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

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Dibenzyl complexes $[Ti(OC_6H_2\text{-}R^1\text{-}6\text{-}R^2\text{-}4)_2\{S(CH_2)_2S\}(CH_2Ph)_2]$ (**2a**−**c**; R^1 = ^{t}Bu, R^2 = Me, **a**; R^1, R^2 = ^{t}Bu, **b**; R^1 = H, R^2 = Me, **c**) with a tetradentate dianionic [OSSO]-type ligand were synthesized from the corresponding titanium dichloro complexes $[Ti(OC_6H_2\text{-}R^1\text{-}6\text{-}R^2\text{-}4)_2\{S(CH_2)_2S\}Cl_2]$ and benzylmagnesium chloride in toluene. NMR spectroscopic monitoring of the reaction of the dibenzyl complex **2b** with $B(C_6F_5)_3$ in bromobenzene indicates the formation of a thermally sensitive benzyl cation $[Ti(OC_6H_2\text{-}^tBu_2\text{-}4,6)_2\{S(CH_2)_2S\}(CH_2Ph)]^+$. ^{1}H 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-dithiapentanediyl-linked ligand $[Ti(OC_6H_2\text{-}^tBu\text{-}6\text{-}R\text{-}4)_2\{S(CH_2)_3S\}(CH_2Ph)_2]$ (**4a**,**b**; R = Me, **a**; R = ^{t}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 $B(C_6F_5)_3$. Using the 1,4-dithiabutanediyl-linked dibenzyl complexes and the activators $[PhNMe_2H][B(C_6F_5)_4]/Al^nOct_3$, 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 ionic[12] or living radical methodologies[13] 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

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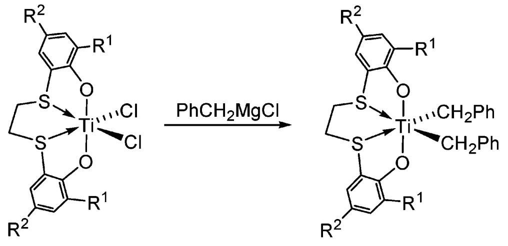
Scheme 1



1a-c **2a-c**

R^1= ^{t}Bu, R^2= Me, **a**
R^1,R^2 = ^{t}Bu, **b**
R^1= H, R^2 = Me, **c**

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 $[Ti(OC_6H_2\text{-}R^1\text{-}6\text{-}R^2\text{-}4)_2\{S(CH_2)_2S\}(CH_2Ph)_2]$ (**2a**−**c**; R^1 = ^{t}Bu, R^2 = Me, **a**; R^1, R^2 = ^{t}Bu, **b**; R^1 = H, R^2 = Me, **c**) were isolated as dark red microcrystals in 20−50% yield by reacting the corresponding dichloro complexes $[Ti(OC_6H_2\text{-}R^1\text{-}6\text{-}R^2\text{-}4)_2\{S(CH_2)_2S\}Cl_2]$ (**1a**−**c**) with an ethereal solution of benzylmagnesium chloride in toluene at −30 °C (Scheme 1). In the ^{1}H NMR spectrum of **2a**, the benzylic protons appear as AB doublets at 3.36 and 3.40 ppm with a coupling constant of $^2J_{HH}$ = 9.2 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 ^{1}H 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 $^1J_{CH}$ = 132.2 Hz. These 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 °C) indicated that both complexes are thermally robust and maintain their chiral C_2-symmetric structure within this temperature range. Above 90 °C, decomposition starts under formation of toluene.

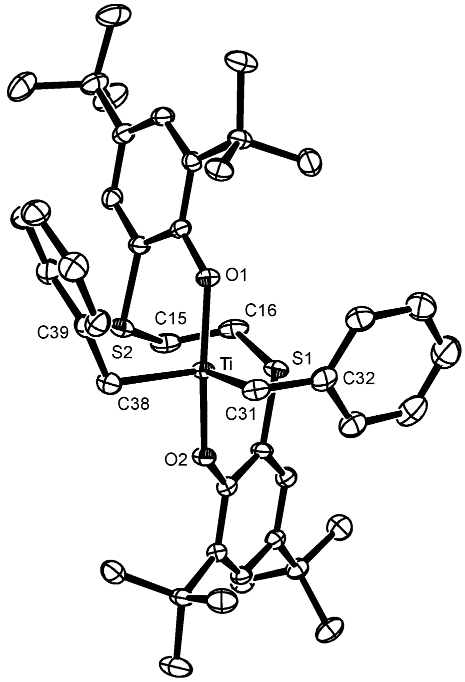


Figure 1. ORTEP diagram of the molecular structure of **2b**. Hydrogen atoms were omitted for clarity; thermal ellipsoids are drawn at the 50% probability level.

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)

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 (C31−Ti−C38 90.57(8)°). The dihedral angles Ti−C31−C32 and Ti−C38−C39 of 116.28(13)° and 97.45(12)° indicate that η^1- as well as η^2-coordination is present in the complex.[20] The elongated titanium sulfur bond distance (Ti−S1 2.8836(7) Å) as compared to the distance Ti−S2 of

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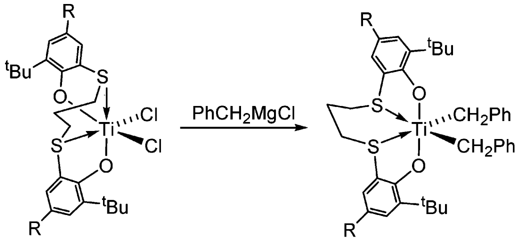
Scheme 2



3a,b **4a,b**

R= Me, **a**

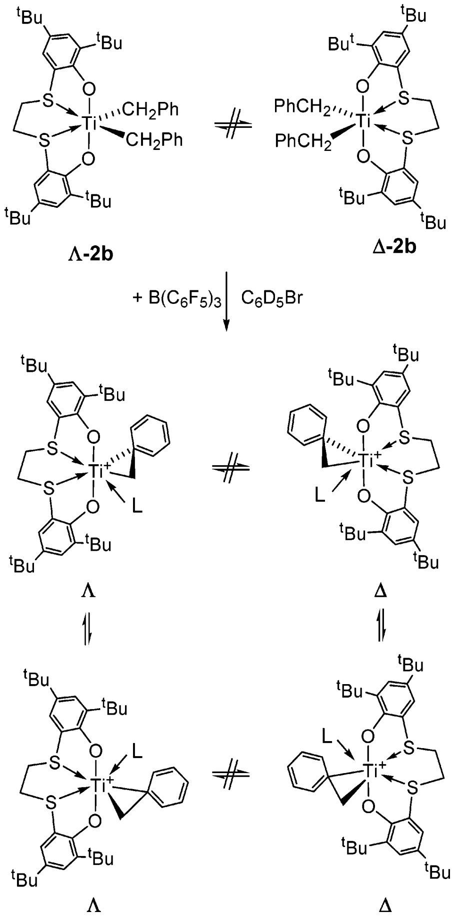
R = ^{t}Bu, **b**

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 $[\mathrm{Hf(OC_6H_2\text{-}^tBu_2\text{-}4,6)_2\{S(CH_2)_2S\}(CH_2Ph)_2}]$.[17a]

In contrast, complex **2c**, which does not carry bulky *ortho*-substituents, was found to be highly fluxional. The ^{1}H NMR spectrum at ambient temperature shows only one singlet at 3.36 ppm for the methylene protons of the benzyl group. The CH_2CH_2 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 CH_2CH_2 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 ^{13}C 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 CH_2 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 $CHCl_3$.

Related benzyl complexes of the 1,5-dithiapentanediyl-linked ligand $[\mathrm{Ti(OC_6H_2\text{-}^tBu\text{-}6\text{-}R\text{-}4)_2\{S(CH_2)_3S\}(CH_2Ph)_2}]$ (**4a**,**b**; R = Me, **a**; R = ^{t}Bu, **b**) were synthesized in an analogous manner (Scheme 2). Similar to the highly fluxional dichloro complex

Scheme 3



Λ-2b **Δ-2b**

Λ **Δ**

Λ **Δ**

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 ^{1}H NMR spectra show singlets for the benzylic protons at 3.59 ppm and the central CH_2 protons of the backbone appear as a higher order multiplet at 1.00 ppm; the SCH_2 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 ^{13}C NMR spectrum the benzylic carbon atom is recorded at 95.15 ppm ($^1J_{CH}$ = 132.4 Hz). The ^{1}H 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 $[\mathrm{Ti(OC_6H_2\text{-}^tBu_2\text{-}4,6)_2\{S(CH_2)_2S\}R}]^+$ is generated as catalytically active species, similar to related nonmetallocene polymerization catalysts.[11] Adding $B(C_6F_5)_3$ to the dibenzyl complex **2b** in bromobenzene-d_5 at −30 °C immediately produced an orange solution. The ^{1}H NMR spectrum shows the signals of the ion pair $[\mathrm{Ti(OC_6H_2{}^tBu_2\text{-}4,6)_2\{S(CH_2)_2S\}(CH_2Ph)}][\mathrm{(PhCH_2)B(C_6F_5)_3}]$, together with a small amount of free bis(phenol) as an impurity. Two-dimensional ^{1}H 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 ^{t}Bu methyl groups. At elevated temperatures, the signals

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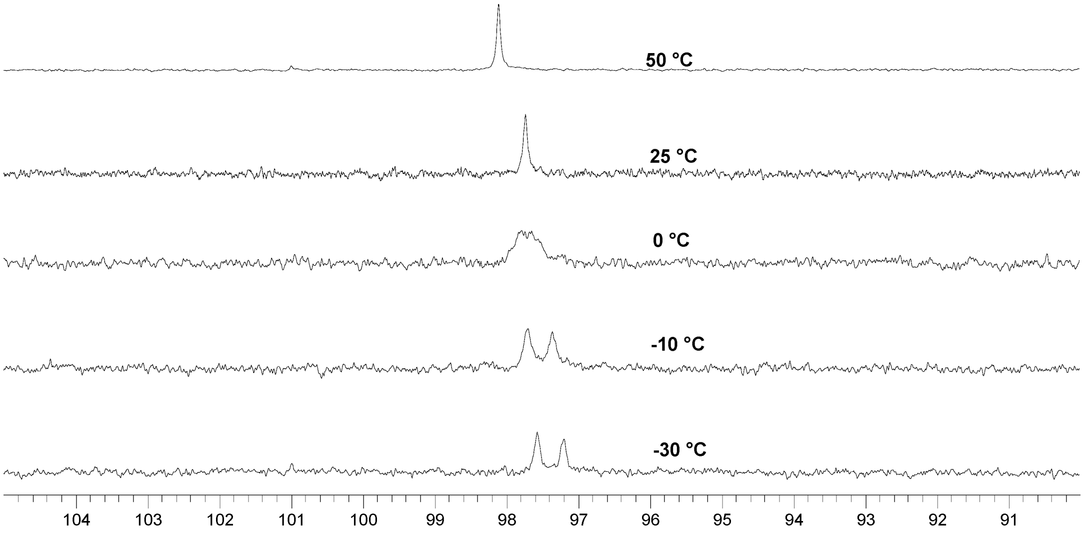

Figure 2. Variable-temperature ^{13}C NMR spectra of the benzyl cation prepared from **2b** and $B(C_6F_5)_3$ in bromobenzene. The expanded region shows the benzyl carbon signals.

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 $^1J_{CH}$ 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 $B(C_6F_5)_3$ with formation of 1,2-diphenylethane and toluene, as indicated by the ^{1}H NMR spectrum. Activation of **4a** and **4b** with $B(C_6F_5)_3$ 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 ^{1}H NMR spectrum. We suspect that the alkyl cation derived from the longer 1,5-dithiapentane bridge more readily undergoes reduction by homolytic dissociation of the alkyl radical to give Ti(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 $[PhNMe_2H][B(C_6F_5)_4]$ in the presence of the trialkylaluminum compound Al^nOct_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 $B(C_6F_5)_3$ 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 [*rr*]

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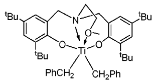
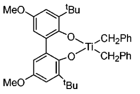
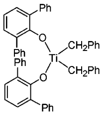
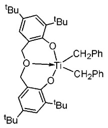
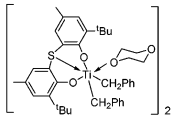
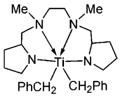
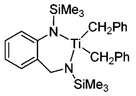
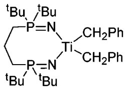
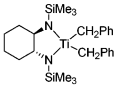
[21] For coordination of $[(PhCH_2)B(C_6F_5)_3]^-$ at a cationic group 4 metal center, see: (a) Pellecchia, C.; Immirzi, A.; Grassi, A.; Zambelli, A. *Organometallics* **1993**, *12*, 4473. (b) Pellecchia, C.; Grassi, A.; Immirzi, A. *J. Am. Chem. Soc.* **1993**, *115*, 1160. (c) Horton, A. D.; de With, 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 ($^1J_{CH}$, 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$_3$(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(C$_6$F$_5$)$_3$ 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 η^2-bonding of the benzyl group rather than by helicity change of the tetradentate ligand. When the dibenzyl complexes were activated with B(C$_6$F$_5$)$_3$ or [PhNMe$_2$H][B(C$_6$F$_5$)] 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-dithiapentanediyl-linked bis(phenolato) ligands are also fluxional and unstable in solution. Reaction of these dibenzyl complexes with B(C$_6$F$_5$)$_3$ results in decomposition.

Table 3. Styrene Polymerization by 2a Activated by [$\mathrm{PhNMe_2H}$][$\mathrm{B(C_6F_5)}$] and $\mathrm{Al^nOct_3}$[a]

run	Al equiv[b]	*t* (h)	% conv	M_n ($\times 10^3$ 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] $\mathrm{Al^nOct_3}$. [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 ^{13}C NMR spectroscopy (see Supporting Information).

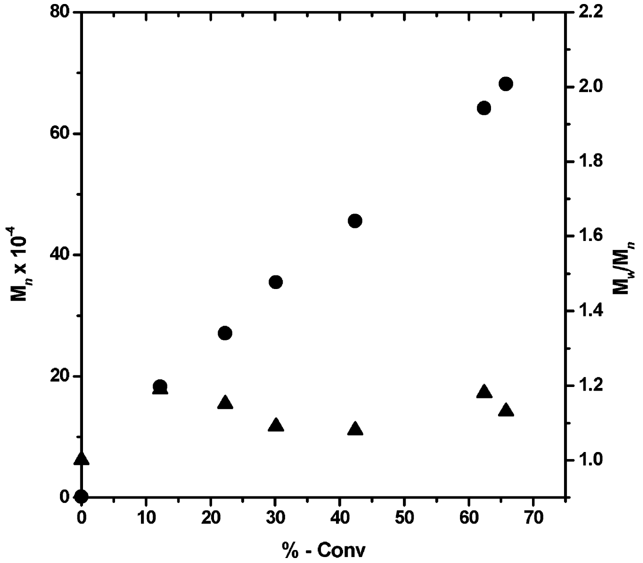


Figure 3. Plot of number-averaged molecular weights M_n and polydispersity index versus conversion during isospecific styrene polymerization using **2a** activated by [$\mathrm{PhNMe_2H}$][$\mathrm{B(C_6F_5)_4}$] and $\mathrm{Al^nOct_3}$.

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-dithiapentanediyl-derived (**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 (^{1}H, 400 MHz; ^{13}C, 101 MHz) in $\mathrm{C_6D_6}$ at 25 °C, unless otherwise stated. All variable-temperature NMR measurements were carried out in toluene-d_8. Chemical shifts for ^{1}H and ^{13}C 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) in 50 mL of toluene at −78 °C was added a 1.0 M solution of $\mathrm{PhCH_2MgCl}$ 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. ^{1}H NMR: δ 1.71 (s, 18 H, $\mathrm{C(CH_3)_3}$), 1.77 (d, 2 H, $^2J_{\mathrm{HH}}$ = 10.0 Hz, $\mathrm{SCH_2}$), 2.07 (s, 6 H, 4-$\mathrm{CH_3}$), 2.27 (d, 2 H, $^2J_{\mathrm{HH}}$ = 10.0 Hz, $\mathrm{SCH_2}$), 3.36 (d, 2 H, $^2J_{\mathrm{HH}}$ = 9.2 Hz, $\mathrm{TiCH_2}$), 3.40 (d, 2 H, $^2J_{\mathrm{HH}}$ = 9.2 Hz, $\mathrm{TiCH_2}$), 6.68 (d, 2 H, $^4J_{\mathrm{HH}}$ = 1.2 Hz, 5-CH), 6.85 (t, 2 H, $^3J_{\mathrm{HH}}$ = 7.2 Hz, *p*-$\mathrm{CH_2Ph}$), 7.06 (t, 4 H, $^3J_{\mathrm{HH}}$ = 7.6 Hz, *m*-$\mathrm{CH_2Ph}$), 7.17 (s, 2 H, 3-CH, overlap with solvent signal), 7.20 (d, 4 H, *o*-$\mathrm{CH_2Ph}$). ^{13}C{^{1}H} NMR (25 °C, $\mathrm{C_6D_6}$): δ 20.79 ($\mathrm{CH_3}$), 29.78 ($\mathrm{C(\mathit{C}H_3)_3}$), 35.45 ($\mathrm{\mathit{C}(CH_3)_3}$), 37.48 ($\mathrm{SCH_2}$), 88.36 ($\mathrm{TiCH_2}$), 120.92 (C-2), 123.70 (*p*-$\mathrm{CH_2Ph}$), 129.55 (*m*-$\mathrm{CH_2Ph}$), 129.90 (C-4), 130.08 (C-3), 130.47 (*o*-$\mathrm{CH_2Ph}$), 131.07 (C-5), 137.49 (C-6), 144.17 (*ipso*-$\mathrm{\mathit{C}H_2Ph}$), 166.26 (C-1). Anal. Calcd for $\mathrm{C_{44}H_{58}O_2S_2Ti}$: C, 70.57; H, 7.17; S, 9.92. Found: C, 69.95; H, 7.30; S, 9.62.

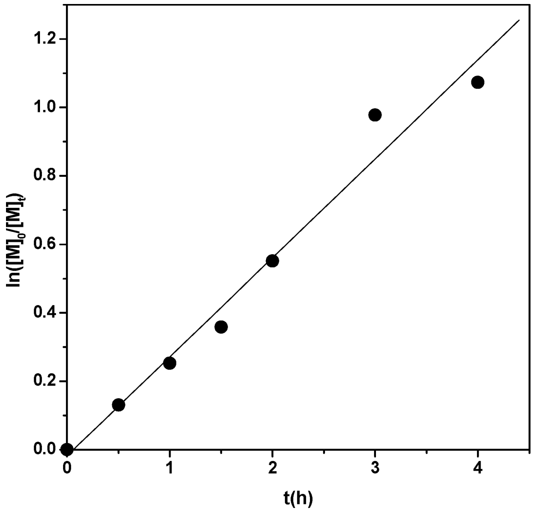


Figure 4. Semilogarithmic plot of styrene conversion against time using **2a** activated by [$\mathrm{PhNMe_2H}$][$\mathrm{B(C_6F_5)_4}$] and $\mathrm{Al^nOct_3}$ (linear fit, R = 0.988).

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 $\mathrm{PhCH_2MgCl}$ 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%. ^{1}H NMR: δ 1.22 (s, 18 H, $\mathrm{C(CH_3)_3}$), 1.75 (s, 18 H, $\mathrm{C(CH_3)_3}$), 1.87 (d, 2 H, $^2J_{\mathrm{HH}}$ = 10.0 Hz, $\mathrm{SCH_2}$), 2.37 (d, 2 H, $^2J_{\mathrm{HH}}$ = 10.0 Hz, $\mathrm{SCH_2}$), 3.27 (d, 2 H, $^2J_{\mathrm{HH}}$ = 8.8 Hz, $\mathrm{TiCH_2}$), 3.34 (d, 2 H, $^2J_{\mathrm{HH}}$ = 8.8 Hz, $\mathrm{TiCH_2}$), 6.84 (t, 2 H, $^3J_{\mathrm{HH}}$ = 7.2 Hz, *p*-$\mathrm{CH_2Ph}$), 7.02 (t, 4 H, $^3J_{\mathrm{HH}}$ = 7.5 Hz, *m*-$\mathrm{CH_2Ph}$), 7.03 (d, 2 H, $^4J_{\mathrm{HH}}$ = 2.4 Hz, 5-CH), 7.16 (d, 4 H, $^3J_{\mathrm{HH}}$ = 7.2 Hz, *o*-$\mathrm{CH_2Ph}$, overlap with solvent signal), 7.52 (d, 2 H, $^4J_{\mathrm{HH}}$ = 2.4 Hz, 3-CH). ^{13}C{H} NMR: δ 30.01 ($\mathrm{C(\mathit{C}H_3)_3}$), 31.65 ($\mathrm{C(\mathit{C}H_3)_3}$), 34.51 ($\mathrm{\mathit{C}(CH_3)_3}$), 35.75 ($\mathrm{\mathit{C}(CH_3)_3}$), 37.84 ($\mathrm{SCH_2}$), 87.57 ($\mathrm{TiCH_2}$), 120.75 (C-2), 123.71 (*p*-$\mathrm{CH_2Ph}$), 125.99 (C-3), 127.87 (C-5), 128.2 (*m*-$\mathrm{\mathit{C}H_2Ph}$, overlap with solvent signal), 130.14 (*o*-$\mathrm{\mathit{C}H_2Ph}$), 136.96 (C-4), 143.19 (C-6), 144.05 (*ipso*-$\mathrm{\mathit{C}H_2Ph}$),166.22 (C-1). Anal. Calcd for $\mathrm{C_{44}H_{58}O_2S_2Ti}$: C, 72.30; H, 8.00, S, 8.77. Found: C 71.57; H, 7.98; S, 8.75.

Dibenzyl{1,4-dithiapentanediyl-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	$C_{47.50}H_{62}O_2S_2Ti$
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
$2\theta_{max}$, 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 PhCH$_2$MgCl 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%). ^{1}H NMR: δ 1.98 (br s, 10 H, 4-CH$_3$ and SCH$_2$), 3.37 (s, 4 H, TiCH$_2$), 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*-CH$_2$Ph), 6.94 (d, 2 H, $^3J_{HH}$ = 7.5 Hz, C6), 7.07 (t, 4 H, $^3J_{HH}$ = 7.5 Hz, *m*-CH$_2$Ph), 7.22 (d, 4 H, $^3J_{HH}$ = 7.5 Hz, *o*-CH$_2$Ph). ^{13}C{^{1}H} NMR: δ 20.35 (4-CH$_3$), 36.92 (SCH$_2$), 89.27 (TiCH$_2$), 116.41 (C-6), 119.80 (C-2), 123.76 (*p*-CH$_2$Ph), 128.58 (*m*-CH$_2$Ph), 129.95 (C-4), 130.67 (*o*-CH$_2$Ph), 132.55 (C-3), 133.37 (C-5), 142.0 (*ipso*-CH$_2$Ph), 167.64 (C-1).

Dibenzyl{1,5-dithiapentanediyl-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 PhCH$_2$MgCl 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. ^{1}H NMR: δ 1.00 (quint, $^3J_{HH}$ = 5.8 Hz, 2 H, CH$_2$), 1.84 (s, 18 H, C(CH$_3$)$_3$), 2.13 (t, $^2J_{HH}$ = 5.8 Hz, 4 H, SCH$_2$), 2.23 (s, 6 H, CH$_3$), 3.59 (s, 4 H, TiCH$_2$), 6.85 (d, 2 H, $^4J_{HH}$ = 1.2 Hz, 5-CH), 6.95 (t, $^3J_{HH}$ = 7.3 Hz, 2 H, *p*-CH$_2$Ph), 7.18 (t, 4 H, $^3J_{HH}$ = 7.3 Hz, *m*-CH$_2$*Ph*), 7.26−7.28 (m, 4 H, overlap with solvent signal, *o*-CH$_2$Ph), 7.29 (s, 2 H, 3-CH). ^{13}C{H} NMR: δ 20.93 (CH$_3$), 22.84 (CH$_2$), 30.03 (C(CH$_3$)$_3$), 34.76 (SCH$_2$), 35.52 (C(CH$_3$)$_3$), 95.15 (TiCH$_2$), 123.06 (C-2), 124.92 (*p*-CH$_2$Ph), 128.38 (*m*-CH$_2$Ph), 128.52 (C-4), 128.86 (C-3), 129.74 (C-5), 130.38 (*o*-CH$_2$Ph), 137.51 (C-6), 146.41 (ipso-CH$_2$*Ph*), 164.79 (C-1). Anal. Calcd for $C_{39}H_{48}O_2S_2Ti$: C, 70.89; H, 7.32; S, 9.70. Found: C, 69.49; H, 7.12; S, 9.85.

Dibenzyl{1,5-dithiapentanediyl-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 PhCH$_2$MgCl 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. ^{1}H NMR: δ 1.25 (s, 18 H, C(CH_3)$_3$), 1.49 (m, 2 H, CH$_2$), 1.57 (s, 18 H, C(CH_3)$_3$), 2.21 (t, 4 H, $^2J_{HH}$ = 7 Hz, SCH$_2$), 3.49 (s, 4 H, TiCH$_2$), 6.68 (s, 2 H, 5-CH), 7.01 (t, 2 H, $^3J_{HH}$ = 6 Hz, *p*-CH$_2$Ph), 7.14 (m, 4 H, overlap with solvent signal, *m*-CH$_2$Ph), 7.18 (m, 4 H, partial overlap with solvent signal, *o*-CH$_2$Ph), 7.52 (d, 2 H, $^4J_{HH}$ = 2.4 Hz, 3-CH). ^{13}C{H} NMR (C$_6$D$_6$, 25 °C): δ 30.00 (C(CH$_3$)$_3$), 31.65 (C(CH$_3$)$_3$), 34.51 (C(CH$_3$)$_3$), 35.75 (C(CH$_3$)$_3$), 37.84 (SCH$_2$), 87.57 (TiCH$_2$), 120.75 (*p*-CH$_2$Ph), 123.71 (C-2), 125.98 (C-3), 127.39 (*o*-CH$_2$Ph, overlap with solvent signal), 127.76 (*m*-CH$_2$Ph), 136.95 (C-4), 143.91 (C-6), 144.04 (*ipso*-CH$_2$Ph), 166.21 (C-1).

Reaction of 2a with B(C$_6$F$_5$)$_3$. To a solid mixture of **2a** (30 mg, 46 μmol) and B(C$_6$F$_5$)$_3$ (28 mg, 55 μmol) in an NMR tube was added a cooled solution of bromobenzene-d_5 at −30 °C, and the reaction was monitored at different temperatures. ^{1}H NMR (C$_6$D$_5$Br, −30 °C): δ 1.33 (s, 9 H, C(CH$_3$)$_3$), 1.35 (s, 18 H, C(CH$_3$)$_3$), 1.46 (s, 9 H, C(CH$_3$)$_3$), 1.81 (m, 2 H, SCH$_2$), 2.0−2.1 (br m, SCH$_2$, overlap with CH$_3$ signals), 2.05 (s, 3 H, CH$_3$), 2.09 (s, 3 H, CH$_3$), 2.13 (s, 3 H, CH$_3$), 2.18 (s, 3 H, CH$_3$), 2.47 (d, 1 H, $^2J_{HH}$ = 9 Hz, SCH$_2$), 2.53 (d, 1 H, $^2J_{HH}$ = 9 Hz, SCH$_2$), 2.74 (d, 1 H, $^2J_{HH}$ = 9 Hz, SCH$_2$), 3.06 (d, 1 H, $^2J_{HH}$ = 9 Hz, SCH$_2$), 3.39 (s, 1 H, TiCH$_2$) overlap with 3.41 (br s, 4 H, BCH$_2$), 3.76 (br s, 2 H, TiCH$_2$), 3.89 (br, 1 H, TiCH$_2$), 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). ^{1}H NMR (C$_6$D$_5$Br, +50 °C): δ 1.42 (s, 18 H, C(CH$_3$)$_3$), 2.05 (d, 2 H, $^2J_{HH}$ = 6.5 Hz, SCH$_2$), 2.17 (s, 6 H, CH$_3$), 2.79 (d, 2 H, $^2J_{HH}$ = 6.5 Hz, SCH$_2$), 3.31 (br s, 2 H, BCH$_2$), 3.79 (d, 1 H, $^2J_{HH}$ = 6.5, TiCH$_2$), 3.94 (d, 1 H, $^2J_{HH}$ = 6.5, TiCH$_2$), 6.7 (s, 2 H, 5-CH), 6.98 (m, 2 H, *m*-TiCH$_2$Ph), 7.06 (m, 1 H, *p*-TiCH$_2$Ph), 7.1−7.2 (m, 5 H, BCH$_2$Ph), 7.15 (m, 2 H, *o*-TiCH$_2$Ph), 7.34 (s, 2 H, 3-CH). ^{13}C{^{1}H} NMR (C$_6$D$_5$Br, −30 °C): δ 20.90, 20.95 (CH$_3$), 29.11, 29.22, 29.41 (C(CH$_3$)$_3$), 32.12 (br s, BCH$_2$), 36.18, 38.31, 39.32, 41.58 (SCH$_2$), 97.19 (TiCH$_2$), 97.57 (TiCH$_2$), 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). ^{13}C{^{1}H} NMR (C$_6$D$_5$Br, +50 °C): δ 20.64 (CH$_3$), 29.57 (C(CH$_3$)$_3$), 31.9 (br s, BCH$_2$), 34.17 (C(CH$_3$)$_3$), 37.94 (SCH$_2$), 41.17 (SCH$_2$), 98.11 (TiCH$_2$), 122.4−140.4 (aromatic signals, overlap with solvent signals), 147.49 (*ipso*-CH$_2$Ph), 163.38 (C-1). ^{11}B NMR (C$_6$D$_5$Br, −30 °C): δ −12.15 (s). ^{19}F NMR (C$_6$D$_5$Br, −30 °C): δ −130.25 (d, $^3J_{FF}$ = 14 Hz, *o*-C$_6$F$_5$), −162.95 (t, $^3J_{FF}$ = 14 Hz, *p*-C$_6$F$_5$), −165.78 (d, $^3J_{FF}$ = 14 Hz, *m*-C$_6$F$_5$).

Reaction of 2b with B(C$_6$F$_5$)$_3$. To a solid mixture of **2b** (32 mg, 43 μmol) and B(C$_6$F$_5$)$_3$ (27 mg, 52 μmol) in an NMR tube was added a cooled solution of bromobenzene-d_5 at −30 °C, and the reaction was monitored at different temperatures. ^{1}H NMR (C$_6$D$_5$Br, −30 °C): δ 1.15 (s, 9 H, C(CH$_3$)$_3$), 1.21 (s, 9 H, C(CH$_3$)$_3$), 1.24 (s, 9 H, C(CH$_3$)$_3$), 1.29 (s, 9 H, C(CH$_3$)$_3$), 1.39 (s, 9 H, C(CH$_3$)$_3$), 1.42 (s, 18 H, C(CH$_3$)$_3$), 1.54 (s, 9 H, C(CH$_3$)$_3$), 1.68 (d, 1 H, $^2J_{HH}$ = 8 Hz, SCH$_2$), 1.89 (m, 2 H, SCH$_2$), 2.06 (m, 1 H, SCH$_2$), 2.22 (m, 1 H, SCH$_2$), 2.52 (m, 1 H, $^2J_{HH}$ = 8 Hz, SCH$_2$), 2.75 (d, 1 H, $^2J_{HH}$ = 8 Hz, SCH$_2$), 3.15 (d, 1 H, $^2J_{HH}$ = 8 Hz, SCH$_2$), 3.35 (m, 1 H, TiCH$_2$), 3.44 (br s, BCH$_2$), 3.78 (s, 1 H, TiCH$_2$), 3.82 (s, 1 H, TiCH$_2$), 3.89 (m, 1 H, TiCH$_2$), 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). ^{1}H NMR (C$_6$D$_5$Br, +60 °C): δ 1.32 (s, 18 H, C(CH$_3$)$_3$), 1.52 (s, 18 H, C(CH$_3$)$_3$), 2.14 (d, 2 H, $^2J_{HH}$ = 7 Hz, SCH$_2$), 2.88 (d, 2 H, $^2J_{HH}$ = 7 Hz, SCH$_2$), 3.37 (br s, 2 H, BCH$_2$), 3.85 (d, 1 H, $^2J_{HH}$ = 4 Hz, TiCH$_2$), 4.01 (d, 1 H, $^2J_{HH}$ = 4 Hz, TiCH$_2$), 6.75−6.90 (m), 6.98 (br), 7.05 (s), 7.15 (br m), 7.40 (br), 7.53 (br) (aromatic signals). ^{13}C NMR (C$_6$D$_5$Br, −30 °C): δ 29.14, 29.28, 29.51, C(CH$_3$)$_3$), 31.34, 31.41, C(CH$_3$)$_3$), 34.60, 34.73, 34.82, 44.88 (C(CH$_3$)$_3$), 35.4 (br, BCH$_2$), 36.0, 37.5, 39.96, 41.73 (SCH$_2$), 97.22 (TiCH$_2$), 97.36 (TiCH$_2$), 119.96−136.42 (aromatic signals, overlap with solvent signals), 146.52, 147.33, 149.01, 149.72 (*ipso*-CH_2Ph), 162.74, 163.58, 164.19 (s, C-1). ^{13}C NMR (C_6D_5Br, +50 °C): δ 29.53 ($C(CH_3)_3$), 31.25 ($C(CH_3)_3$), 34.68 ($C(CH_3)_3$), 34.91 ($C(CH_3)_3$), 37.81 (br, BCH_2), 41.54 (SCH_2), 89.35 ($TiCH_2$), 121.08−149.80 (aromatic signals, overlap with solvent signals), 163.30 (C-1). ^{11}B NMR (C_6D_5Br, −30 °C): δ −12.23 (s). ^{19}F NMR (C_6D_5Br, −30 °C): δ −130.23 (d, $^3J_{FF} = 14$ Hz, *o*-C_6F_5), −162.98 (t, $^3J_{FF} = 14$ Hz, *p*-C_6F_5), −165.80 (d, $^3J_{FF} = 14$ Hz, *m*-C_6F_5).

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 Kα 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 $[Hf(OC_6H_2\text{-}^tBu_2\text{-}4,6)_2\text{-}\{S(CH_2)_2S\}(CH_2Ph)_2]$.[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 μmol) was added, followed by a 4.5 mM solution of $[PhNMe_2H][B(C_6F_5)]$ in toluene (2 mL; 9.0 μmol) and a 5 mM solution of tri(*n*-octyl)aluminum in hexane/toluene (1−3 mL; 5−15 μmol). 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.

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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 ^{13}C NMR spectra of the reaction mixture of **2a** with $B(C_6F_5)_3$. ^1H and ^{13}C NMR spectra of isotactic polystyrene obtained by titanium complex **2a** activated with $[PhNMe_2H][B(C_6F_5)_4]/Al^nOct_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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