

Living Isospecific Styrene Polymerization by Chiral Benzyl Titanium Complexes That Contain a Tetradentate [OSSO]-Type Bis(phenolato) Ligand

Klaus Beckerle, Ramanujachary Manivannan, Thomas P. Spaniol, and Jun Okuda*

Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, D-52056 Aachen, Germany

Received January 17, 2006

Dibenzyl complexes $[\text{Ti}(\text{OC}_6\text{H}_2\text{-R}^1\text{-6-R}^2\text{-4})_2\{\text{S}(\text{CH}_2)_2\text{S}\}(\text{CH}_2\text{Ph})_2]$ (**2a–c**; $\text{R}^1 = \text{'Bu}$, $\text{R}^2 = \text{Me}$, **a**; $\text{R}^1, \text{R}^2 = \text{'Bu}$, **b**; $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Me}$, **c**) with a tetradentate dianionic [OSSO]-type ligand were synthesized from the corresponding titanium dichloro complexes $[\text{Ti}(\text{OC}_6\text{H}_2\text{-R}^1\text{-6-R}^2\text{-4})_2\{\text{S}(\text{CH}_2)_2\text{S}\}\text{Cl}_2]$ and benzylmagnesium chloride in toluene. NMR spectroscopic monitoring of the reaction of the dibenzyl complex **2b** with $\text{B}(\text{C}_6\text{F}_5)_3$ in bromobenzene indicates the formation of a thermally sensitive benzyl cation $[\text{Ti}(\text{OC}_6\text{H}_2\text{-'Bu}_2\text{-4,6})_2\{\text{S}(\text{CH}_2)_2\text{S}\}(\text{CH}_2\text{Ph})]^\dagger$. ^1H NMR spectra at -30°C show two C_1 -symmetric diastereomers in a 55:45 ratio, suggesting slow epimerization on the NMR time scale at this temperature. The benzyl complex **2c**, which does not bear bulky *ortho*-substituents, was found to be fluxional and unstable in solution. Related benzyl complexes of the 1,5-dithiapentanediy-linked ligand $[\text{Ti}(\text{OC}_6\text{H}_2\text{-'Bu-6-R-4})_2\{\text{S}(\text{CH}_2)_3\text{S}\}(\text{CH}_2\text{Ph})_2]$ (**4a,b**; $\text{R} = \text{Me}$, **a**; $\text{R} = \text{'Bu}$, **b**) were synthesized in an analogous manner and were also shown to be highly fluxional and unstable in solution, decomposing immediately upon addition of $\text{B}(\text{C}_6\text{F}_5)_3$. Using the 1,4-dithiabutanediyl-linked dibenzyl complexes and the activators $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{Al}^n\text{Oct}_3$, the living isospecific polymerization of styrene could be achieved for the first time. The resulting isotactic polystyrenes show narrow molecular weight distributions ($M_w/M_n < \sim 1.2$). A linear relation between the number-averaged molecular weights M_n and the monomer conversion was observed.

Introduction

The introduction of structurally well-defined α -olefin polymerization catalysts has rejuvenated the area of initiator design for the living/controlled polymerization of α -olefins.^{1–7} Following the pioneering work by Doi et al. on the vanadium-initiated living polymerization of propylene in the 1980s,⁸ the goal of both stereospecific and living polymerization of α -olefins has been recently achieved by Sita et al. using structurally well-

defined chiral half-sandwich zirconium complexes.⁹ The design of post-metallocene initiators^{10,11} provides important contributions to modern macromolecular synthesis, since conventional living ionic¹² or living radical methodologies¹³ usually do not allow influencing the stereospecificity during chain propagation.

Whereas syndiospecific styrene polymerization by titanium half-sandwich titanium complexes has been well established,¹⁴ a controlled version of this polymerization has become known only recently.¹⁵ Isotactic polystyrene was already described in

(1) For reviews, see: (a) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223. (b) Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2236.

(2) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 1008.

(3) (a) Baumann, R.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 3830. (b) Liang, L. C.; Schrock, R. R.; Davis, W. M.; McConville, D. H. *J. Am. Chem. Soc.* **1999**, *121*, 5797. (c) Mehrkhodavandi, P.; Schrock, R. R. *J. Am. Chem. Soc.* **2001**, *123*, 10746.

(4) (a) Saito, J.; Mitani, M.; Mohri, J.; Ishii, S.; Yoshida, Y.; Matsugi, T.; Kojoh, S.; Kashiwa, N.; Fujita, T. *Chem. Lett.* **2001**, 576. (b) Kojoh, S.; Matsugi, T.; Saito, J.; Mitani, M.; Fujita, T.; Kashiwa, N. *Chem. Lett.* **2001**, 822. (c) Saito, J.; Mitani, M.; Onda, M.; Mohri, J.; Ishii, S.; Yoshida, Y.; Nakano, T.; Tanaka, H.; Matsugi, T.; Kojoh, S.; H.; Kashiwa, N.; Fujita, T. *Macromol. Rapid Commun.* **2001**, *22*, 1072.

(5) (a) Tian, J.; Hustad, P. D.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 5134. (b) Mason, A. F.; Coates, G. W. *J. Am. Chem. Soc.* **2004**, *126*, 16326.

(6) (a) Hagihara, H.; Shiono, T.; Ikeda, T. *Macromolecules* **1998**, *31*, 3184. (b) Hasan, T.; Ioku, A.; Nishii, K.; Shiono, T.; Ikeda, T. *Macromolecules* **2001**, *34*, 3142. (c) Fukui, Y.; Murata, M.; Soga, K. *Macromol. Rapid Commun.* **1999**, *20*, 637.

(7) (a) Killian, C. M.; Tempel, D. J.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **2001**, *123*, 10754. (b) Camacho, D. H.; Guan, Z. *Macromolecules* **2005**, *38*, 2544.

(8) (a) Doi, Y.; Keii, T. *Adv. Polym. Sci.* **1986**, *73/74*, 201. (b) Doi, Y.; Tokuhito, N.; Soga, K. *Makromol. Chem., Macromol. Chem. Phys.* **1989**, *190*, 643.

(9) (a) Jayaratne, K. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 958. (b) Jayaratne, K. C.; Keaton, R. J.; Hennigsen, D. A.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 10490. (c) Keaton, R. J.; Jayaratne, K. C.; Hennigsen, D. A.; Koterwas, L. A.; Sita, L. R. *J. Am. Chem. Soc.* **2001**, *123*, 10754. (d) Keaton, R. J.; Jayaratne, K. C.; Hennigsen, D. A.; Koterwas, L. A.; Sita, L. R. *J. Am. Chem. Soc.* **2001**, *123*, 6197. (e) Zhang, Y.; Kissounko, D. A.; Fetting, J. C.; Sita, L. R. *Organometallics* **2003**, *22*, 21. (f) Zhang, Y.; Keaton, R. J.; Sita, L. R. *J. Am. Chem. Soc.* **2003**, *125*, 9062. (g) Zhang, Y.; Sita, L. R. *J. Am. Chem. Soc.* **2004**, *126*, 7776.

(10) (a) Tshuva, E. Y.; Goldberg, I.; Kol, M. *J. Am. Chem. Soc.* **2000**, *122*, 10706. (b) Segal, S.; Goldberg, I.; Kol, M. *Organometallics* **2005**, *24*, 200.

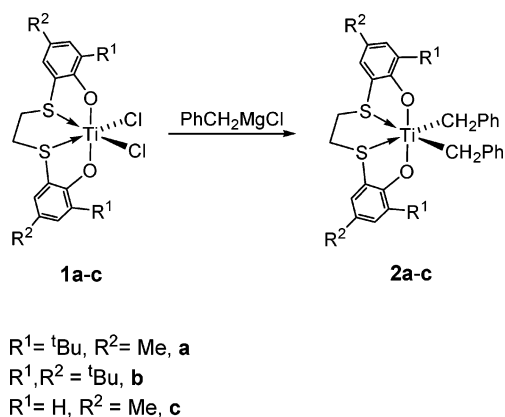
(11) For reviews on post-metallocene α -olefin polymerization catalysts, see: (a) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428. (b) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283.

(12) Szwarc, M.; Van Beylen, M. *Ionic Polymerization and Living Polymers*; Chapman & Hall: New York, 1993.

(13) For reviews, see: (a) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921. (b) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689.

(14) (a) Ishihara, N.; Seimiya, T.; Kuramoto, M.; Uoi, M. *Macromolecules* **1986**, *19*, 2464. (b) Ishihara, N.; Kuramoto, M.; Uoi, M. *Macromolecules* **1988**, *21*, 3356. For reviews, see: (c) Po, R.; Cardi, N. *Prog. Polym. Sci.* **1996**, *21*, 47. (d) Tomotsu, N.; Ishihara, N.; Newmann, T. H.; Malanga, M. T. *J. Mol. Catal., A: Chem.* **1998**, *128*, 167. (e) Pellicchia, C.; Grassi, A. *Top. Catal.* **1999**, *7*, 125.

Scheme 1



the early days of Ziegler–Natta catalysis.¹⁶ However, only recently was a post-metallocene catalyst precursor with a [OSSO]-type ligand introduced that upon methylaluminoxane (MAO) activation allows the efficient preparation of isotactic polystyrene of high molecular weight.^{17,18} Here we show that living isospecific polymerization of styrene is possible when dibenzyl titanium complexes with this ligand are used as structurally characterized precursors.

Results and Discussion

Synthesis and Structure of the Dibenzyl Complexes. The dibenzyl titanium complexes $[\text{Ti}(\text{OC}_6\text{H}_2\text{-R}^1\text{-6-R}^2\text{-4})_2\{\text{S}(\text{CH}_2)_2\text{S}\}(\text{CH}_2\text{Ph})_2]$ (**2a–c**; $R^1 = \text{tBu}$, $R^2 = \text{Me}$, **a**; $R^1, R^2 = \text{tBu}$, **b**; $R^1 = \text{H}$, $R^2 = \text{Me}$, **c**) were isolated as dark red microcrystals in 20–50% yield by reacting the corresponding dichloro complexes $[\text{Ti}(\text{OC}_6\text{H}_2\text{-R}^1\text{-6-R}^2\text{-4})_2\{\text{S}(\text{CH}_2)_2\text{S}\}\text{Cl}_2]$ (**1a–c**) with an ethereal solution of benzylmagnesium chloride in toluene at $-30\text{ }^\circ\text{C}$ (Scheme 1). In the ^1H NMR spectrum of **2a**, the benzylic protons appear as AB doublets at 3.36 and 3.40 ppm with a coupling constant of $^2J_{\text{HH}} = 9.2\text{ Hz}$. The protons of the methylene backbone appear as AA'BB' doublet-like multiplets at 1.77 and 2.27 ppm. The complex **2b** shows a similar ^1H NMR spectral pattern. The ^{13}C NMR spectra of both compounds show a singlet for the benzylic carbon atoms at 88.36 and 87.57 ppm, respectively, with a coupling constant of $^1J_{\text{CH}} = 132.2\text{ Hz}$. These

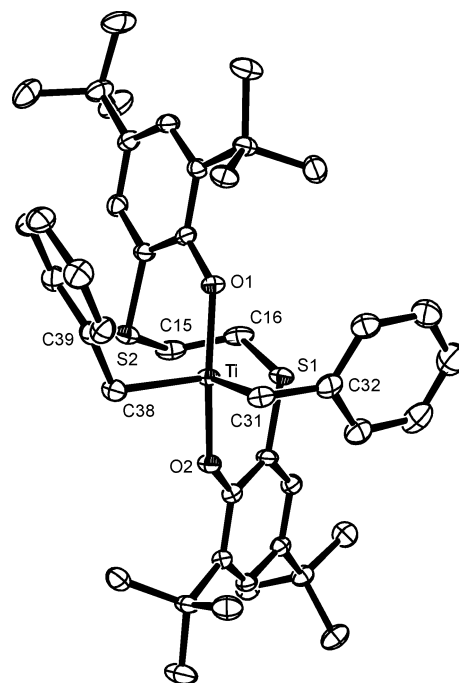


Figure 1. ORTEP diagram of the molecular structure of **2b**. Hydrogen atoms were omitted for clarity; thermal ellipsoids are drawn at the 50% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in **2b**

Ti–O1	1.8732(13)	Ti–O2	1.8758(13)
Ti–S1	2.8836(7)	Ti–S2	2.7472(7)
Ti–C31	2.149(2)	Ti–C38	2.137(2)
O1–Ti–O2	157.55(6)	O1–Ti–S1	72.23(4)
O1–Ti–S2	86.06(4)	O1–Ti–C31	100.59(7)
O1–Ti–C38	100.77(7)	O2–Ti–S1	92.57(4)
O2–Ti–S2	73.69(4)	O2–Ti–C31	93.18(7)
O2–Ti–C38	96.71(7)	S1–Ti–S2	74.14(2)
S1–Ti–C31	81.67(6)	S1–Ti–C38	168.23(6)
S2–Ti–C31	151.66(6)	S2–Ti–C38	115.45(6)
C31–Ti–C38	90.57(8)	Ti–S1–C2	92.27(7)
Ti–S1–C15	106.27(7)	C2–S1–C15	101.88(9)
Ti–C31–C32	116.28(13)	Ti–C38–C39	97.45(12)

values are higher than the expected values for a η^1 -coordinated benzyl group (122 to 126 Hz), suggesting a partial η^2 -coordination at the titanium center.¹⁹ Variable-temperature NMR studies (-70 to $+90\text{ }^\circ\text{C}$) indicated that both complexes are thermally robust and maintain their chiral C_2 -symmetric structure within this temperature range. Above $90\text{ }^\circ\text{C}$, decomposition starts under formation of toluene.

Single crystals of **2b** were obtained from a toluene/hexane mixture. The ORTEP diagram for the structure is shown in Figure 1, and selected bond lengths and bond distances are provided in Table 1. The molecular structure shows a C_2 -symmetrical [OSSO]-type ligand with the two benzyl groups in the *cis*-position ($\text{C31–Ti–C38 } 90.57(8)^\circ$). The dihedral angles Ti–C31–C32 and Ti–C38–C39 of $116.28(13)^\circ$ and $97.45(12)^\circ$ indicate that η^1 - as well as η^2 -coordination is present in the complex.²⁰ The elongated titanium sulfur bond distance ($\text{Ti–S1 } 2.8836(7)\text{ Å}$) as compared to the distance Ti–S2 of

(15) (a) Kawabe, M.; Murata, M. *Macromol. Chem. Phys.* **2001**, *202*, 2440. (b) Kawabe, M.; Murata, M. *Macromol. Chem. Phys.* **2001**, *202*, 1799. (c) Kawabe, M.; Murata, M.; Soga, K. *Macromol. Rapid Commun.* **1999**, *20*, 569.

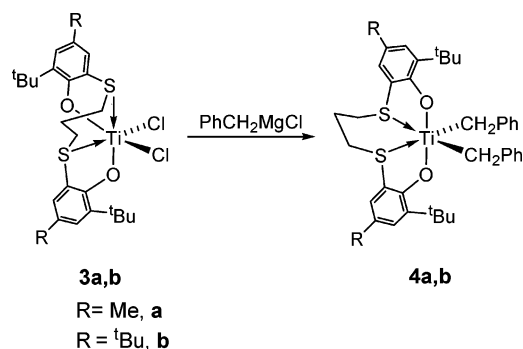
(16) (a) Natta, G.; Pino, P.; Corradini, P.; Danusso, F.; Mantica, E.; Mazzanti, G.; Moraglio, G. *J. Am. Chem. Soc.* **1955**, *77*, 1708. (b) Natta, G.; Corradini, P. *Makromol. Chem.* **1955**, *16*, 77. (c) Overberger, C.; Mark, H. *J. Polym. Sci.* **1959**, *35*, 381. (d) Kern, R. J.; Hurst, H. G.; Richard, W. *J. J. Polym. Sci.* **1960**, *45*, 195.

(17) (a) Capacchione, C.; Proto, A.; Ebeling, H.; Mülhaupt, R.; Möller, K.; Spaniol, T. P.; Okuda, J. *J. Am. Chem. Soc.* **2003**, *125*, 4964. (b) Capacchione, C.; D'Acunzi, M.; Motta, O.; Oliva, L.; Proto, A.; Okuda, J. *Macromol. Chem. Phys.* **2004**, *205*, 370. (c) Capacchione, C.; Manivannan, R.; Barone, M.; Beckerle, K.; Centore, R.; Oliva, L.; Proto, A.; Tuzi, A.; Spaniol, T. P.; Okuda, J. *Organometallics* **2005**, *24*, 2971. (d) Capacchione, C.; Proto, A.; Ebeling, H.; Mülhaupt, R.; Möller, K.; Manivannan, R.; Spaniol, T. P.; Okuda, J. *J. Mol. Catal. A: Chem.* **2004**, *213*, 137. (e) Beckerle, K.; Capacchione, C.; Ebeling, H.; Manivannan, R.; Mülhaupt, R.; Proto, A.; Spaniol, T. P.; Okuda, J. *J. Organomet. Chem.* **2004**, *689*, 4636.

(18) For other α -olefin polymerization using this type of catalysts, see: (a) Proto, A.; Capacchione, C.; Venditto, V.; Okuda, J. *Macromolecules* **2003**, *36*, 9249. (b) Capacchione, C.; Proto, A.; Okuda, J. *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 2815. (c) Capacchione, C.; De Carlo, F.; Zannoni, C.; Okuda, J.; Proto, A. *Macromolecules* **2004**, *37*, 8918. (d) Capacchione, C.; Proto, A.; Ebeling, H.; Mülhaupt, R.; Okuda, J. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1908.

(19) For examples of η^2 -coordinated benzyl groups at titanium, see: (a) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 902. (b) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willet, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111. (c) Bochmann, M.; Lancaster, S. J.; *Organometallics* **1993**, *12*, 633. (d) Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Malik, A. K. M. *Organometallics* **1994**, *13*, 2335.

Scheme 2

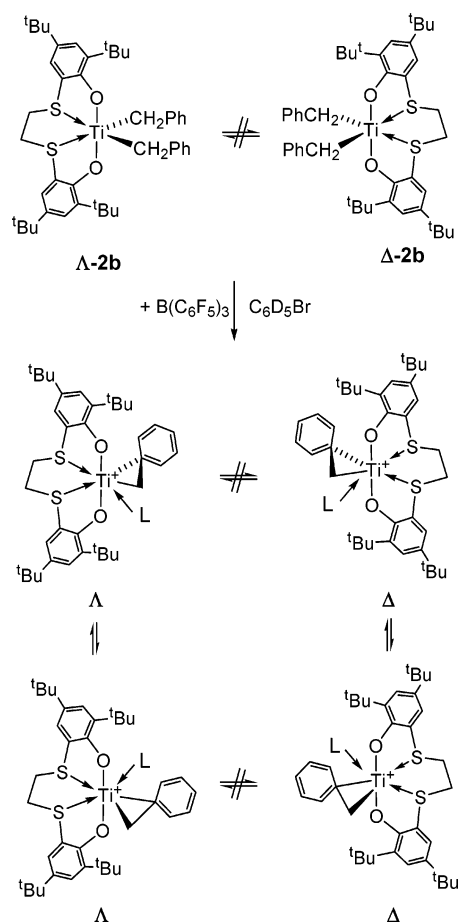


2.7472(7) Å can be explained by the stronger *trans*-influence of the η^2 -coordinated benzyl group in the solid state. The two oxygen ligands of the phenol are in the apical position, and the O1–Ti–O2 angle of 157.55(6)° significantly differs from linearity. The overall structure of **2b** is virtually analogous to that found for the hafnium complex [Hf(OC₆H₂-^tBu₂-4,6)₂{S(CH₂)₂S}(CH₂Ph)₂].^{17a}

In contrast, complex **2c**, which does not carry bulky *ortho*-substituents, was found to be highly fluxional. The ¹H NMR spectrum at ambient temperature shows only one singlet at 3.36 ppm for the methylene protons of the benzyl group. The CH₂CH₂ protons of the backbone within the bis(phenolato) ligand appear as a broad singlet at 1.98 ppm, overlapping with the signals of the *para* methyl groups. At temperatures below –20 °C, the CH₂CH₂ protons of the backbone appear as two broad doublets at 1.78 and 2.23 ppm. The benzylic protons still are recorded as a singlet at –20 °C, but at –55 °C, they appear as an AB quartet, which at –80 °C give rise to two broad singlets at 3.02 and 3.08 ppm. Consistent with these results, the ¹³C NMR spectrum at ambient temperature shows one signal at 36.92 ppm for the carbon atoms of the backbone and a single resonance at 89.87 ppm for the η^2 -coordinated CH₂ group (¹J_{CH} = 134 Hz). At temperatures above 40 °C, the complex starts to decompose under formation of 1,2-diphenylethane, indicating low stability in solution. Even at room temperature, **2c** was not stable in solution for more than 4 h. The decomposition resulted in the formation of a dark-colored solid that was insoluble in hydrocarbon solvents and CHCl₃.

Related benzyl complexes of the 1,5-dithiapentanediy-linked ligand [Ti(OC₆H₂-^tBu-6-R-4)₂{S(CH₂)₃S}(CH₂Ph)₂] (**4a,b**; R = Me, **a**; R = ^tBu, **b**) were synthesized in an analogous manner (Scheme 2). Similar to the highly fluxional dichloro complex

Scheme 3



3a,^{17c} the dibenzyl complex **4a** was configurationally fluxional within the temperature region of –70 to +80 °C with C_s-symmetry in solution. At room temperature, the ¹H NMR spectra show singlets for the benzylic protons at 3.59 ppm and the central CH₂ protons of the backbone appear as a higher order multiplet at 1.00 ppm; the SCH₂ protons are recorded as a triplet-like higher order multiplet at 2.13 ppm. At –70 °C, the benzylic protons appear as two broad singlets at 3.38 and 3.58 ppm and coalesce to a broad singlet at –35 °C. In the ¹³C NMR spectrum the benzylic carbon atom is recorded at 95.15 ppm (¹J_{CH} = 132.4 Hz). The ¹H NMR spectrum of **4b** is similar to that of **4a**. Upon standing at room temperature for more than 8 h, solutions of the complexes **4a,b** decompose under formation of toluene, indicating that these complexes are less stable than their 1,4-dithiabutanediyl-bridged counterparts **2a,b**. The high solubility of this complex in all common solvents precluded us from isolating this compound in pure form.

Generation of Benzyl Cations. For the MAO-activated dichloro complexes **1a,b**, we assume that an alkyl cation [Ti(OC₆H₂-^tBu₂-4,6)₂{S(CH₂)₂S}R]⁺ is generated as catalytically active species, similar to related nonmetallocene polymerization catalysts.¹¹ Adding B(C₆F₅)₃ to the dibenzyl complex **2b** in bromobenzene-*d*₅ at –30 °C immediately produced an orange solution. The ¹H NMR spectrum shows the signals of the ion pair [Ti(OC₆H₂-^tBu₂-4,6)₂{S(CH₂)₂S}(CH₂Ph)](PhCH₂)B(C₆F₅)₃, together with a small amount of free bis(phenol) as an impurity. Two-dimensional ¹H NMR spectra allowed us to assign the signals. At low temperature (–30 °C), two sets of signals of intensity ratio 55:45 are found; coalescence is observed at ca. 0 °C, where only one broad signal is observed for the ^tBu methyl groups. At elevated temperatures, the signals

(20) For bond angles, bond distances, and NMR spectroscopic data of other titanium dibenzyl complexes, see Table 2 and the following references: (a) Bassi, I. W.; Allegra, G.; Scordamaglia, R.; Chioccola, G. *J. Am. Chem. Soc.* **1971**, *93*, 3787. (b) Scholz, J.; Rehbaum, F.; Thiele, K. H.; Goddard, R.; Betz, P.; Krüger, C. *J. Organomet. Chem.* **1993**, *443*, 93. (c) Groysman, S.; Tshuva, E. Y.; Goldberg, I.; Kol, M.; Goldschmidt, Z.; Shuster, M. *Organometallics* **2004**, *23*, 5291. (d) van der Linden, A.; Schaverien, C. J.; Meijboom, N.; Ganter, C.; Orpen, A. G. *J. Am. Chem. Soc.* **1995**, *117*, 3008. (e) Thorn, M. G.; Etheridge, Z. C.; Fanwick, P. E.; Rothwell, I. P. *J. Organomet. Chem.* **1999**, *591*, 148. (f) Reimer, V.; Spaniol, T. P.; Okuda, J.; Ebeling, H.; Tuchbreiter, A.; Mülhaupt, R. *Inorg. Chim. Acta* **2003**, *345*, 221. (g) Fokken, S.; Reichwald, F.; Spaniol, T. P.; Okuda, J. *J. Organomet. Chem.* **2002**, *663*, 158. (h) Duchateau, R.; Cremer, U.; Harmsen, R. J.; Mohamud, S. I.; Abbenhuis, H. C. L.; van Santen, R. A.; Meetsma, A.; Thiele, S. K. H.; van Tol, M. F. H.; Kranenburg, M. *Organometallics* **1999**, *18*, 5447. (i) Carpentier, J. F.; Martin, A.; Swenson, D. C.; Jordan, R. F.; *Organometallics* **2003**, *22*, 4999. (j) Jeon, Y.-M.; Heo, J.; Lee, W. M.; Chang, T.; Kim, K. *Organometallics* **1999**, *18*, 4107. (k) Siemeling, U.; Kölling, L.; Stämmler, A.; Stämmler, H.-G. *J. Chem. Soc., Dalton Trans.* **2002**, 3277. (l) Tsui, B.; Swenson, D. C.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1997**, *16*, 1392. (m) Minhas, R. K.; Scoles, L.; Wong, S.; Gambarotta, S. *Organometallics* **1996**, *15*, 1113.

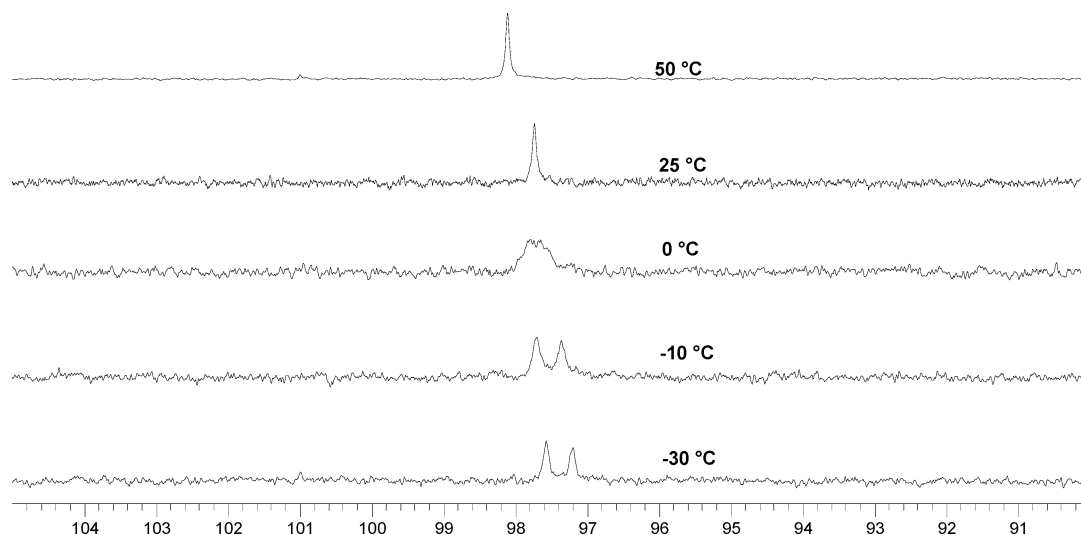


Figure 2. Variable-temperature ^{13}C NMR spectra of the benzyl cation prepared from **2b** and $\text{B}(\text{C}_6\text{F}_5)_3$ in bromobenzene. The expanded region shows the benzyl carbon signals.

become sharp. Above ca. 70 °C, slow decomposition sets in. The proton signals of the BCH_2 group at 3.4 ppm as well as the ^{19}F and ^{11}B NMR spectra suggest the presence of a solvent-separated ion pair.²¹

The two diastereomers can be distinguished in the ^{13}C NMR spectrum at low temperature (−30 °C), where the signal for the TiCH_2 carbon appears at 97.22 and 97.36 ppm (of equal intensity). The $^1J_{\text{CH}}$ value of 151 Hz indicates an η^2 -bonding nature of the benzyl group. The ^{13}C NMR spectra at −30 °C show that the ratio of both C_1 -symmetric diastereomers is nearly equal and suggests that epimerization does not occur on the NMR time scale at this temperature (Scheme 3). Coalescence is observed at −5 °C. Above this temperature, only one signal is observed, corresponding to only one species with C_2 -symmetry (Figure 2). The free energy of activation for this epimerization process was estimated to be $\Delta G^\ddagger = 52 \pm 4$ kJ/mol. We explain this fluxional behavior by the formation of an η^2 -bonded benzyl cation that coordinates either a solvent molecule or the anion, leading to diastereomeric pairs with pseudo-seven-coordinate configuration. We assume that the helicity change or Δ, Λ interconversion does not occur, but cannot exclude it conclusively at this time.

Similar NMR spectra were obtained for the cation generated from **2a**. The benzyl cations derived from the complexes **2a** and **2b** were stable within the same temperature range and decompose slowly at elevated temperature, giving 1,2-diphenylethane and toluene.

Complex **2c** immediately decomposed upon reaction with $\text{B}(\text{C}_6\text{F}_5)_3$ with formation of 1,2-diphenylethane and toluene, as indicated by the ^1H NMR spectrum. Activation of **4a** and **4b** with $\text{B}(\text{C}_6\text{F}_5)_3$ in bromobenzene at −30 °C led to a color change of the initially dark red solution to pale red; only broad resonances attributable to (paramagnetic) decomposition products could be observed in the ^1H NMR spectrum. We suspect that the alkyl cation derived from the longer 1,5-dithiapentane bridge more readily undergoes reduction by homolytic dissocia-

tion of the alkyl radical to give $\text{Ti}(\text{III})$ species than the corresponding complex with a 1,4-dithiabutane bridge.²²

Styrene Polymerization. Polymerization data of styrene using the dibenzyl titanium complex **2a** activated with $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ in the presence of the trialkylaluminum compound Al^iOct_3 are presented in Table 3. The molecular weight of the polymers increases linearly with the conversion up to ca. 70% (Figure 3). The semilogarithmic plot of monomer conversion against time also shows linearity (Figure 4). In all of these experiments, the polydispersity remains low ($M_w/M_n < \sim 1.2$), and there is no consistent trend toward a broader molecular weight distribution upon increasing conversion. The larger molecular weight distribution of some samples is caused by varying amounts of a byproduct of higher molecular weight. Closer examination of these bimodal distributions shows that both fractions have a narrow molecular weight distribution ($M_w/M_n < \sim 1.1$) and that the molecular weight of the byproduct is twice the molecular weight of the main fraction. We assume that this byproduct is formed during aerobic workup by coupling of two polymer chains via a radical mechanism.²³ The initiator efficiencies < 100% result in molecular weights higher than the calculated values.

Activation of the benzyl complex with $\text{B}(\text{C}_6\text{F}_5)_3$ is possible, but leads to slightly broader molecular weight distributions, most probably because of the stronger coordinating character of the anion compared to that of the perfluorinated borate. The presence of aluminum alkyl is essential for the polymerization, although an excess does not influence the polymerization behavior. It is probably involved in “masking” the *N,N*-dimethylaniline that would coordinate at the active center.

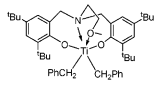
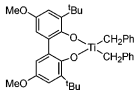
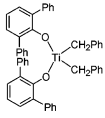
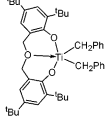
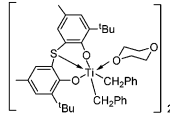
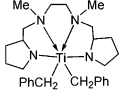
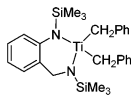
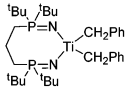
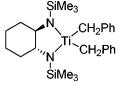
DSC measurements of the polymers show melting temperatures of ca. 210 °C. These T_m values are slightly lower than those of high molecular weight isotactic polystyrenes,^{17a,c} but given the relatively low molecular weight of the samples, these values can be regarded as typical. ^{13}C NMR spectroscopic analysis of the samples revealed perfect isotacticity with $[\text{rr}]$

(21) For coordination of $[(\text{PhCH}_2)\text{B}(\text{C}_6\text{F}_5)_3]^-$ at a cationic group 4 metal center, see: (a) Pellecchia, C.; Immirzi, A.; Grassi, A.; Zambelli, A. *Organometallics* **1993**, *12*, 4473. (b) Pellecchia, C.; Grassi, A.; Immirzi, A. *J. Am. Chem. Soc.* **1993**, *115*, 1160. (c) Horton, A. D.; de With, J.; van der Linden, A. J.; van de Weg, H. *Organometallics* **1996**, *15*, 2672. (d) Horton, A. D.; de With, J. *Organometallics* **1997**, *16*, 5424.

(22) Borkowsky, S. L.; Baenziger, N. C.; Jordan, R. F. *Organometallics* **1993**, *12*, 486.

(23) (a) Odian, G. *Principles of Polymerization*, 3rd ed.; John Wiley: New York, 1991; p 403. (b) Takaki, M.; Asami, R.; Kuwata, R. *Macromolecules* **1979**, *12*, 378. (c) Asami, R.; Takaki, M.; Hanahata, H. *Macromolecules* **1983**, *16*, 628.

Table 2. Structural Comparisons of Some Benzyl Titanium Complexes

Compound	d(Ti-CH ₂) (Å)	Ti-CH ₂ -Ph (deg)	¹³ C NMR δ (¹ J _{CH} , Hz)	Ref.
Ti(CH ₂ Ph) ₄	2.13(3), 2.13(3), 2.15(3), 2.14(3)	88(2), 98(2), 108(2), 116(2)	98.4 (132.0)	20a
Ti(η ⁵ -C ₅ H ₅) ₂ (CH ₂ Ph) ₂	2.239(6), 2.210(5)	120.8(4), 123.1(4)	92.5 (125.8)	20b
2b	2.137(2), 2.149(2)	97.45(12), 116.28(13)	87.57 (132.2)	this work
	2.128(4), 2.129(4)	120.3(3), 120.7(3)	-	20c
	2.075(11), 2.080(12)	100.0(7), 106.5(6)	87.0	20d
	2.078(5), 2.091(5)	102.1(3), 113.1(1)	94.0	20e
	2.086(5), 2.109(4)	102.8(3), 103.6(3)	86.0	20f
	2.115(2), 2.170(3)	116.1(2), 121.8(2)	90.0 and 97.4	20g
Ti{η ⁵ -C ₅ H ₅ (SiMe ₃) ₂ -1,3}(OSiPh ₃)(CH ₂ Ph) ₂	2.140(2), 2.145(2)	113.54(14), 118.49(15)	86.83 (127.0)	20h
	2.190(7), 2.210(7)	122.9(5)	81.9 (120.0)	20i
	2.114(4), 2.138(4)	92.5(3), 118.5(2)	82.5 (123.4)	20j
	2.157(5), 2.165(4)	107.0(2)	65.6	20k
	2.143(2)	113.7(1)	75.2 (117.0)	20l
Ti{N(SiMe ₃) ₂ } ₂ (CH ₂ Ph) ₂	2.092(5), 2.109(4)	119.2(3), 120.7(3)	99.2	20m

> 95%. Finally, we have confirmed by acetone extraction that the polymer samples are not contaminated with atactic polystyrene that might have been formed by radical or cation initiation.

Conclusion

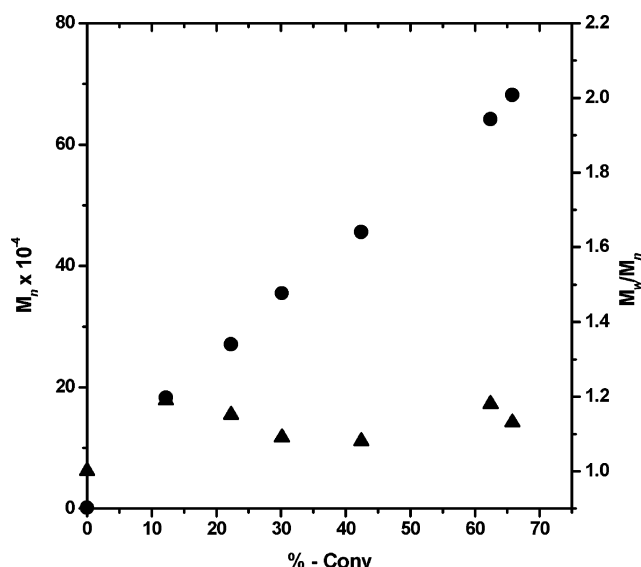
Chiral titanium dibenzyl complexes with bulky *ortho* substituents in the 1,4-dithiabutanediylbis(phenolato) ligand do not undergo Δ,Λ interconversion on the NMR time scale. Reaction of these complexes with B(C₆F₅)₃ gives rise to two diastereomeric benzyl cations in a 55:45 ratio at lower temperatures. However, at higher temperatures epimerization occurs, by labile

solvent/anion coordination and η²-bonding of the benzyl group rather than by helicity change of the tetradentate ligand. When the dibenzyl complexes were activated with B(C₆F₅)₃ or [PhNMe₂H][B(C₆F₅)] in the presence of trialkylaluminum, isospecific polymerization of styrene could be performed in a living fashion for the first time. Complexes that do not bear *ortho* substituents in the aromatic ring of the phenol moiety are fluxional in solution and rapidly decompose in solution. The corresponding dibenzyl complexes with 1,5-dithiapentanediyllinked bis(phenolato) ligands are also fluxional and unstable in solution. Reaction of these dibenzyl complexes with B(C₆F₅)₃ results in decomposition.

Table 3. Styrene Polymerization by **2a** Activated by [PhNMe₂H][B(C₆F₅)₄] and AlⁿOct₃^a

run	Al equiv ^b	t (h)	% conv	$M_n (\times 10^3 \text{ g mol}^{-1})$	M_w/M_n	efficiency ^c	T_m (°C)
1	1	0.5	12.2	18.3	1.19	35	n.d.
2	1	1	22.3	27.1	1.15	43	n.d.
3	1	1.5	30.1	35.1	1.09	44	n.d.
4	1	2	42.4	49.9	1.08	48	n.d.
5	1	3	62.4	64.1 ^d	1.18	50	n.d.
6	1	4	65.8	67.1 ^d	1.13	50	207 ^e
7	1	5	90.8	106.1 ^d	1.27	45	210
8	2	2	78.9	72.5	1.19	57	215
9	3	2	71.3	67.0	1.20	55	217

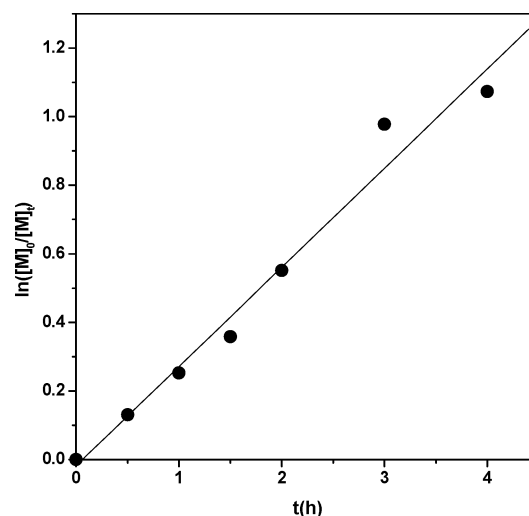
^a Conditions: [Ti] = 10^{−3} M, [B] = 0.9 × 10^{−3} M in 10 mL of toluene; [styrene]/[Ti] = 500; T = 25 °C. ^b AlⁿOct₃. ^c Efficiency defined as the percentage of active initiators, calculated from the observed number of polymer chains relative to the theoretical ones, assuming that each titanium complex initiates one polymer chain. ^d Bimodal. ^e [rr] > 95% by ¹³C NMR spectroscopy (see Supporting Information).

**Figure 3.** Plot of number-averaged molecular weights M_n and polydispersity index versus conversion during isospecific styrene polymerization using **2a** activated by [PhNMe₂H][B(C₆F₅)₄] and AlⁿOct₃.

Experimental Section

General Considerations. All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. Diethyl ether was distilled from sodium benzophenone ketyl; hexane and toluene were purified by distillation from sodium/triglyme benzophenone ketyl. Titanium tetrachloride (ALFA or Strem), 25 wt % tri-*n*-octylaluminum solution in hexane, and 1 M benzylmagnesium chloride solution in diethyl ether (Aldrich) were used as received. Dichloro titanium complexes of 1,4-dithiabutanediyl- (**1a–c**) and 1,5-dithiapentanediy- (**3a,b**) ligands were prepared according to published procedures.^{17c} All other chemicals were commercially available and used after appropriate purification. NMR spectra were recorded on a Bruker DRX 400 spectrometer (¹H, 400 MHz; ¹³C, 101 MHz) in C₆D₆ at 25 °C, unless otherwise stated. All variable-temperature NMR measurements were carried out in toluene-*d*₈. Chemical shifts for ¹H and ¹³C spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. Assignments were verified by correlated spectroscopy. Elemental analyses were performed by the Microanalytical Laboratory of this department.

Dibenzyl{1,4-dithiabutanediyl-2,2'-bis(6-*tert*-butyl-4-methylphenoxy)}titanium (2a**).** To a solution of **1a** (1.51 g, 2.80 mmol)

**Figure 4.** Semilogarithmic plot of styrene conversion against time using **2a** activated by [PhNMe₂H][B(C₆F₅)₄] and AlⁿOct₃ (linear fit, R = 0.988).

in 50 mL of toluene at −78 °C was added a 1.0 M solution of PhCH₂MgCl in diethyl ether (0.89 g, 5.9 mL, 5.9 mmol) dropwise over a period of 15 min, and the dark red colored mixture stirred for 1 h at −78 °C. The dark red colored solution was then gradually allowed to warm to 0 °C and stirred for 2 h at the same temperature. After filtration the solution was concentrated to 3 mL, an equal volume of hexane was added, and the mixture was stored at −20 °C to afford 0.83 g of a red-brown powder in 46% yield. ¹H NMR: δ 1.71 (s, 18 H, C(CH₃)₃), 1.77 (d, 2 H, ²J_{HH} = 10.0 Hz, SCH₂), 2.07 (s, 6 H, 4-CH₃), 2.27 (d, 2 H, ²J_{HH} = 10.0 Hz, SCH₂), 3.36 (d, 2 H, ²J_{HH} = 9.2 Hz, TiCH₂), 3.40 (d, 2 H, ²J_{HH} = 9.2 Hz, TiCH₂), 6.68 (d, 2 H, ⁴J_{HH} = 1.2 Hz, 5-CH), 6.85 (t, 2 H, ³J_{HH} = 7.2 Hz, *p*-CH₂Ph), 7.06 (t, 4 H, ³J_{HH} = 7.6 Hz, *m*-CH₂Ph), 7.17 (s, 2 H, 3-CH, overlap with solvent signal), 7.20 (d, 4 H, *o*-CH₂Ph). ¹³C{¹H} NMR (25 °C, C₆D₆): δ 20.79 (CH₃), 29.78 (C(CH₃)₃), 35.45 (C(CH₃)₃), 37.48 (SCH₂), 88.36 (TiCH₂), 120.92 (C-2), 123.70 (*p*-CH₂Ph), 129.55 (*m*-CH₂Ph), 129.90 (C-4), 130.08 (C-3), 130.47 (*o*-CH₂Ph), 131.07 (C-5), 137.49 (C-6), 144.17 (*ipso*-CH₂Ph), 166.26 (C-1). Anal. Calcd for C₄₄H₅₈O₂S₂Ti: C, 70.57; H, 7.17; S, 9.92. Found: C, 69.95; H, 7.30; S, 9.62.

Dibenzyl{1,4-dithiabutanediyl-2,2'-bis(4,6-di-*tert*-butylphenoxy)}titanium (2b**).** To a solution of **1b** (1.70 g, 2.74 mmol) in toluene at −78 °C was added a 1.0 M solution of PhCH₂MgCl in diethyl ether (0.83 g, 5.5 mL, 5.50 mmol) dropwise over a period of 15 min, and the dark red colored mixture stirred for 1 h at −78 °C. The dark red colored solution was then gradually allowed to warm to 0 °C and stirred for 2 h at 0 °C. After filtration the solution was concentrated to 3 mL, an equal volume of *n*-hexane was added, and the mixture was stored at −20 °C to afford 0.88 g of dark red microcrystals; yield 45%. ¹H NMR: δ 1.22 (s, 18 H, C(CH₃)₃), 1.75 (s, 18 H, C(CH₃)₃), 1.87 (d, 2 H, ²J_{HH} = 10.0 Hz, SCH₂), 2.37 (d, 2 H, ²J_{HH} = 10.0 Hz, SCH₂), 3.27 (d, 2 H, ²J_{HH} = 8.8 Hz, TiCH₂), 3.34 (d, 2 H, ²J_{HH} = 8.8 Hz, TiCH₂), 6.84 (t, 2 H, ³J_{HH} = 7.2 Hz, *p*-CH₂Ph), 7.02 (t, 4 H, ³J_{HH} = 7.5 Hz, *m*-CH₂Ph), 7.03 (d, 2 H, ⁴J_{HH} = 2.4 Hz, 5-CH), 7.16 (d, 4 H, ³J_{HH} = 7.2 Hz, *o*-CH₂Ph, overlap with solvent signal), 7.52 (d, 2 H, ⁴J_{HH} = 2.4 Hz, 3-CH). ¹³C{¹H} NMR: δ 30.01 (C(CH₃)₃), 31.65 (C(CH₃)₃), 34.51 (C(CH₃)₃), 35.75 (C(CH₃)₃), 37.84 (SCH₂), 87.57 (TiCH₂), 120.75 (C-2), 123.71 (*p*-CH₂Ph), 125.99 (C-3), 127.87 (C-5), 128.2 (*m*-CH₂Ph, overlap with solvent signal), 130.14 (*o*-CH₂Ph), 136.96 (C-4), 143.19 (C-6), 144.05 (*ipso*-CH₂Ph), 166.22 (C-1). Anal. Calcd for C₄₄H₅₈O₂S₂Ti: C, 72.30; H, 8.00; S, 8.77. Found: C 71.57; H, 7.98; S, 8.75.

Dibenzyl{1,4-dithiapentanediy-2,2'-bis(4-methylphenoxy)}titanium (2c**).** To a suspension of **1c** in 2 mL diethyl ether (1.01

Table 4. Experimental Data for the Crystal Structure Determinations of 2b

formula	C _{47.50} H ₆₂ O ₂ S ₂ Ti
fw	777.02
cryst size, mm	0.63 × 0.26 × 0.14
cryst color	dark red
cryst syst	triclinic
space group	P $\bar{1}$ (no. 2)
a, Å	9.4075(18)
b, Å	15.683(3)
c, Å	16.292(3)
α , deg	104.389(5)
β , deg	102.912(5)
γ , deg	103.148(5)
V, Å ³	2165.1(7)
Z	2
ρ_{calcd} , g cm ⁻³	1.192
μ , mm ⁻¹	0.330
F(000)	834
2 θ_{max} , deg	1.35 to 26.06
index ranges	h, -11 to 11 k, -19 to 19 l, -20 to 20
no. of reflns measd	25 373
no. of indep reflns	8507 [R(int) = 0.0428]
no. of params	548
GOF	1.024
final R indices R ₁ , wR ₂ (obsd data)	0.0422/0.1011
final R indices R ₁ , wR ₂ (all data)	0.0561/0.1083
largest e-max., e-min., e Å ⁻³	0.477/-0.229

g, 2.38 mmol) at -30 °C was added dropwise a 1.0 M solution of PhCH₂MgCl in diethyl ether (0.76 g, 5.0 mL, 5.01 mmol) and stirred for 1 h at the same temperature. Then, 15 mL of diethyl ether was added at -30 °C, and the solution was then gradually allowed to warm to ambient temperature and stirred for 4 h. The solution was filtered, concentrated, and stored at -30 °C to afford a dark red powder; yield 0.27 g (22%). ¹H NMR: δ 1.98 (br s, 10 H, 4-CH₃ and SCH₂), 3.37 (s, 4 H, TiCH₂), 6.65 (d, 2 H, ⁴J_{HH} = 1.5 Hz, C5), 6.86 (d, 2 H, ³J_{HH} = 7.5 Hz, C3), 6.87 (t, 2 H, ³J_{HH} = 7.5 Hz, *p*-CH₂Ph), 6.94 (d, 2 H, ³J_{HH} = 7.5 Hz, C6), 7.07 (t, 4 H, ³J_{HH} = 7.5 Hz, *m*-CH₂Ph), 7.22 (d, 4 H, ³J_{HH} = 7.5 Hz, *o*-CH₂Ph). ¹³C{¹H} NMR: δ 20.35 (4-CH₃), 36.92 (SCH₂), 89.27 (TiCH₂), 116.41 (C-6), 119.80 (C-2), 123.76 (*p*-CH₂Ph), 128.58 (*m*-CH₂Ph), 129.95 (C-4), 130.67 (*o*-CH₂Ph), 132.55 (C-3), 133.37 (C-5), 142.0 (*ipso*-CH₂Ph), 167.64 (C-1).

Dibenzyl{1,5-dithiapentanediy-2,2'-bis(6-*tert*-butyl-4-methylphenoxy)}titanium (4a). To a solution of **3a** (0.63 g, 1.13 mmol) in diethyl ether at -30 °C was added dropwise 1.0 M PhCH₂MgCl in diethyl ether (0.34 g, 2.3 mL, 2.30 mmol), and the mixture was stirred for 1 h at the same temperature. The solution was then gradually allowed to warm to ambient temperature and stirred for 6 h. The solution was filtered and concentrated to give 0.28 g of dark red powder; yield 37%. Analytical samples were obtained from a toluene/diethyl ether mixture at 0 °C. ¹H NMR: δ 1.00 (quint, ³J_{HH} = 5.8 Hz, 2 H, CH₂), 1.84 (s, 18 H, C(CH₃)₃), 2.13 (t, ²J_{HH} = 5.8 Hz, 4 H, SCH₂), 2.23 (s, 6 H, CH₃), 3.59 (s, 4 H, TiCH₂), 6.85 (d, 2 H, ⁴J_{HH} = 1.2 Hz, 5-CH), 6.95 (t, ³J_{HH} = 7.3 Hz, 2 H, *p*-CH₂Ph), 7.18 (t, 4 H, ³J_{HH} = 7.3 Hz, *m*-CH₂Ph), 7.26–7.28 (m, 4 H, overlap with solvent signal, *o*-CH₂Ph), 7.29 (s, 2 H, 3-CH). ¹³C{¹H} NMR: δ 20.93 (CH₃), 22.84 (CH₂), 30.03 (C(CH₃)₃), 34.76 (SCH₂), 35.52 (C(CH₃)₃), 95.15 (TiCH₂), 123.06 (C-2), 124.92 (*p*-CH₂Ph), 128.38 (*m*-CH₂Ph), 128.52 (C-4), 128.86 (C-3), 129.74 (C-5), 130.38 (*o*-CH₂Ph), 137.51 (C-6), 146.41 (*ipso*-CH₂Ph), 164.79 (C-1). Anal. Calcd for C₃₉H₄₈O₂S₂Ti: C, 70.89; H, 7.32; S, 9.70. Found: C, 69.49; H, 7.12; S, 9.85.

Dibenzyl{1,5-dithiapentanediy-2,2'-bis(4,6-di-*tert*-butylphenoxy)}titanium (4b). To a solution of **3b** (0.64 g, 1.0 mmol) in toluene at -78 °C was added dropwise PhCH₂MgCl in diethyl ether (0.35 g, 2.2 mL, 2.2 mmol), and the mixture was stirred for 1 h at the same temperature. The reaction mixture was gradually allowed to warm to 0 °C and stirred for 2 h. The solution was

filtered and concentrated to afford a dark red oil. Repeated attempts to crystallize failed. ¹H NMR: δ 1.25 (s, 18 H, C(CH₃)₃), 1.49 (m, 2 H, CH₂), 1.57 (s, 18 H, C(CH₃)₃), 2.21 (t, 4 H, ²J_{HH} = 7 Hz, SCH₂), 3.49 (s, 4 H, TiCH₂), 6.68 (s, 2 H, 5-CH), 7.01 (t, 2 H, ³J_{HH} = 6 Hz, *p*-CH₂Ph), 7.14 (m, 4 H, overlap with solvent signal, *m*-CH₂Ph), 7.18 (m, 4 H, partial overlap with solvent signal, *o*-CH₂Ph), 7.52 (d, 2 H, ⁴J_{HH} = 2.4 Hz, 3-CH). ¹³C{¹H} NMR (C₆D₆, 25 °C): δ 30.00 (C(CH₃)₃), 31.65 (C(CH₃)₃), 34.51 (C(CH₃)₃), 35.75 (C(CH₃)₃), 37.84 (SCH₂), 87.57 (TiCH₂), 120.75 (*p*-CH₂Ph), 123.71 (C-2), 125.98 (C-3), 127.39 (*o*-CH₂Ph, overlap with solvent signal), 127.76 (*m*-CH₂Ph), 136.95 (C-4), 143.91 (C-6), 144.04 (*ipso*-CH₂Ph), 166.21 (C-1).

Reaction of 2a with B(C₆F₅)₃. To a solid mixture of **2a** (30 mg, 46 μ mol) and B(C₆F₅)₃ (28 mg, 55 μ mol) in an NMR tube was added a cooled solution of bromobenzene-*d*₅ at -30 °C, and the reaction was monitored at different temperatures. ¹H NMR (C₆D₅Br, -30 °C): δ 1.33 (s, 9 H, C(CH₃)₃), 1.35 (s, 18 H, C(CH₃)₃), 1.46 (s, 9 H, C(CH₃)₃), 1.81 (m, 2 H, SCH₂), 2.0–2.1 (br m, SCH₂, overlap with CH₃ signals), 2.05 (s, 3 H, CH₃), 2.09 (s, 3 H, CH₃), 2.13 (s, 3 H, CH₃), 2.18 (s, 3 H, CH₃), 2.47 (d, 1 H, ²J_{HH} = 9 Hz, SCH₂), 2.53 (d, 1 H, ²J_{HH} = 9 Hz, SCH₂), 2.74 (d, 1 H, ²J_{HH} = 9 Hz, SCH₂), 3.06 (d, 1 H, ²J_{HH} = 9 Hz, SCH₂), 3.39 (s, 1 H, TiCH₂) overlap with 3.41 (br s, 4 H, BCH₂), 3.76 (br s, 2 H, TiCH₂), 3.89 (br, 1 H, TiCH₂), 6.31 (s, 1 H), 6.43 (br d, 1 H), 6.56 (d, 2 H), 6.74–6.85 (m), 6.98–7.05 (m, overlap with solvent signals), 7.12 (m), 7.17–7.21 (m), 7.38 (m, 1 H), 7.48 (m, 2 H). ¹H NMR (C₆D₅Br, +50 °C): δ 1.42 (s, 18 H, C(CH₃)₃), 2.05 (d, 2 H, ²J_{HH} = 6.5 Hz, SCH₂), 2.17 (s, 6 H, CH₃), 2.79 (d, 2 H, ²J_{HH} = 6.5 Hz, SCH₂), 3.31 (br s, 2 H, BCH₂), 3.79 (d, 1 H, ²J_{HH} = 6.5, TiCH₂), 3.94 (d, 1 H, ²J_{HH} = 6.5, TiCH₂), 6.7 (s, 2 H, 5-CH), 6.98 (m, 2 H, *m*-TiCH₂Ph), 7.06 (m, 1 H, *p*-TiCH₂Ph), 7.1–7.2 (m, 5 H, BCH₂Ph), 7.15 (m, 2 H, *o*-TiCH₂Ph), 7.34 (s, 2 H, 3-CH). ¹³C{¹H} NMR (C₆D₅Br, -30 °C): δ 20.90, 20.95 (CH₃), 29.11, 29.22, 29.41 (C(CH₃)₃), 32.12 (br s, BCH₂), 36.18, 38.31, 39.32, 41.58 (SCH₂), 97.19 (TiCH₂), 97.57 (TiCH₂), 122.4–149.8 (aromatic signals and solvent signals), 162.58 (s, C-1), 162.79 (s, C-1), 163.61 (s, C-1), 164.06 (s, C-1). ¹³C{¹H} NMR (C₆D₅Br, +50 °C): δ 20.64 (CH₃), 29.57 (C(CH₃)₃), 31.9 (br s, BCH₂), 34.17 (C(CH₃)₃), 37.94 (SCH₂), 41.17 (SCH₂), 98.11 (TiCH₂), 122.4–140.4 (aromatic signals, overlap with solvent signals), 147.49 (*ipso*-CH₂Ph), 163.38 (C-1). ¹¹B NMR (C₆D₅Br, -30 °C): δ -12.15 (s). ¹⁹F NMR (C₆D₅Br, -30 °C): δ -130.25 (d, ³J_{FF} = 14 Hz, *o*-C₆F₅), -162.95 (t, ³J_{FF} = 14 Hz, *p*-C₆F₅), -165.78 (d, ³J_{FF} = 14 Hz, *m*-C₆F₅).

Reaction of 2b with B(C₆F₅)₃. To a solid mixture of **2b** (32 mg, 43 μ mol) and B(C₆F₅)₃ (27 mg, 52 μ mol) in an NMR tube was added a cooled solution of bromobenzene-*d*₅ at -30 °C, and the reaction was monitored at different temperatures. ¹H NMR (C₆D₅Br, -30 °C): δ 1.15 (s, 9 H, C(CH₃)₃), 1.21 (s, 9 H, C(CH₃)₃), 1.24 (s, 9 H, C(CH₃)₃), 1.29 (s, 9 H, C(CH₃)₃), 1.39 (s, 9 H, C(CH₃)₃), 1.42 (s, 18 H, C(CH₃)₃), 1.54 (s, 9 H, C(CH₃)₃), 1.68 (d, 1 H, ²J_{HH} = 8 Hz, SCH₂), 1.89 (m, 2 H, SCH₂), 2.06 (m, 1 H, SCH₂), 2.22 (m, 1 H, SCH₂), 2.52 (m, 1 H, ²J_{HH} = 8 Hz, SCH₂), 2.75 (d, 1 H, ²J_{HH} = 8 Hz, SCH₂), 3.15 (d, 1 H, ²J_{HH} = 8 Hz, SCH₂), 3.35 (m, 1 H, TiCH₂), 3.44 (br s, BCH₂), 3.78 (s, 1 H, TiCH₂), 3.82 (s, 1 H, TiCH₂), 3.89 (m, 1 H, TiCH₂), 6.48 (br d, 1 H), 6.55 (br s, 1 H), 6.68 (br d, 1 H), 6.86 (br), 6.94–7.02 (br m), 7.29 (br), 7.44 (br), 7.48 (br), 7.53 (aromatic signals). ¹H NMR (C₆D₅Br, +60 °C): δ 1.32 (s, 18 H, C(CH₃)₃), 1.52 (s, 18 H, C(CH₃)₃), 2.14 (d, 2 H, ²J_{HH} = 7 Hz, SCH₂), 2.88 (d, 2 H, ²J_{HH} = 7 Hz, SCH₂), 3.37 (br s, 2 H, BCH₂), 3.85 (d, 1 H, ²J_{HH} = 4 Hz, TiCH₂), 4.01 (d, 1 H, ²J_{HH} = 4 Hz, TiCH₂), 6.75–6.90 (m), 6.98 (br), 7.05 (s), 7.15 (br m), 7.40 (br), 7.53 (br) (aromatic signals). ¹³C NMR (C₆D₅Br, -30 °C): δ 29.14, 29.28, 29.51, C(CH₃)₃), 31.34, 31.41, C(CH₃)₃), 34.60, 34.73, 34.82, 44.88 (C(CH₃)₃), 35.4 (br, BCH₂), 36.0, 37.5, 39.96, 41.73 (SCH₂), 97.22 (TiCH₂), 97.36 (TiCH₂), 119.96–136.42 (aromatic signals, overlap with solvent

signals), 146.52, 147.33, 149.01, 149.72 (*ipso*-CH₂Ph), 162.74, 163.58, 164.19 (s, C-1). ¹³C NMR (C₆D₅Br, +50 °C): δ 29.53 (C(CH₃)₃), 31.25 (C(CH₃)₃), 34.68 (C(CH₃)₃), 34.91 (C(CH₃)₃), 37.81 (br, BCH₂), 41.54 (SCH₂), 89.35 (TiCH₂), 121.08–149.80 (aromatic signals, overlap with solvent signals), 163.30 (C-1). ¹¹B NMR (C₆D₅Br, –30 °C): δ –12.23 (s). ¹⁹F NMR (C₆D₅Br, –30 °C): δ –130.23 (d, ³J_{FF} = 14 Hz, *o*-C₆F₅), –162.98 (t, ³J_{FF} = 14 Hz, *p*-C₆F₅), –165.80 (d, ³J_{FF} = 14 Hz, *m*-C₆F₅).

Crystal Structure Analysis of 2b. Crystallographic data for **2b** are summarized in Table 1. Single-crystals suitable for X-ray crystal structure analysis were obtained by slow evaporation of toluene as toluene solvate inside the glovebox at ambient temperature. The data collection was performed using ω scans on a Bruker AXS diffractometer with graphite-monochromated Mo K α radiation at 120(2) K. The data collection as well as the data reduction and correction for absorption was carried out using the program system SMART.^{24a} The structure was solved using the program SHELXS-86^{24b} and was found to be isotypic to [Hf(OC₆H₂-ⁱBu₂-4,6)₂–{S(CH₂)₂S}(CH₂Ph)₂].^{17a} From the measured reflections, all independent reflections were used, and the parameters were refined by full-matrix least-squares against all F_o^2 data (SHELXL-97)^{24c} and refined with anisotropic thermal parameters. For the graphical

representation, ORTEP-III for Windows was used as implemented in the program system WINGX.^{24d}

Styrene Polymerization. A 25 mL Schlenk tube was charged with toluene (calculated for an overall volume of 10 mL; toluene and styrene were dried over sodium and calcium hydride, respectively, and degassed three times before use). A 0.01 M solution of **2a** in toluene (1 mL, 10 μ mol) was added, followed by a 4.5 mM solution of [PhNMe₂H][B(C₆F₅)] in toluene (2 mL; 9.0 μ mol) and a 5 mM solution of tri(*n*-octyl)aluminum in hexane/toluene (1–3 mL; 5–15 μ mol). This mixture was stirred for 20 min, 500 mg of styrene (4.80 mmol), if not stated otherwise in Table 3, was added, and the mixture was stirred for the time given in Table 3. The reaction mixture was quenched by addition of 0.1 mL of acidified methanol, and the polymer was precipitated from 100 mL of acidified methanol and dried in vacuo at 60 °C for several hours.

Acknowledgment. Financial support by the EU Commission (FP6 project: NMP3-CT-2005-516972), the Deutsche Forschungsgemeinschaft, and the Fonds der Chemischen Industrie is gratefully acknowledged. R.M. thanks the Alexander von Humboldt Foundation for a postdoctoral fellowship.

Supporting Information Available: Tables of all crystal data and refinement parameters, atomic parameters including hydrogen atoms, thermal parameters, and bond lengths and angles for **2b**. Variable-temperature ¹H and ¹³C NMR spectra of the reaction mixture of **2a** with B(C₆F₅)₃. ¹H and ¹³C NMR spectra of isotactic polystyrene obtained by titanium complex **2a** activated with [PhNMe₂H][B(C₆F₅)₄]/AlⁿOct₃. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM060047E

(24) (a) Siemens. *ASTRO, SAINT, and SADABS. Data Collection and Processing Software for the SMART System*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1996. (b) Sheldrick, G. M. *SHELXS-86, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1986. (c) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997. (d) Farrugia, L. J. WinGX—Version 1.64.02, An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single-Crystal X-Ray Diffraction Data. *J. Appl. Crystallogr.* **1999**, 32, 837.