Macromolecules **1989**, *22*, 3205-3210

Di- and Tetrafunctional Initiators for the Living Ring-Opening Olefin Metathesis Polymerization of Strained Cyclic Olefins[†]

Wilhelm Risse, David R. Wheeler, Louis F. Cannizzo, and Robert H. Grubbs*

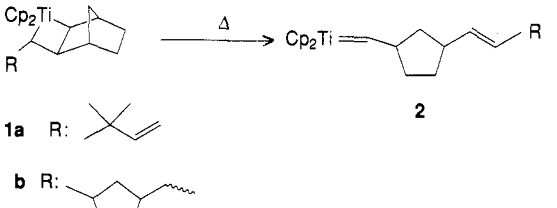
Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125.

Received September 20, 1988; Revised Manuscript Received January 4, 1989

ABSTRACT: The low-temperature photochemical reaction of a titanacyclobutane compound with molecules containing two and four norbornene rings gave bis- and tetrakis(titanacyclobutanes). These compounds were applied as di- and tetrafunctional initiators for the living ring-opening olefin metathesis polymerization (ROMP) of norbornene. The rate of polymerization proceeded at approximately 2 and 4 times the rate of polymerization with a monometallacycle compound. The resulting living polymers were end-capped by Wittig reactions with ketones. Polymers of controlled molecular weight (M_n = 5540–10 700) with polydispersity indexes (PDIs) of 1.15–1.49 were prepared.

Introduction

α,β,α'-Trisubstituted[1] bis(η^5-cyclopentadienyl)titanacyclobutanes 1 derived from strained cyclic olefins such as norbornene cleave thermally in a productive fashion (eq 1) to relieve the ring strain. In the presence of excess norbornene, the unstable carbene structure 2 is trapped to form a new titanacycle. Repeated metallacycle cleavage and formation results in the living ring-opening olefin metathesis polymerization (ROMP) of norbornene.[2,3]



(1)

Titanacyclobutane 3,[4] derived from 3,3-dimethylcyclopropene, is an initiator for the synthesis of polynorbornene living at one end.

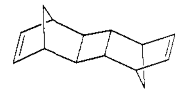
3

The present work demonstrates the novel synthesis of two-ended, living polynorbornene from bis(titanacyclobutane) compounds and the preparation of star-shaped polynorbornene from a tetrakis(titanacyclobutane)derivative.

Results and Discussion

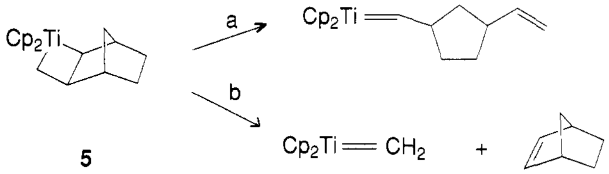
Synthesis of Di- and Tetrafunctional Initiators. The ring-opening polymerization of norbornene with chain growth in two or more directions requires a molecule that incorporates two or more identical units capable of initiating the polymerization. For this purpose, we synthesized compounds containing two or four titanacyclobutane structures. Obtaining a narrow molecular weight distribution of the resulting polymers requires that all initiating metallacycle units undergo productive metathesis at a rate similar to or higher than the rate of chain propagation. We considered structures containing several equivalent titanacyclobutane units derived from the same strained cyclic olefin to be good candidates to serve as multifunctional initiators.

The (2 + 2) cycloaddition of norbornadiene catalyzed by hexacarbonylbis(triphenylphosphine)dicobalt(0)[5] is known to give a mixture of the *exo-trans-exo*-diene 4 and the isomeric *exo-trans-endo*-diene along with higher molecular weight material. Diene 4 was isolated by preparative scale vapor-phase chromatography. This diene was used in the synthesis of a bis(titanacyclobutane) complex.



4

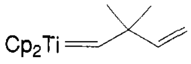
It has been shown that metallacycle 5 cleaves both productively (eq 2a) and nonproductively (eq 2b).[1] The formation of "$Cp_2Ti{=}CH_2$" would reduce the functionality of a multifunctional initiator, resulting in a less well-defined polymerization. Therefore, to ensure the exclusive productive cleavage, it is more desirable to use α,β,α'-trisubstituted titanacyclobutane derivatives than the corresponding α,β-disubstituted metallacycles.



(2)

Monometallacycle 1a could not be cleanly prepared by the thermochemical reaction of 3 with norbornene. Even at temperatures as low as 20 °C, formation of 1a competes with ring-opening and the addition of a second equivalent of norbornene to 1a.[2] Similar behavior was observed when 4 was reacted with 3 at temperatures between 0 and 20 °C. Monitoring the reaction by ^{1}H NMR spectroscopy revealed that when the olefinic signals of 4 had totally disappeared, approximately 50% of 3 remained unreacted. No reaction occurred at temperatures lower than 0 °C.

A recent study[6] demonstrated that 3 could be ring-opened at temperatures well below 0 °C by low-temperature photolysis. This reaction generates the same titanium alkylidene 6 from 3 as does thermolysis. This reaction was used to generate titanacycle 1a that was not contaminated with higher oligomers. The photochemical reaction of 1a and norbornene (λ > 300 nm) for 1.5 h at −78 °C yielded 1a in greater than 90% yield. Metallacycle 1a is relatively inert photochemically; thus, no secondary photolysis products were observed after 1.5 h of reaction time.



6

[†] Contribution No. 7859.

0024-9297/89/2222-3205$01.50/0

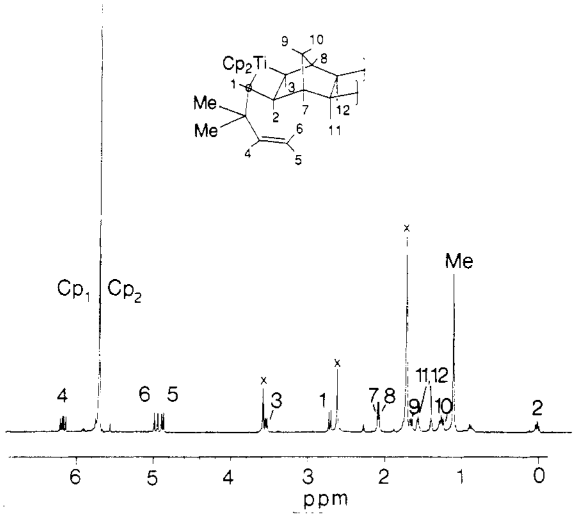
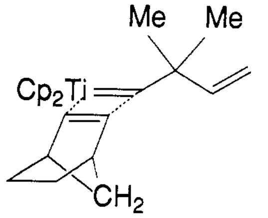


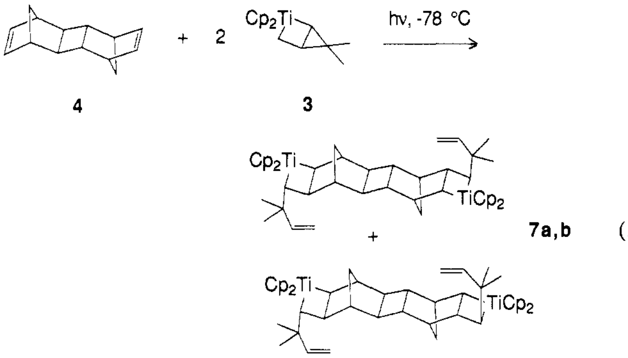
Figure 1. The 400-MHz ^{1}H NMR spectrum of bis(metallacycle) **7a,b** in d_8-THF (× = solvent signals at −20 °C.



6

Figure 2. Transition state for the approach of norbornene to the titanium alkylidene **6**.

In an analogous fashion, **3** was photolyzed in the presence of the diene **4** at −78 °C. The formation of two isomers **7a** and **7b**, which differ in the relative position of the Cp$_2$T fragments, was observed (eq 3).



(3)

The exclusive exo addition of a titanium alkylidene to norbornene has been previously established. The indicated trans configuration for the α'- and β-substituents of the metallacycle is based on the results of difference NOE experiments. Irradiation of the proton signal at 1.10 ppm (corresponding to the two methyl groups of the α'-substituent) enhances signals at 0.02, 2.08, 2.70, and 4.96 ppm, assigned as H$_2$, H$_7$, H$_1$, and H$_6$, respectively (see Figure 1) without substantial enhancement of the signal for the bridge proton H$_9$. The trans configuration of the α'- and β-substituents indicates that the photochemical formation of the trisubstituted titanacyclobutane structure proceeds predominantly by a transition state in which the norbornene approaches the alkylidene with the –(CH$_2$)– bridge pointing away from the two methyl groups, as outlined in Figure 2.

This transition state is also preferred in the thermochemical polymerization of norbornene initiated by **3** at 75 °C. The resulting polymer contains a 3,3-dimethyl-1,4-pentadienyl end group with a 75% trans configuration for the internal olefinic double bond. The stereochemistry was determined by ^{1}H NMR spectroscopy (Figure 3).

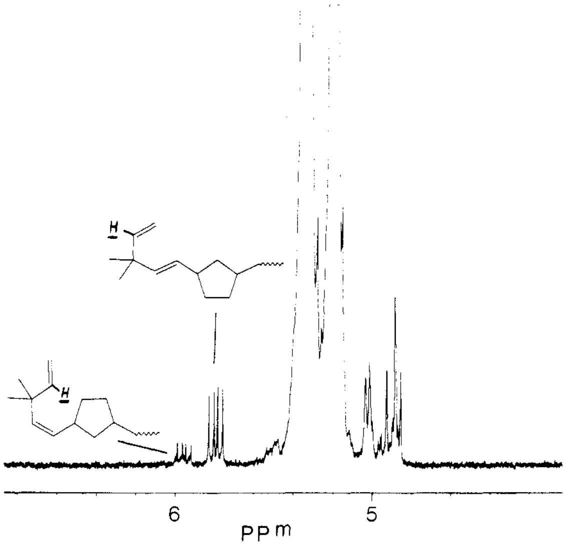
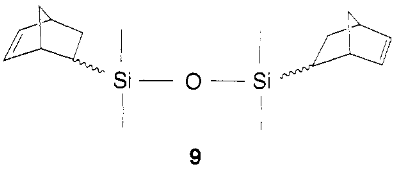


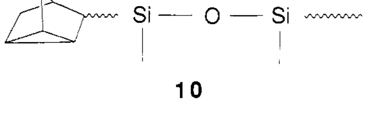
Figure 3. The 400-MHz ^{1}H NMR spectrum (CDCl$_3$) of the olefinic region of polynorbornene obtained by thermolysis of initiator **3** in the presence of norbornene. The signals at δ 5.78 and 5.94 correspond to the indicated proton of the 3,3-dimethyl-1,4-pentadienyl end group with trans and cis configuration, respectively, for the internal olefinic double bond.

The photolytic generation of **7a,b** was carried out in d_8-THF (THF = tetrahydrofuran) and d_8-toluene. In both solvents, one of the isomeric bis(titanacycles) precipitated from solutions stored at −20 °C (the maximum temperature for storing the solutions for 48 h without decomposition). Isomers **7a** and **7b** exhibit significantly different chemical shifts in d_8-toluene (in contrast to d_8-THF), thus allowing the precipitation process to be followed by ^{1}H NMR spectroscopy (Figure 4a,b). After 24 h, the intensity of the signals at 1.18, 1.30, 2.22, 2,36, and 3.63 ppm for the two diastereotopic methyl groups, H$_7$, H$_8$, and H$_3$, respectively, is decreased (Figure 4b). The corresponding signals for the dominating species at δ 1.13, 1.22, 2.32, 2.42, and 3.68 are nearly identical with the signals for **1a** (δ 1.11, 1.20, 2.30, 2.42, and 3.70; Figure 4c). The long-range shielding effect[7] of the α'-substituent is expected to be similar for **1a** and the centrosymmetric isomer **7a**. This suggests that **7b** with the C_2 symmetry axis is the less soluble isomer.

Hydrosilation[8,9] of norbornadiene results in compounds with two and more norbornene units. Norbornadiene and 1,1,3,3-tetramethyldisiloxane were reacted at 80 °C in the presence of 0.5 mol % of hexachloroplatinic acid to give disiloxane **9** (six different isomers). The exo/endo rate is 58/42 (determined by ^{1}H NMR spectroscopy, Figure 5). Nine percent of the hydrosilation proceeded by an undesirable side reaction, 2,6-addition, to provide the nortricyclene structure **10**.



9



10

Table I
Polynorbornene with Diphenylethenyl End Groups, Prepared from Di- and Tetrametallacyclobutanes

no.	I[a]	T/°C[b]	M_n(theor)[c]	M_n(GPC)[d]	M_n(corr)[e]	PDI[f]	f[g]
1	**7a,b**	75	7300	15900	8250	1.1	1.8
2	**7a,b**	70	9700	20700	10700	1.3	1.8
3	**12**	75	4700	10700	5540	1.3	1.7
4	**13**	75	13400	17700	9170	1.5	3.1

[a] Multifunctional initiator. [b] Reaction temperature. [c] Molecular weight calculated from the ratio of monomer to initiator. [d] Number average molecular weight determined by GPC (vs polystyrene standards). [e] Corrected molecular weight determined by dividing M_n(GPC) by a factor of 1.93. [f] Polydispersity index. [g] Number of diphenylethenyl end groups determined by ^{1}H NMR spectroscopy.

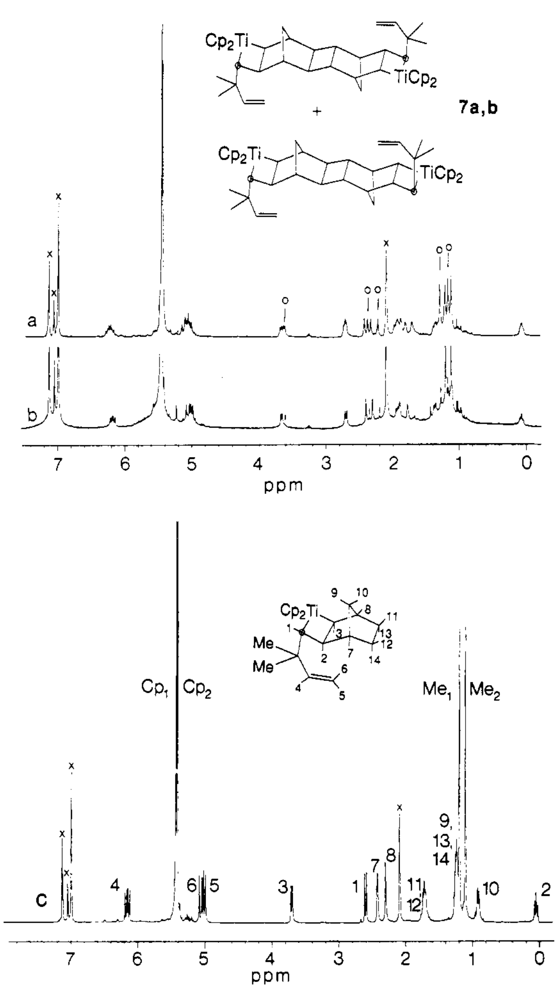
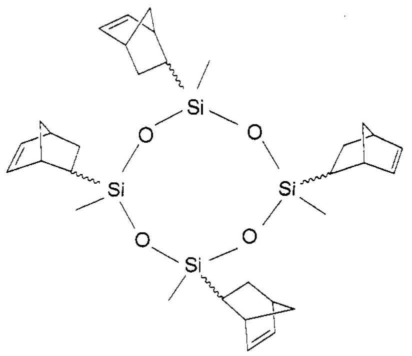


Figure 4. ^{1}H NMR spectra of **7a,b** (d_8-toluene) (a) immediately after the synthesis (× = solvent signals, ○ = signals for the less soluble isomer) and (b) after 24 h at −20 °C; (c) ^{1}H NMR spectrum of **1a** (in d_8-toluene). All spectra at −20 °C.

Under the same conditions, the reaction of norbornadiene and 1,3,5,7-tetramethylcyclotetrasiloxane gave the tetraolefin **11** (in theory, 64 isomers are possible).



11

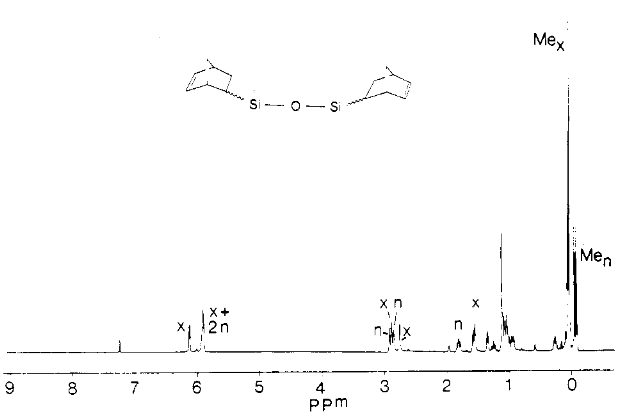
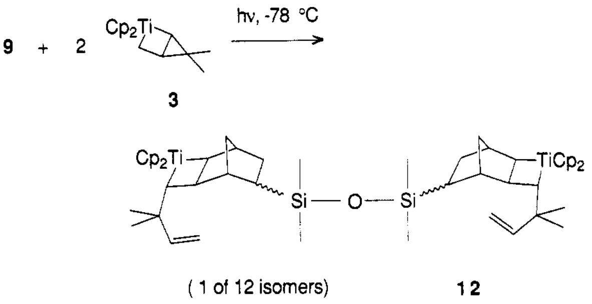
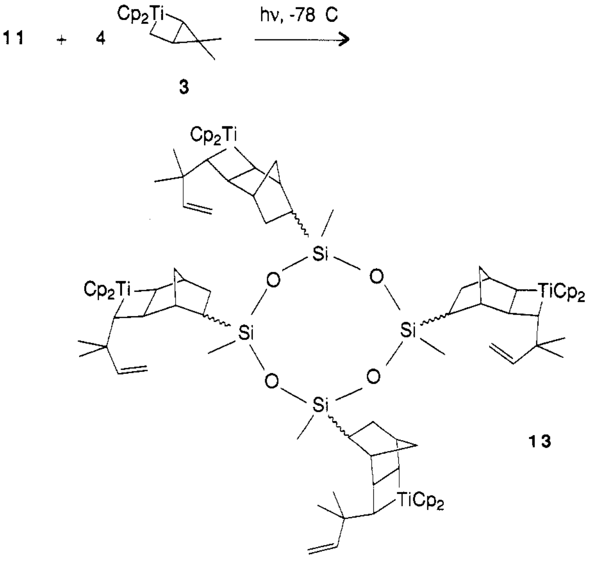


Figure 5. ^{1}H NMR spectrum of diolefin **9** (CDCl$_3$). Signals × and n correspond to protons of the exo and endo isomers, respectively.

Diolefin **9** and tetraolefin **11** were subjected to low-temperature photolysis in the presence of 2 and 4 equiv of **3**, respectively, to produce bis(metallacycle) **12** (eq 4) and tetrakis(metallacycle) **13** (eq 5).



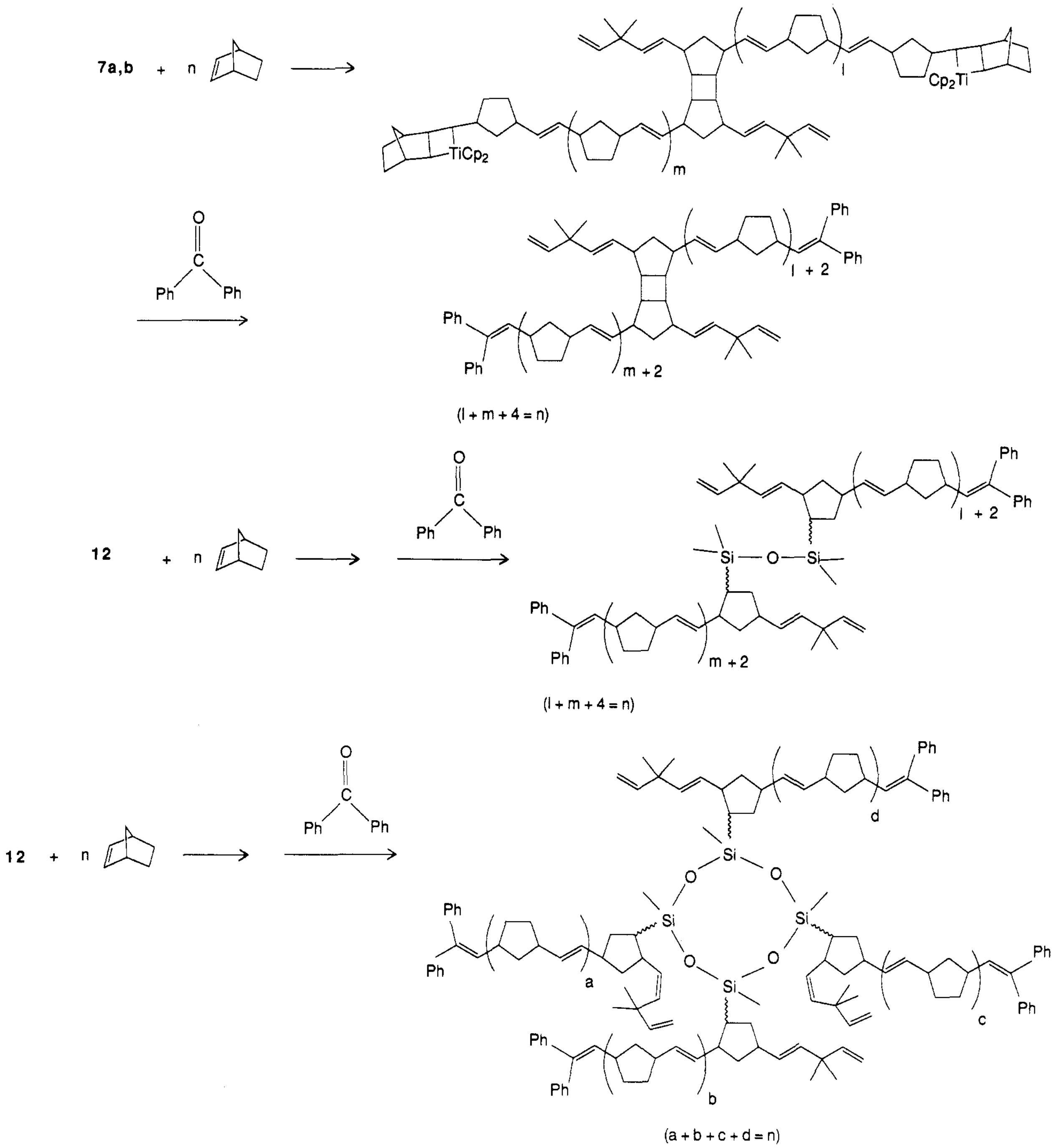
(4)



(5)

Polymerization of Norbornene. Bis(metallacycles) **7a,b** and **12** and tetrakis(metallacycle) **13** were prepared in situ and used as initiators for the polymerization of norbornene (Table I). The conversion of norbornene to

Scheme I



(6a)

(6b)

(6c)

polynorbornene was monitored by ^{1}H NMR spectroscopy. All the polymerizations showed a zero-order dependence of the polymerization rate on the concentration of monomer, which corresponds to the zero-order kinetics of norbornene polymerization with monometallacycle **3**.[2] The monomer consumption rate was 50 and 44 equiv/h at 75 °C for polymerizations with **7a,b** and **12**, respectively. These rates correspond to twice the rate of polymerization with **3** (22.7 equiv/h at 73 °C).[2] The polymerization with the tetrakis(metallacycle) proceeded at approximately 4 times this value (87 equiv/h). The resulting metallacycle-ended polymers were reacted with benzophenone to give polynorbornene chains with diphenylethenyl end groups (eq 6a–c Scheme I). These end groups are suitable to determine the number of propagation sites. Previous studies[10] have demonstrated a high efficiency (84–100% conversion) for this Wittig reaction of titanacyclobutanes linked to a polymer chain.

The number of diphenylethenyl end groups (equivalent to the number of living end groups) was determined by ^{1}H NMR spectroscopy by determining the ratio of the intensity of the signals for the aromatic protons (d 7.10–7.40, m, 10 H) to the intensity of the signals for the olefinic (d 5.20–5.35, m) and the allylic protons (d 2.84, m; 2.49, m) of the polynorbornene chain. The calculated ratios are given in column 7 of Table I. The molecular weights of the polymers (Table I) were determined by gel permeation chromatography (GPC). Previous work[11] has shown that polystyrene standards give approximately twice the correct value of the molecular weight for polynorbornene. A correction factor of 1.93 (determined by vapor-phase osmometry)[12] was used in Table I to give a more realistic estimate of the molecular weights.

Among the multifunctional initiators of Table I, the bismetallacycle **7a,b** derived from the norbornadiene dimer **4** gave the lowest polydispersities. The polymerization with

7a,b at 75 °C (first polymerization of Table I) resulted in a narrower molecular weight distribution (PDI = 1.15) than the reaction at 70 °C (PDI = 1.27). This is probably due to the precipitation of a small fraction of **7a,b** during the photochemical synthesis. The precipitate dissolved at 75 °C within about 2 min, allowing uniform initiation for the first polymerization of Table I. The much slower dissolution of the precipitate at 70 °C (within 20 min) resulted in a longer initiation period and hence a higher polydispersity. The GPC curve of the polymer prepared from the disiloxane-based initiator **12** shows a small shoulder at about half the molecular weight of the peak molecular weight, resulting in an increased value for the polydispersity index (PDI = 1.32). Apparently, a small amount of initiator molecules are monofunctional due to the presence of the nortricyclene structure **10**. Incorporation of **12** into the polymer chain is demonstrated by the NMR spectrum, which shows a broad signal at δ 0.06 corresponding to the $-SiMe_2$ protons.

M_n(corr) for the product of the fourth polymerization of Table I is an approximate value and is considerably smaller than the theoretical molecular weight calculated from the ratio of monomer/initiator. This M_n(corr) is expected to be in error since the hydrodynamic volume of the star-branched polymer has a different molecular weight dependence than the related linear products. The high PDI (1.5) and low end group analysis (3.1) for this polymer are due to a number of factors. The GPC curve for this star-branched polymer is biomodal and shows about 20 wt % of a low molecular weight fraction. In addition, the average number of growing arms is expected to be less than 4 per initiator due to the inefficiency (91% selectivity to the norbornene functionality) of the hydrosilation reaction. If each arm of the star is formed with 91% selectivity, only 69% of the initiators have four living arms. Improvements in this approach will require developments in the hydrosilation catalysis and not the polymerization reactions.

Conclusion and Outlook

Compounds with two or four titanacyclobutane structures have been developed for the initiation of ring-opening olefin metathesis polymerization. These initiators provide for polymer growth in two and four directions. A previous study[14] has shown that well-defined block copolymers with narrow molecular weight distributions can be prepared by the subsequent addition of differnt cyclic olefins, such as *endo-* and *exo*-dicyclopentadiene, benzonorbornadiene, and 6-methylbenzonorbornadiene. The synthesis of an ABA-type triblock copolymer with a monofunctional initiator requires two changes of monomers and thus three different polymerization steps. In the future, ABA-block copolymers can be made from bis(metallacyclobutanes) by preparing the middle block B first and changing monomer only once. Another new application can be the connection of a two-ended living soft segment B with two hard segments A containing carbonyl end groups to give a triblock copolymer with the properties of a thermoplastic elastomer.

Experimental Section

General Procedures. All work involving air- and/or moisture-sensitive compounds was performed using standard high-vacuum, Schlenk, or drybox (Vacuum Atmospheres) techniques. Argon was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4-Å molecular sieves. ^1H NMR spectra were recorded on JEOL FX-90Q (89.60 MHz) and JEOL GX-400 (399.65 MHz) spectrometers. Difference NOE experiments were performed according to published procedures.[15]

Preparative gas chromatography was carried out on a Varian Aerograph Model 920 instrument with a 5 ft × 1/4 in. 15% SE-30 on Chromosorb W column. Flash chromatography was performed by the procedure of Still et al.[16] using silica gel 60 (230–400 mesh ATM, EM reagents).

Gel permeation chromatography utilized Shodex KF-803, KF-804, and KF-805 columns and a Knauer differential refractometer. All GPC analyses were performed on 0.5% w/v solutions of polymer in dichloromethane. An injection volume of 0.200 mL and a flow rate of 1.5 mL/min were used. Calibration was based on narrow-dispersity polystyrene standards (Polysciences) ranging from M_n = 3550 to 600 000. The molecular weight averages and distribution were calculated by standard procedures from the refractive index and were not corrected for peak broadening.[17]

A 350-W high-pressure Hanovia lamp was used for the photochemical reactions. A Pyrex Dewar (transparent for $\lambda \geq 300$ nm) was used for cooling (dry ice/isopropyl alcohol) to −78 °C The photolysis reactions were performed in a Young NMR tube equipped with a Teflon valve. Oil bath temperatures for all polymerizations were maintained at a constant value (±0.3 °C) by use of a I^2R Therm-O-Watch.

Materials. Metallacycle **3** was prepared as previously described.[4] Norbornene and norbornadiene were purchased from Aldrich, refluxed over Na, and distilled prior to use. Benzophenone (Aldrich) was recrystallized from toluene. Hexacarbonylbis(triphenylphosphine)dicobalt(0) (Alfa) and hexachloroplatinic acid (hydrate) (Aldrich) were used without any further purification. *exo-trans-exo*-Diene **4** was prepared according to the procedure by Trecker et al.[5] and purified by preparative gas chromatography. 1,1,3,3-Tetramethyldisiloxane and 1,3,5,7-tetramethylcyclotetrasiloxane (Petrarch) were distilled under argon. Toluene, d_8-toluene, and d_8-THF were vacuum transferred first from Na and then from Na/K into a dry vessel equipped with a Teflon valve closure and stored under argon.

Preparation of 1a. A NMR tube (Young) equipped with a Teflon valve closure was charged with 5.3 mg (20.2 μmol) of titanacycle **3** and 2.3 mg (24.5 μmol) of norbornene. Toluene (0.5 mL) was added, and the NMR tube was cooled to −78 °C. The dark red solution was photolyzed at −78 °C for 1.5 h. The solution was evaporated to dryness at −20 °C. d_8-Toluene was vacuum transferred onto the solid residue (96% yield). ^1H NMR at −20 °C, assignment as in Figure 4c and chemical shift vs residual solvent: δ 6.16 (dd, J_{45} = 10.7 Hz, J_{46} = 17.6 Hz, 1 H, H_4), 5.43 (s, 5 H, Cp), 5.41 (s, 5 H, Cp), 5.07 (d, J_{64} = 17.6 Hz, 1 H, H_6), 5.01 (d, J_{54} = 10.7 Hz, 1 H, H_5), 3.70 (d, J_{32} = 9.0 Hz, 1 H, H_3), 2.60 (d, J_{12} = 11.5 Hz, 1 H, H_1), 2.42 (br s, 1 H, H_7), 2.30 (br s, 1 H, H_8), 1.72 (br m, 2 H, $H_{11,12}$), 1.24 (br m, 3 H, $H_{9,13,14}$), 1.20 (s, 3 H, Me), 1.11 (s, 3 H, Me), 0.92 (d, $J_{10,9}$ = 9.7 Hz, 1 H, H_{10}), 0.05 (pt, J_{23} = 9.8 Hz, J_{21} = 10.7 Hz, 1 H, H_2). Assignment of the ^1H spectrum was aided by a two-dimensional ^1H–^1H correlated spectrum.

Preparation of 7a,b. A solution of 1.6 mg (8.70 μmol) of **4** and 5.1 mg (19.5 μmol) of titanacycle **3** in 0.5 mL of toluene was photolyzed at −78 °C for 1.5 h as in the preparation of **1** (94% yield). ^1H NMR (d_8-THF) at −20 °C, assignment as in Figure 1 and shifts vs residual solvent: δ 6.18 (dd, J_{45} = 17 Hz, J_{46} = 11 Hz, 1 H, H_4), 5.72 (5 H, Cp), 5.71 (5 H, Cp), 4.96 (d, J_{54} = 17 Hz, 1 H, H_5), 4.87 (d, J_{64} = 11 Hz, 1 H, H_6), 3.53 (d, J_{32} = 11 Hz, 1 H, H_3), 2.70 (d, J_{12} = 11 Hz, 1 H, H_1), 2.08 (s, 1 H, H_7), 2.07 (s, 1 H, H_8), 1.64 (d, $J_{9,10}$ = 9 Hz, 1 H, H_9), 1.58 (d, $J_{11,12}$ = 5 Hz, 1 H, H_{11} or H_{12}), 1.41 (d, $J_{12,11}$ = 5 Hz, H_{12} or H_{11}), 1.27 (d, $J_{10,9}$ = 9 Hz, 1 H, H_{10}), 1.10 (s, 3 H, Me), 1.09 (s, 3 H, Me), 0.02 (pt, J_{21} = 11 Hz, J_{23} = 11 Hz, H_2). Assignment of the ^1H spectrum was aided by a two-dimensional ^1H–^1H correlated spectrum.

Polymerization of Norbornene with 7a,b. In a NMR tube with a Teflon valve closure, a d_8-toluene solution of **7a,b** (8.7 μmol) was prepared as described previously. Norbornene (66.2 mg, 0.70 mmol) was vacuum transferred into the NMR tube. The reaction mixture was heated to 75 °C (oil bath), and the reaction was monitored by NMR spectroscopy. The polymerization was temporarily stopped by cooling with ice water after 28, 53, and 78 min of reaction time to record NMR spectra. After each stop, the reaction was restarted again by heating to 75 °C and finally ended after 94 min of reaction time (90% conversion). The conversion of monomer was determined from the intensity of the olefinic signals (δ 5.94) of unreacted norbornene and the residual protons of the solvent (δ 6.95–7.20). Benzophenone (55 mg, 30.2 μmol) was added and the mixture heated to 75 °C to cap the reactive titanacyclobutane end groups. The initial dark red solution became pale orange after 0.5 h. After cooling, the solution was flash chromatographed (toluene) and the solvent evaporated. The residue was redissolved in 0.5 mL of toluene. The polymer was isolated by precipitation with methanol. The polymer was redissolved in toluene and reprecipitated with methanol twice. The product was dried under vacuum (10^{-3} Torr) for 24 h, yield 45 mg (76%). The other polymerizations of Table I (with **12** and **13** as initiators) were performed in a similar fashion.

Preparation of 9. A Schlenk flask was charged with 6.76 g (73.5 mmol) of norbornadiene and 170 μL (38 μmol) of a H_2PtCl_6 solution (1 g of H_2PtCl_6 in 1 mL of ethanol and 9 mL of 1,2-dimethoxyethane). By syringe, 1.32 mL (7.46 mmol) of 1,1,3,3-tetramethyldisiloxane was added. The mixture was stirred for 8 h in an oil bath at 70 °C. The reaction mixture was flash chromatographed. The unreacted norbornadiene was removed by vacuum distillation. The product **9** was purified by distillation at 89 °C (7×10^{-3} Torr), isolated yield 2.06 g (89%). ^1H NMR ($CDCl_3$): δ 6.12 (dd, J_1 = 5.6 Hz, J_2 = 2.9 Hz, 1 H, H(x)), 5.90 (m, 3 H, H(x) + 2 H(n)), 2.92 (br s, 1 H, H(n)), 2.88 (br s, 1 H, H(x)), 2.85 (br s, 1 H, H(n)), 2.75 (br s, 1 H, H(x)), 1.96 (l, nortricyclene), 1.80 (m, 1 H, H(n)), 1.56 (m, 1 H, H(x)), 1.34 (d, J = 7.8 Hz, 1 H, H(n)), 1.24 (l, nortricyclene), 1.11–0.98 (m, 5 H, 3 H(x) + 2 H(n)), 0.93 (dd, J_1 = 5.6 Hz, J_2 = 11.0 Hz, 1 H, H(n)), 0.58 (l, nortricyclene), 0.26 (m, H, H(x)), 0.04 (m, 6 H, 2 Me, H(x)), −0.07 (m, 3 H, H(n)). (H(x) and H(n) correspond to protons of the exo and endo product, respectively). The exo/endo rate is 58/42.

Preparation of Tetraolefin 11. A mixture of 18 g (0.196 mol) of norbornadiene, 400 μL (89 μmol) of H_2PtCl_6 solution (same solution as for **9**), and 1.2 g (5 mmol) of 1,3,5,7-tetramethylcyclotetrasiloxane was heated to 80 °C for 12 h. The reaction mixture was flash chromatographed, and unreacted norbornadiene was removed by distillation. About 10 mol % of a mixture of norbornadiene dimers ((2 + 2) cycloadducts) was formed during the reaction. A vacuum (10^{-3} Torr, 25 °C) was applied for 12 h to remove the norbornadiene dimers, yield 2.9 g (95%) of a bright yellow oil. ^1H NMR ($CDCl_3$): δ 6.10 (br s, 1 H, H(x)), 5.94 (br s, 3 H, 1 H(x) + 2 H(n)), 2.93–2.80 (m, 4 H, 2 H(x) + 2 H(n)), 1.98 (l, nortricyclene), 1.79 (br s, 1 H, H(n)), 1.65 (br m, 1 H, H(x)), 1.33 (br s, 1 H, H(n)), 1.24 (l, nortricyclene), 1.15–0.95 (br m, 6 H, 3 H(x) + 3 H(n)), 0.62 (l, nortricyclene), 0.28 (br s, 1 H, H(x)), 0.08 (br m, 3 H, Me, H(x)), −0.06 (m, 3 H, Me, H(n)). H(x) and H(n) = protons of the exo and endo product, respectively. The exo/endo ratio is 50/50.

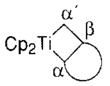
Generation of 12 and 13. Compounds **12** and **13** were prepared in situ by the photochemical reaction of **9** and **11** with 2 and 4 equiv of **3**, respectively. The reaction conditions were analogous to those used in the preparation of **7a**,**b**. **12**: ^1H NMR (d_8-toluene): 6.5–6.2 (br m, 1 H), 5.60–5.40 (m, 10 H), 5.2–5.0 (m, 2 H), 3.9–3.8 (m, 1 H), 2.75–2.42 (m, 2 H), 1.9–1.6 (m, 2 H), 1.5–1.0 (m, 8 H), 0.75 (m, 1 H), 0.4–0.3 (m, 6 H), 0.2 (m, 1 H). **13**: ^1H NMR (d_8-toluene): 6.5–6.2 (m, 1 H), 5.7–5.5 (m, 10 H), 5.1 (m, 2 H), 3.8 (br s, 1 H), 2.7 (br s, 2 H), 1.7–1.5 (m, 2 H), 1.5–1.0 (m, 6 H), 0.6 (br s, 3 H), 0.3 (br m, 1 H).

Acknowledgment. We gratefully acknowledge the National Science Foundation (CHE 8520517), the 3M Corp., and the Rohm and Haas Co. for financial support and the Deutsche Forschungsgemeinschaft (DFG) for a postdoctoral fellowship to W.R. We especially thank Lynda K. Johnson for her very kind and generous advice on preparing the manuscript.

Registry No. **1a**, 99798-42-2; **3**, 99798-41-1; **4**, 1624-12-0; **7a**, 120711-23-1; **7b**, 120828-67-3; **9**, 120687-11-8; **11**, 120687-12-9; **12**, 120711-24-2; **13**, 120711-25-3; poly(norbornene), 25038-76-0.

References and Notes

(1) The ring positions of the titanacyclobutane ring for metallacycles derived from cyclic olefins are discussed as shown (see also ref 2):



(2) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733.

(3) Reviews on olefin metathesis: (a) Dragutan, V.; Balaban, A. T.; Dimonie, M. *Olefin Metathesis and Ring-Opening Polymerization of Cyclo-Olefins*: Wiley-Interscience: Chichester, 1985. (b) Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983). (c) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press Ltd.: Oxford, 1982; Vol. 8, pp 499–551. (d) Banks, R. L. *Catal. (London)* **1981**, *4*, 100. (e) Basset, J. M.; Leconte, M. *CHEMTECH* **1980**, *10*, 762. (f) Katz, T. J.; Lee, S. J.; Shippey, M. A. *J. Mol. Catal.* **1980**, *8*, 219. (g) Calderon, N. J. *J. Macromol. Sci. Rev.* **1972**, *C7* (1), 105.

(4) Gilliom, L. R.; Grubbs, R. H. *Organometallics* **1986**, *5*, 721.

(5) Arnold, D. R.; Trecker, J. D.; Whipple, E. B. *J. Am. Chem. Soc.* **1965**, *87*, 2596.

(6) Tumas, W.; Wheeler, D. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 6182.

(7) Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd. ed.; Pergamon Press: Oxford, 1969.

(8) Review on hydrosilation: Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407–447.

(9) The preparation and characterization of the similar compound trimethylsilyl-3-bicyclo(2.2.1)heptene-5 is reported in: (a) Gassend, R.; Limouzin, Y.; Maire, J. C. *Org. Magn. Reson.* **1974**, *6*, 259. (b) Kuivila, H. G.; Warner, C. R. *J. Org. Chem.* **1964**, *29*, 2845.

(10) Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* **1987**, *20*, 1488.

(11) (a) Katz, T. L.; Lee, S. J. Acton, N. *Tetrahedron Lett.* **1976**, 4247. (b) Katz, T. J.; Acton, N. *Ibid.* **1976**, 4251.

(12) Risse, W.; Grubbs, R. H. submitted for publication in *Macromolecules*.

(13) Martin, M. K.; Ward, T. C.; McGrath, J. E. In *Anionic Polymerization*; McGrath, J. E., Ed.; ACS Symposium Series 164; American Chemical Society: Washington DC., 1981.

(14) Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* **1988**, *21*, 1961.

(15) Hall, L. D.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1980**, *102*, 5703. Sanders, J. K. M.; Mersh, J. D. *Prog. Nucl. Magn. Reson. Spectrosc.* **1982**, *15*, 353.

(16) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(17) Yau, W. W.; Kirkland, J. J.; Bly, D. D. *Modern Size-Exclusion Chromatography*; Wiley: New York, 1979.