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

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A series of titanium dichloro and di(isopropoxy) complexes with a 1,4-dithiabutanediyl-linked bis(4,6-disubstituted phenolato) ligand [Ti(OC_6H_2-6-R^1-4-R^2)$_2${S(CH_2)$_2$S}X_2] (X = Cl, **2a**−**i**, O^{i}Pr, **3a**−**i**; R^1 = H, Me, ^{i}Pr, ^{t}Bu, 2-phenyl-2-propyl; R^2 = H, Me, ^{t}Bu, OMe, 2-phenyl-2-propyl) were synthesized by reacting the corresponding linked bis(phenol) (HOC_6H_2-6-R^1-4-R^2)$_2${S(CH_2)$_2$S} (**1a**−**i**) with the titanium precursor TiX_4. The NMR spectra of the dichloro complexes Ti(OC_6H_2-6-R^1-4-R^2)$_2${S(CH_2)$_2$S}Cl_2] (**2a**−**d**) with small ortho substituents R^1 = H, Me, ^{i}Pr are in agreement with a C_2-symmetrical helical structure, but the complexes become fluxional at higher temperatures. The corresponding di(isopropoxy) complexes [Ti(OC_6H_2-6-R^1-4-R^2)$_2${S(CH_2)$_2$S}(O^{i}Pr)$_2$] (**3a**−**d**) are fluxional in solution at room temperature due to rapid interconversion between the Δ and Λ isomers. In contrast, both dichloro and di(isopropoxy) complexes **2e**−**i** and **3e**−**i** with bulky ortho substituents R^1 = ^{t}Bu and 2-phenyl-2-propyl exhibit a rigid C_2-symmetrical helical structure in solution up to 100 °C. The helical structure with *trans*-O,O, *cis*-S,S, *cis*-Cl,Cl ("α-*cis*") is confirmed by the single-crystal structure analysis of two dichloro complexes [Ti(OC_6H_2-6-R^1-4-R^2)$_2${S(CH_2)$_2$S}Cl_2] (**2e**, R^1 = ^{t}Bu, R^2 = Me; **2i**, R^1, R^2 = 2-phenyl-2-propyl). Related dichloro and di(isopropoxy) complexes that contain a 1,5-dithiapentanediyl-linked bis(4,6-disubstituted phenolato) ligand [Ti(OC_6H_2-6-R^1-4-R^2)$_2${S(CH_2)$_3$S}X_2] (R^1 = ^{t}Bu; R^2 = Me, ^{t}Bu, OMe; X = Cl, **5a**−**c**; O^{i}Pr, **6a**−**c**) were synthesized in an analogous fashion and shown by NMR spectroscopy to be conformationally flexible at room temperature. This fluxionality can be explained by a twisting of one five-membered chelate ring, converting the *trans*-O,O ("α-*cis*") to the *cis*-O,O ("*β*-*cis*") isomer. A crystal structure determination of ligand [Ti(OC_6H_2^{t}Bu$_2$-4,6)$_2${S(CH_2)$_3$S}(O^{i}Pr)$_2$] (**6b**) revealed the *trans*-O,O, *cis*-S,S, *cis*-Cl,Cl ("α-*cis*") isomer. Upon activation with methylaluminoxane, the stereorigid derivatives **2e**−**i** efficiently polymerize styrene to give isotactic polystyrene, whereas the conformationally flexible complexes **2a**−**d** produce atactic polystyrene with negligible activity. Under the same conditions, complexes with the 1,5-dithiapentanediyl-linked ligand **5a**,**b** and **6b**,**c** polymerized styrene syndiospecifically with low activity.

Introduction

Currently there is considerable activity in developing stereospecific α-olefin polymerization catalysts that do not feature the ubiquitous bis(η^5-cyclopentadienyl) ligand framework.[1] In contrast to the symmetry-related stereocontrol in Brintzinger-type *ansa*-zirconocene catalysts,[2] the design of ligand spheres for the catalytically active metal center in chiral nonmetallocene catalysts appears to be rather challenging.[3] Furthermore, homogeneous nonmetallocene catalysts hold promise as models that may provide valuable insights into the nature of the stereospecific active sites of the industrially employed heterogeneous catalysts.[4]

So far there have been no general ways to control the stereoselectivity during the coordinate polymerization of styrene.[5] Syndiotactic polystyrene, discovered by Ishihara et al. at Idemitsu and commercialized as a high melting, fast crystallizing, chemically resistant thermoplastic,[6] is produced by trivalent mono(cyclopentadienyl)titanium catalysts of the type [Ti(η^5-$C_5R'_5$)R]$^+$.[7] Isotactic polystyrene, discovered almost half a century ago, is still best produced by heterogeneous Ziegler-type catalysts.[8,9] Except for detailed works by Tkatchenko et al. on isospecific styrene oligomerization using phos-

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phine-supported nickel cations[10] and for a recent report on isospecific styrene polymerization by isopropylidene-linked Brintzinger-type zirconocenes by Arai et al.,[11] the synthesis of isotactic polystyrene by single-site organometallic catalysts remained virtually unknown.

To design stereoselective α-olefin polymerization catalyst precursors based on a bis(phenolato) ligand framework,[12,13] we set out to investigate a number of differently substituted linked bis(phenolato) ligands. Our initial results were not encouraging,[13b] since in contrast to the situation for the Brintzinger-type *ansa*-metallocenes, we failed to observe any stereorigidity in the resulting group 4 metal complexes. The use of a hemilabile sulfide link,[14] which connects the two phenolato moieties in titanium complexes of the type $[Ti\{S(OC_6H_2\text{-}{}^tBu\text{-}6\text{-}Me\text{-}4)_2\}Cl_2]$, was known to promote syndiospecific styrene polymerization.[13a,c,15] Recently, group 4 metal catalyst precursors based on 1,4-dithiabutanediyl-linked bis(phenolate) of the type $[Ti(OC_6H_2\text{-}{}^tBu_2\text{-}4,6)_2\text{-}\{S(CH_2)_2S\}X_2]$ ($X = Cl, O^iPr$) were found to efficiently polymerize styrene to give isotactic polystyrene.[16,17] When the 1,5-dithiapentanediyl-linked bis(phenolate)

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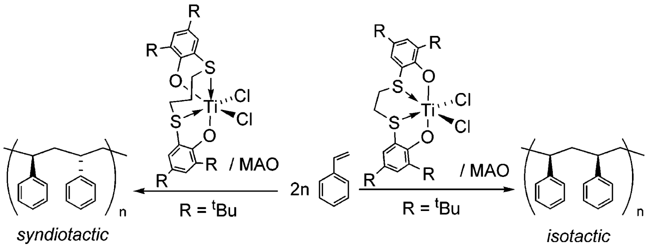
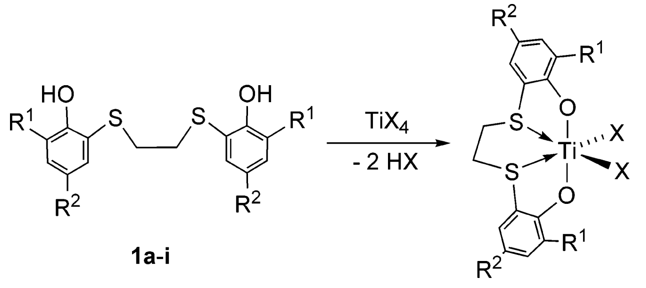
Scheme 1



Scheme 2

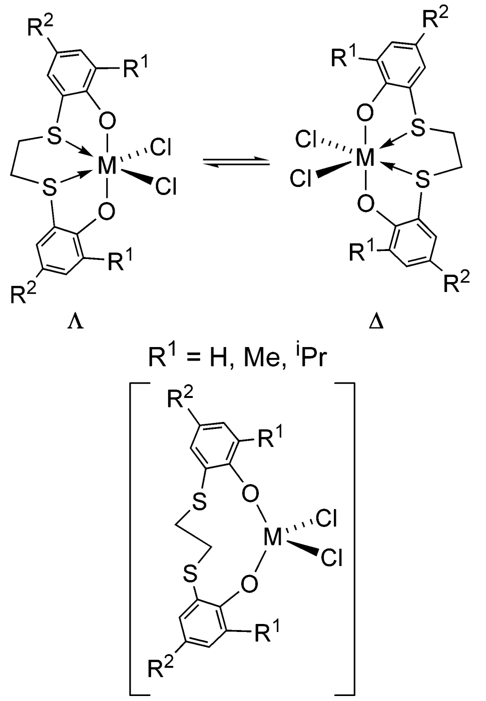


1a-i

R^1,R^2 = H, **a**
R^1= H, R^2 = Me, **b**
R^1,R^2 = Me, **c**
R^1= ^{i}Pr, R^2 = ^{t}Bu, **d**
R^1= ^{t}Bu, R^2= Me, **e**
R^1,R^2 = ^{t}Bu, **f**
R^1= ^{t}Bu, R^2= OMe, **g**
R^1 = CMe_2Ph, R^2 = Me, **h**
R^1,R^2 = CMe_2Ph, **i**

X = Cl, **2a-i**
X= O^{i}Pr, **3a-i**

Scheme 3



complexes with a longer trimethylene backbone in the ligand were employed, syndiospecific styrene polymerization was observed (Scheme 1).[16] We report here the synthesis and structural characterization of a series of titanium-based precursors, with the aim of comprehensively mapping the substituent effect of this [OSSO]-type ligand on the catalyst precursors' structure, the activity, and stereoselectivity during styrene polymerization.[18]

Results and Discussion

Synthesis and Structure of the 1,4-Dithiabutanediyl-Linked Complexes. The 1,4-dithiabutanediyl-linked bis(phenols) $(HOC_6H_2\text{-}6\text{-}R^1\text{-}4\text{-}R^2)_2\{S(CH_2)_2S\}$ (**1a**–**i**, R^1 = H, Me, ^{i}Pr, ^{t}Bu, 2-phenyl-2-propyl; R^2 = H, Me, ^{t}Bu, OMe, 2-phenyl-2-propyl), prepared in analogy to the published procedure,[16a] reacted with titanium tetrachloride to afford the dichloro complexes $[Ti(OC_6H_2\text{-}6\text{-}R^1\text{-}4\text{-}R^2)_2\{S(CH_2)_2S\}Cl_2]$ (**2a**–**i**) in practically quantitative yields (Scheme 2). Not only the solubility but also the configurational stability was found to strongly depend on the nature of the ortho substituents R^1 in the phenol rings. Initially we assumed a C_2-symmetric ground state structure for all of these dichloro complexes, based on the most reasonable coordination of the tetradentate ligand (*trans*-O,O, *cis*-S,S, *cis*-Cl,Cl; “α-*cis*”).[19] However, it became evident that the presence of large ortho substituents is required to stabilize this chiral configuration in solution. The ^1H NMR spectroscopic data for the sparingly soluble complex **2a** in THF-d_8, independently reported previously by Erker et al., indicated fluxional behavior.[12m] The complex $[Ti(OC_6H_3\text{-}Me\text{-}4)_2\{S(CH_2)_2S\}Cl_2]$ (**2b**) derived from linked *para*-cresol was shown to be fluxional and to contain a mirror plane (overall C_{2v} structure) above 70 °C ($\Delta G^{\ddagger} = 66.3 \pm 2$ kJ mol^{-1}) according to variable-temperature ^1H NMR spectra in $C_2D_2Cl_4$. This suggests that a rapid enantiomerization between the Λ, Δ isomers occurs in solution, possibly via a tetrahedrally coordinated transition state (Scheme 3). ^1H and ^{13}C NMR spectroscopic data of the 1,4-dithiabutanediyl-linked complexes **2e**–**i** are in agreement with a C_2-symmetric structure with *cis*-chloro ligands (*trans*-O,O, *cis*-S,S, *cis*-Cl,Cl). This chiral structure is retained at least up to temperatures of +100 °C, as can be concluded from the presence of an AA′BB′ pattern for the CH_2CH_2 backbone (Scheme 4). When the *tert*-butyl groups in the ortho position of the ligand are replaced by the ^{i}Pr groups, the stereorigidity is apparently lost, as can be seen from the considerable broadening of the CH_2CH_2 backbone signals above 80 °C for complex **2d**.

The complexes **2c**, **2e**, and **2i** were further characterized by X-ray crystallography, and the results confirm the C_2-symmetrical configuration for the complexes in the solid state. The ORTEP diagrams for **2e** and **2i** are shown Figures 1 and 2 (see Supporting Information for **2c**). All bond parameters are unexceptional for these octahedral complexes of tetravalent titanium, as has previously been revealed for the parent complex **2a**.[12m] It is noteworthy that the relatively short titanium–sulfur bond distances (average Ti–S lengths: 2.65 Å for

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(18) For zirconocene catalysts, remarkable control of the stereoselectivity during propylene polymerization by ligand variations, including conformational changes, has been achieved: Lin, S.; Waymouth, R. M. *Acc. Chem. Res.* **2002**, *35*, 765.

(19) Two other configurational isomers, *cis*-O,O, *cis*-S,S, *cis*-Cl,Cl (“*β-cis*”); *trans*-O,O, *cis*-S,S, *trans*-Cl,Cl (“*trans*”), are conceivable. See: von Zelewsky, A. *Stereochemistry of Coordination Compounds*; Wiley: Chichester, 1996; p 116.

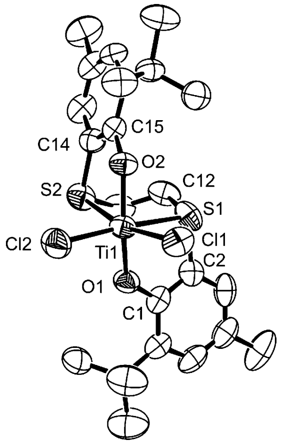
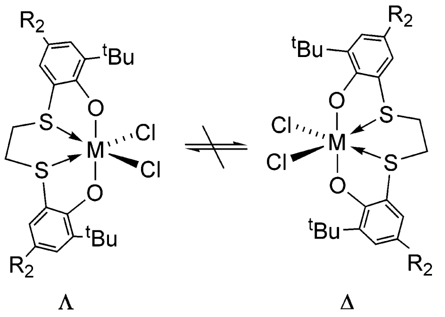


Figure 1. ORTEP diagram of the molecular structure of **2e** (Δ isomer). Only one of the crystallographically independent molecules is shown. Hydrogen atoms were omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ti1−O1 1.855(5), Ti1−O2 1.849(5), Ti1−Cl1 2.262(2), Ti1−Cl2 2.254(3), Ti1−S1 2.647(3), Ti1−S2 2.647(3), O1−Ti1−O2 156.7(2), S1−Ti1−S2 78.37(8), Cl1−Ti1−Cl2 103.40(10).

Scheme 4



2a,[12m] 2.64 Å for **2c**, 2.65 Å for **2e**; 2.61 Å for **2i**) seem to contribute to the stabilization of the helical configuration.[20] There are no significant differences in the bond parameters of **2a**, and **2c** and those of **2e** and **2i** with bulky ortho substituents. Despite the presumed hemilabile nature of the titanium−sulfur bond,[14] this dative bond is strong enough to render the tetradentate [OSSO] coordination stereorigid in solution, whenever ortho substituents bulkier than ^{i}Pr are present.

The di(isopropoxy) complexes $[Ti(OC_6H_2\text{-}6\text{-}R^1\text{-}4\text{-}R^2)_2\{S(CH_2)_2S\}(O^iPr)_2]$ (**3a**−**i**, R^1 = H, Me, ^{i}Pr, ^{t}Bu, 2-phenyl-2-propyl; R^2 = H, Me, ^{t}Bu, OMe, 2-phenyl-2-propyl) were synthesized by reacting the corresponding bis(phenols) **1a**−**i** with titanium tetra(isopropoxide) and isolated in excellent yields. As confirmed by an X-ray structure determination of **3h**, the C_2-symmetrical structure can be assumed for the configuration of the entire series. In analogy with the behavior of the dichloro complexes **2a**−**i**, the di(isopropoxy) complexes with the 1,4-dithiabutanediyl link are configurationally stable in solution only if the ligand features large ortho substituents R^1. For instance, the ^{1}H NMR spectra of the complexes **3h** up to a temperature of 105 °C display a typical AB spin pattern for the four protons of the CH_2CH_2 bridge, indicating molecular C_2-symmetry. In contrast, the di(isopropoxy) complexes **3a**−**d** with smaller ortho substituents R^1 display a pattern of broad signals at room temperature, suggesting a fluxional structure. In the ^{1}H NMR spectrum of $[Ti(OC_6H_3Me\text{-}4)_2\{S(CH_2)_2S\}(O^iPr)_2]$ (**3b**) at ambient temperature, the protons of the CH_2CH_2 bridge appear as a broad singlet at 2.29 ppm. At 60 °C one sharp singlet for the protons of the CH_2CH_2 bridge along with one doublet for both isopropoxy methyl groups suggest a structure with a mirror plane. Below 10 °C these signals decoalesce and the protons of the CH_2CH_2 bridge give rise to an AB pattern, while the isopropoxy groups are recorded as two doublets due to the diastereotopic nature of the methyl groups (Figure 3). The free enthalpy of activation for this process was estimated to be $\Delta G^\ddagger = 56.2 \pm 2$ kJ mol^{-1} (T_c = 23 °C). Likewise, Eyring analysis for **3a** and **3c** leads to similar activation barriers (**3a**: $\Delta G^\ddagger = 56.5 \pm 1$ kJ mol^{-1}; T_c = 14 °C; **3c**: $\Delta G^\ddagger = 58.6 \pm 2$ kJ mol^{-1}, T_c = 46 °C). Evidently, the presence of large ortho substituents is essential for maintaining the configurational stability above room temperature. Otherwise rapid interconversion between the Δ and Λ isomers of the complexes occurs (Scheme 5). This type of fluxionality, which is commonly observed for octahedral complexes with two bidentate ligands, suggests that the mechanism may not involve bond rupture, as observed for the nondissociative inversions of (β-diketonato)titanium(IV)[21] or diolatobis(acetylacetonato)titanium(IV) complexes.[22] At this time, however, we cannot

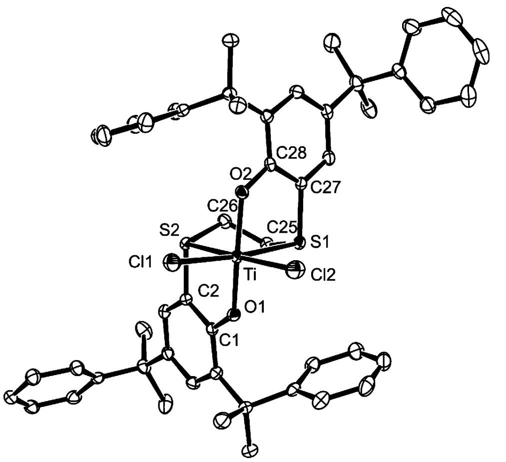


Figure 2. ORTEP representation of the structure of **2i** (Λ isomer). Hydrogen atoms were omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ti−O1 1.8627(13), Ti−O2 1.8678(12), Ti−Cl1 2.2427(6), Ti−Cl2 2.2524(6), Ti−S1 2.6160(6), Ti−S2 2.5962(6), O1−Ti−O2 155.46(6), O1−Ti−Cl1 96.62(4), O1−Ti−Cl2 98.35(4), O2−Ti−Cl1 98.74(4), O2−Ti−Cl2 96.87(4), Cl1−Ti−Cl2 102.49(3), O1−Ti−S2 83.46(4), O2−Ti−S2 77.80(4), Cl1−Ti−S2 168.81(2), Cl2−Ti−S2 88.54(2), O1−Ti−S1 77.15(4), O2−Ti−S1 84.65(4), Cl1−Ti−S1 87.00(2), Cl2−Ti−S1 169.99(2), S2−Ti−S1 82.11(2).

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(20) Titanium−sulfur bond distances of tbmp complexes (tbmp = $S(OC_6H_2\text{-}^tBu\text{-}6\text{-}Me\text{-}4)_2$) are in the range 2.6−2.9 Å: (a) 2.719(1) Å in $[Ti(tbmp)(O^iPr)_2]_2$: Porri, L.; Ripa, A.; Colombo, P.; Miano, E.; Capelli, S.; Meille, S. V. *J. Organomet. Chem.* **1996**, *213*, 514. (b) 2.704(1) Å in $Ti(tbmp)(C_6H_4CH_2NMe_2)Cl$: Fokken, S.; Spaniol, T. P.; Kang, H.-C.; Massa, W.; Okuda, J. *Organometallics* **1996**, *15*, 5069. (c) 2.637(1) Å in $Ti(dtbmp)I_2$: ref 14d. (d) 2.8699(6) Å in $Ti(tbmp)(CH_2C_6H_5)_2(1,4\text{-dioxane})_{0.5}$: Fokken, S.; Reichwald, F.; Spaniol, T. P.; Okuda, J. *J. Organomet. Chem.* **2002**, *663*, 158. (e) 2.907(1) Å in Ti(tbmp)CpCl: Amor, F.; Fokken, S.; Kleinhenn, T.; Spaniol, T. P.; Okuda, J. *J. Organomet. Chem.* **2001**, *621*, 3. (f) 2.664(2) Å in $[Ti(tbmp)Cl_2]_2$: Nakayama, Y.; Watanabe, K.; Ueyama, N.; Nakamura, A.; Harada, A.; Okuda, J. *Organometallics* **2000**, *19*, 2498.

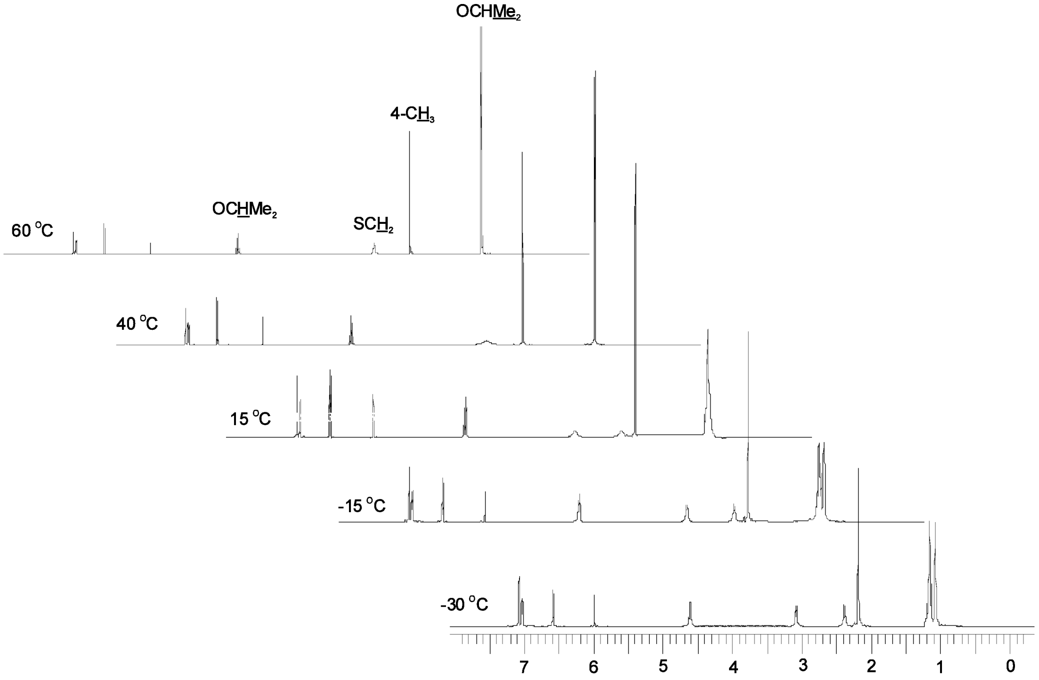
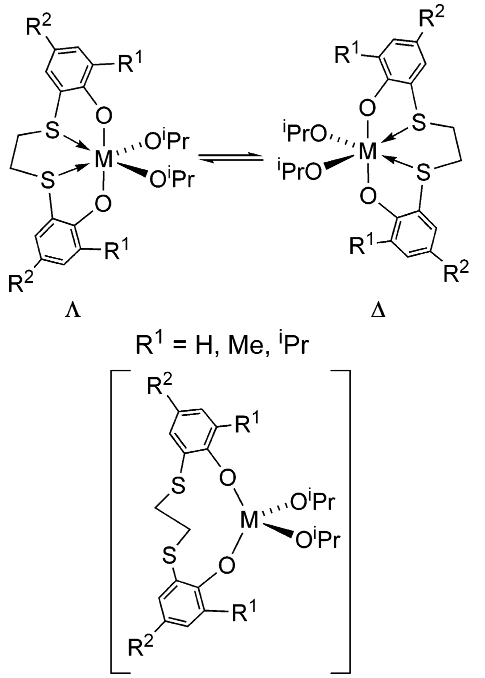
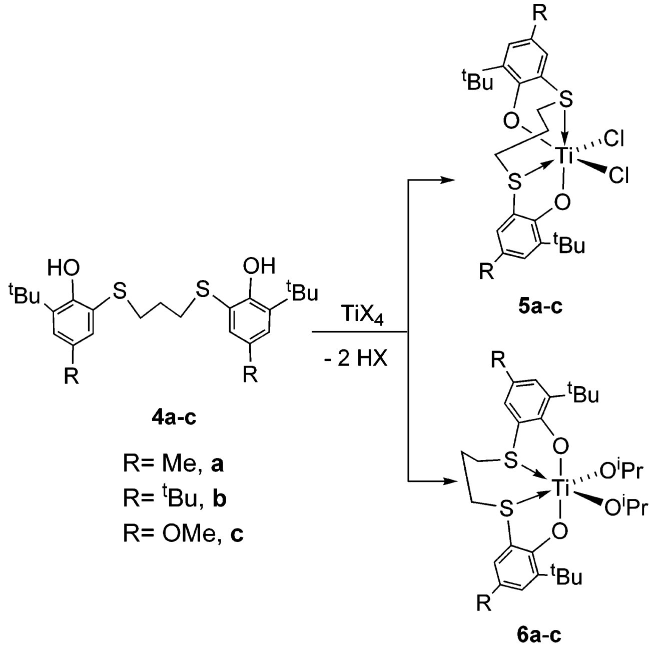


Figure 3. Variable-temperature ^{1}H NMR spectra of the di(isopropoxy) complex [Ti(OC$_6$H$_3$Me-4)$_2${S(CH$_2$)$_2$S}(O^{i}Pr)$_2$] (**3b**) in C$_2$D$_2$Cl$_4$.

Scheme 5



Scheme 6



exclude significant weakening of at least one titanium−sulfur bonding during the interconversion.[14] Although the fluxional behavior of octahedral complexes with two or three bidentate ligands is well documented in the literature,[23] the structure of complexes that contain a "linear"[3i,u,v,4,12m,p,24] (in contrast to the more common branched or "tripodal"[3p−t,12q−s]) tetradentate ligand has been studied only occasionally.

Synthesis and Structure of the 1,5-Dithiapentanediyl-Linked Complexes. When 1,5-dithiapentanediyl-linked bis(phenols) were reacted with titanium tetrachloride and tetra(isopropoxide), the corresponding complexes [Ti(OC$_6$H$_2$-6-^{t}Bu-4-R)$_2${S(CH$_2$)$_3$S}X$_2$] (R = Me, **a**, ^{t}Bu, **b**, OMe, **c**; X = Cl, **5**; O^{i}Pr, **6**) were obtained in good yields (Scheme 6). In contrast to the dichloro complexes with the 1,4-dithiabutandiyl-linked bis(phenolato) ligand, analogous complexes with the 1,5-dithiapentanediyl-linked bis(phenolato) ligand [Ti(OC$_6$H$_2$-6-^{t}Bu-4-R)$_2${S(CH$_2$)$_3$S}Cl$_2$] (**5a**−**c**) were found to be fluxional at ambient temperature, even with *tert*-butyl groups as ortho substituents. The low-temperature NMR spectra of **5a** showed the following feature: when

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[21] Fay, R. C.; Lindmark, A. F. *J. Am. Chem. Soc.* **1975**, *97*, 5928.

[22] (a) Baggett, N.; Poolton, D. S. P.; Jennings, W. B. *J. Chem. Soc., Chem. Commun.* **1975**, 239. (b) Baggett, N.; Poolton, D. S. P.; Jennings, W. B. *J. Chem. Soc., Dalton Trans.* **1979**, 1128.

[23] Serpone, N.; Bickley, D. *Progr. Inorg. Chem.* **1972**, *17*, 391.

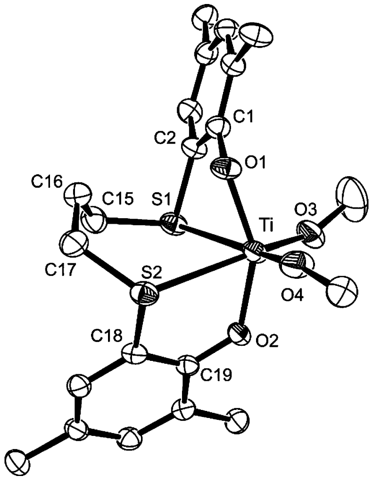


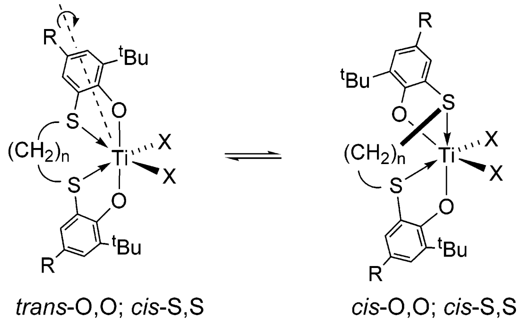
Figure 4. ORTEP representation of the structure of **6b**. Hydrogen atoms were omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Methyl groups of the *tert*-butyl and isopropoxy groups have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti−O1 1.9117(17), Ti−O2 1.9102(16), Ti−O3 1.7731(19), Ti−O4 1.7733(18), Ti−S1 2.7800(8), Ti−S2 2.7467(8), O1−Ti−O2 150.36(8), O1−Ti−O3 98.67(8), O1−Ti−O4 97.28(8), O2−Ti−O3 96.60(8), O2−Ti−O4 102.40(8), O3−Ti−O4 106.84(10), O1−Ti−S1 73.60(5), O1−Ti−S2 86.64(6), O2−Ti−S1 82.69(5), O2−Ti−S2 72.15(5), O3−Ti−S1 84.83(7), O3−Ti−S2 163.06(7), O4−Ti−S1 166.41(7), O4−Ti−S2 88.28(7), S2−Ti−S1 81.25(2).

cooled to −30 °C, the six CH_2 protons of the backbone appeared as broad signals in the region of 1.81−3.75 ppm. The *tert*-butyl groups were recorded as two signals at 1.27 and 1.43 ppm and the 4-methyl groups at 2.27 and 2.33 ppm, indicating that the complex is highly fluxional even at low temperatures. These ^1H NMR spectroscopic data are in accordance with the unsymmetrical structure found in the crystalline state. According to a crystal structure determination, the ground state configuration of the analogous complex **5b** corresponds to the C_1-symmetrical *cis*-O,O, *cis*-S,S isomer, as reported previously.[16a,c] A similar pattern for the NMR signals was observed for **5c**.

The di(isopropoxy) complexes of the 1,5-dithiapentanediyl-linked bis(phenolato) ligand **6a**−**c** are configurationally fluxional in the temperature range of −80 to +80 °C, exhibiting apparent C_s-symmetry in solution. The NMR spectra for **6a** are as follows: Whereas the two methyl groups of the isopropoxy group are recorded as one sharp doublet at 1.24 ppm, the four SCH_2 protons appeared as a triplet-like multiplet at 2.35 ppm and the two central CH_2 protons appeared as a higher-order multiplet at 1.21 ppm. A crystallographic structure determination of **6b** revealed that this complex adopts a C_2-symmetrical configuration with *cis*-arranged isopropoxy (O3−Ti−O4 = 106.84(10)°) and thioether groups with titanium−sulfur distances of Ti−S1 2.7800(8) Å and Ti−S2 2.7467(8) Å. The two bulky phenolato ligand moieties adopt the *trans*-coordination with the O1−Ti−O2 angle of 150.36(8)° (Figure 4).

The structure of this di(isopropoxy) complex **6b** (*trans*-O,O, *cis*-S,S, *cis*-Cl,Cl; "α-*cis*") is distinct from that of the dichloro complex **5b** (*cis*-O,O, *cis*-S,S, *cis*-Cl,Cl; "*β*-*cis*"),[16a] suggesting that for the 1,5-dithiapentanediyl-linked bis(phenolato) complexes more than one configuration is accessible. For the dichloro complexes **5a**−**c**, the observed NMR pattern can be explained by an interconversion between the (helical) C_2-symmetric (*trans*-O,O, *cis*-S,S, *cis*-Cl,Cl) and C_1-symmetric (*cis*-O,O, *cis*-S,S, *cis*-Cl,Cl) configuration (Scheme 7). This process can be envisaged as twisting of one of the OTiS five-membered chelate rings. This process is obviously more facile for complexes with the longer and conformationally more flexible 1,5-dithiapentanediyl link than those with the 1,4-dithiabutanediyl link.[24]

Scheme 7



Styrene Polymerization. Polymerization results of the various titanium catalyst precursors in toluene at temperatures of 40 or 50 °C using MAO as cocatalyst are compiled in Table 1. The configurationally flexible catalyst precursors with small ortho substituents **2a**−**d** produced atactic polystyrene with low activity and with broad molecular weight distribution upon activation with MAO. These results indicate that the tetradentate ligand does not offer a robust framework under the activation and/or polymerization conditions. Complexes **2e**−**i** produced isotactic polystyrene, whereas the 1,5-dithiapentadienyl complexes **5a**,**b** and **6b**,**c** produced syndiotactic polystyrene. Generally, the chloro complexes were found to be more active than the corresponding di(isopropoxy) complexes for the isospecific catalysts. The activity for styrene polymerization was particularly high for the precursors with the ortho-cumyl groups **2h** and **2i**. In the case of the polymerization initiated by MAO-activated **2i**, nearly all styrene was consumed within 5 min of initiation. The isotactic polystyrene showed a narrow molecular weight distribution, in analogy with the polystyrenes obtained using the complexes bearing a *tert*-butyl group at the ortho positions.[16a] The activity of complex **2g** is significantly decreased compared with that of **2e** and **f**, probably due to the electronic influence of the electron releasing para-methoxy substituent.[25]

Conclusion

Titanium dichloro and di(isopropoxy) complexes with a 1,4-dithiabutanediyl-linked bis(4,6-disubstituted phe-

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[24] Knight, P. D.; Scott, P. *Coord. Chem. Rev.* **2003**, *242*, 125. Balsells, J.; Caroll, P. J.; Walsh, P. J. *Inorg. Chem.* **2001**, *40*, 5568. For examples of "classical" coordination compounds of tetradentate thioether ligands, see: Nikles, D. E.; Powers, M. J.; Urbach, F. L. *Inorg. Chem.* **1983**, *22*, 3210. van Rijn, J.; Driessen, W. L.; Reedijk, J.; Lehn, J.-M. *Inorg. Chem.* **1985**, *23*, 3584. Kim, Y.-S.; Tian, W.; Kim, Y.; Jun, M. J. *Polyhedron* **1997**, *16*, 3807.

[25] The critical role of bulky ortho and electron-withdrawing substituents in phenolato-based polymerization catalysts are well-known: cf. ref. For similar trends in nickel catalysts, see: Wang, C.; Friedrich, S.; Younkin, T. R.; Li, R. T.; Grubbs, R. H.; Bansleben, D. A.; Day, M. W.; *Organometallics* **1998**, *17*, 3149. Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460.

Table 1. Polymerization of Styrene by Methylaluminoxane-Activated Titanium Complexes

complex	yield (g)	activity[a]	M_n ($\times 10^{-4}$)[b]	M_w/M_n[b]	T_m (°C)[c]
2a[d]	0.08	4	1.2	82	
2b[e]	0.10	7	193.5	1.57	
			0.7	1.88	
2c[d]	0.08	4	1.2	50	
2d[d]	0.09	5	n.d.	n.d.	
2e[e]	8.20	518	101.3	1.57	222
2f[e]	1.55	1543	265.4	2.0	223
2g[e]	0.21	13	91.0	1.66	222
			1.0	1.76	
2h[d]	3.47	175	70.0	1.9	225
2i[e,f]	5.40	682	31.4	2.36	223
3b[g]	0.03	4	168.6	1.50	
			0.7	1.71	
3e[g]	0.09	10	57.3	1.86	217
			0.5	1.76	
3h[d]	4.28	267	48.0	2.0	223
3i[g]	0.66	79	100.0	1.87	223
			0.2	1.48	
5a[e]	0.06	4	0.7	2.89	268
5b[e]	0.16	3	n.d.	n.d.	264
6b[e]	0.15	3	n.d.	n.d.	267
6c[g]	0.03	5	89.1	1.78	
			0.5	1.71	

[a] Activity: g (polymer)/(mmol catalyst) [styrene mol/L]·h. [b] Determined by GPC. n.d. = not determined. [c] Determined by DSC. [d] Polymerization conditions: 10 μmol Ti complex; [Al]/[Ti] = 500; [styrene] = 3.5 mol/L (10 mL); toluene (15 mL); $T = 50$ °C; reaction time 1 h. [e] Polymerization conditions: 2.5 μmol Ti complex; [Al]:[Ti] = 1500; [styrene] = 3.5 mol/L (10 mL); toluene (15 mL); $T = 40$ °C; reaction time 2 h. [f] Reaction time: 1 h. [g] Polymerization conditions: 2.5 μmol Ti complex; [Al]:[Ti] = 1500; [styrene] = 1.75 mol/L (5 mL); toluene (20 mL); $T = 40$ °C; reaction time 2 h.

nolato) ligand were examined in styrene polymerization upon activation with methylaluminoxane. The role played by the ligand's peripheral substituents in determining the activity and stereoselectivity is evidently related to the effect of these substituents on the stereorigidity of the catalyst precursors. Complexes bearing less bulky ortho-substituents R^1 in the aromatic ring (H, Me, ^{i}Pr) allow a rapid Δ, Λ interconversion on the NMR time scale, while the complexes with bulkier groups (^{t}Bu, CMe$_2$Ph) are stereorigid at temperatures up to 100 °C. Small ortho-substituents lead to configurational lability at room temperature and result in the loss of both activity and stereoselectivity. The atactic polystyrene formed with these complexes may not result from coordinate polymerization. When titanium dichloro and di(isopropoxy) complexes with the longer, more flexible 1,5-dithiapentanediyl-linked bis(phenolato) ligands are examined, syndiospecific polymerization with relatively low activity is observed. The ground state structures of these catalyst precursors do not show any preference for one of the two configurational isomers with *trans*- or *cis*-O,O arrangement of the phenolato ligands. Such a flexible ligand sphere may result in the generation of syndiospecific sites, most probably trivalent alkyl titanium centers formed from homolysis of the methyl cation.[7] Only the configurationally stable 1,4-dithiabutanediyl-linked phenolates with bulky ortho-substituents appear to be capable of stabilizing a C_2-symmetric, helical ligand sphere at the titanium center and thereby provide an active site for the isospecific styrene polymerization.[4] We will soon report the generation of the benzyl cations with this type of [OSSO] ligand sets and the controlled isospecific polymerization of styrene.[26]

Experimental Section

General Considerations. All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. Diethyl ether and THF were distilled from sodium benzophenone ketyl; pentane, hexane, and toluene were purified by distillation from sodium/triglyme benzophenone ketyl. 4-*tert*-Butyl-2-isopropylphenol and 4-methyl-2-(2-phenyl-2-propyl)phenol were synthesized following a literature procedure.[27] 1,4-Dithiabutanediyl-2,2′-bis(4,6-di-*tert*-butylphenol) (**1f**), dichloro{1,4-dithiabutanediyl-2,2′-bis-(4,6-di-*tert*-butylphenoxy)}titanium (**2f**), di(isopropoxy){1,4-dithiabutanediyl-2,2′-bis(4,6-di-*tert*-butylphenoxy)}titanium (**3f**), 1,5-dithiapentanediyl-2,2′-bis(4,6-di-*tert*-butylphenol) (**4b**), dichloro{1,5-dithiapentanediyl-2,2′-bis(4,6-di-*tert*-butylphenoxy)}-titanium (**5b**), and di(isopropoxy){1,5-dithiapentanediyl-2,2′-bis(4,6-di-*tert*-butylphenoxy)}titanium (**6b**) were prepared according to published procedures.[16a] The required thiophenols were prepared following a literature procedure.[28] Methylaluminoxane (MAO) in toluene was purchased from Aldrich. Titanium tetrachloride and titanium tetra(isopropoxide) (ALFA or Strem) were used as received. 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 C$_6$D$_6$ at 25 °C, unless otherwise stated. Chemical shifts for ^{1}H and ^{13}C spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. Elemental analyses were performed by the Microanalytical Laboratory of this department. Molecular weights of the polymers were measured using gel permeation chromatography (GPC) at 30 °C in THF and calibrated with respect to polystyrene standards.

1,4-Dithiabutanediyl-2,2′-bis(phenol) (1a).[29] This compound was prepared in the same manner as 1,4-dithiabutanediyl-2,2′-bis(4,6-di-*tert*-butylphenol) (**1f**)[16a,27] starting from phenol; yield 4.75 g (85%). ^{1}H NMR (CDCl$_3$, 25 °C): δ 2.80 (s, 4 H, SCH$_2$), 6.73 (s, 2 H, OH), 6.89 (dd, $^3J_{HH} = 7.7$ and 8.2 Hz, 2 H, 4-CH), 7.01 (d, $^3J_{HH} = 8.2$ Hz, 2 H, 6-CH) 7.28 (dd, $^3J_{HH} = 8.2$ and 7.7 Hz, 2 H, 5-CH), 7.42 (d, $^3J_{HH} = 7.7$ Hz, 2 H, 3-CH). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 35.7 (SCH$_2$), 115.1 (C-4), 117.3 (C-2), 121.0 (C-5), 131.6 (C-3), 136.1 (C-6), 158.5 (C-1). Anal. Calcd for C$_{14}$H$_{14}$O$_2$S$_2$: C, 60.40; H, 5.07. Found: C, 60.36; H, 5.13.

1,4-Dithiabutanediyl-2,2′-bis(4-methylphenol) (1b). This compound was prepared in the same manner as 1,4-dithiabutanediyl-2,2′-bis(4,6-di-*tert*-butylphenol) (**1f**)[16a,27] starting from 4-methylphenol. Crystallization of the crude product from chloroform afforded a colorless powder in 58% yield. ^{1}H NMR (CDCl$_3$, 25 °C): δ 2.25 (s, 6 H, CH$_3$), 2.80 (s, 4 H, SCH$_2$), 6.57 (s, 2 H, OH), 6.89 (d, $^3J_{HH} = 8.3$ Hz, 2 H, 2-CH), 7.07 (d, $^3J_{HH} = 8.3$ Hz, 2 H, 4-CH), 7.22 (s, 2 H, 6-CH). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 20.25 (CH$_3$), 35.80 (SCH$_2$), 114.79 (C-6) 116.93 (C-2), 130.23 (C-4), 132.15 (C-5), 136.07 (C-3), 154.90 (C-1). Anal. Calcd for C$_{16}$H$_{18}$O$_2$S$_2$: C, 62.71; H, 5.92; S, 20.93. Found: C, 61.89; H, 6.19; S, 20.88.

1,4-Dithiabutanediyl-2,2′-bis(4,6-dimethylphenol) (1c). This compound was isolated in 58% yield as colorless crystals following a procedure analogous to that to prepare **1a** starting from 2,4-dimethylphenol. The crude product was recrystallized as colorless crystals from a 1:1 acetone/acetonitrile mixture. ^{1}H NMR (CDCl$_3$, 25 °C): δ 2.20 (s, 6 H, 6-CH$_3$), 2.23 (s, 6 H, 4-CH$_3$), 2.79 (s, 4 H, SCH$_2$), 6.67 (s, 2 H, OH), 6.94 (d, $^4J_{HH} =$

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2.4 Hz, 2 H, 3-CH), 7.06 (d, $^4J_{HH}$ = 2.4 Hz, 2 H, 5-CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 16.4 (6-CH_3), 20.3 (4-CH_3), 35.8 (SCH_2), 116.3 (C-2), 124.2. (C-6), 129.4 (C-4), 133.4 (C-3), 133.5 (C-5), 153.2 (C-1). Anal. Calcd for $C_{18}H_{22}O_2S_2$: C, 64.63; H, 6.63. Found: C, 64.58; H, 6.38.

1,4-Dithiabutanediyl-2,2′-bis(4-*tert*-butyl-6-isopropylphenol) (1d). This compound was isolated in 54% yield as colorless crystals following a procedure analogous to that to prepare **1a** starting from 4-*tert*-butyl-2-isopropylphenol. The crude product was recrystallized from a 1:1 acetone/acetonitrile mixture. ^1H NMR ($CDCl_3$, 25 °C): δ 1.24 (d, $^3J_{HH}$ = 7.0 Hz, 12 H, $CH(CH_3)_2$), 1.27 (s, 18 H, $C(CH_3)_3$), 2.82 (s, 4 H, SCH_2), 3.28 (septet, $^3J_{HH}$ = 7.0 Hz, 2 H, $CH(CH_3)_2$), 6.79 (s, 2 H, OH), 7.21 (d, $^4J_{HH}$ = 2.3 Hz, 2 H, 3-CH), 7.28 (d, $^4J_{HH}$ = 2.4 Hz, 2 H, 5-CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 22.7 ($CH(CH_3)_2$), 28.4 ($CH(CH_3)_2$), 31.7 ($C(CH_3)_3$), 34.5 ($C(CH_3)_3$), 36.4 (SCH_2), 116.6 (C-2), 125.7 (C-3), 130.2 (C-5), 134.3 (C-6), 143.3 (C-4), 152.4 (C-1). Anal. Calcd for $C_{28}H_{42}O_2S_2$: C, 70.84; H, 8.92. Found: C, 70.74; H, 8.84.

1,4-Dithiabutandiyl-2,2′-bis(6-*tert*-butyl-4-methylphenol) (1e). This compound was prepared in the same manner as 1,4-dithiabutanediyl-2,2′-bis(4,6-di-*tert*-butyl-phenol) (**1f**)[16a,27] starting from 2-*tert*-butyl-4-methylphenol. Crystallization of the crude product from toluene gave a white powder in 94% yield. ^1H NMR ($CDCl_3$, 25 °C): δ 1.38 (s, 18 H, $C(CH_3)_3$), 2.23 (s, 6 H, CH_3), 2.78 (s, 4 H, SCH_2), 7.04 (s, 2 H, OH), 7.06 (d, $^4J_{HH}$ = 1.8 Hz, 2 H, 3-CH), 7.11 (d, $^4J_{HH}$ = 1.8 Hz, 2 H, 5-CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 20.6 (4-CH_3), 29.4 ($C(CH_3)_3$), 34.9 ($C(CH_3)_3$), 36.1 (SCH_2), 117.8 (C-2), 128.9 (C-4), 129.7 (C-5), 133.6 (C-3), 135.9 (C-6), 153.3 (C-1). Anal. Calcd for $C_{24}H_{32}O_2S_2$: C, 68.85; H, 8.19; S, 15.32. Found: C, 68.70; H, 7.98; S, 15.33.

1,4-Dithiabutandiyl-2,2′-bis(6-*tert*-butyl-4-methoxyphenol) (1g). This compound was prepared in the same manner as 1,4-dithiabutanediyl-2,2′-bis(4,6-di-*tert*-butylphenol) (**1f**)[16a,27] starting from 2-*tert*-butyl-4-methoxyphenol and isolated in 61% yield as colorless crystals. ^1H NMR δ: 1.46 (s, 18 H, $C(CH_3)_3$), 2.42 (s, 4 H, SCH_2), 3.32 (s, 6 H, OCH_3), 6.82 (d, $^4J_{HH}$ = 3 Hz, 2 H, 6-CH), 6.85 (s, 2 H, OH) 7.06 (d, $^4J_{HH}$ = 3 Hz, 2 H, 4-CH). $^{13}C\{^1H\}$ NMR: δ 29.5 ($C(CH_3)_3$), 35.4 ($C(CH_3)_3$), 36.1 (SCH_2), 55.3 (OCH_3), 116.6 (C-3), 117.4 (C-5), 118.4 (C-2), 137.6 (C-4), 150.4 (C-6), 153.1 (C-1). Anal. Calcd for $C_{24}H_{32}O_4S_2$: C, 63.96; H, 7.60; S, 14.23. Found: C, 64.04; H, 7.58; S, 14.74.

1,4-Dithiabutanediyl-2,2′-bis{4-methyl-6-(2-phenyl-2-propyl)phenol} (1h). This compound was prepared in the same manner as 1,4-dithiabutanediyl-2,2′-bis(4,6-di-*tert*-butylphenol) (**1f**)[16a,27] starting from 4-methyl-2-(2-phenyl-2-propyl)phenol. The crude product was purified by chromatography (hexane/ethyl acetate, 12:1) affording **1h** as colorless crystals in 30% yield. ^1H NMR ($CDCl_3$, 25 °C): δ 1.68 (s, 12 H, $C(CH_3)_2$), 2.30 (s, 6 H, 4-CH_3), 2.60 (s, 4 H, SCH_2), 6.38 (s, 2 H, OH), 7.09−7.25 (m, 14 H, 3-CH, 5-CH and Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 21.0 (4-CH_3), 29.7 ($C(CH_3)_2$), 35.8 (SCH_2), 42.4 ($C(CH_3)_2$), 118.6 (C-2), 125.6. (C-4′), 125.8 (C-2′), 128.1 (C-3′), 129.1 (C-6), 129.7 (C-5) 133.8 (C-3) 135.5 (C-4) 150.5 (C-1′) 152.9 (C-1). Anal. Calcd for $C_{34}H_{38}O_2S_2$: C, 75.23; H, 7.06. Found: C, 75.21; H, 6.96.

1,4-Dithiabutanediyl-2,2′-bis{4,6-di(2-phenyl-2-propyl)phenol} (1i). This compound was prepared in the same manner as 1,4-dithiabutanediyl-2,2′-bis(4,6-di-*tert*-butylphenol) (**1f**)[16a,27] starting from 2,4-di(2-phenyl-2-propyl)phenol. Crystallization of the crude product from pentane gave a white powder in 63% yield. ^1H NMR ($CDCl_3$, 25 °C): δ 1.67 (s, 12 H, $C(CH_3)_2$), 1.69 (s, 12 H, $C(CH_3)_2$), 2.56 (s, 4 H, SCH_2), 6.51 (s, 2 H, OH), 7.18−7.34 (m, 24 H, 3-CH, 5-CH and Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 29.33 ($C(CH_3)_2$), 30.92 ($C(CH_3)_2$), 35.48 (SCH_2), 42.37 ($C(CH_3)_2$), 42.56 ($C(CH_3)_2$), 117.79 (C-2), 125.34, 125.50, 125.66, 126.60, 127.61, 127.88, 127.98 (C-3), 131.98 (C-5), 134.73 (C-6), 142.01 (C-4), 150.18, 150.48, 152.69 (C-1). Anal. Calcd for $C_{50}H_{54}O_2S_2$: C, 79.95; H, 7.25; S, 8.54. Found: C, 80.04; H, 7.32; S, 8.71.

Dichloro{1,4-dithiabutanediyl-2,2′-bis(phenoxy)}titanium (2a). To a stirred solution of **1a** (1.00 g, 3.60 mmol) in 25 mL of toluene was added neat titanium tetrachloride (0.68 g, 3.60 mmol) at −10 °C. The mixture was warmed to room temperature and stirred for 1 h. All volatiles were removed under reduced pressure, and the resulting red solid was washed with pentane and dried in vacuo; yield 1.36 g (98%). ^1H NMR spectroscopic data in THF-d_8 are in agreement with those reported in the literature.[12m] Anal. Calcd for $C_{14}H_{12}Cl_2O_2S_2Ti$: C, 42.55; H, 3.06. Found: C, 42.05; H, 3.05.

Dichloro{1,4-dithiabutanediyl-2,2′-bis(4-methylphenoxy)}titanium (2b). To a solution of **1b** (1.61 g, 5.30 mmol) in CH_2Cl_2 was added titanium tetrachloride (1.01 g, 5.30 mmol) dropwise at −10 °C. The mixture was warmed to room temperature and stirred for 6 h at this temperature. The dark red solution was evaporated and washed twice with pentane to give a red powder; yield 1.8 g (82%). This compound was insoluble in hydrocarbons and only sparingly soluble in CH_2Cl_2 and $CHCl_3$. ^1H NMR ($C_2D_2Cl_4$, −20 °C): δ 2.27 (s, 6H, 4-CH_3), 2.75 (d, $^2J_{HH}$ = 10.3 Hz, 2 H, SCH_2), 3.25 (d, $^2J_{HH}$ = 10.3 Hz, 2 H, SCH_2), 6.72 (d, $^3J_{HH}$ = 8.2 Hz, 4 H, 5-CH, 6-CH), 7.11−7.31 (m, 2 H, 3-CH). ^1H NMR ($C_2D_2Cl_4$, 100 °C): δ 2.34 (s, 6 H, 4-CH_3), 2.99 (s, 4 H, SCH_2), 6.79 (d, $^2J_{HH}$ = 8.2 Hz, 4 H, 5-CH, 6-CH), 7.11−7.29 (m, 2 H, 3-CH). Anal. Calcd for $C_{16}H_{16}Cl_2O_2S_2Ti$: C, 45.41; H, 3.81; S, 15.15. Found: C, 45.91; H, 3.41; S, 15.65.

Dichloro{1,4-dithiabutanediyl-2,2′-bis(4,6-dimethylphenoxy)}titanium (2c). This compound was obtained as a burgundy-red powder in 96% yield following an analogous procedure reported to prepare **2a**. ^1H NMR ($CDCl_3$, 25 °C): δ 2.26 (s, 6 H, 6-CH_3), 2.30 (s, 6 H, 4-CH_3), 2.70 (d, $^2J_{HH}$ = 10.3 Hz, 2 H, SCH_2), 3.14 (d, $^2J_{HH}$ = 10.3 Hz, 2 H, SCH_2), 6.99 (d, $^4J_{HH}$ = 2.3 Hz, 2 H, 5-CH), 7.05 (d, $^4J_{HH}$ = 2.3 Hz, 2 H, 3-CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 16.8 (6-CH_3), 20.8 (4-CH_3), 40.7 (SCH_2), 118.2 (C-2), 125.1 (C-4), 130.1 (C-5), 132.7 (C-6), 134.9 (C-3), 167.2 (C-1). Anal. Calcd for $C_{18}H_{20}Cl_2O_2S_2Ti$: C, 47.91; H, 4.47. Found: C, 47.66; H, 4.30.

Dichloro{1,4-dithiabutanediyl-2,2′-bis(4-*tert*-butyl-6-isopropylphenoxy)}titanium (2d). This compound was prepared in a manner analogous to that to prepare **2a** starting with **1d** and was obtained as a dark red powder in 95% yield. ^1H NMR ($CDCl_3$, 25 °C): δ 1.29 (s, 18 H, $C(CH_3)_3$), 1.32 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$), 2.70 (d, $^2J_{HH}$ = 10.2 Hz, 2 H, SCH_2), 3.30 (d, $^2J_{HH}$ = 10.3 Hz, 2 H, SCH_2), 3.32 (septet, $^3J_{HH}$ = 6.8 Hz, 2 H, $CH(CH_3)_2$), 7.16 (d, $^4J_{HH}$ = 2.2 Hz, 2 H, 5-CH), 7.29 (d, $^4J_{HH}$ = 2.2 Hz, 2 H, 3-CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 22.5 ($CH(CH_3)_2$), 29.8 ($CH(CH_3)_2$), 31.7 ($C(CH_3)_3$), 34.9 ($C(CH_3)_3$), 40.8 (SCH_2), 118.4 (C-2), 126.3 (C-5), 127.2 (C-3), 135.2 (C-4), 146.5 (C-6), 166.4 (C-1). Anal. Calcd for $C_{28}H_{40}Cl_2O_2S_2Ti$: C, 56.85; H, 6.82. Found: C, 56.62; H, 6.70.

Dichloro{1,4-dithiabutanediyl-2,2′-bis(6-*tert*-butyl-4-methylphenoxy)}titanium (2e). A suspension of **1e** (1.01 g, 2.40 mmol) in 20 mL of toluene was treated with a solution of titanium tetrachloride (0.46 g, 2.40 mmol) in 10 mL of toluene at −78 °C. After stirring for 15 min at this temperature and 2 h at room temperature, the red solution was stored at −30 °C overnight. The precipitate was separated to give 1.04 g of a red powder (81%). ^1H NMR: δ 1.58 (s, 18 H, $C(CH_3)_3$), 2.03 (s, 6 H, 4-CH_3), 2.15 (d, $^2J_{HH}$ = 10.3 Hz, 2 H, SCH_2), 2.35 (d, $^2J_{HH}$ = 10.3 Hz, 2 H, SCH_2), 6.60 (d, $^4J_{HH}$ = 1.3 Hz, 2 H, 3-CH), 7.07 (d, $^4J_{HH}$ = 1.3 Hz, 2 H, 5-CH). $^{13}C\{^1H\}$ NMR: δ 20.8 (CH_3), 29.7 ($C(CH_3)_3$), 35.4 ($C(CH_3)_3$), 40.1 (SCH_2), 120.3 (C-2), 130.4 (C-5), 130.6 (C-3), 132.3 (C-6), 137.5 (C-4), 167.5 (C-1). Anal. Calcd for $C_{24}H_{32}Cl_2O_2S_2Ti\cdot 1/2C_7H_8$: C, 56.45; H, 6.14; S, 11.16. Found: C, 56.08; H, 6.09; S, 11.43.

Dichloro{1,4-dithiabutanediyl-2,2′-bis(6-*tert*-butyl-4-methoxyphenoxy)}titanium (2g). A suspension of **1g** (2.33 g, 5.20 mmol) in 20 mL of toluene was treated with a solution of titanium tetrachloride (0.98 g, 5.20 mmol) in 10 mL of toluene at −78 °C. After stirring for 15 min at this temperature and 2 h at room temperature, the red solution was stored at

−30 °C overnight. The precipitate was separated to give 2.94 g of a red powder (88%). ^{1}H NMR (CDCl$_3$, 25 °C): δ 1.46 (s, 18 H, C(C*H*$_3$)$_3$), 2.61 (d, $^2J_{HH}$ = 10.4 Hz, 2 H, SCH$_2$), 3.2 (d, $^2J_{HH}$ = 10.4 Hz, 2 H, SCH$_2$), 3.73 (s, 6 H, OCH$_3$), 6.72 (d, $^4J_{HH}$ = 2.9 Hz, 2 H, 6-CH), 6.93 (d, $^4J_{HH}$ = 2.9 Hz, 2 H, 4-CH). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 29.2 (C(*C*H$_3$)$_3$), 35.4 (*C*(CH$_3$)$_3$), 40.2 (SCH$_2$), 55.8 (OCH$_3$), 112.9 (C-5), 117.1 (C-3), 120 (C-2), 138.8 (C-4), 154.9 (C-6), 163.4 (C-1). Anal. Calcd for $C_{24}H_{32}Cl_2O_4S_2Ti$: C, 50.80; H, 5.68; S, 11.30. Found: C, 50.50; H, 5.99; S, 11.55.

Dichloro{1,4-dithiabutanediyl-2,2′-bis[4-methyl-6-(2-phenyl-2-propyl)phenoxy]}titanium (2h). This compound was prepared in a manner analogous to that to prepare **2b** using **1h**, and a brick red powder was obtained in 96% yield. ^{1}H NMR (CD$_2$Cl$_2$, 25 °C): δ 1.64 (s, 6 H, C(C*H*$_3$)$_2$Ph), 1.80 (s, 6 H, C(C*H*$_3$)$_2$Ph) 2.10 (d, $^2J_{HH}$= 10.2 Hz, 2 H, SCH$_2$), 2.31 (s, 6 H, 4-CH$_3$) 2.88 (d, $^2J_{HH}$ = 10.2 Hz, 2 H, SCH$_2$), 6.98−7.33 (m, 14 H, 3-CH, 5-CH and Ph). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C): δ 21.3 (4-CH$_3$), 27.4 (C(*C*H$_3$)$_2$), 30.7 (C(*C*H$_3$)$_2$), 40.8 (SCH$_2$), 42.6 (*C*(CH$_3$)$_2$), 120.3 (C-2), 126.3 (C-4′), 126.6 (C-2′), 128.3 (C-3′), 130.7 (C-3), 130.9 (C-5), 132.1 (C-4), 137.7 (C-6), 150.3 (C-1′), 166.8 (C-1). Anal. Calcd for $C_{34}H_{36}Cl_2O_2S_2Ti$: C, 61.92; H, 5.50. Found: C, 61.63; H, 5.37.

Dichloro{1,4-dithiabutanediyl-2,2′-bis[4,6-bis(2-phenyl-2-propyl)phenoxy]}titanium (2i). Neat titanium tetrachloride (0.78 g, 4.09 mmol) was added at −10 °C dropwise to a solution of **1i** (3.07 g, 4.09 mmol) in 30 mL of pentane. The mixture was warmed to room temperature and stirred for 2 h at the same temperature. A red powder precipitated from pentane, which was washed twice with 30 mL of pentane and dried in a vacuum; yield 3.20 g (90%). Crystals were obtained from a mixture of CH$_2$Cl$_2$ and pentane (3:1). ^{1}H NMR (CD$_2$Cl$_2$, 25 °C): δ 1.57 (s, 6 H, C(CH$_3$)$_2$), 1.68 (s, 6 H, C(C*H*$_3$)$_2$), 1.69 (s, 6 H, C(C*H*$_3$)$_2$), 1.79 (s, 6 H, C(C*H*$_3$)$_2$), 2.06 (d, $^2J_{HH}$ = 10.6 Hz, 2 H, SCH$_2$), 2.84 (d, $^2J_{HH}$ = 10.6 Hz, 2 H, C*H*$_2$), 7.06 (d, $^4J_{HH}$ = 2.2 Hz, 2 H, 3- or 5-CH), 7.11−7.14 (m, 2 H, *Ph*), 7.20−7.26 (m, 14 H, *Ph*), 7.30−7.34 (m, 4 H, C(CH$_3$)$_2$*Ph*), 7.38 (d, $^4J_{HH}$ = 2.2 Hz, 2 H, 3 or 5-CH). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C): δ 27.00 (C(CH$_3$)$_2$), 30.39 (C(*C*H$_3$)$_2$), 31.03 (*C*(CH$_3$)$_2$), 31.12 (*C*(CH$_3$)$_2$), 40.71 (C(*CH*$_3$)$_2$), 42.55 (SCH$_2$), 43.13 (*C*(CH$_3$)$_2$), 119.93 (C-2), 125.58 (C-3), 126.19, 126.33, 127.00 (C-5), 128.14, 128.46, 128.58, 128.63, 137.07 (C-6), 145.78 (C-4), 150.01 (*ipso*-C, C(CH$_3$)$_2$*Ph*), 150.57 (*ipso*-C, C(CH$_3$)$_2$*Ph*), 166.56 (C-1). Anal. Calcd for $C_{50}H_{52}Cl_2O_2S_2Ti$: C, 69.20; H, 6.04; S, 7.39. Found: C, 68.81; H, 6.58; S, 7.63.

Di(isopropoxy){1,4-dithiabutanediyl-2,2′-bis(phenoxy)}titanium (3a). To a stirred solution of **1a** (600 mg, 2.15 mmol) in 25 mL of toluene was added titanium tetra(isopropoxide) (615 mg, 2.15 mmol). The resulting yellow solution was further stirred for 1 h. All volatiles were removed under reduced pressure, and the resulting orange-yellow solid was washed with pentane and dried in vacuo; yield 0.93 g (98%). ^{1}H NMR (CDCl$_3$, −20 °C): δ 1.15 (d, $^3J_{HH}$ = 6.2 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.22 (d, $^3J_{HH}$ = 6.2 Hz, 6 H, CH(C*H*$_3$)$_2$), 2.46 (d, $^2J_{HH}$ = 10.3 Hz, 2 H, SCH$_2$), 3.14 (d, $^2J_{HH}$ = 10.3 Hz, 2 H, SCH$_2$), 4.72 (septet, $^3J_{HH}$ = 6.2 Hz, 2 H, C*H*(CH$_3$)$_2$), 6.76−6.82 (m, 4 H, C$_6$H$_4$), 7.30−7.32 (m, 4 H, C$_6$H$_4$). ^{13}C{^{1}H} NMR: δ 26.1 (CH(*C*H$_3$)$_2$)), 37.6 (SCH$_2$), 81.1 (*C*(CH$_3$)$_3$), 117.2 (C-2), 117.7 (C-4), 119.5 (C-5), 132.8 (C-3), 134.1 (C-6), 171.8 (C-1). Anal. Calcd for $C_{20}H_{26}O_4S_2Ti$: C, 54.30; H, 5.92. Found: C, 54.20; H, 5.83.

Di(isopropoxy){1,4-dithiabutanediyl-2,2′-bis(4-methylphenoxy)}titanium (3b). To a solution of **1b** (0.68 g, 2.26 mmol) in pentane was added titanium tetra(isopropoxide) (0.64 g, 2.26 mmol) at room temperature and stirred overnight. The orange solution was then filtered and concentrated. The concentrated solution was left standing at 0 °C to afford 0.79 g of an orange powder; yield 76%. ^{1}H NMR (C$_2$D$_2$Cl$_4$, 25 °C): δ 1.18 (d, $^3J_{HH}$ = 6.2 Hz, 12 H, OCH(C*H*$_3$)$_2$), 2.26 (s, 6 H, 4-CH$_3$), 2.72 (br s, 4 H, SCH$_2$), 4.69 (septet, $^3J_{HH}$ = 6.2 Hz, 2 H, OC*H*(CH$_3$)$_2$), 6.62 (d, $^2J_{HH}$ = 8.2 Hz, 2 H, 3-,5-,6-CH), 7.03−7.08 (m, 4 H, 3-,5-,6-CH). ^{1}H NMR (C$_2$D$_2$Cl$_4$, −15 °C): δ 1.10 (d, $^3J_{HH}$ = 6.1 Hz, 6 H, OCH(C*H*$_3$)$_2$), 1.17 (d, $^3J_{HH}$ = 6.1 Hz, 6 H, OCH(C*H*$_3$)$_2$), 2.19 (s, 6 H, 4-CH$_3$), 2.39 (d, $^2J_{HH}$ = 9.7 Hz, 2 H, SCH$_2$), 3.06 (d, $^2J_{HH}$ = 9.7 Hz, 2 H, SCH$_2$), 4.62 (septet, $^3J_{HH}$ = 6.2 Hz, 2 H, OC*H*(CH$_3$)$_2$), 6.58 (d, $^2J_{HH}$ = 8.2 Hz, 2 H, 3-,5-,6-CH), 7.05−7.07 (m, 4 H, 3-,5-,6-CH). ^{1}H NMR (C$_2$D$_2$Cl$_4$, 60 °C): δ 1.21 (d, $^3J_{HH}$ = 6.2 Hz, 12 H, OCH(C*H*$_3$)$_2$), 2.24 (s, 6 H, 4-CH$_3$), 2.75 (s, 4 H, SCH$_2$), 4.72 (septet, $^3J_{HH}$ = 6.2 Hz, 2 H, OC*H*(CH$_3$)$_2$), 6.65 (d, $^2J_{HH}$ = 8.2 Hz, 2 H, 3-,5-,6-CH), 7.04−7.09 (m, 4 H, 3-,5-,6-CH). ^{13}C{^{1}H} NMR (C$_2$D$_2$Cl$_4$, 25 °C): δ 20.38 (4-CH$_3$), 25.94 (OCH(*C*H$_3$)$_2$), 37.35 (SCH$_2$), 80.50 (O*C*H(CH$_3$)$_2$), 116.90 (C-1), 126.67 (C-5), 127.13 (C-6), 133.25 (C-4), 133.73 (C-3), 169.41 (C-2). Anal. Calcd for $C_{22}H_{30}O_4S_2Ti$: C, 56.16; H, 6.43; S, 13.63. Found: C, 55.26; H, 7.13; S, 13.93.

Di(isopropoxy){1,4-dithiabutanediyl-2,2′-bis(4,6-dimethylphenoxy)}titanium (3c). This compound was obtained as an orange-yellow powder in 97% yield following the procedure reported to prepare **3a** from **1b**. ^{1}H NMR (CDCl$_3$, −20 °C): δ 1.21 (d, $^3J_{HH}$ = 6.1 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.26 (d, $^3J_{HH}$ = 6.2 Hz, 6 H, CH(C*H*$_3$)$_2$), 2.19 (s, 6 H, 6-CH$_3$), 2.21 (s, 6 H, 4-CH$_3$), 2.43 (d, $^2J_{HH}$ = 10.1 Hz, 2 H, SCH$_2$), 3.10 (d, $^2J_{HH}$ = 10.1 Hz, 2 H, SCH$_2$), 4.78 (septet, $^3J_{HH}$ = 6.1 Hz, 2 H, C*H*(CH$_3$)$_2$), 6.94 (s, 4 H, C$_6$H$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 17.3 (6-CH$_3$), 20.6 (4-CH$_3$), 25.6 (OCH(*C*H$_3$)$_2$), 37.6 (SCH$_2$), 80.0 (O*C*H(CH$_3$)$_2$), 115.3 (C-2), 125.6 (C-4), 127.8 (C-6), 130.6 (C-5), 133.8 (C-3), 167.4 (C-1). Anal. Calcd for $C_{24}H_{34}O_4S_2Ti$: C, 57.82; H, 6.87. Found: C, 57.61; H, 6.66.

Di(isopropoxy){1,4-dithiabutanediyl-2,2′-bis(4-*tert*-butyl-6-isopropylphenoxy)}titanium (3d). This compound was obtained as a yellow powder in 97% yield following the procedure reported to prepare **3a** from **1d**. ^{1}H NMR (CDCl$_3$, 25 °C): δ 1.22−1.26 (overlapping d, d, s, 42 H, OC*H*(CH$_3$)$_2$, CH(C*H*$_3$)$_2$, C(C*H*$_3$)$_3$), 2.38 (d, $^2J_{HH}$ = 9.2 Hz, 2 H, SCH$_2$), 3.05 (d, $^2J_{HH}$ = 9.2 Hz, 2 H, SCH$_2$), 3.32 (septet, $^3J_{HH}$ = 6.9 Hz, 2 H, C*H*(CH$_3$)$_2$), 4.78 (septet, $^3J_{HH}$ = 6.1 Hz, 2 H, OC*H*(CH$_3$)$_2$), 7.09 (d, $^4J_{HH}$ = 2.4 Hz, 2 H, 5-CH) 7.29 (d, $^4J_{HH}$ = 2.4 Hz, 2 H, 3-CH). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 22.6 (CH(*C*H$_3$)$_2$), 25.7 (OCH(*C*H$_3$)$_2$), 28.8 (*C*H(CH$_3$)$_2$), 31.8 (C(*C*H$_3$)$_3$), 34.5 (*C*(CH$_3$)$_3$), 37.7 (SCH$_2$), 79.8 (O*C*H(CH$_3$)$_2$), 115.4 (C-2), 125.5 (C-5), 126.6 (C-3), 135.4 (C-4), 141.5 (C-6), 166.5 (C-1). Anal. Calcd for $C_{34}H_{54}O_4S_2Ti$: C, 63.93; H, 8.52. Found: C, 63.58; H, 8.47.

Di(isopropoxy){1,4-dithiabutanediyl-2,2′-bis-(6-*tert*-butyl-4-methylphenoxy)}titanium (3e). A solution of titanium tetra(isopropoxide) (0.72 g, 2.55 mmol) in 10 mL of toluene was added to a suspension of **1e** (1.07 g, 2.55 mmol) in 40 mL of toluene at −25 °C. The solution turned immediately yellow. After stirring for 2 h at room temperature, the solvent was evaporated in a vacuum and the crude product recrystallized from 7 mL of hexane at −30 °C to give 1.17 g of a yellow powder; yield 79%. ^{1}H NMR: δ 1.27 (d, $^3J_{HH}$ = 6.2 Hz, 12 H, OCH(C*H*$_3$)$_2$), 1.65 (s, 18 H, C(C*H*$_3$)$_3$), 2.10 (s, 6 H, 4-CH$_3$), 2.17 (d, $^2J_{HH}$ = 10.4 Hz, 2 H, SCH$_2$), 2.43 (d, $^2J_{HH}$ = 10.4 Hz, 2 H, SCH$_2$), 4.85 (septet, $^3J_{HH}$ = 6.2 Hz, 2 H, OC*H*(CH$_3$)$_2$), 6.87 (d, $^4J_{HH}$ = 2.2 Hz, 2 H, 3-CH), 7.14 (d, $^4J_{HH}$ = 2.2 Hz, 2 H, 5-CH). ^{13}C{^{1}H} NMR: δ 20.8 (CH$_3$), 26.2 (OCH(*C*H$_3$)$_2$), 29.7 (C(*C*H$_3$)$_3$), 35.4 (*C*(CH$_3$)$_3$), 37.5 (SCH$_2$), 79.9 (O*C*H(CH$_3$)$_2$), 117.4 (C-2), 127.4 (C-6), 130.1 (C-5), 131.2 (C-3), 137.5 (C-4), 167.8 (C-1). Anal. Calcd for $C_{30}H_{46}O_4S_2Ti$: C, 61.84; H, 7.96; S, 11.01. Found: C, 62.03; H, 8.50; S, 11.04.

Di(isopropoxy){1,4-dithiabutanediyl-2,2′-bis-(6-*tert*-butyl-4-methoxyphenoxy)}titanium (3g). A solution of titanium tetra(isopropoxide) (0.63 g, 2.16 mmol) in 10 mL of toluene was added to a suspension of **1g** (0.97 g, 2.16 mmol) in 40 mL of toluene at −25 °C. The solution became immediately orange. After stirring for 15 min at that temperature and for 2 h at room temperature, the solution was concentrated in a vacuum. Then it was stored at −30 °C overnight. The residue was separated to give 0.92 g of a red powder in 71% yield. ^{1}H NMR: δ 1.300 (d, $^3J_{HH}$ = 6.1 Hz, 6 H, OCH(C*H*$_3$)$_2$), 1.301 (d, $^3J_{HH}$ = 6.1 Hz, 6 H, OCH(C*H*$_3$)$_2$), 1.62 (s, 18 H,

$C(CH_3)_3$), 2.22 (d, $^{2}J_{HH}$ = 10.2 Hz, 2 H, SCH_2), 2.53 (d, $^{2}J_{HH}$ = 10.2 Hz, 2 H, SCH_2), 3.34 (OCH_3), 4.87 (septet, $^{3}J_{HH}$ = 6.1 Hz, 2 H, $OCH(CH_3)_2$), 6.69 (d, $^{4}J_{HH}$ = 2.2 Hz, 2 H, 3-CH), 7.13 (d, $^{4}J_{HH}$ = 2.2 Hz, 2 H, 5-CH). $^{13}C\{^{1}H\}$ NMR: δ 26.2 ($OCH(CH_3)_2$), 29.5 ($C(CH_3)_3$), 35.6 ($C(CH_3)_3$), 37.4 (SCH_2), 55.4 (OCH_3), 79.8 ($OCH(CH_3)_2$), 113.9 (C-5), 116.9 (C-2), 117.5 (C-3), 138.8 (C-4), 152.5 (C-6), 167.8 (C-1). Anal. Calcd for $C_{30}H_{46}O_6S_2Ti \cdot 0.5C_7H_8$: C, 60.89; H, 7.63; S, 9.71. Found: C, 60.20; H, 7.87; S, 9.88.

Di(isopropoxy){1,4-dithiabutanediyl-2,2′-bis[4-methyl-6-(2-phenyl-2-propylphenoxy)]}titanium (3h). This compound was obtained as a yellow powder in 97% yield following the procedure reported to prepare **3a** from **1h**. ^{1}H NMR ($CDCl_3$, 25 °C): δ 0.90, (d, $^{3}J_{HH}$ = 6.1 Hz, 6 H, $OCH(CH_3)_2$), 1.66 (s, 6 H, $C(CH_3)_2Ph$), 1.71 (s, 6 H, $C(CH_3)_2Ph$) 1.97 (d, $^{2}J_{HH}$= 10.5 Hz, 2 H, SCH_2), 2.25 (s, 6 H, 4-CH_3), 2.77 (d, $^{2}J_{HH}$ = 10.5 Hz, 2 H, SCH_2), 4.21 (septet, $^{3}J_{HH}$ = 6.1 Hz, 1 H, $OCH(CH_3)_2$), 6.92−7.19 (m, 14 H, 3-CH, 5-CH and Ph). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 25 °C): δ 21.0 (4-CH_3), 24.3 ($OCH(CH_3)$), 28.6 ($C(CH_3)_2$), 29.7 ($C(CH_3)_2$), 37.3 (SCH_2), 47.0 ($C(CH_3)_2$), 79.1 $OCH(CH_3)$), 117.4 (C-2), 124.8 (C-4′), 124.8 (C-2′), 126.8 (C-4),127.6 (C-3′), 129.7 (C-5), 131.3 (C-3), 136.9 (C-6), 151.0 (C-1′), 161.6 (C-1). Anal. Calcd for $C_{40}H_{50}O_4S_2Ti$: C, 67.97; H, 7.13. Found: C, 67.87; H, 7.03.

Di(isopropoxy){1,4-dithiabutanediyl-2,2′-bis[(2-phenyl-2-propyl)phenoxy]}titanium (3i). Titanium tetra(isopropoxide) (0.15 g, 0.53 mmol) was added to a solution of **1i** (0.41 g, 0.53 mmol) in pentane at room temperature and stirred overnight. The orange-yellow solution was evaporated, redissolved in 5 mL of pentane, and filtered. The concentrated solution was stored at −30 °C, affording 0.41 g of yellow crystals; yield 85%. ^{1}H NMR: δ 1.08 (d, $^{3}J_{HH}$ = 6.1 Hz, 6 H, $OCH(CH_3)_2$), 1.09 (d, $^{3}J_{HH}$ = 6.1 Hz, 6 H, $OCH(CH_3)_2$), 1.59 (s, 12 H, $C(CH_3)_2$), 1.76 (s, 6 H, $C(CH_3)_2$), 1.87 (s, 6 H, $C(CH_3)_2$), 1.93 (d, $^{2}J_{HH}$ = 10.1 Hz, 2 H, SCH_2), 2.34 (d, 2 H, $^{2}J_{HH}$ = 10.1 Hz, SCH_2), 4.46 (septet, 2 H, $^{3}J_{HH}$ = 6.1 Hz, $OCH(CH_3)_2$), 7.05−7.28 (m, 18 H, Ph), 7.37 (d, 4 H, $^{3}J_{HH}$ = 7.3 Hz, Ph), 7.45 (d, 2 H, $^{4}J_{HH}$ = 2.5 Hz, 3- or 5-CH). $^{13}C\{^{1}H\}$ NMR: δ 25.91 ($C(CH_3)_2$), 25.95 ($C(CH_3)_2$), 28.4 ($C(CH_3)_2$), 29.97 ($OCH(CH_3)_2$), 31.13 ($C(CH_3)_2$), 37.35 (SCH_2), 42.69 ($C(CH_3)_2$), 42.75 ($C(CH_3)_2$), 79.50 ($OCH(CH_3)_2$), 117.46 (C-2), 125.17, 125.90, 126.31, 126.05, and 129.22 (*o*-, *m*-, *p*-C of *Ph*), 136.79 (C-6), 140.45 (C-4), 151.11 (*ipso*-C, $(CH_3)_2Ph$), 151.32 (*ipso*-C, $C(CH_3)_2Ph$), 167.15 (C-1). Anal. Calcd for $C_{56}H_{66}O_4S_2Ti$: C, 73.50; H, 7.27; S, 7.01. Found: C, 73.07; H, 7.09; S, 7.41.

1,5-Dithiapentanediyl-2,2′-bis(6-*tert*-butyl-4-methylphenol) (4a). This compound was prepared in the same manner as **4b** starting from 2-*tert*-butyl-4-methylphenol and isolated as colorless crystals in 40% yield. ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.36 (s, 18 H, $C(CH_3)_3$), 1.73 (quintet, 2 H, $^{3}J_{HH}$ = 7.2 Hz, CH_2), 2.15 (s, 6 H, 4-CH_3), 2.68 (t, 4 H, $^{3}J_{HH}$ = 7.2 Hz, SCH_2), 6.96 (s, 2 H, OH), 7.00 (d, 2 H, $^{4}J_{HH}$ = 1.6 Hz, 3-or 5-CH), 7.04 (d, 2 H, $^{4}J_{HH}$ = 1.6 Hz, 3-or 5-CH). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 25 °C): δ 20.45 (4-CH_3), 29.24 ($C(CH_3)_3$), 34.09 (CH_2), 34.71 ($C(CH_3)_3$), 35.10 (SCH_2), 118.47 (C-1), 128.53(C-3), 129.28 (C-6), 133.35 (C-4), 135.52 (C-5), 152.15 (C-2). Anal. Calcd for $C_{25}H_{36}O_2S_2$: C, 69.40; H, 8.39; S, 14.82. Found: C, 70.34; H, 8.58; S, 14.64.

1,5-Dithiapentanediyl-2,2′-bis(6-*tert*-butyl-4-methoxyphenol) (4c). This compound was prepared in the same manner as **4b** starting from 2-*tert*-butyl-4-methoxyphenol and isolated as colorless crystals in 55% yield. ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.37 (quintet, 2 H, $^{3}J_{HH}$ = 7.3 Hz, CH_2), 1.38 (s, 18 H, $C(CH_3)_3$), 2.79 (t, 4 H, $^{3}J_{HH}$ = 7.3 Hz, SCH_2), 3.75 (s, 6 H, 4-OCH_3), 6.79 (s, 2 H, OH), 6.85 (d, 2 H, $^{4}J_{HH}$ = 3.0 Hz, 3-or 5-CH), 6.89 (d, 2 H, $^{4}J_{HH}$ = 3.0 Hz, 3- or 5-CH). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 25 °C): δ 29.24 ($C(CH_3)_3$), 35.15 ($C(CH_3)_3$), 35.27 (SCH_2), 55.75 (OCH_3), 116.21 (C-4), 116.50(C-6), 118.67 (C-1), 137.28 (C-3), 149.72 (C-5), 152.15 (C-2). Anal. Calcd for $C_{25}H_{36}O_4S_2$: C, 64.62; H, 7.81; O, 13.77; S, 13.80. Found: C, 64.34; H, 7.58; S, 14.04.

Dichloro{1,5-dithiapentanediyl-2,2′-bis(6-*tert*-butyl-4-methylphenoxy)}titanium (5a). To a solution of **4a** (3.08 g, 7.10 mmol) in pentane was added dropwise titanium tetrachloride (1.35 g, 7.10 mmol) at −10 °C. The mixture was warmed to room temperature and stirred for 2 h at the same temperature. The dark red powder obtained was washed twice with 30 mL of pentane and dried in a vacuum; yield 3.20 g (84%). ^{1}H NMR (toluene-d_8, 25 °C): δ 1.38−1.61 (br s, 22 H, $C(CH_3)_3$, CH_2), 2.08 (6 H, overlapped with solvent, 4-CH_3), 2.89 (br s, 2H, CH_2), 6.49 (s, 2 H, 3-or 5-CH), 6.93 (s, 2 H, 3-or 5-CH). ^{1}H NMR (toluene-d_8, −40 °C): δ 1.34 (s, 11 H, $C(CH_3)_3$, CH_2), δ 1.57 (s, 9 H, $C(CH_3)_3$), 1.97 (s, 3 H, 4-CH_3), 2.07 (3 H, overlapped with solvent, 4-CH_3), 2.32 (br s, 1 H, CH_2), 2.78 (br t, 1 H, CH_2), 2.95 (br d, 1 H, CH_2), 3.15 (b t, 1 H, CH_2), 6.41 (br s, 2 H, 3-or 5-CH), 6.85 (br s, 1 H, 3- or 5-CH), 6.89 (br s, 1 H, 3-or 5-CH). $^{13}C\{^{1}H\}$ NMR (toluene-d_8, −40 °C): δ 20.82 (CH_3), 21.17 (CH_3), 29.36 ($C(CH_3)_3$), 29.59 ($C(CH_3)_3$), 34.11 (CH_2), 34.71 ($C(CH_3)_3$), 35.13 (SCH_2), 35.36 (SCH_2), 121.47 (C-2), 127.84 (C-3), 127.99 (C-3′), 128.70 (C-5), 128.90 (C-5′), 132.81 (C-4), 133.04 (C-4′), 136.35 (C-6), 136.90 (C-6′), 162.99 (C-1), 163.04 (C-1′). Anal. Calcd for $C_{25}H_{34}Cl_2O_2S_2Ti$: C, 54.65; H, 6.24; S, 11.67. Found: C, 55.45; H, 6.44; S, 11.97.

Dichloro{1,5-dithiapentanediyl-2,2′-(6-*tert*-butyl-4-methoxyphenoxy)}titanium (5c). To a solution of **4c** (2.11 g, 4.50 mmol) in pentane was added dropwise titanium tetrachloride (0.85 g, 4.50 mmol) at −10 °C. The mixture was warmed to room temperature and stirred for 2 h at the same temperature. The dark red powder obtained was washed twice with 15 mL of pentane and dried in a vacuum; yield 2.10 g (80%). ^{1}H NMR (toluene-d_8, 25 °C): δ 1.27 (m, 4 H, CH_2), 1.44 (br s, 18 H, $C(CH_3)_3$), 2.76 (br s, 2H, CH_2), 3.33 (s, 6 H, 4-OCH_3), 6.29 (s, 2 H, 3-CH) 6.78 (s, 2 H, 5-CH). ^{1}H NMR (toluene-d_8, −40 °C): δ 1.17 (br s, 2 H, SCH_2), 1.33 (s, 9 H, $C(CH_3)_3$), 1.54 (s, 9 H, $C(CH_3)_3$), 2.17 (br s, 1 H, CH_2), 2.77 (br s, 1 H, SCH_2), 3.01 (br s, 1 H, SCH_2), 3.20 (s, 3 H, OCH_3), 3.31 (s, 3 H, OCH_3), 6.30 (s, 2 H, 3-CH) 6.71 (s, 1 H, 5-CH), 6.81 (s, 1 H, 5-CH). $^{13}C\{^{1}H\}$ NMR (toluene-d_8, −40 °C): δ 29.13 ($C(CH_3)_3$), 29.36 ($C(CH_3)_3$), 33.78 ($C(CH_3)_3$), 34.55 (CH_2), 35.38 (SCH_2), 35.63 (SCH_2), 54.82 (OCH_3), 55.16 (OCH_3), 109.82 (C-3), 111.51 (C-3′), 113.24 (C-5), 114.73 (C-5′), 121.79 (C-2), 137.61 (C-6), 138.41 (C-6′), 155.66 (C-4), 155.75 (C-4′), 159.33 (C-1), 159.53 (C-1′). Anal. Calcd for $C_{25}H_{34}Cl_2O_4S_2Ti$: C, 51.64; H, 5.89; S, 11.03. Found: C, 52.84; H, 6.19; S, 11.43.

Di(isopropoxy){1,5-dithiapentanediyl-2,2′-bis-(6-*tert*-butyl-4-methylphenoxy)}titanium (6a). To a solution of **4a** (0.60 g, 1.38 mmol) in pentane was added titanium tetra(isopropoxide) (0.40 g, 1.38 mmol) at room temperature, and the mixture was stirred overnight. The yellow solution was then filtered and concentrated. The concentrated solution left at 0 °C afforded 0.61 g of a pale yellow powder; yield 73%. ^{1}H NMR: δ 1.21 (m, 2 H, CH_2), 1.24 (d, $^{3}J_{HH}$ = 6.1 Hz, 12 H, $OCH(CH_3)_2$), 1.69 (s, 18 H, $C(CH_3)_3$), 2.15 (s, 6 H, 4-CH_3), 2.35 (higher order t, 4H, SCH_2), 4.87 (septet, $^{3}J_{HH}$ = 6.1 Hz, 2 H, $OCH(CH_3)_2$), 6.98 (d, $^{4}J_{HH}$ = 2.1 Hz, 2 H, 3-CH), 7.15 (d, $^{4}J_{HH}$ = 2.1 Hz, 2 H, 5-CH). $^{13}C\{^{1}H\}$ NMR: δ 22.75 (CH_2), 26.12 ($OCH(CH_3)_2$), 29.67 ($C(CH_3)_3$), 29.79 ($C(CH_3)_3$), 35.13 ($C(CH_3)_3$), 35.38 ($C(CH_3)_3$), 36.53 (SCH_2), 80.08 ($OCH(CH_3)_2$), 122.37 (C-2), 127.39 (C-4), 128.29(C-3), 130.61 (C-5), 36.93 (C-6), 165.89 (C-1). Anal. Calcd for $C_{31}H_{48}O_4S_2Ti$: C, 62.40; H, 8.11; S, 10.75. Found: C, 63.26; H, 8.51; S, 11.15.

Di(isopropoxy){1,5-dithiapentanediyl-2,2′-bis-(6-*tert*-butyl-4-methoxyphenoxy)}titanium (6c). To a solution of **4c** (0.65 g, 1.40 mmol) in pentane was added titanium tetra(isopropoxide) (0.40 g, 1.40 mmol) at room temperature, and the mixture was stirred overnight. The orange solution was then filtered and concentrated. The concentrated solution left at 0 °C afforded 0.52 g of an orange powder; yield 60%. ^{1}H NMR (toluene-d_8): δ 1.20 (d, $^{3}J_{HH}$ = 6.2 Hz, 12 H, $OC(CH_3)_2$), 1.32 (m, 2 H, CH_2), 1.62 (s, 18 H, $C(CH_3)_3$), 2.41 (higher order

Table 2. Experimental Data for the Crystal Structure Determinations of the Complexes 2c, 2e, 2i, 3h, and 6b

	2c	**2e**	**2i**	**3h**	**6b**
Crystal Data					
formula	$C_{18}H_{20}Cl_2O_2S_2Ti$	$C_{24}H_{32}Cl_2O_2S_2Ti\cdot 1/2C_6D_6$	$C_{50}H_{52}Cl_2O_2S_2Ti$	$C_{40}H_{50}O_4S_2Ti$	$C_{37}H_{60}O_4S_2Ti$
fw	451.25	580.52	867.84	706.82	680.87
cryst size, mm	0.50 × 0.25 × 0.25	0.70 × 0.20 × 0.16	0.53 × 0.39 × 0.08	0.50 × 0.30 × 0.15	0.40 × 0.25 × 0.20
cryst color	dark red	dark red	red	yellow	yellow
cryst system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
a, Å	17.974(4)	15.774(3)	10.643(2)	19.415(4)	37.699(6)
b, Å	8.713(3)	22.616(3)	32.663(5)	10.550(3)	9.209(1)
c, Å	26.134(4)	17.275(2)	12.708(2)	19.990(4)	26.836(3)
α, deg	90	90	90	90	90
β, deg	150.73(3)	102.70(1)	90.061(3)	109.15(3)	122.117(7)
γ, deg	90	90	90	90	90
V, Å^3	2001.1(9)	6012.0(16)	4417.7(13)	3867.9(16)	7890.9(18)
Z	4	8	4	4	8
ρ_{calcd}, g cm^{-3}	1.498	1.283	1.305	1.214	1.146
μ, mm^{-1}	0.912	0.622	0.448	0.367	0.357
F(000)	928	2408	1824	1504	2944
Data Collection					
$2\theta_{max}$, deg	3.2 to 27.5	3.0 to 28.0	1.3 to 28.3	3.2 to 27.5	2.6 to 28.3
index ranges	h −23 to 23; k −11 to 9; l -31 to 31	h 0 to 19; k 0 to 29; l −22 to 22	h −14 to 14; k −43 to 43; l −16 to16	h −25 to 23; k −13 to 12; l −20 to 25	h −50 to 50; k −12 to 12; l −35 to 35
no. of reflns measd	24 590	13 393	60 832	23 267	34 881
no. of indep reflns	4502 [R(int) = 0.0662]	12 890 [R(int) = 0.0656]	10 966 [R(int) = 0.0610]	8358 [R(int) = 0.0738]	9747 [R(int) = 0.0462]
no. of params	292	797	722	424	554
GOF	1.031	0.968	1.021	1.022	1.001
final R indices R_1, wR_2 (obsd data)	0.0400, 0.0921	0.0821, 0.1521	0.0424, 0.0951	0.0626, 0.1387	0.0518, 0.1361
final R indices R_1, wR_2 (all data)	0.0706, 0.1044	0.2369, 0.2072	0.0604, 0.1035	0.1552, 0.1751	0.0919, 0.1557
largest e-max, e-min, e Å^{-3}	0.365, −0.674	0.487, −0.432	0.479, −0.336	0.480, −0.350	0.933, −0.567

t, 2 H, CH$_2$), 3.41 (s, 6 H, OCH$_3$), 4.83 (septet, $^3J_{HH}$ = 6.2 Hz, 2 H, OC(CH_3)$_2$), 6.77 (d, $^4J_{HH}$ = 2.2 Hz, 2 H, 3-CH), 7.05 (d, $^4J_{HH}$ = 2.2 Hz, 2 H, 5-CH). ^{13}C{^{1}H} NMR (toluene-d_8): δ 23.05 (CH$_2$), 26.21 (OCH(CH$_3$)$_2$), 29.58 (C(CH$_3$)$_3$), 35.66 (SCH$_2$), 36.56 (C(CH$_3$)$_3$), 55.36 (OCH$_3$), 79.98 (OCH(CH$_3$)$_2$), 113.69 (C-3), 115.96 (C-5), 122.12 (C-2′), 124.97 (C-2), 137.50 (C-6′), 138.17 (C-6), 152.56 (C-4), 165.89 (C-1). Anal. Calcd for $C_{31}H_{48}O_6S_2Ti$: C, 59.22; H, 7.70; S, 10.20. Found: C, 60.02; H, 8.27; S, 10.52.

Crystal Structure Analysis of 2c, 2e, 2i, 3h, and 6b. Relevant crystallographic data of **2c**, **2e**, **2i**, **3h**, and **6b** are summarized in Table 2. Crystals suitable for X-ray analysis of **2c** and **3h** were obtained from toluene solution at −20 °C, of **2e** by slow evaporation of a C$_6$D$_6$ solution at room temperature, of **6b** in an analogous manner from a toluene solution, and of **2i** from a 1:1 CH$_2$Cl$_2$/pentane mixture at room temperature. Data collections were performed with graphite-monochromated Mo Kα radiation using φ scans + ω scans on a Bruker AXS diffractometer at 296(2) K (**2e**), 120(2) K (**2i**), and 203(2) K (**6b**) and on a Bruker-Nonius Kappa CCD diffractometer at 173(2) K (**2c**) and at 298(2) K (**3h**). The data collections as well as the data reductions and corrections for absorption were carried out using the program systems SMART[30a] and COLLECT.[30b] The structures were solved using the programs SHELXS-86[30c] and SIR97.[30d] 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)[30e] and refined with anisotropic thermal parameters. Compound **2e** crystallizes with two crystallographically independent molecules. The unit cell incorporates the solvent molecule benzene. Compound **6b** shows disorder in one of the isopropyl groups as well as in one *tert*-butyl group. Split positions of equal intensity were introduced. For the graphical representation, ORTEP-III for Windows was used as implemented in the program system WINGX.[30f]

General Procedure for Styrene Polymerization. Variant a: To a 100 mL Schlenk flask were added 15 mL of toluene, 10 mL of styrene, and MAO (2.25 mL, 10 wt % in toluene) and stirred at 40 °C for 15 min. The polymerization was initiated by adding 25 μmol of catalyst precursor as a toluene solution. The mixture was stirred for 2 h, after which time 1 mL of 2-propanol was added and the mixture stirred for 10 min. The contents were then poured into acidified methanol (300 mL). The obtained polymer was filtered and washed two times with methanol. The resulting polymers were dried overnight at 60 °C in a vacuum to constant weight.

Variant b: Polymerizations were carried out in a 100 mL Schlenk flask equipped with magnetic stirring bars and thermostated to the desired temperature. The reactor was charged with the specific amount of MAO (Al/Ti = 500) into the glovebox. Toluene (15 mL), toluene solution of the catalyst (1 mL, 1 × 10^{-2} mmol), and styrene were sequentially charged, and the resulting mixture was strongly stirred for 1 h. The polymerization was quenched by the fast introduction of 30 mL of ethanol/HCl. The polymer was filtered, washed several

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(30) (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) *Collect. Data Collection Software*; Nonius BV, 1997−2000. (c) Sheldrick, G. M. *SHELXS-86, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1986. (d) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115. (e) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997. (f) 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.

times with fresh ethanol, and dried under vacuum until constant weight.

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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 **2c**, **2e**, **2i**, **3i**, and **6b** are given. This material is available free of charge via the Internet at http://pubs.acs.org.

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