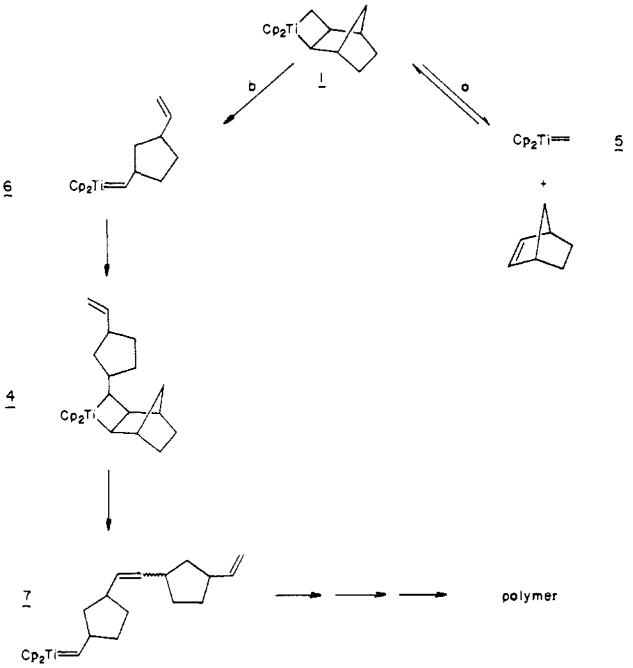


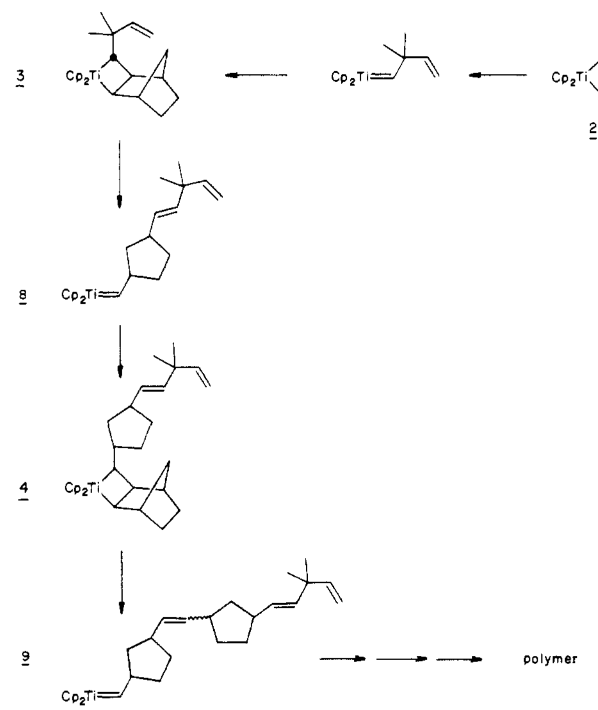
Figure 6. 400-MHz ^{1}H NMR spectra in C_6D_6 showing the incorporation of deuterated norbornene into the polymer: (a) after polymerization of norbornene-d_0; (b) after polymerization of norbornene-d_2; (c) after polymerization of additional norbornene-d_0.

Scheme I



All the data presented here are consistent with the mechanisms outlined in Schemes I and II.[22] Metallacycle **1** can cleave to a carbene–olefin complex in two possible ways. Path a is nonproductive but rapidly reversible. Path b leads to substituted titanacarbene **6**. Titanacarbene **6** is trapped by norbornene, forming an α,β,α′-trisubstituted metallacycle, **4**. Cleavage of **4** affords substituted carbene **7** which when trapped by norbornene again produces trisubstituted metallacycle. Propagation in this manner

Scheme II



yields a growing chain of ring-opened polynorbornene attached to the α' position of a trisubstituted titanacyclobutane analogous to **4**.

A direct route to the chain-propagating metallacycles **4** is afforded by thermolysis of **3** 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 by isolation, spectral evidence, and/or trapping studies. Metallacycles **1** and **2** are fully characterized. Trisubstituted metallacycle **3** could not be cleanly isolated; however, ^{1}H and ^{13}C spectra are consistent with the assigned structure. Furthermore, the expected product **8a** was obtained from reaction of **3** with benzophenone.

In Schemes I and II all the chain-propagating metallacycles have been labeled **4**. 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 is attached to a secondary carbon. In contrast, the α' position for **3** is attached to a tertiary center. Since the metallacycles **4** 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.

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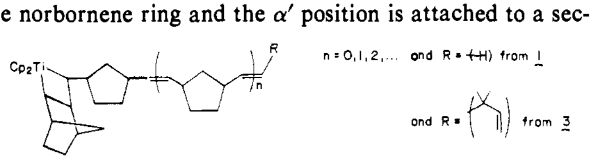
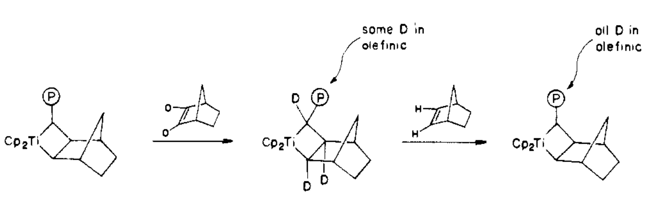


The NMR signals at δ 3.67 and −0.22 are observed throughout polymerizations with both catalysts. Since they occur in regions characteristic of α and β protons on titanacyclobutanes, they are attributed to the α and β protons of the chain-propagating metallacycles **4**. Further substantiation of this assignment is provided by the incorporation of deuterium at these positions when norbornene-d_2 is added to the growing polymer chain. The deuterium 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 **5a**, **6a**, and **7a** from reaction with **1** suggests the presence of titanacarbenes **5**, **6**, and **7**. Product **7a** presumably arises by addition of free norbornene, formed by the nonproductive cleavage of **1** (path a), to **6** and subsequent trapping of **7**. 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 **6a** and decrease in the amount of **7a** is observed. Ninety-five percent of the norbornene initially present in metallacycle **1** can be accounted for in the products of reaction 3. Under these conditions, addition of 2 equiv of benzophenone effectively prevents polymerization.



Similarly, the production of hydrocarbons **8a** and **9a** on thermolysis of **3** supports the intermediacy of titanacarbenes **8** and **9**. Since no additional norbornene was added to the reaction, the presence of **9a** suggests that trisubstituted metallacycle **4** (n = 0) is the major impurity in samples of **3**. The fact that an increased amount of **9a** and a decreased amount of **8a** were obtained when **3** was prepared by reaction of **2** and norbornene for 3.0 h rather than the usual 1.5 h confirms the suggestion that the metallacycle impurities obtained with **3** result from a competitive reaction of **3** 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.[23] In fact, few such cases have been observed in the kinetics of homogeneous polymerizations.[24] In this case the observed zero-order dependence is consistent with rate-determining unimolecular cleavage of metallacycle **4** 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 was observed for polymerizations with **3** suggests rapid formation of the chain-carrying metallacycles **4**. Since **3** is substituted on the α'-carbon by a tertiary carbon while **4** has a secondary carbon attached at that position and since the stability of other titanacyclobutanes is sensitive to increased steric bulk on the ring, **3** is expected to be less stable than **4**. Because ring-opening affords structurally analogous carbenes **8** and **9**,[25] the initiation reaction (cleavage of **3**) is arguably faster than propagation (cleavage of **4**). Experimentally, by the time a spectrum could be recorded in the kinetic studies at 73 °C, no signals attributable to **3** remained.

In contrast, polymerizations catalyzed by **1** do show an induction period. The length of this period does not depend on the concentration of either **1** or norbornene. The NMR studies showing the appearance of signals attributed to **4** as **1** disappears suggest

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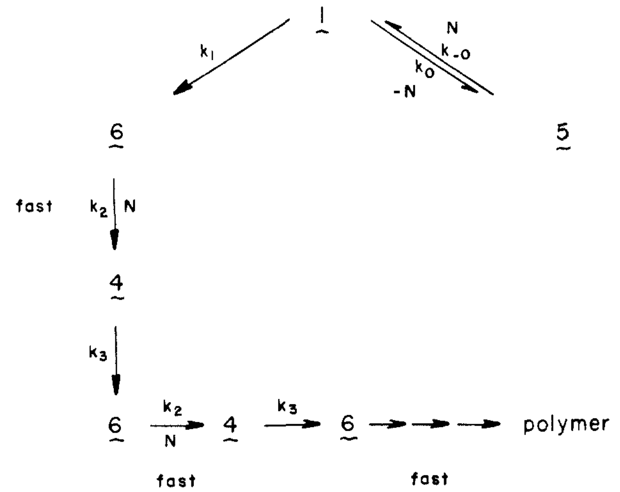
[22] The issue of formation of a carbene–olefin complex prior to addition producing metallacycle vs. direct insertion to give metallacycle is not considered here.

[23] Cooper, W. In "Comprehensive Chemical Kinetics"; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier Scientific Publishing Company: Amsterdam, 1976; Vol. 15, p 155.

[24] Several reported cases of zero-order dependence in monomer include the following: Thoi, H. H.; Reddy, B. S. R.; Rooney, J. J. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 3307. Oreskin, I. A.; Tinyakova, E. I.; Dolgoplosk, B. A. *Vysokomol. Soedin.*, *A11* **1969**, 1840 (as reported in: Dawans, F.; Teyssié, P. *Ind. Eng. Chem. Prod. Res. Dev.* **1971**, *10*, 261). Hamann, S. D.; Murphy, A. J.; Solomon, D. M.; Willing, R. I. *J. Macromol. Sci., Chem.* **1972**, *A6*, 771. Fontana, C. M.; Kidder, G. A. *J. Am. Chem. Soc.* **1948**, *70*, 3745.

[25] Each carbene is α'-substituted by a secondary group. They differ only by the central ring-opened norbornene unit present in **9**.

Scheme III



that the induction period is due to slow conversion of **1** to **4**. The interaction of the α′-substituent of **4** and the Cp groups on titanium should destabilize **4** relative to the unsubstituted **1**. Consequently, cleavage of **1** (initiation) should be slower than cleavage of **4** (propagation).

Making the assumptions that k_{-1}, k_{-2}, and k_{-3} are all slow compared to the forward reactions[26] and assuming the steady-state approximation for all titanacarbenes (see Scheme III)[27] led to the prediction that

$$-\frac{d[N]}{dt} = k_1[\mathbf{1}] + k_3[\mathbf{4}] \qquad (1)$$

where $k_1[\mathbf{1}]$ corresponds to the first-order decay of initiator **1** and the $k_3[\mathbf{4}]$ term corresponds to the first-order decay of each of the chain-carrying metallacycles **4**. Once the initiation period is over, the overall concentration of **4** 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 **1**. The constant k_1 is set equal to the rate constant obtained from monitoring the first-order disappearance of **1** 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 **3** ($k_3 = 2.4 \times 10^{-3}$ s^{-1}). A plot obtained using eq 2 with $[\mathbf{1}]_0 = 0.035$ M is shown in Figure 7 along with the experimental data

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

where

$$A = \frac{k_1 - k_3}{k_1}[\mathbf{1}]_0 \text{ and } B = k_3[\mathbf{1}]_0$$

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 eq 1 and the mechanisms presented in Schemes I and II.

Stereochemistry of the Polymers. 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 **6**. Decomposition of the subsequent metallacycle occurs without isomerization, affording a trans double bond for trans metallacycles **4t** and a cis double bond for cis metallacycles **4c**. In fact, olefin exchange has been shown to occur with retention of stereochemistry for other titanacyclobutane systems.[5c]

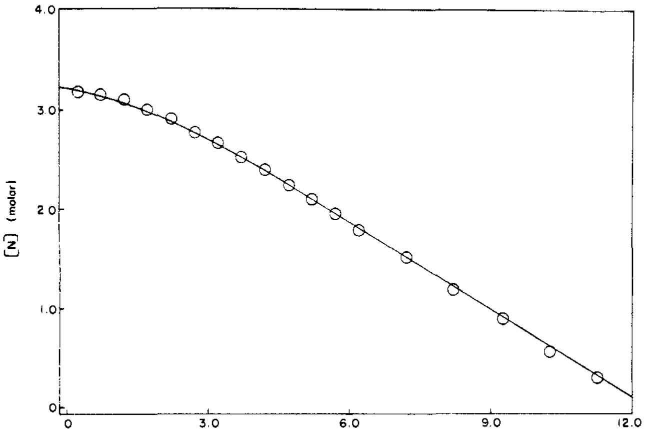
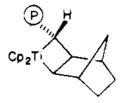
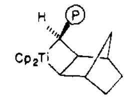


Figure 7. Experimental data and the calculated curve for the kinetics for the polymerization of norbornene with **1** at 65 °C. Circles (○) are used to indicate experimental data. The solid line (—) indicates the theoretical curve derived as described in the text.



4t



4c

The experimentally observed trans to cis ratio of 62:38 suggests some trans perference 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,[28] presumably due to secondary metathesis[29] 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 reaction. A true thermodynamic mixture of double bond isomers on polynorbornene would have a much lower cis content.[30] Also, the same cis to trans ratio is observed at low conversion and throughout the polymerization.

Although other explanations have been presented[32-35] to explain observed stereochemistries in polymers prepared with different catalyst systems, consideration of the steric interactions in the

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(26) 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 $k_{-2}[\mathbf{4}]$ is expected to be slower than $k_3[\mathbf{4}]$ since productive cleavage (ring-opening) relieves the strain of the bicyclic system while nonproductive cleavage (loss of norbornene) requires generation of a strained olefin. Both pathways afford structurally similar carbenes **6** from the metallacycles **4**.

(27) The kinetic indistinguishability of all chain-propagating metallacycles **4** and the kinetic indistinguishability of all α-substituted carbenes (labeled **6** in Scheme III) are assumed.

(28) Reference 2b, p 540.

(29) Rief, L.; Höcker, H. *Macromolecules* **1984**, *17*, 952 and references therein.

(30) The Δ*H* for isomerization of *trans*-2,5-dimethyl-3-hexene to the cis isomer has been measured at 25 °C as 1.9 kcal/mol.[31] 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.

(31) Turner, R. B.; Jarrett, A. D.; Goebel, P.; Mallon, B. J. *J. Am. Chem. Soc.* **1973**, *95*, 790.

(32) Katz, T. J.; Hersh, W. H. *Tetrahedron Lett.* **1977**, 585. Ott, K. C.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 2942.

(33) Calderon, N.; Ofstead, E. A.; Judy, W. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 401. Ofstead, E. A.; Lawrence, J. P.; Senyek, M. L.; Calderon, N. *J. Mol. Catal.* **1980**, *8*, 227.

(34) Basset, J. M.; Bilhou, J. L.; Mutin, R.; Theolier, A. *J. Am. Chem. Soc.* **1975**, *97*, 7376.

(35) Hamilton, J. G.; Ivin, K. T.; McCann, G. M.; Rooney, J. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1379. Thoi, H. H.; Ivin, K. J.; Rooney, J. J. *J. Mol. Catal.* **1982**, *15*, 245. Reference 24a.

transition state for titanacyclobutane formation explains satisfactorily the polynorbornene cis to trans ratio reported here.

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.[36] The sixth column of Table III lists corrected molecular weight data for the ring-opened polynorbornenes reported here. Comparison with theoretical values suggests high efficiencies in catalyst for polymerization with **1** and **3**.

Since polymerizations with **1** have a slower rate of initiation than propagation while polymerizations with **3** show no induction period, the molecular weight distributions of polymers obtained form **1** should be broader than those of polymers made with **3**. As stated in the Results section, the polydispersity is always lower for polymers of comparable M_n when **3** is the catalyst. The d values of polymers from **1** rapidly decrease with increased conversion, while those for polymers from **3** remain roughly constant throughout the polymerization. This trend is consistent with slow first-order decay of initiator **1** and rapid initiation with **3**.

The molecular weight distributions obtained for catalysis by both **1** and **3** are narrow. Gold,[37] 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 **3** have polydispersities as low as 1.08. The extremely narrow distributions obtained by some anionic systems[38] were not obtained here. One factor in this system which may broaden the distribution is the presence of the two different propagating species **4c** and **4t** with different stabilities and different rates of propagation.

Conclusions

Narrow and controlled molecular weights in product polymers, high efficiency in catalyst, absence of chain transfer or termination, and characterizable chain-carrying intermediates are requirements of a living polymerization system.[39] Since the polymerizations of norbornene initiated by titanacyclobutanes **1** and **3** have these characteristics, they are living. While a number of anionic[40] and cationic[41,42] living polymers are known, there are few examples of coordinative polymerization systems that are living.[43] This system is the only living polymerization system for the ring-opening polymerization of cyclic olefins reported to date.[44-47] 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.

Titanacyclobutanes are unique among metathesis systems in that the metallacycles appear to be the principal chain-carrying species rather than metal carbenes.[2b,5] Titanacyclobutanes **1**, **3**, and **4** 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[2b]—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 **1** and **3**.

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 an MO-40-1 purification train and a DK-3E Dri-Kool.

Materials. Tebbe reagent[9] and metallacycle **2**[7] were prepared according to literature procedures. Norbornene was purchased from Aldrich Chemical Co. and was refluxed over sodium and distilled prior to use. The norbornene-*2,3*-d_2[48] was kindly provided by Dr. J. K. Stille. *N,N*-Dimethylaminopyridine (Aldrich) and benzophenone (Aldrich) were recrystallized from hot toluene. Dimethyl sulfide, 1,1-diphenylethylene, tetraphenylethylene, 2,6-di-*tert*-butyl-4-methylphenol (BHT), and Sudan III dye were purchased from Aldrich Chemical Co. *trans*-1,2-Diphenylethylene was purchased from MCB Reagents. Cyclopentane-1,3-dicarboxaldehyde was prepared according to a literature procedure.[49] 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 ^{1}H; 22.53 MHz ^{13}C), a JEOL GX-400 (399.65 MHz ^{1}H; 100.40 MHz ^{13}C; 61.25 MHz ^{2}H), or a Bruker WM-500 (500.13 MHz ^{1}H). Temperatures were measured by using $\Delta\nu(CH_2OH)_2$ and were constant to ±0.5 °C. Difference NOE experiments were performed according to published procedures.[50] 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 × 15 m DB1). Preparative gas chromatography was performed on a Varian Aerograph Model 920 instrument with a 5 ft × 1/4 in. 15% SE-30 on Chromosorb W column (column a) or a 2 ft × 1/4 in. 5% SE-30 on Chromosorb W column (column b). 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. 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,

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(36) Katz, T. J.; Lee, S. J.; Acton, N. *Tetrahedron Lett.* **1976**, 4247. Katz, T. J.; Acton, N. *Ibid.* **1976**, 4251.

(37) Gold, L. *J. Chem. Phys.* **1958**, *28*, 91.

(38) Polydispersities as low as 1.01 have been obtained. Morton, M.; Fetters, L. J. *Rubber Chem. Technol.* **1975**, *48*, 359.

(39) Flory, P. *J. Am. Chem. Soc.* **1940**, *62*, 1561.

(40) Szwarc, M. "Carbanions, Living Polymers, and Electron Transfer Processes"; Wiley-Interscience Publications: New York, 1968. Szwarc, M. In "Advances in Polymer Science"; Springer-Verlag: Berlin, 1983; Vol. 49.

(41) Miyamoto, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1984**, *17*, 265. Mandal, B. M.; Kennedy, J. P. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 833. Yamshita, Y.; Chiba, K. *Polym. J.* **1973**, *4*, 200. Berger, G.; Levy, M.; Vofsi, D. *J. Polymn. Sci. B* **1966**, *4*, 183. Dreyfuss, M. P.; Dreyfuss, P. *Polymer* **1965**, *6*, 93.

(42) Lal, J. "Elastomers and Rubber Elasticity"; Marke, J. E., Ed.; ACS: Washington, D.C., 1982; ACS Symp. Ser. No. 193, pp 214–227.

(43) See, for example: Hadjiandreou, P.; Julémont, M.; Teyssié, P. *Macromolecules* **1984**, *17*, 2455 and ref 6 therein. Doi, Y.; Ueki, S.; Keii, T. *Macromolecules* **1979**, *12*, 814. Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706. Hetler, W. R.; Sogah, D. Y.; Webster, O. W.; Trost, B. M. *Macromolecules* **1984**, *17*, 1415.

(44) One patent claims the preparation of polynorbornene with controlled molecular weight. Fr. Demande 2, 298.560 (Nippon Oil Co.). *Chem. Abstr.* **1977**, *86*, 122050n.

(45) A polypentenamer with a narrow molecular weight distribution has been prepared. The distribution, however, broadens with time. Pakuro, N. I.; Gantmakher, A. R.; Dolgoblosk, B. A. *Dokl. Akad. Nauk. SSSR* **1975**, *223*, 868, as discussed in ref 2a, p 228.

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Lincoln. Oil bath temperatures for all polymerizations were maintained at 65.0 ± 0.2 °C by use of an I^2R Therm-O-Watch. Ozone was obtained with use of a Welsbach generator.

Preparation of 1. A solution of norbornene (3.3 g, 35.8 mmol) in CH_2Cl_2 (7 mL) was degassed by 3 freeze–pump–thaw cycles. Addition of the norbornene solution to Tebbe reagent (5.0 g, 17.6 mmol) dissolved in 13 mL of 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 **1** as red crystals. ^{1}H NMR (500 MHz, C_6D_6) assignment as in Figure 1a and shifts vs. residual solvent: δ 5.47 (s, 5 H, Cp_1), 5.29 (s, 5 H, Cp_2), 3.51 (d, J_{14} = 9.0 Hz, 1 H, H_1), 3.11 (dd, J_{24} = 10.5 Hz, J_{23} = 8.5 Hz, 1 H, H_2), 2.27 (br s, 1 H, H_6), 2.25 (br s, 1 H, H_5), 1.91 (pt, J_{32} = 8.5 Hz, J_{34} = 8.5 Hz, J_{34} = 8.5 Hz, 1 H, H_3), 1.67 (m, 2 H, H_9 and H_{10}),1.22 (m, 2 H, H_{11} and H_{12}), 1.08 (d, J_{78} = 9.0 Hz, 1 H, H_7), 0.86 (d, J_{87} = 9.0 Hz, 1 H, H_8), 0.14 (pq, J_{41} = 9.0 Hz, J_{42} = 10.5 Hz, J_{43} = 8.5 Hz, 1 H, 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 ^{1}H spectrum was aided by a two-dimensional ^{1}H–^{1}H correlated spectrum. ^{13}C NMR (22.53 MHz, C_6D_6) chemical shifts vs. C_6D_6: δ 109.22, 108.44, 107.46 (C_α), 76.40 (C_α'), 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 ^{1}H–^{13}C correlated spectrum. Anal. Calcd for $C_{18}H_{22}Ti$: C, 75.52; H, 7.75. Found: C, 75.28; H, 7.84.

Preparation of 3. To **2** (0.25 g, 9.6 mmol) was added a solution of norbornene (0.15 g, 15.6 mmol) in benzene (3 mL). The reaction mixture was stirred for 1.5 h at 20 °C. Volatiles were removed under vacuum to afford 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 **3** with roughly 30% impurity assigned as **4** (n = 0). The estimate of the relative amount of **4** is based on integration of the ^{1}H NMR signals at δ 0.08 and −0.22. Reaction of **2** (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 **3** with 30% **4**. An identical reaction stirred for 3 h at 20 °C shows 50% **4**. ^{1}H NMR (400 MHz, C_6D_6) assignment as in Figure 2b, peaks attributed to **4** indicated by I, and shifts vs. residual solvent: δ 6.14 (dd, J_{45} = 17.5 Hz, J_{46} = 10.5 Hz, 1 H, H_4), 5.49 (5 H, Cp), 5.46 (5 H, Cp), 5.43–5.31 (I, singlets, Cp), 5.04 (dd, J_{54} = 17.5 Hz, J_{56} = 1.5 Hz, 1 H, H_5), 4.97 (dd, J_{64} = 10.5 Hz, J_{65} = 1.5 Hz, 1 H, H_6), 3.72 (br d, J_{13}= 10.0 Hz, 1 H, H_1), 3.66 (I, m, H_α), 2.63 (d, J_{23} = 11.0 Hz, 1 H, H_2), 2.41 (br s, 1 H, H_8), 2.30 (s, 1 H, H_7), 1.67 (m, 2 H), 1.21–1.17 (m, 3 H), 1.18 (s, 3 H, Me), 1.12 (s, 3 H, Me), 0.90 (d, 1 H, J = 12.0 Hz), 0.08 (pt, J_{31} = 10.5 Hz, J_{32} = 10.5 Hz, 1 H, 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. ^{13}C NMR (400 MHz, C_6D_6) chemical shifts vs. C_6D_6: δ 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. 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 1 with Benzophenone. To three flasks, each containing **1** (50 mg, 0.17 mmol) in 1.5 mL of 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 the mixture was cooled 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 **5a**, **6a**, and **7a** were determined by capillary VPC analysis of the solutions. Response factors for **6a** and **7a** were assumed on the basis of carbon number.

Isolation of 5a, 6a, and 7a. To **1** (0.15 g, 0.52 mmol) in 4.0 mL of C_6H_6 was added benzophenone (0.10 g, 0.55 mmol). The solution was stirred at 65 °C for 10 h. After being cooled to 23 °C, the solution was diluted with 20 mL of 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 of 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 peaks. Preliminary purification by preparative layer chromatography (silica, hexane) was followed by isolation of the three fractions by preparative VPC on column a.

5a (6.0 mg): Identification based on comparison of NMR spectral data with data from an authentic sample and by coinjection by capillary VPC.

6a (13.0 mg): ^{1}H NMR (500 MHz, $CDCl_3$) shifts vs. added Me_4Si: δ 7.4–7.1 (m, 10 H), 5.97 (d, 1 H), 5.80 (ddd, 1 H), 4.96 (d, 1 H), 4.88 (d, 1 H), 2.64 (m, 1 H), 2.45 (m, 1 H), 1.93 (m, 1 H), 1.80 (m, 2 H), 1.51 (m, 2 H), 1.25 (m, 1 H). ^{13}C NMR (22.53 MHz, $CDCl_3$) shifts vs. 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.

7a (2.0 mg): ^{1}H NMR (500 MHz, $CDCl_3$) shifts vs. added Me_4Si: δ 7.4–7.1 (m, 10 H), 5.97 (d, 1 H), 5.79 (m, 1 H), 5.22 (m, 1 H), 4.96 (d, 1 H), 4.86 (d, 1 H), 2.8–2.3 (m, 4 H), 1.9–0.9 (m, 12 H); 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 6a and 7a. To a solution of 4.5 mg of **6a** in 1.0 mL of 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 a 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 dimethyl sulfoxide, *cis*-1,3-dicarboxycyclopentane, and benzophenone. The molar ratio of benzophenone to dialdehyde was 1.0:0.7. Response factors were measured by using authentic samples.

Ozonolysis of **7a** was performed as described above with 0.6 mg of **7a** in 0.25 mL of MeOH. The molar ratio of benzophenone to dialdehyde was 1.0:1.7.

Reaction of 3 with Benzophenone. To two flasks, each containing **2** (50 mg, 0.19 mmol) in 1.0 mL of 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 of 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 the solutions were cooled 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 **8a** and **9a** were determined by capillary VPC analysis of the solutions. Response factors were assumed on the basis of carbon number.

Isolation of 8a and 9a. To **2** (50 mg, 0.19 mmol) in 1.0 mL of C_6D_6 was added norbornene (40 mg, 0.42 mmol). The solution was stirred for 1.5 h at 23 °C. Volatiles were removed under vacuum, 1.0 mL of C_6D_6 and 70 mg of benzophenone (0.38 mmol) were added, and the solution was stirred at 40 °C for 10 h. After the mixture was cooled to 23 °C, 10 mL of 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 **8a**. 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 **9a** is based primarily on high-resolution GC/MS results.

8a: ^{1}H NMR (400 MHz, $CDCl_3$) shift vs. added Me_4Si: δ 7.4–7.1 (m, 10 H), 5.95 (d, 1 H, J = 9.8 Hz), 5.77 (dd, 1 H, J = 10.6, 17.4 Hz), 5.35 (d, 1 H, J = 15.6 Hz), 5.29 (dd, 1 H, J = 6.1, 15.6 Hz), 4.90 (dd, 1 H, J = 15.0, 17.4 Hz), 4.87 (dd, 1 H, J = 1.5, 10.6 Hz), 2.58 (m, 1 H), 2.37 (m, 1 H), 1.86 (m, 1 H), 1.75 (m, 2 H), 1.51 (m, 1 H), 1.42 (m, 1 H), 1.22 (m, 1 H), 1.05 (s, 6 H). ^{13}C NMR (100.40 MHz, $CDCl_3$) shift vs. 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.

9a: ^{1}H NMR (400 MHz, $CDCl_3$) shift vs. added Me_4Si: 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 8a and 9a. The products **8a** and **9a** were ozonized by the same procedure described above for **6a** and **7a**. Solutions of 1.0 mg of **8a** or **9a** in 0.25 mL of MeOH were used. The molar ratio of benzophenone to *cis*-1,3-dicarboxycyclopentane obtained for **8a** was 1.0:0.5 and that obtained for **9a** 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 of benzene and 0.5 mL of octane. The solution was further degassed by 2 freeze–pump–thaw cycles and then diluted with additional benzene to 50 mL total volume (1.75 M).

To **1** (20 mg, 0.07 mmol) or **2** (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 of 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 of 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 of **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 a flow rate of 1.0 mL/min were used. Calibration was based on narrow dispersity polystyrene standards (Polysciences) ranging from MW = 3550 to 600000 and was repeated with each analysis. The molecular weight averages and distribution were calculated by standard procedures[50] from the refractive index trace and were not corrected for peak broadening.

Kinetics of Polymerization with 1 and 3. Stock 0.09 and 0.18 M solutions of **1** and **2** in C_6D_6 were prepared. A stock 5.3 M solution of norbornene in C_6D_6 containing 0.4 M added C_6H_6 was prepared. NMR tubes (5 mL) were charged with appropriate aliquots of the stock solutions diluted where necessary with additional C_6D_6 to provide 0.5 mL total solution. The tubes were kept at 23 °C for 1.5 h to allow for conversion of **2** to **3** 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 the samples were allowed 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_6H_6 signal. To obtain rate data for polymerization with **1** 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] vs. t yielded k_{obsd}. Activation parameters were obtained from least-squares analysis of ln k_1/T vs. $1/T$ plots, where $k_1 = k_{obsd}/[\text{catalyst}]$.

Kinetics of Disappearance of 1. An NMR sample with $[\mathbf{1}]_0 = 0.035$ M and $[\mathrm{N}]_0 = 3.2$ M was prepared form stock solutions as described above and stored at −10 °C until use. Approximately 2 μL of 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 sample was allowed to reach thermal equilibrium, spectra were obtained at regular intervals. The disappearance of **1** was monitored by integration of the signal for H_α of **1** at δ 3.51 vs 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 Figure 7).

Incorporation of Norbornene-d_2 into the Polymer. To **2** (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 and then at 65 °C for 1 h. The volatiles were removed under vacuum and replaced with 0.5 mL of C_6D_6. A ^{1}H NMR spectrum was recorded. The C_6D_6 was removed under vacuum and replaced with 0.5 mL of C_6H_6 containing 12 mg (0.12 mmol) of norbornene-d_2. A ^{2}H NMR spectrum was recorded. The NMR tube was heated at 60 °C in the probe for the JEOL GX-400 for 30 min, allowing polymerization of 90% of the norbornene-d_2. The sample was cooled and a ^{2}H spectrum was recorded. The volatiles were removed under vacuum and replaced with 0.5 mL of C_6D_6 containing 20 mg (0.21 mmol) of norbornene. A ^{1}H NMR spectrum was recorded. The NMR tube was heated t 65 °C in the probe of the NMR spectrometer for 15 min. The sample was cooled and a ^{1}H spectrum was recorded. The volatiles were removed under vacuum and replaced with 0.5 mL of C_6H_6. A ^{2}H spectrum was recorded. All spectra were recorded at 23 °C.

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Supplementary Material Available: Two-dimensional ^{1}H–^{1}H correlated NMR spectra of **1** and **3**, two-dimensional ^{13}C–^{1}H correlated NMR spectra of **1** and **3**, and details of the two-dimensional NMR experiments (5 pages). Ordering information is given on any current masthead page.

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