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Ring-Opening Metathesis Polymerization of Norbornene with Titanium Alkylidenes Generated by Thermolysis of Dimethyltitanocene and Related Cyclopentadienyltitanium(IV) Derivatives

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Abstract: Heating norbornene in the presence of catalytic amounts of dimethyltitanocene, cyclopentadienyltrimethyltitanium(IV), chlorodimethylcyclopentadienyltitanium(IV), and bis[(trimethylsilyl)methyl]titanocene resulted in the ring-opening metathesis polymerization of norbornene. Presumably, the in-situ generation of free or complexed titanium alkylidene intermediates is responsible for these polymerizations. The use of tetrahydrofuran as the solvent had a significant inhibitory effect that varied with the initiator used. This effect was confirmed with the measurement of kinetic data. This substituent-dependent solvent effect was attributed to changes in the relative contributions of nucleophilic and neutral resonance structures, in agreement with recent theoretical calculations.

Introduction

The ring-opening metathesis polymerization (ROMP) of cyclic olefins has been an area of many fascinating recent developments. The pioneering work of Grubbs,[1] Schrock,[2] and others[3] has provided valuable mechanistic information and led to the synthesis of new polymeric materials.[4] Among the most effective initiators that were developed for this type of polymerization are several preformed and thermally stable alkylidene complexes[2b,5] ($L_nM{=}CHR$) of molybdenum,[6] tungsten,[7] tantalum,[8] rhenium,[9] and ruthenium.[10] Herein we report a new method for ROMP initiation involving dialkyltitanium(IV) derivatives.

Titanium-based initiators have played a key role in the development of ROMP. The first reported example of this kind of polymerization involved the ROMP of norbornene with a mixture derived from $TiCl_4$ and EtMgBr or $LiAlR_4$.[11] Also, the first living polymerization of this type was demonstrated with norbornene and titanacyclobutanes.[12] The use of preformed titanium alkylidenes ($L_nTi{=}CHR$) for this purpose, however, remains elusive since these compounds are generally unstable and have not been isolated in a pure form, although phosphine complexes have been prepared.[13] The parent titanocene methylidene species (**3**, Scheme I) was studied computationally[14] and has been postulated as an intermediate in the reactions of the Tebbe reagent[15] (**1**) and during the thermolysis of titanacyclobutanes[16] (**4**).

We have recently shown that dimethyltitanocene (**2**) is a convenient and practical alternative to **1** for carbonyl methylenations[17,18] and the preparation of titanacyclobutenes.[19] We have also found that the dibenzyl-,[20] bis[(trimethylsilyl)-

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[1] Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907.

[2] (a) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158. (b) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1.

[3] For general reviews see: (a) Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983. (b) Grubbs, R. H. *Compr. Organomet. Chem.* **1982**, *8*, 499. (c) Amass, A. J. *Compr. Polym. Sci.* **1989**, *4*, 109. (d) Feast, W. J. *Compr. Polym. Sci.* **1989**, *4*, 135. (e) Novak, B. M.; Risse, W.; Grubbs, R. H. *Adv. Polym. Sci.* **1992**, *102*, 47.

[4] For example, (a) polybenzvalene: Swager, T. M.; Dougherty, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2793. (b) Polycyclooctatetraene: Klavetter, F. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7807. (c) Polyacetylene: Swager, T. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 4413. (d) Saunders, R. S.; Cohen, R. E.; Schrock, R. R. *Macromolecules* **1991**, *24*, 5599.

[5] Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley & Sons: New York, 1988.

[6] (a) Schrock, R. R.; Krouse, S. A.; Knoll, K.; Feldman, J.; Murdzek, J. S.; Yang, D. C. *J. Mol. Catal.* **1986**, *46*, 243. (b) Schoettel, G.; Kress, J.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1989**, 1062. (c) Bazan, G. C.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378. (d) Bazan, G. C.; Schrock, R. R.; Cho, H. N.; Gibson, V. C. *Organometallics* **1991**, *24*, 4495.

[7] (a) Schrock, R. R.; Feldman, J.; Cannizzo, L. F.; Grubbs, R. *Macromolecules* **1987**, *20*, 1169. (b) Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L.; DiMare, M.; Schofield, M.; Anhaus, J.; Walbosrsky, E.; Evitt, E.; Kruger, C.; Bertz, P. *Organometallics* **1990**, *9*, 2262. (c) Blosch, L. L.; Abboud, K.; Boncella, J. M. *J. Am. Chem. Soc.* **1991**, *113*, 7066. (d) Couturier, J. L.; Paillet, C.; Leconte, M.; Basset, J. M.; Weiss, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 628. (e) van Der Schaaf, P. A.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1992**, 717.

[8] Wallace, K. C.; Liu, A. H.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 4964.

[9] (a) Toreki, R.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2448. (b) Toreki, R.; Schrock, R. R.; Vale, M. G. *J. Am. Chem. Soc.* **1991**, *113*, 3610. (c) Herrmann, W. A.; Wagner, W.; Fleggner, U. N.; Volkhardt, U.; Komber, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1636.

[10] (a) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542. (b) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H.; Ailler, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 3974. (c) Hamilton, J. G.; Marquess, D. G.; O'Neill, T. J.; Rooney, J. J. *J. Chem. Soc., Chem. Commun.* **1990**, 119.

[11] (a) Anderson, A. W.; Merkling, N. G. U.S. Patent 2,721,189, 1955; *Chem. Abstr.* **1955**, *50*, 3008. (b) Eleuterio, H. C. U.S. Patent 3,074,913, 1957; *Chem. Abstr.* **1961**, *55*, 16005. (c) Truett, W. L.; Johnson, D. R.; Robinson, I. M.; Montague, B. A. *J. Am. Chem. Soc.* **1960**, *82*, 2337.

[12] Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733.

[13] (a) Gilliom, L. R.; Grubbs, R. H. *Organometallics* **1986**, *5*, 721. (b) van De Heisteeg, B. J. J.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *J. Organomet. Chem.* **1986**, *310*, C25. (c) Meinhart, J. D.; Anslyn, E. V.; Grubbs, R. H. *Organometallics* **1989**, *8*, 583. (d) Binger, P.; Muller, P.; Benn, R.; Mynott, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 610.

[14] (a) Francl, M. M.; Pietro, W. J.; Hout, R. F., Jr.; Hehre, W. J. *Organometallics* **1983**, *2*, 281; **1983**, *2*, 815. (b) Gregory, A. R.; Mintz, E. A. *J. Am. Chem. Soc.* **1985**, *107*, 2179.

[15] (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (b) Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3270. (c) 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. (d) Pine, S. H.; Pettit, R. J.; Geib, G. D.; Cruz, S. G.; Gallego, C. H.; Tijerina, T.; Pine, R. D. *J. Org. Chem.* **1985**, *50*, 1212.

[16] (a) Howard, T. R.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 6876. (b) Ikariya, T.; Ho, S. C. H.; Grubbs, R. H. *Organometallics* **1985**, *4*, 199. (c) Gilliom, L. R.; Grubbs, R. H. *Organometallics* **1986**, *5*, 721. (d) Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 4880.

[17] Petasis, N. A.; Bzowej, E. I. *J. Am. Chem. Soc.* **1990**, *112*, 6392.

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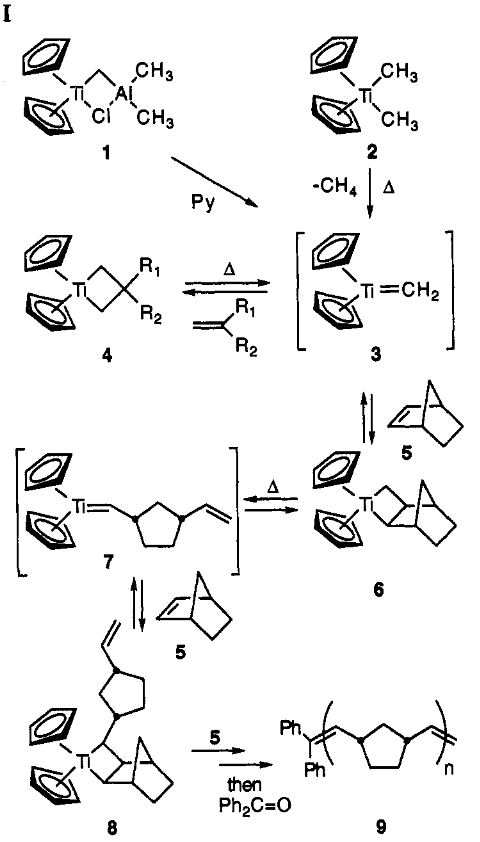
Scheme I



methyl]-,[21] and bis(cyclopropyl)titanocenes[22] behave similarly. A noteworthy feature of these titanocene derivatives is that they are easily prepared by the addition of the corresponding lithium reagents to titanocene dichloride. They are also reasonably stable to air and water, eliminating the need for special techniques.

Although the methylidenetitanocene species (**3**) has not been directly observed, it is a likely intermediate in the thermal reactions of **2** with various substrates. Other mechanisms, however, involving the initial complexation of **2** with the substrate are also possible. In this case the same products may be obtained by a subsequent *ligand-promoted α-abstraction*,[23] or by a migratory insertion followed by elimination. Therefore, in an effort to probe the formation of **3** during the thermolysis of **2**, we investigated the ability of **2** to initiate the ROMP of norbornene.

In spite of the detailed thermolysis studies[24] of **2**, its application in the polymerization of silanes,[25] and its use as a cocatalyst with aluminum reagents in Ziegler–Natta polymerizations[26] and with tungsten compounds in olefin metathesis,[27] to our knowledge the ROMP capability of **2** was not previously documented. As reported herein, dimethyltitanocene (**2**) and several related titanium(IV) derivatives can indeed serve as effective ROMP initiators.

Table I. Polymerization of Norbornene (**5**) Initiated with **2**, **10**, **11**, and **14**

entry	init	**5** (equiv)	proc[a]	solvent	concn[b]	*t*(h)	M_n[c]	poly-dispersity
1	**2**	100	A	THF	2.5	5	9800	1.33
2	**2**	100	A	THF	5	5	11 300	1.53
3	**2**	100	A	THF	5	8	19 100	1.25
4	**2**	100	A	THF	12.5	5	20 300	1.33
5	**2**	200[d]	A[d]	THF	12.5	10[d]	30 200	1.65
6	**2**	200	A	THF	30	10	28 000	1.62
7	**2**	100	B	toluene	7.5	12	55 500	1.36
8	**2**	100	B	toluene	5	18	37 700	1.52
9	**2**	100	B	toluene	2.5	24	50 000	1.40
10	**10**	100	B	THF	25	15	34 000	1.33
11	**11**	100	B	THF	5	8	16 800	1.76
12	**11**	100	B	THF	10	20	24 200	1.62
13	**14**	100	C	THF	5	5	9900	1.55
14	**14**	100	B	toluene	5	12	33 700	2.05[e]
15	**14**	100	B	toluene	7.5	12	33 200	2.15[e]

[a] Procedure A: The mixture of monomer **5** (10 equiv) and initiator (1 equiv) was heated for 1 h, and then the remaining monomer was added and heating was continued. Procedure B: All of monomer **5** (100 equiv) and the initiator (1 equiv) was heated in a single step. Procedure C: The mixture of monomer **5** (100 equiv) and initiator (1 equiv) in 10% of the total solvent was heated for 1 h and then the remaining 90% of the solvent was added and heating was continued. [b] Final monomer concentration. [c] Determined by GPC with polystyrene standards.[28] [d] This is a continuation of entry 4, involving the addition of 100 equiv of monomer after 5 h of heating. [e] Trimodal distribution (Figure 1b).

Results

Formation of Titanacyclobutane 6. Upon heating an NMR sample of a 1:1 solution of dimethyltitanocene (**2**) and norbornene (**5**) in benzene-d_6 at 55 °C for 1 h, we noted the appearance of peaks corresponding to the titanacyclobutane adduct **6**.[12] All of the peaks corresponding to **6** could be identified, including the two Cp peaks at 5.30 and 5.47 ppm and the characteristic doublet for H_1 at 3.51 ppm and doublet of doublets for H_2 at 3.11 ppm. Variable amounts of oligomers were also present, suggesting that the titanacyclobutane ring-opening of **6** to **7** takes place under the same conditions, thereby triggering the initiation process.

Polymerization of Norbornene (5) with Dimethyltitanocene (2). During our initial studies of the polymerization of **5** with **2** we observed a significant solvent effect. Thus, heating a THF solution of a 100:1 mixture of monomer (**5**, 5 M) and initiator (**2**, 0.05 M) in a sealed flask at 70 °C (procedure B, Table I) did not produce any polymer, while a toluene solution under identical conditions showed smooth polymerization. However, if the experiment was carried out in two stages (procedure A, Table I), the polymerization could be performed even in THF. At first, a THF solution of a 10:1 mixture of **5** (5 M) and **2** (0.5 M) was heated for 1 h under argon at reflux, forming mostly the titanacyclobutane **6**. Subsequent addition of more monomer and solvent, further heating, and termination with benzophenone led to the formation of polynorbornene **9**. This polymer was identified by its ^{1}H- and ^{13}C-NMR spectra.[12] A 63:37 ratio of trans to cis olefins was observed, indicating a similarity with other titanium initiators.[12] Gel permeation chromatography (GPC) showed monomodal and relatively narrow molecular weight distribution (Figure 1a) with polydispersities ranging from 1.25 to 1.65 (Table I).

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(18) For synthetic applications see: (a) Petasis, N. A.; Patane, M. A. *Tetrahedron Lett.* **1990**, *31*, 6799. (b) Csuk, R.; Glanzer, B. I. *Tetrahedron* **1991**, *47*, 1655. (c) DeShong, P.; Rybczynski, P. J. *J. Org. Chem.* **1991**, *56*, 3207. (d) Swenton, J. S.; Bradin, D.; Gates, B. D. *J. Org. Chem.* **1991**, *56*, 6156. (e) Petasis, N. A.; Bzowej, E. I. *Tetrahedron Lett.* **1993**, *34*, 1721.

(19) Petasis, N. A.; Fu, D.-K. *Organometallics* **1993**, *12*, in press.

(20) Petasis, N. A.; Bzowej, E. I. *J. Org. Chem.* **1992**, *57*, 1327.

(21) Petasis, N. A.; Akritopoulou, I. *Synlett.* **1992**, 665.

(22) Petasis, N. A.; Bzowej, E. I. *Tetrahedron Lett.* **1993**, *34*, 943.

(23) Ruppercht, G. A.; Messerle, L. W.; Fellmann, J. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6236.

(24) (a) Latyaeva, V. N.; Vyshinskaya, L. I.; Mar'in, V. P. *Zh. Obshch. Khim.* **1976**, *46*, 628. (b) Alt, H. G.; Di Sanzo, F. P.; Rausch, M. D.; Uden, P. C. *J. Organomet. Chem.* **1976**, *107*, 257. (c) Erskine, G. J.; Wilson, D. A.; McCowan, J. D. *J. Organomet. Chem.* **1976**, *114*, 119. (d) Erskine, G. J.; Hartgerink, J.; Weinberg, E. L.; McCowan, J. D. *J. Organomet. Chem.* **1979**, *170*, 51. (e) Razuvaev, G. A.; Mar'in, V. P.; Andrianov, Y. A. *J. Organomet. Chem.* **1979**, *174*, 67.

(25) (a) Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059. (b) Review: Corey, J. Y. *Adv. Silicon Chem.* **1991**, *1*, 327.

(26) (a) Soga, K.; Yanagihara, H. *Makromol. Chem.* **1988**, *189*, 2839. (b) Soga, K.; Lee, D. H.; Shiono, T.; Kashiwa, N. *Makromol. Chem.* **1989**, *190*, 2683. (c) Soga, K.; Yanagihara, H.; Lee, D. H. *Makromol. Chem.* **1989**, *190*, 37. (d) Soga, K.; Uozumi, T.; Yanagihara, H. *Makromol. Chem.* **1989**, *190*, 31. (e) Soga, K.; Yanagihara, H. *Macromolecules* **1989**, *22*, 2875.

(27) (a) Tsuji, J.; Hashiguchi, S. *Tetrahedron Lett.* **1980**, *21*, 2955. (b) Tsuji, J.; Hashiguchi, S. *J. Organomet. Chem.* **1980**, *218*, 69.

(28) The actual (corrected) molecular weight was previously (ref 12) estimated to be one-half of the molecular weight measured with polystyrene standards.

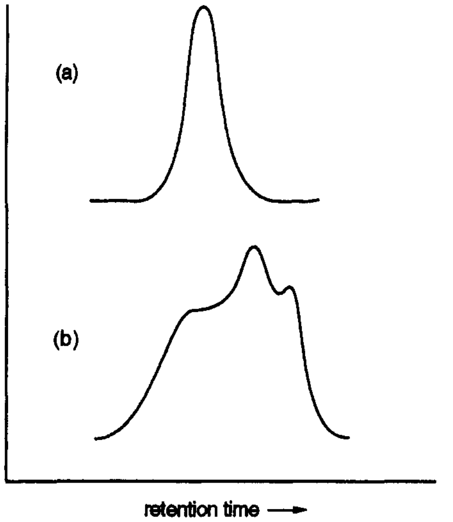

Figure 1. GPC traces of the polymers obtained after 12 h by polymerization of **5** in toluene with (a) initiator **2** and (b) initiator **14**.

Scheme II

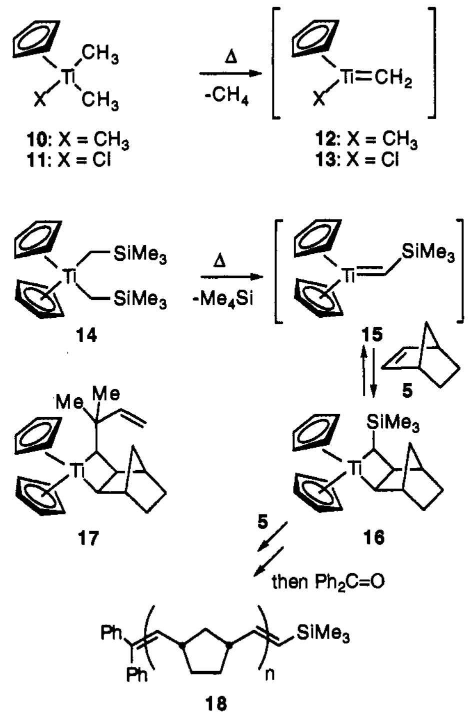

Table I lists the results of the polymerization of norbornene (**5**) in refluxing THF or in toluene at 80 °C using **2**, **10**, **11**, and **14** as initiators under a variety of conditions. Higher concentration (entry 4 vs 1 and 2), longer reaction time (entry 3 vs 2), or more equivalents of monomer (entry 5) increased the molecular weight of the polymer. Also the polydispersity of the polymer could be improved by using a lower monomer concentration and slow monomer addition (entry 1) or dilution of the reaction mixture during the polymerization process (entries 2 and 3). The molecular weights for similar reaction times varied with the initial monomer concentration (entries 1, 2, and 4).

Polymerization of Norbornene (5) with 10 and 11. In an effort to find milder conditions for the formation of the initiating titanium methylidene species, we also studied the ROMP activity of **10** and **11**, the precursors of **12** and **13**, respectively (Scheme II). Compounds **10** and **11** were prepared from cyclopentadienyltitanium trichloride and methyllithium,[29] and used in situ without purification. We found that both **10** and **11** are effective ROMP initiators and initiate the polymerization at lower concentrations and lower temperatures. Furthermore, THF does not inhibit the ROMP activity of these initiators, allowing a single-step polymerization to be utilized (Table I, procedure B).

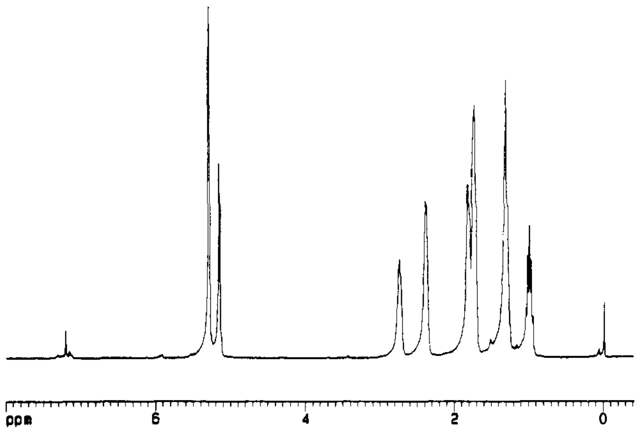

Figure 2. ^{1}H-NMR spectrum (500 MHz, C_6D_6) of polymer **18** obtained by heating a 100:1 mixture of **5** and **14** in toluene at 80 °C and termination with benzophenone.

Polymerization of Norbornene (5) with 14. In order to accelerate the initiation relative to the propagation and hence lower the polydispersity, we also examined the ROMP behavior of bis[(trimethylsilyl)methyl]titanocene (**14**). In a comparative study[30] we have previously found that **14** reacts with alkynes to form titanacyclobutenes faster than **2**. Similarly, higher reactivity can be expected for the reactions of **14** with alkenes. Thus, thermolysis of **14** should form the alkylidene intermediate **15**, which in the presence of **5** should give the α-trimethylsilyl-substituted titanacyclobutane **16** (Scheme II). For steric and electronic reasons[31] **16** should undergo a more facile ring-opening than a propagating species such as **8** (Scheme I). A similar effect was previously noted with compound **17**, which gave lower polydispersities than **6**.[12] While **14** could be prepared according to the literature,[32] by adding 2 equiv of Me_3SiCH_2Li to Cp_2TiCl_2, we found[21] that this process gives variable amounts of $CpTi(CH_2SiMe_3)_3$. For this reason we developed a reliable two-step procedure, involving the sequential addition of Me_3SiCH_2MgBr and Me_3SiCH_2Li.

By using **14** as the initiator in toluene, we found that, under conditions similar to those used for **2**, the polymerization was seemingly faster. While the actual propagation rates are nearly the same in both cases, the polymerization appears faster with **14**, due to a faster accumulation of the initial alkylidene (**15**), which results in an increase in the concentration of the propagating species. After termination with benzophenone and evaporation of the volatiles, the obtained polymer gave the characteristic ^{1}H-NMR spectrum (Figure 2), indicating the incorporation of the trimethylsilyl group at one terminus and the diphenylethylene moiety at the other. While at its initial stages the polymerization had a monomodal molecular weight distribution, at conversions over 85% the polymer had a trimodal distribution (Figure 1b), suggesting the occurrence of chain transfer, either intermolecularly or intramolecularly (backbiting).

Similarly to **2**, the polymerization of **5** with **14** could not take place in THF under single-step conditions (procedure B). Contrary to **2**, however, the polymerization with **14** in THF was

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[29] Giannini, U.; Cesca, S. *Tetrahedron Lett.* **1960**, 19.

[30] Petasis, N. A.; Fu, D.-K. Unpublished results.

[31] Finch, W. C.; Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2406.

[32] (a) Collier, M. R.; Lappert, M. F.; Truelock, M. M. *J. Organomet. Chem.* **1970**, *25*, C36. (b) Wozniak, B.; Ruddick, J. D.; Wilkinson, G. *J. Chem. Soc. A* **1971**, 3116. (c) Collier, M. R.; Lappert, M. F.; Pearce, R. *J. Chem. Soc., Dalton Trans.* **1973**, 445. (d) Green, M. L. H.; Lucas, C. R. *J. Organomet. Chem.* **1974**, *73*, 259. (e) Sakurai, H.; Umino, H. *J. Organomet. Chem.* **1977**, *142*, C49.

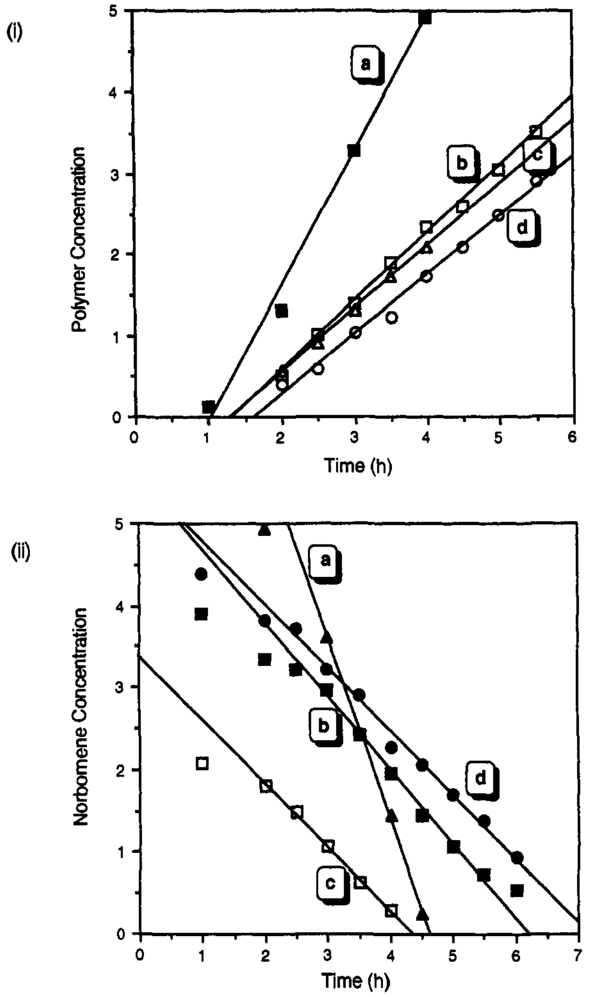

Figure 3. (i) Increase in polymer concentration and (ii) decrease in norbornene concentration in benzene-d_6 at 80 °C. The concentrations were determined by ^{1}H NMR, in relationship to a ferrocene internal standard. The plots have ρ values greater than 0.99. Conditions: **a**, 1 equiv of bis[(trimethylsilyl)methyl]titanocene (**14**), 50 equiv of norbornene (**5**); **b**, 1 equiv of dimethyltitanocene (**2**), 50 equiv of norbornene (**5**); **c**, 1 equiv of dimethyltitanocene (**2**), 25 equiv of norbornene (**5**); **d**, 1 equiv of dimethyltitanocene (**2**), 50 equiv of norbornene (**5**), 10 equiv of THF. On the basis of the graphs shown in i, the following relative polymerization rates[33] were determined: $k_a/k_b = 1.93$, $k_b/k_c = 1.10$, $k_b/k_d = 1.16$.

also inhibited under the two-step process involving a higher initial ratio of initiator per monomer (procedure A). We found, nevertheless, that this process could proceed smoothly at higher initial concentrations (procedure C).

Kinetic Studies. In order to quantify the observed reactivity trends and further understand this process, we carried out kinetic studies with the use of NMR spectroscopy (Figure 3). The relative polymerization rates[33] were determined with respect to the initiator used (conditions a vs b), monomer concentration (conditions b vs c), and the presence of THF (conditions b vs d). The increase in polymer concentration is shown in Figure 3 (i). From these data, it is clear that initiator **14** is faster than **2** ($k_a/k_b = 1.93$). Also, halving the monomer concentration (conditions c) resulted only in a small decrease in the polymerization rate ($k_b/k_c = 1.10$), indicating a close to zero-order reaction. Also, the addition of 10 equiv of THF (conditions d) resulted in a moderate decrease in rate ($k_b/k_d = 1.16$).

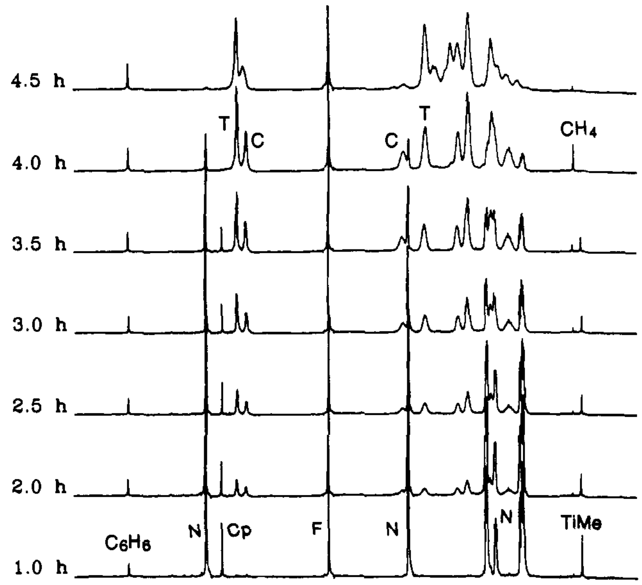

Figure 4. ^{1}H-NMR spectra (360 MHz) obtained under conditions c (initiator **2**, 25 equiv of norbornene, in benzene-d_6 at 80 °C). N = norbornene, F = ferrocene internal standard, C = cis olefin in polymer, and T = trans olefin in polymer.

The effects of conditions a–d on the decrease in norbornene (**5**) concentration are shown in Figure 3 (ii). Initially, during the first 1–2 h of the reaction, a much slower drop in norbornene concentration is observed. Once the polymerization begins, however, a linear concentration decrease is observed, indicating a zero-order propagation process. This induction period, also observed with **6**,[12] is the consequence of the dual role of **5** in forming **6** and in being the monomer in the polymerization. Not surprisingly, the monomer-derived rates observed during the propagation stage are consistent with those discussed above for the increase in polymer concentration.

Toward the end of these kinetic measurements, at over 85% conversions, we could also observe chain transfer and/or back-biting, as mentioned above. Figure 4 shows the NMR spectra obtained at various intervals, under conditions c (initiator **2**, 25 equiv of norbornene, in benzene-d_6 at 80 °C). Interestingly, these secondary reactions took place preferably at the internal cis olefinic bonds. As shown in the spectrum obtained at 4.5 h, the previously increasing peaks corresponding to the cis olefin started to decrease, while some new peaks started to appear.

Discussion

Early detailed studies[24] on the thermolysis of dimethyltitanocene (**2**) have postulated the formation of methylidenetitanocene (**3**) and suggested that this highly reactive species leads to the rapid autocatalytic decomposition of **2**. We have previously demonstrated[17] that this "self-destruction" of **2** is prevented in the presence of carbonyl compounds, which undergo smooth methylenation via either **3** or an alternate pathway. This finding has prompted us to explore other ways to harness the reactivity of **3** or other similar species generated in this manner.

Herein we focus on the reaction with norbornene (**5**). Thus, we have shown with NMR spectroscopy that **5** is indeed converted to the titanacyclobutane **6**, which can then serve as a ROMP initiator.[12] This process is kinetically more complex than the polymerization initiated with the titanacyclobutane **6**, which was studied in detail by Gilliom and Grubbs.[12] Thus, while the propagation may be zero order in monomer, the initial induction period is more complicated by the participation of monomer **5** in the formation of **6**. Similar results were observed with **10**, **11**, and **14**.

The ROMP capability of these dialkyltitanium derivatives (**19**, Scheme III) is strong evidence for the intermediacy of a titanium

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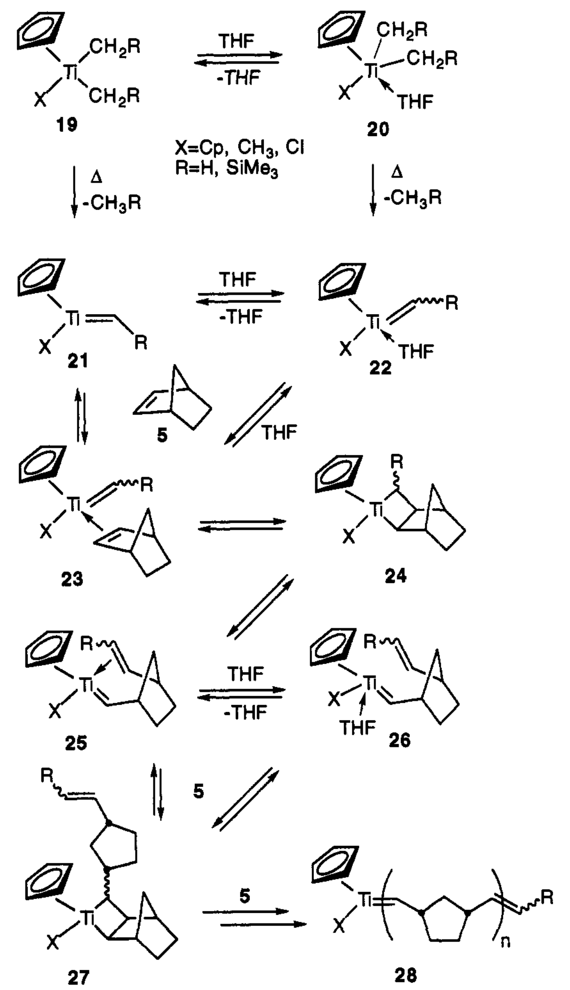
[33] The term "polymerization rate" as used here does not imply propagation rate, which is roughly the same in all cases due to only remote changes in the structure of the propagating alkylidene. The observed differences in the polymerization rates are apparently due to differences in the rate of formation of the initiating species, which leads to differences in the *concentration* of the propagating alkylidene.

Scheme III



alkylidene species during their thermolysis. It is still not clear, however, if **19** is directly converted to a highly reactive free titanium alkylidene (**21**). It is also possible that prior complexation with norbornene or the solvent gives a new complex, such as **20** or a Cp-slipped variant, which is directly converted to the complexed alkylidene (**22**) via a *ligand-promoted α-abstraction.*[23] Further transformation to **24** and subsequent ring-opening would give **25**, which triggers the polymerization. Thus, the polymerization requires both the formation of a titanium alkylidene species and its conversion to the titanacyclobutane **24**. Although the rate-determining step is presumably the irreversible loss of methane or tetramethylsilane (from **19** or **20**), the outcome of the polymerization depends heavily on the solvent and the substituents X and R.

Solvent Effects. During our olefination studies[17] with **2** we had noted that the reaction was faster in tetrahydrofuran (THF) than in toluene or hexane. This solvent effect could be correlated with the polarity of the solvent and attributed to the intermediacy of a polar intermediate, such as a titanocene–carbonyl complex. Interestingly, an opposite effect, related to the solvent's Lewis basicity, would be expected for the ROMP polymerization. Other studies[4b,6d,8,34] have shown that Lewis bases such as THF, pyridine, and trimethylphosphine tend to complex with the alkylidene intermediates, resulting in a slower propagation process. In some cases, preferential complexation with the propagating alkylidene and prevention of chain transfer and backbiting results in a smaller polydispersity.[8,34]

Similar arguments can be used to explain the remarkable solvent effects observed during the ROMP of **5** reported herein. For example, polymerizations in toluene presumably take place via **19** → **21** → **23** → **24** → **25** → **27**, while in THF additional pathways, such as **19** → **20** → **22**, may suppress or even inhibit polymer formation. Also, it is likely that the propagating alkylidene species forms an intramolecular complex with the neighboring olefinic bond (**25**).[35] In the presence of THF, **25** may be in equilibrium with **26**, resulting in a slower propagation. In the case of **2**, this type of interference by THF could be responsible for the complete shutdown of the polymerization, thereby preventing the single-step polymerization from taking place. This may also indicate that THF complexation in this case is mostly nonproductive, and the resulting complexes (e.g. **22** or **26**) may deactivate the titanium species or lead to other products. However, as the relative amount of **5** is increased (as in the two-step process), the relative amount of norbornene adducts is also increased, leading to the formation of the titanacyclobutane intermediates (**24** and **27**). Apparently, once it is formed, the titanacyclobutane **24** is capable of ROMP initiation, even in the presence of excess THF added during the second step. In agreement with steric effects, these observations may indicate that THF binds more strongly to the less substituted methylidene (**22**, X = Cp, R = H) than to the propagating alkylidene (**26**, X = Cp, R = H).

The fact that similar THF-inhibition was not observed with **10** or **11** may be attributed to a more reactive intermediate (e.g. **22**, X = CH_3, Cl, R = H), which can still react with **5** to form **23** and **24**. The lower titanium electron count could be a determining factor in these systems.

With the (trimethylsilyl)methyl derivative **14**, THF inhibition has prevented even the two-step polymerization (procedure A) from taking place in this solvent, although it proceeds at high concentrations (procedure C) and in toluene (procedure B). Since the propagating alkylidene (**25**, X = Cp, R = $SiMe_3$) is almost identical with that obtained with **2**, the inhibiting effect of THF in this case may be attributed to the more facile formation of **22** (X = Cp, R = $SiMe_3$), resulting from the increased electrophilic character of titanium, as discussed below.

Taken together, these results suggest that the polymerization is affected not only by the ease of formation of the alkylidene intermediates, but also by their propensity to bind with either nonbonding electrons (in THF) or π-electrons (in **5**). Of special significance to the propagation is the ability of the alkylidene intermediates (**21** or **22**) to react with **5** to form titanacyclobutanes. This can be accomplished via prior loss of THF and trapping of the resulting free carbene with **5** in an S_N1 manner. Also possible is an initial direct displacement of THF by **5** in an S_N2 fashion, followed by a rapid transformation of the olefin–carbene complex (**23**) to the titanacyclobutane (**24**).[36] For example, the unhindered methylidenes derived from **10** and **11** could react readily with **5**, while the more crowded complexes derived from **2** and to a larger extent **14** are expected to be less reactive toward **5**.

Substituent Effects. The differences in the ROMP activity of **2**, **10**, **11**, and **14** can be analyzed in terms of the electronic structure of the corresponding alkylidene intermediates, according to recent theoretical calculations by Cundari and Gordon.[37] In this study, the effects of ligands and substituents on the major resonance contributors to the structures of a series of titanium alkylidenes (**32–36**) were determined (Scheme IV).[37] It was shown that the relative contribution of nucleophilic resonance structures (**29**) increases in this series, while the contributions of neutral resonance structures (**30**) and electrophilic ones (**31**) decrease. In general, higher olefin metathesis activity is observed

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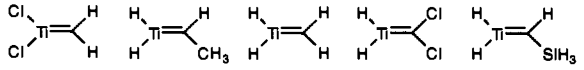
(34) Wu, Z.; Wheeler, D. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 146.

(35) We thank a referee for suggesting this type of intermediate.

(36) (a) Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 4880. (b) Upton, T. H.; Rappe, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 1206.

(37) (a) Cundari, T. R.; Gordon, M. S. *J. Am. Chem. Soc.* **1991**, *114*, 539. (b) Cundari, T. R.; Gordon, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 5231. (c) Cundari, T. R.; Gordon, M. S. *Organometallics* **1992**, *11*, 55.

Scheme IV. Resonance Structure Contributions in Various Titanium Alkylidenes According to Cundari and Gordon[a]



		32	**33**	**34**	**35**	**36**
29	$\overset{\oplus\leftarrow\ominus}{\mathrm{Ti-C}}$	42 %	46%	48 %	50%	52%
30	$\mathrm{Ti{=}C}$	51%	48%	46%	45%	43%
31	$\overset{\ominus\rightarrow\oplus}{\mathrm{Ti-C}}$	7%	6%	5%	5%	4%

[a] Reference 37.

with Schrock-type[38] alkylidenes that have a higher component of nucleophilic resonance structures, while the electrophilic Fischer-type alkylidenes do not behave this way.[39]

Our experimental results are in agreement with these calculations, if we make the reasonable assumption[16,36b,40] that the *relative* reactivities of the titanium alkylidenes **13**, **25**, **3**, and **15** are correlated with those of the calculated prototypes **32**, **33**, **34**, and **36**. Thus, the relatively narrow polydispersities observed with **2** may be explained by the higher reactivity of **34** vs **33**, which can reflect a higher relative reactivity of the initial methylidene (**3**) vs the propagating alkylidene (**25** and homologues). Also, the lack of THF inhibition during the polymerizations with **10** and **11** is explainable in terms of a more neutral titanium metal in **32** as compared to **34**, which supresses THF coordination to titanium.[41] The above calculations also predict the silyl derivative **36**, and consequently **15**, to be a more reactive metathesis initiator, in agreement with our experimental results. Similarly, the inhibition of ROMP by THF in this case may be the result of THF-binding to a more electrophilic titanium, resulting from the interaction of silicon's empty d-orbital with the alkylidene carbon.

Another interesting consequence of Cundari and Gordon's calculations[37] is the comparison of the resonance contributions in **35** and **34**, which suggests that electron-withdrawing substituents on the alkylidene carbon should increase the olefin metathesis activity. Preliminary results with dibenzyltitanocene derivatives[20] confirm this observation. Thus, while the unsubstituted dibenzyltitanocene could not initiate the ROMP of **5**, the corresponding bis(*m*-chlorobenzyl)titanocene was a very effective initiator.[42] Further studies are currently in progress to probe these substituent effects.

Conclusions

We have demonstrated that dimethyltitanocene (**2**) as well as three other related titanium(IV) derivatives (**10**, **11**, and **14**) can serve as initiators for the ROMP of norbornene. Presumably, this polymerization is initiated by a thermally generated titanium alkylidene (**3**, **12**, **13**, and **15**), confirming the formation of such species during the thermolysis of dialkyltitanocenes. Initial complexation of the solvent or norbornene with the titanium(IV) initiator prior to the α-elimination process may also be involved. It is noteworthy that, despite the involvement of additional initiation steps, i.e. the conversion of **2** to **3** and then to **6**, only a small increase in the polydispersity was observed, relative to the use of pure **6**.

The use of THF as the solvent inhibited the ROMP activity of **14** and to a lesser extent the activity of **2**, but had no effect on **10** or **11**. This substituent-dependent solvent effect and the variations in the polydispersity could be explained in terms of steric and electronic factors resulting from the relative amount of contributing nucleophilic and neutral resonance structures.

Since the dialkyltitanocene ROMP initiators reported herein are easily derived from organolithium precursors, they are potentially applicable to block copolymer synthesis, in combination with anionic polymerization. The suitability of this process for the synthesis of new, interesting materials is being investigated.

Experimental Section

^{1}H- and ^{13}C-NMR spectra were recorded in benzene-d_6 on Bruker AMX-500, AM-360, or AC-250 instruments. Gel permeation chromatographic analysis of the molecular weight distribution of the polymers was performed on a Waters system, comprising a U6K injector, a 510 solvent delivery system, an R401 differential refractometer, and a Maxima 820 data station. The retention times were calibrated with monodispersed polystyrene standards, and HPLC-grade THF was used as the eluant.

Materials. All chemicals were purchased from Aldrich. Norbornene was purified by distillation over Na. THF was distilled from Na and benzophenone. Dimethyltitanocene (**2**) was prepared by the literature method.[43]

Two-Step Polymerization of Norbornene (5) with Dimethyltitanocene (2) in THF. A 10:1 mixture of monomer and initiator was prepared by adding **2** (102 mg, 0.5 mmol) to a solution of freshly distilled norbornene (**5**, 0.49 g, 5 mmol) in THF (1.0 mL). This solution was syringe-transferred into a vacuum-dried 50-mL flask and refluxed under argon for 1 h. Another portion (4.41 g, 45 mmol) of **5** in THF (4 mL) was then added, and the mixture was heated at reflux for 5 h or more. The reaction mixture maintained a deep red color during the polymerization period. Some reactions were diluted by adding more THF during polymerization in order to get better polydispersities. The polymerization was terminated by adding benzophenone (100 mg, 0.55 mmol) and continuing heating for 30 min. Evaporation of the solvent and excess monomer or precipitation with methanol gave polymer **9** in yields ranging between 65–85%.

One-Step Polymerization of Norbornene (5) with Dimethyltitanocene (2) in Toluene. A solution of **2** (102 mg, 0.5 mmol) and norbornene (**5**, 4.9 g, 50 mmol) in toluene (10 mL) was stirred at 80 °C for several hours. The reaction mixture kept a deep red color during the polymerization. Termination with benzophenone and evaporation of the volatiles gave polymer **9**.

Preparation of Cyclopentadienyltrimethyltitanium(IV) (10) and Polymerization of Norbornene (5). To a suspension of $CpTiCl_3$ (0.10 g, 0.48 mmol) in THF (5.0 mL) cooled to -50 °C under argon was syringe-transferred a solution of methyllithium (1.6 mL, 0.88 M, 1.41 mmol). The reaction mixture was stirred at -50 to 0 °C for 1 h. To the resulting brown solution was added norbornene (4.9 g, 50 mmol) dissolved in THF (3.0 mL), and the solution was heated to reflux while being stirred for 20 h. Termination with benzophenone and evaporation of the volatiles gave polymer **9**.

Preparation of Chlorodimethylcyclopentadienyltitanium(IV) (11) and Polymerization of Norbornene (5). To a suspension of $CpTiCl_3$ (0.10 g, 0.48 mmol) in THF (5.0 mL) cooled to -50 °C under argon was syringe-transferred a solution of methyllithium (1.0 mL, 0.88 M, 0.88 mmol). The reaction mixture was kept stirring at -50 to 0 °C for 1 h. Freshly distilled norbornene (**5**, 4.9 g, 50 mmol) dissolved in THF (2.0 mL) was added to the mixture, and the flask was heated to reflux for 15 h. The reaction mixture was green during the polymerization. Termination with benzophenone and evaporation of the volatiles gave polymer **9**.

Bis[(trimethylsilyl)methyl]titanocene (14). To a suspension of Cp_2TiCl_2 (0.50 g, 2 mmol) in diethyl ether (20 mL) cooled to -50 °C under argon was syringe-transferred a diethyl ether solution of Me_3SiCH_2MgCl (3 mL, 1.0 M, 3 mmol). The reaction mixture was stirred for 2 h while being warmed to room temperature, and then it was poured into ice water (50 mL). The organic layer was extracted three times with diethyl ether (3 × 10 mL) and dried over magnesium sulfate. Removal of the solvent gave $Cp_2Ti(Cl)CH_2SiMe_3$ as a bright orange solid (0.54 g, 90%). To a solution of $Cp_2Ti(Cl)CH_2SiMe_3$ (0.54 g, 1.7 mmol) in diethyl ether (18 mL) cooled to −78 °C under argon was syringe-transferred a diethyl ether solution of Me_3SiCH_2Li (2.2 mL, 1.0 M, 2.2 mmol). The reaction mixture was stirred at this temperature for 1 h and warmed to room temperature over 30 min. Addition to ice water, extraction with diethyl ether (3 × 10 mL), drying over magnesium sulfate, filtration, and evaporation of the solvent gave pure $Cp_2Ti(CH_2SiMe_3)_2$

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(38) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.

(39) For a theoretical comparison of nucleophilic and electrophilic metal carbenes see: Taylor, T. E.; Hall, M. B. *J. Am. Chem. Soc.* **1984**, *106*, 1576.

(40) For additional recent examples of using Cl_2Ti or H_2Ti instead of Cp_2Ti during high-level calculations see: (a) Jolly, C. A.; Marynick, D. S. *J. Am. Chem. Soc.* **1989**, *111*, 7968. (b) Kuribayashi, H. K.; Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1992**, *114*, 2359.

(41) The nearly nonpolar nature of the Ti=C bond of **12** was previously postulated from localized molecular orbital calculations: Marynick, D. S.; Kirkpatrick, C. M. *J. Am. Chem. Soc.* **1985**, *107*, 1993.

(42) Petasis, N. A.; Fu, D.-K.; Bzowej, E. I. Unpublished results.

(43) Clauss, v. K.; Bestian, H. *Justus Liebigs Ann. Chem.* **1962**, 8.

(**14**) as a yellow solid (0.60 g, 95%): ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.07 (s, 10H, Cp), 0.87 (s, 4H, CH_2), –0.09 (s, 18H, $SiMe_3$); ^{13}C NMR (63 MHz, $CDCl_3$) δ 111.98 (Cp), 64.52 (CH_2), 2.88 ($SiMe_3$).

Polymerization of Norbornene (5) with Bis[(trimethylsilyl)methyl]titanocene (14). A solution of **14** (0.094 g, 0.25 mmol) and norbornene (2.5 g, 25 mmol) in toluene (10 mL) was stirred at 80 °C for 12 h. The reaction mixture kept a deep red color during the polymerization. Termination with benzophenone and evaporation of the volatiles gave polymer **18**.

Kinetics under Conditions b. A solution of **2** (10.1 mg, 0.05 mmol), norbornene (245 mg, 2.5 mmol), and ferrocene (18.5 mg, 0.1 mmol) in benzene-d_6 (0.5 mL) was placed in an NMR tube. The solution was degassed under vacuum upon cooling to –78 °C, and the tube was filled with argon, sealed, and placed in an oil bath heated at 80 °C. At the indicated intervals the 360-MHz ^{1}H-NMR spectra of the mixture were recorded. The peak integrals for monomer and polymer were divided with the integral of the ferrocene reference and plotted (Figure 3). The ρ value for all of the plots was >0.99.

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Supplementary Material Available: NMR spectra of **6**, **9**, and **14** (3 pages). Ordering information is given on any current masthead page.