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Article

Synthesis, Structure, and Olefin Polymerization Activity of Titanium Complexes Bearing Asymmetric Tetradentate [OSNO]-Type Bis(phenolato) Ligands

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A series of chiral linear tetradentate bis(phenols) that contain both sulfur and nitrogen donors of the type [2,2′-(HOC_6H_2-6-^{t}Bu-4-R^1)$_2$$SC_6H_{10}NR^2$] [$R^1$ = Me (**a**), ^{t}Bu (**b**); R^2 = H (**1**), Me (**2**)], [2,2′-(HOC_6H_2-4,6-^{t}Bu$_2$)$_2$$SC_6H_{10}$N═CH] (**3**), and [2,2′-(HOC_6H_2-4,6-^{t}Bu$_2$)$_2$$SC_6H_{10}NHCH_2$] (**4**) were synthesized. The reaction of these bis(phenols) with TiX_4 (X = Cl, O^{i}Pr) afforded the corresponding C_1-symmetric titanium complexes [Ti{2,2′-(OC_6H_2-6-^{t}Bu-4-R^1)$_2$$SC_6H_{10}NR^2$}-$X_2$] [$R^1$ = Me (**a**), ^{t}Bu (**b**); R^2 = H, X = Cl (**5a**, **5b**), O^{i}Pr (**6a**); R^2 = Me, X = Cl (**7a**, **7b**), O^{i}Pr (**8a**)], [Ti{2,2′-(OC_6H_2-4,6-^{t}Bu$_2$)$_2$$SC_6H_{10}$N═CH}Cl$_2$] (**9**), and [Ti{2,2′-(OC_6H_2-4,6-^{t}Bu$_2$)$_2$$SC_6H_{10}NHCH_2$}Cl$_2$] (**10**). The formation of titanium complexes **5**−**8** proceeded diastereoselectively, but a mixture of two isomers (**a** and **b**) was obtained for **9** and **10**. The configuration of the ligand around the metal center was determined by a combination of NMR spectroscopy and single-crystal X-ray diffraction studies of **5b**, **7b**, **8a**, **9b**, **10a**, and **10b**. All titanium complexes were configurationally stable in solution up to 100 °C. For compounds **5**−**8**, cis-α and cis-β_2 coordination modes of the ligand were observed, depending on the nitrogen substituent and the auxiliary ligand. In compounds **9** and **10**, both configurations coexist and do not interconvert at elevated temperatures, but HCl catalyzes the isomerization of **10a** to **10b**. Upon activation with methylaluminoxane, [Ti{OSNO}X_2] complexes show moderate activity in the polymerization of styrene and trace activity in the polymerization of 1-hexene.

Introduction

During the past 50 years, homogeneous Ziegler−Natta polymerization catalysts have been developed from mere model systems for heterogeneous systems to highly active olefin polymerization catalysts.[1,2] Especially, group 4 *ansa*-metallocenes and half-sandwich catalysts have been instrumental in the study of reaction mechanisms and structure−property relationships, offering a high degree of control over the nature of the polyolefin product.[3,4] Currently, there is

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considerable interest in the development of stereospecific olefin polymerization catalysts that do not feature the ubiquitous cyclopentadienyl ligand.[5] An important family of postmetallocene catalysts are group 4 metal complexes based on bis(aryloxide) ligands that have additional coordinating heteroatoms.[6−19] Successful examples are phenoxyimine-based catalysts, which show high activity and selectivity for the (co)polymerization of a broad range of α-olefins but rather low activity for the polymerization of styrene.[6,7,20,21]

To design stereoselective olefin polymerization catalyst precursors based on a bis(phenolato) ligand framework, a number of differently sulfur-linked bis(phenolato) ligands have been investigated.[18a−18d,22] In contrast to stronger donor atoms, the soft sulfur atom interacts more weakly with the hard metal center, thus stabilizing the reactive cationic metal center without deactivating it. This effect has been proposed to account for the higher ethylene polymerization activity of some sulfur-bridged bis(phenolato)-titanium systems in comparison to methylene-bridged or biaryloxide analogues.[23] Recently, we have shown that group 4 metal catalyst precursors based on α,β-dithiaalkanediyl-linked [OSSO]-type bis(phenolato) ligands were able to efficiently polymerize styrene to give isotactic polystyrene upon activation of the dihalide complex with methylaluminoxane (MAO).[18e,18f,24,25] Living isospecific polymerization of styrene is possible with borane- or borate-activated [Ti{OSSO}$(CH_2Ph)_2$] complexes,[26] and optically active oligostyrenes can be generated by catalysts with enantiopure [OSSO]-type ligands.[18f,27] Remarkably, these catalysts are active only for the oligomerization of aliphatic olefins, albeit with high activity.[28]

Kol et al. have reported on similar linear [ONNO]-type bis(phenolato) group 4 catalysts, which are suitable for the synthesis of isotactic poly(1-hexene).[11] We were intrigued by the question of whether the use of linked bis(phenolato) ligands with mixed sulfur and nitrogen donors could combine the advantages of both parent ligand families in olefin polymerization catalysis.[29] In this paper, we report on the synthesis and coordination chemistry of titanium complexes bearing tetradentate, cyclohexanediyl-bridged [OSNO]-type hybrid ligand systems and explore their styrene and 1-hexene polymerization activity.

Results and Discussion

Synthesis of Bis(phenols). Ligand precursors **1a** and **1b** were synthesized as racemates via a multistep route (Scheme 1). Nucleophilic attack of an *o*-aminophenol on cyclohexene oxide at 120 °C afforded a ring-opened *trans*-aminocyclohexanol. In a one-pot synthesis in diethyl ether, the amino group was protected by CH_3SO_3H, after which the sulfonamide underwent intramolecular

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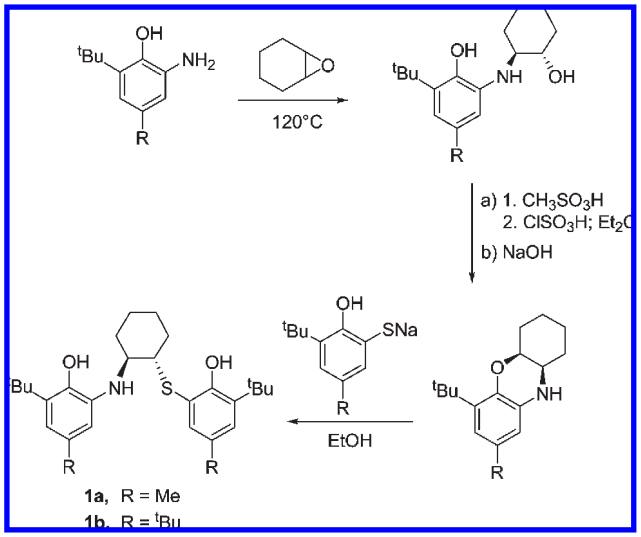
Scheme 1

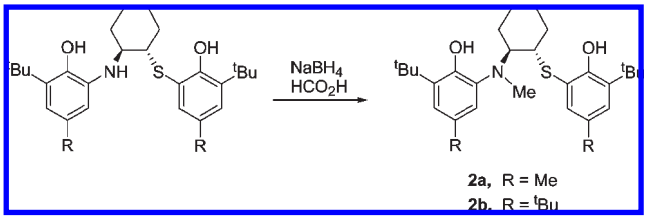


ring closure after the subsequent addition of $ClSO_3H$ and NaOH to give a hexahydrophenoxazine intermediate in 76% overall yield.[30] In the last reaction step, bis(phenols) **1a** and **1b** were obtained by nucleophilic attack of an arenethiolate on tetrahydrophenoxazine in refluxing ethanol. Control over the stereochemistry of every substitution step allows the (racemic) ligand precursors **1a** and **1b** to be obtained selectively in the trans-N,S configuration. Compound **1a** is an air-sensitive solid, whose color will change from white to green in solution and in the solid state upon exposure to air. In contrast, bis (phenol) **1b** is air-stable. The N-methylated analogues **2a** and **2b** could be prepared in good yield by the reaction of **1a** and **1b** with $NaBH_4$ in a formic acid solution (Scheme 2).[31] Both **2a** and **2b** could be isolated as air-stable white solids.

Bis(phenol) **3**, a salen-[OSSO] hybrid, was prepared by a two-step procedure, as shown in Scheme 3. The first step is a nucleophilic ring-opening reaction of an aziridine by an arenethiolate in methanol to give racemic (2-aminocyclohexylthio)phenol with the desired trans-N,S stereochemistry. Schiff-base condensation of this amine with the appropriate hydroxybenzaldehyde in refluxing methanol afforded **3** as a yellow solid in moderate yield.[32] Upon reduction of the imine bond of **3** with $NaBH_4$ in a mixture of methanol and diethyl ether, hybrid bis(phenol) **4** could be obtained in high yield as a white solid.

Synthesis and Structure of Titanium Complexes 5−8. The reaction of bis(phenols) **1** and **2** with TiX_4 (X = Cl, O^iPr) in toluene proceeded cleanly to afford the corresponding [Ti{OSNO}X_2] complexes **5**−**8** in high (X = Cl) or low (X = O^iPr) yield (Scheme 4).[33] There are three conceivable configurational isomers for octahedral complexes featuring a linear tetradentate [ABBA] ligand of which the chiral-at-metal cis-α and cis-β conformers

Scheme 2



exist as two stereoisomers (Δ and Λ) (Figure 1).[34] Titanium complexes supported by [OSSO] and many [ONNO]-type ligands adopt cis-α or cis-β configurations. For symmetrical bis(phenols), these types of coordination isomerism can be distinguished by NMR spectroscopy, where the symmetry is reflected in the spectra. The lack of symmetry in [OSNO] bis(phenolato) ligands complicates elucidation of the complex geometry by NMR spectroscopy. Although the selective synthesis of racemic trans-N,S-bridged bis(phenols) only allows for the presence of two enantiomers, upon complexation to the metal center 8 cis-α and 16 cis-β diastereomers are possible, taking into account the chiral cyclohexanediyl bridge and nitrogen donor, which becomes chiral upon coordination.[35] The cis-β isomers can now be divided into cis-β_1 and cis-β_2 subclasses, where cis-β_1 is defined as having the auxiliary ligand X in the equatorial plane trans to the higher CIP priority central donor atom.[36] We have demonstrated for cyclohexanediyl-bridged complexes [Ti{OSSO}X_2] (X = Cl, O^iPr) and [V{OSSO}(O)Cl] that the reaction of bis(phenol) with the metal center is diastereoselective.[18f,27a,37] Observation of a single product by NMR spectroscopy in the synthesis of complexes **5**−**8** suggests that diastereoselectivity extends to these cyclohexanediyl-bridged mixed-donor complexes.

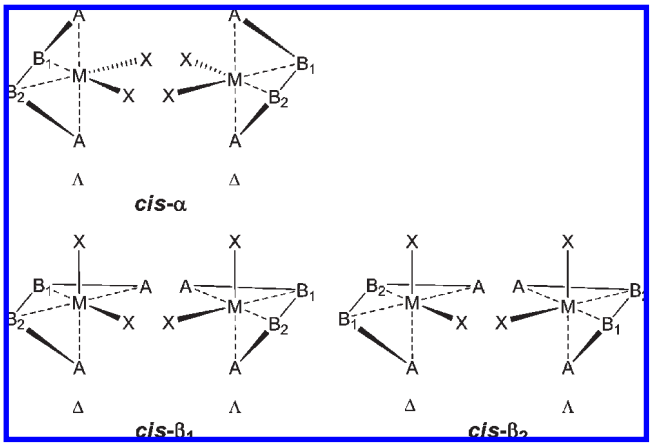


Figure 1. Chiral geometries for asymmetric tetradentate ligands around an octahedral metal center.

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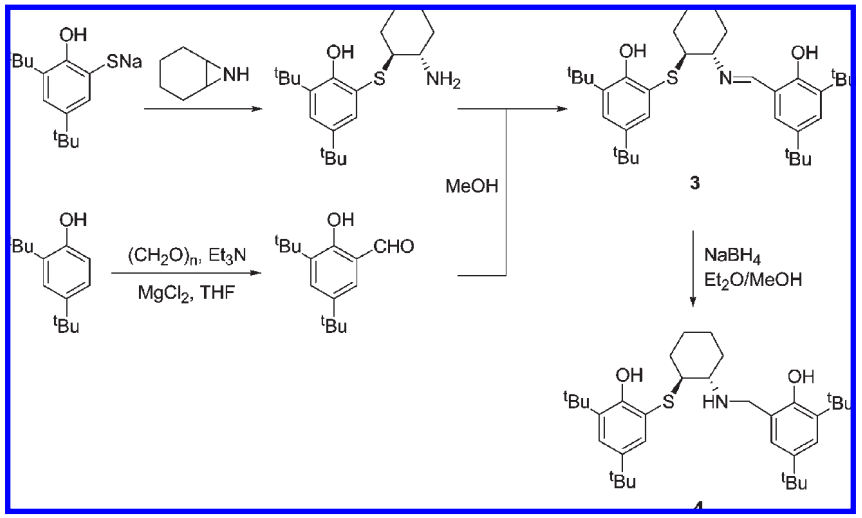
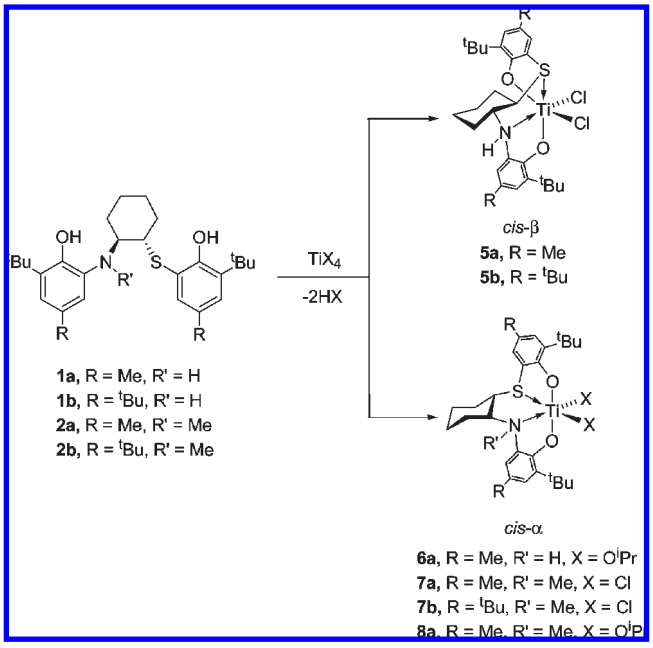
Scheme 3



Scheme 4



Because of the asymmetric nature of the complexes, ^{1}H NMR spectroscopy of complexes **5**−**8** shows four doublet aromatic hydrogen signals and four resonances for the aryl substituents. The spectra of **5a**, **5b**, and **6a** show doublet NH resonances at 5.22, 5.24, and 4.28 ppm, respectively; compounds **7a**, **7b**, and **8a** display N−Me resonances at 3.22, 3.23, and 2.84 ppm. All complexes are structurally rigid in solution up to 100 °C. Some obvious differences between **5a**, **5b**, **6a**, **7a**, **7b**, and **8a** were observed in the ^{1}H NMR spectra. While for complexes **6**−**8** all resonances for the cyclohexanediyl bridge can be found 3 ppm upfield, one of the cyclohexanediyl protons for complexes **5a** and **5b** is shifted downfield to 4.0 ppm. Furthermore, **5a** and **5b** display a high-field-shifted ^{t}Bu resonance at 0.90 ppm, whereas for complexes **6**−**8**, all ^{t}Bu resonances lie between 1.3 and 1.6 ppm. In comparison, cyclohexanediyl-bridged [Ti{OSSO}X_2] complexes (X = Cl, O^{i}Pr) feature ^{t}Bu resonances between 1.2 and 1.6 ppm and cyclohexanediyl resonances upfield of 2.9 ppm. The dissimilar nature of the NMR spectra of **5a** and **5b** indicates that the configuration of the [OSNO] ligand around the metal center differs from those of complexes **6**−**8** and from [Ti{OSSO}X_2]. In order to further investigate the absolute structure of these complexes, single crystals of **5b**, **7b**, and **8a** were grown for X-ray crystallography. The combination of X-ray analysis and NMR spectroscopy shows that the configuration of the [OSNO] ligand around the titanium center strongly depends on the amine substituent R′ and on the auxiliary ligand X. The dichloro complexes derived from bis(phenols) **1a** and **1b** (R′ = H) have cis-β_2 configuration. Conversely, all diisopropoxy and dichloro complexes derived from **2a** and **2b** (R′ = Me) show cis-α configuration.

A single-crystal X-ray structure analysis of **5b** (Figure 2) revealed that this complex adopts a cis-β configuration in a distorted octahedral environment. The S-bound aryl oxygen atom occupies the apical position, and the other donor atoms lie in the equatorial plane, with the sulfur and N-bound phenolato oxygen atoms occupying trans positions [S−Ti−O2 = 153.60(11)°]. Both oxygen atoms are bound to the titanium center in a cis fashion with an O1−Ti−O2 bond angle of 94.22(15)°. The equatorial aryl group is bent upward by 37.42(19)° out of the Ti−N−O2 plane, which fixes the stereogenic nitrogen atom in the *S* configuration for the (*R*,*R*)-cyclohexanediyl bridge and vice versa. The Ti−S bond distance of 2.5956(16) Å is relatively short in comparison to literature values observed for related bis(phenolato) complexes (2.58−2.88 Å) but compares well with Ti−S bond distances of the isostructural cis-β complex [Ti{2,2′-(OC$_6$H$_2$-4,6-^{t}Bu$_2$)$_2$-SC$_3$H$_6$S}Cl$_2$] [2.5789(8) and 2.6035(8) Å].[38] Comparison of the Ti−N bond in **5b** [2.254(4) Å] with that of cis-α complex **7b** [2.305(6) Å] shows that in both structures the nitrogen atom is firmly coordinated to the titanium center and that, while likely contributing to their stability, their respective configurations are determined by the N-substituent. For the (*R*,*R*)-cyclohexanediyl-bridged ligand, changing from a cis-β to cis-α configuration confers an *R* configuration on the nitrogen atom. In the solid-state structure of **7b**

(38) For structural details, see the Supporting Information of ref 18f.

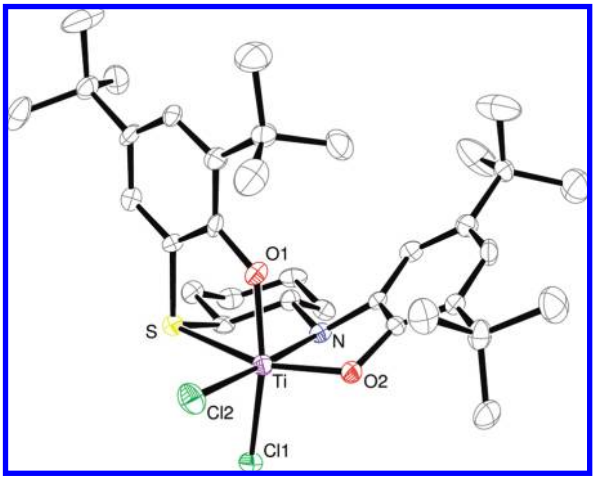


Figure 2. ORTEP diagram of **5b** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti−O1 1.855(3), Ti−O2 1.834(3), Ti−S 2.5956(16), Ti−N 2.254(4), Ti−Cl1 2.3470(16), Ti−Cl2 2.2781(16); O1−Ti−O2 94.22(15), S−Ti−N 77.98(11), Cl1−Ti−Cl2 95.14(6).

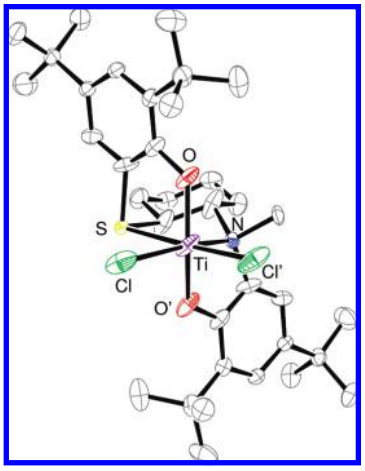


Figure 3. ORTEP diagram of **7b** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted, and a single disordered structure is shown for clarity. Primed atoms are related by the symmetry transformation $(-x, y, -z+{}^{2}/_{3})$. Selected bond lengths (Å) and angles (deg): Ti−O 1.861(3), Ti−S 2.653(2), Ti−N 2.305(6), Ti−Cl 2.2647(12); O−Ti−O′ 158.47(18), S−Ti−N 78.17(19), Cl−Ti−Cl′ 101.63(8).

(Figure 3), the titanium center occupies a special position in the crystal lattice. The resulting crystallographic C_2 symmetry of the molecule leads to disorder in the *N*-methyl and sulfur positions. The sulfur atoms are located between the nitrogen and methyl carbon atoms on the N−C bond axis, which suggests that in the solid state *N*-methyl and sulfur require approximately the same amount of space.

The solid-state structure of **8a** shows the expected cis-α configuration of the [OSNO] ligand, forced by the *N*-methyl substituent (vide supra) and isopropoxy ligands (Figure 4). The Δ isomer of **8a** features a (*R*,*R*)-cyclohexanediyl bridge, which signifies a break from the trend observed for cyclohexanediyl-bridged [OSSO]-type complexes and [OSNO] complex **7b** that only Δ,*S*,*S* and Λ,*R*,*R* isomers are observed. The observation of a single species of **8a** by NMR spectroscopy shows that diastereoselectivity upon complexation is not lost but reversed. The sulfur and *N*-methyl positions are disordered in this crystal as well, but the disorder in both **7b** and **8a** affects

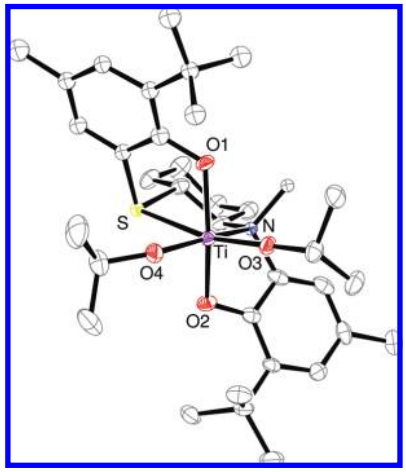


Figure 4. ORTEP diagram of **8a** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted, and a single disordered structure is shown for clarity. Selected bond lengths (Å) and angles (deg): Ti−O1 1.949(2), Ti−O2 1.942(2), Ti−O3 1.777(2), Ti−O4 1.790(2), Ti−S 2.6550(11), Ti−N 2.336(3); O1−Ti−O2 157.33(9), O3−Ti−O4 108.02(10), S−Ti−N 76.62(8).

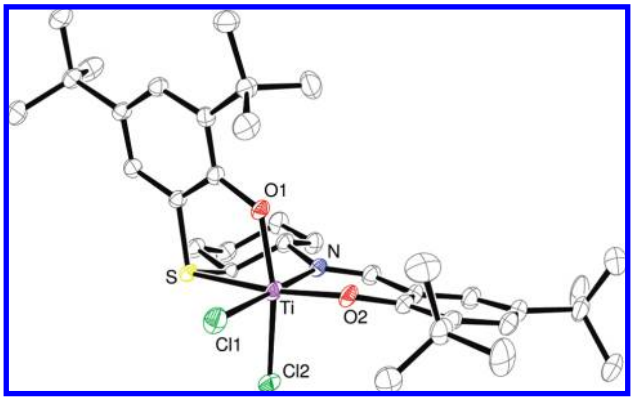
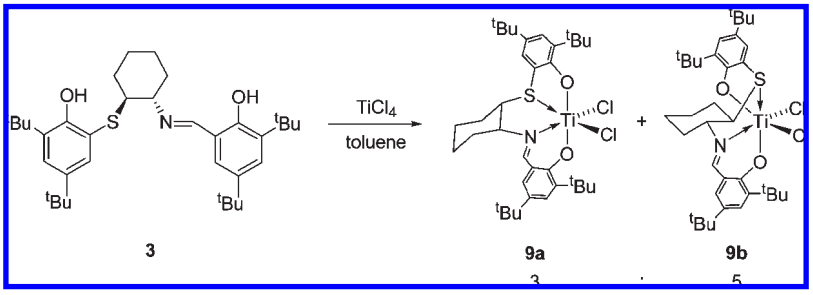


Figure 5. ORTEP diagram of **9b** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti−O1 1.8614(17), Ti−O2 1.8020(17), Ti−S 2.5493(8), Ti−N 2.201(2), Ti−Cl1 2.2718(8), Ti−Cl2 2.3415(8); O1−Ti−O2 99.35(8), S−Ti−N 79.89(5), Cl1−Ti−Cl2 93.21(3).

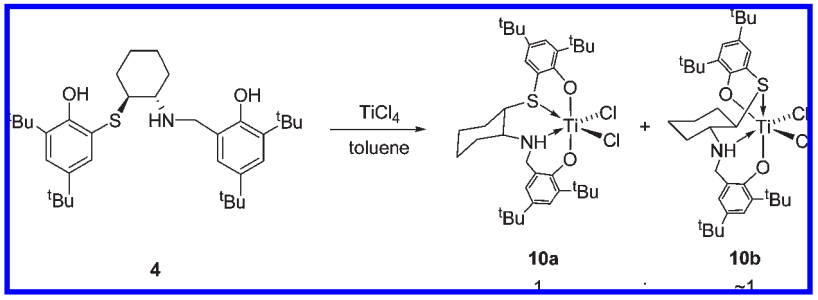
neither the stereochemistry of the coordinating nitrogen atom nor the stereochemistry of the complex as a whole.

Synthesis and Structure of Titanium Complexes 9 and 10. In contrast to the synthesis of complexes **5**−**8**, the reaction of hybrid bis(phenol) **3** with titanium tetrachloride in toluene at −30 °C afforded a mixture of two compounds (**9a** and **9b**) in an approximate ratio of 3:5 as determined from ^{1}H NMR (Scheme 5). Both isomers are stable for weeks in solution at room temperature. When heated to 100 °C for several hours, no interconversion between **9a** and **9b** was observed by NMR spectroscopy. Major isomer **9b** could be isolated after several recrystallizations from toluene/pentane; isomer **9a** was only identified by NMR spectroscopy of the mixture and was tentatively assigned a cis-α geometry based on analogy with complex **10a** (vide infra). From NMR spectroscopy of **9b**, the imine moiety can be clearly distinguished as a doublet at 8.35 ppm (^{1}H) and 161.0 ppm (^{13}C). The presence of four singlets for the ^{t}Bu groups and a downfield-shifted cyclohexane resonance at 3.47 ppm suggest a C_1-symmetric cis-β complex.

Scheme 5



Scheme 6



Single crystals suitable for X-ray analysis, grown from a toluene solution, corroborate that **9b** adopts the same cis-β_2 configuration that was observed for **5b** (Figure 5). The extra carbon spacer of the imine moiety in the ligand relieves some of the distortion in the octahedral complex, which manifests itself in an increase of the S−Ti−O2 bond angle from 153.60(11)° (**5b**) to 163.90(6)°. In contrast to **5b**, the N-bound arene and coplanar imine are bent downward out of the Ti−N−O2 plane by 10.13(15)°, which leads to an increase in the bond angle of the cis-coordinated oxygen atoms to 99.35(8)° [**5b**, 94.22(15)°]. The Ti−S and Ti−N bond distances [2.5493(8) and 2.201-(2) Å, respectively] are shorter than those in **5b** and **7b**, but the Ti−N bond distance is longer than that of analogous titanium salen complexes (2.12−2.16 Å).[39]

Analogous to **3**, the reaction of **4** with $TiCl_4$ results in the formation of two species (**10a** and **10b**) in an approximate ratio of 1:1 (Scheme 6). The ^1H and ^{13}C NMR spectra of the resulting mixture are too complicated to yield any useful structural information. While growing crystals for X-ray analysis, the two isomers could be easily distinguished and visually separated because of their different crystal shapes. The solid-state structure of **10a** (see the Supporting Information) has cis-α geometry, with structural parameters closely resembling those of **7b**. The extra methylene group allows for more flexibility of the ligand, in which the aryl group is tilted slightly inward. In a similar fashion, **10b** (see the Supporting Information) is closely related to the cis-β_2 complexes **5b** and **9b**. Upon reduction of the double bond, the six-membered titanacycle becomes puckered, with the nitrogen atom adopting the same conformation as that in **5b**. ^1H NMR data for **10a** and **10b** support the observed geometries in the solid state and are consistent with NMR data observed for complexes **5**−**8**: while for **10a**, all cyclohexanediyl resonances are observed upfield of 2.75 ppm, for **10b**, one of the cyclohexanediyl resonances is shifted downfield to 3.84 ppm. The NCH_2 resonances were observed at 3.92/4.66 ppm (**10a**) and 3.85/4.28 ppm (**10b**).

Compounds **10a** and **10b** are stable in solution and do not interchange at temperatures up to 100 °C. The high energy barrier for isomerization suggests that their formation may be kinetically controlled. Furthermore, **10a** and **10b** may be generated in a dynamic process, catalyzed by HCl liberated during the reaction. The acid may protonate the nitrogen donor of the ligand, which is then detached from the titanium center, thus lowering the energy barrier for isomerization. A proposed mechanism is shown in Scheme 7. A similar mechanism might also apply to the formation of **9a** and **9b**. To test this hypothesis, an experiment was performed in which a catalytic amount (10 mol %) of HCl in diethyl ether was added to a toluene solution of a mixture of **10a** and **10b**. After 24 h, it was observed by NMR spectroscopy that isomerization had taken place to give **10b**. This observation supports the hypothesis of acid-catalyzed isomerization and establishes **10b** with cis-β_2 configuration as the more stable isomer.

Polymerization Activity. Compounds **5**−**10** were tested for styrene polymerization activity in toluene at 40 and 50 °C, using MAO as the cocatalyst (Table 1). Upon activation, **5a** and **5b** produced highly isotactic (*mm* > 90%) polystyrene of relatively high molecular weight and low polydispersity with moderate activity. Complexes **7b**, **8a**, **9b**, **10a**, and **10b** show low activity and give low molecular weight atactic polystyrenes. Gel permeation chromatography (GPC) spectra for **7**−**10** show very

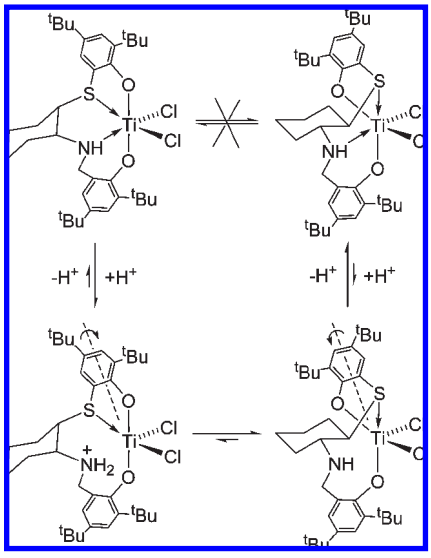
(39) (a) DiMauro, E. F.; Mamai, A.; Kozlowski, M. *Organometallics* **2003**, *22*, 850–855. (b) Belokon, Y. N.; Carta, P.; Gutnov, A. V.; Maleev, V.; Moskalenko, M. A.; Yashkina, L. V.; Ikonnikov, N. S.; Voskoboev, N. V.; Khrustalev, V. N.; North, M. *Helv. Chim. Acta* **2002**, *85*, 3301–3312. (c) Tararov, V. I.; Hibbs, D. E.; Hursthouse, M. B.; Ikonnikov, N. S.; Abdul Malik, K. M.; North, M.; Orizu, C.; Belokon, Y. N. *Chem. Commun.* **1998**, 387–388. (d) Kim, I.; Ha, Y. S.; Zhang, D. F.; Ha, C.-S.; Lee, U. *Macromol. Rapid Commun.* **2004**, *25*, 1319–1323.

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

precatalyst	yield (mg)	activity[a]	$M_n(\times 10^4)$[b]	M_w/M_n[b]	tacticity[c]
5a[d]	440	50	6.88	1.8	isotactic
5b[d]	480	55	9.97	1.9	isotactic
7b[d]	60	6.9	1.81	18	atactic
7b[e]	110	6.3	1.35	21	atactic
8a[d]	46	5.3	1.43	23	atactic
8a[d]	46	5.3	1.43	23	atactic
9b[d]	68	7.8	2.05	15	atactic
9b[e]	68	3.9	1.00	4.9	atactic
10b[d]	70	8.0	1.63	18	atactic
10a + **10b**[d]	67	7.8	1.20	23	atactic

[a] Activity: kg of polymer (mol of catalyst)$^{-1}$ [styrene, mol L^{-1}]$^{-1}$ h^{-1}. [b] Determined by GPC. [c] Determined by ^{13}C NMR spectroscopy. [d] Polymerization conditions: 1.25 μmol of Ti complex, [Al]/[Ti] = 1500, [styrene] = 3.5 mol L^{-1} (5 mL), toluene (7.5 mL), T = 40 °C, t = 2 h. [e] Polymerization conditions: 2.5 μmol of Ti complex, [Al]/[Ti] = 1500, [styrene] = 3.5 mol L^{-1} (10 mL), toluene (15 mL), T = 50 °C; t = 2 h.

Scheme 7



broad bimodal or multimodal molecular weight distributions, which suggest the presence of multiple active species. No apparent relationship exists between the configuration of the precatalyst and the polymer microstructure: whereas **5a** and **5b** (cis-β_2) give isotactic polystyrene, **10b** does not, and cis-α precatalysts such as **7b** and **8a** give atactic polystyrene. In preliminary tests for 1-hexene polymerization activity of titanium complexes bearing [OSNO] ligands, only trace activity was observed.[40]

Conclusion

Complexation of unsymmetric [OSNO]-type bis(phenolate) ligands to a [TiX$_2$] fragment (X = Cl, O^{i}Pr) proceeds diastereoselectively for ligands where the nitrogen donor is directly attached to the arene. The coordination geometry of the ligand around the metal center is determined by the nitrogen substituent and by the ligands X. For the half-salen and -salan ligands that feature an extra carbon spacer between the arene and nitrogen donor, both cis-α and cis-β_2 isomers were observed. For the latter, it was demonstrated that HCl catalyzes the isomerization toward the thermodynamically more stable cis-β_2 isomer. In polymerization catalysis, rather than combining the best properties of [ONNO] and [OSSO] catalyst families, poor 1-hexene polymerization activity and loss of isotacticity for styrene polymerization were observed. It remains to be explored how the structure of the active species is related to this observation because fairly little is known on the ligand dynamics of the alkyl cation.[26,28]

Experimental Section

General Considerations. All operations were performed under an inert atmosphere of argon using standard Schlenk-line and glovebox techniques. Diethyl ether was distilled from sodium benzophenone ketyl; pentane and toluene were purified by distillation from sodium/triglyme benzophenone ketyl; dichloromethane was distilled from calcium hydride. Deuterated solvents were dried over sodium or calcium hydride and degassed prior to use. Mercaptophenols,[41] aminophenols,[42] and 7-azabicyclo[4.1.0]heptane[43] were prepared analogously to literature procedures. Titanium tetrachloride and titanium tetra(isopropoxide) were used as received; all other chemicals were commercially available and were used after appropriate purification. Methylaluminoxane (MAO) in toluene (10 wt %) was purchased from Aldrich and used as received. NMR spectra were recorded on a Bruker DRX 400 spectrometer (^{1}H, 400.1 MHz; ^{13}C, 100.6 MHz) in $CDCl_3$ at 25 °C unless stated otherwise. Chemical shifts were referenced internally using 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. GPC measurements were carried out on an Agilent 1100 series instrument at 35 °C using tetrahydrofuran as a solvent against a polystyrene standard.

2-*tert*-Butyl-6-(2-hydroxycyclohexylamino)-4-methylphenol. A mixture of 2-amino-6-*tert*-butyl-4-methylphenol (2.82 g, 15.7 mmol) and cyclohexene oxide (1.74 mL, 17.2 mmol) was heated at 120 °C for 3 h. Upon cooling, the reaction mixture became a glasslike material. After the addition of hexane initially, all material dissolved, but after standing at room temperature, a white solid precipitated. The solid was collected and washed with cooled hexane under an argon atmosphere to give 2.65 g (61%) of a white solid. ^{1}H NMR: δ 0.95−1.45 (m, 4H, C_6H_{10} CH, overlap with $C(CH_3)_3$), 1.40 (s, 9H, $C(CH_3)_3$), 1.60−1.80 (m, 2H, C_6H_{10} CH), 2.03 (br s, 2H, C_6H_{10} CH), 2.24 (br s, 3H, CH_3), 2.77 (br s, 1H, CHO), 3.45 (br s, 1H, CHN), 6.66 (br s, 1H, C_6H_2), 6.76 (br s, 1H, C_6H_2). ^{13}C{^{1}H} NMR: δ 21.01 (CH_3), 24.45 ($C(CH_3)_3$), 29.66 ($C_6H_{10}CH_2$), 31.21 ($C_6H_{10}CH_2$), 34.29 ($C(CH_3)_3$), 63.14 (CHO), 74.72 (CHN), 120.03 (C_6H_2 CH), 121.96 (C_6H_2 CH), 128.21 (C_6H_2), 134.27 (C_6H_2), 135.80 (C_6H_2), 146.49 (C_6H_2). Anal. Calcd for $C_{17}H_{27}NO_2$: C, 73.61; H, 9.81; N, 5.05. Found: C, 73.64; H, 10.08; N, 5.03.

6-*tert*-Butyl-8-methyl-2,3,4,4a,10,10a-hexahydrophenoxazine. To a solution of 2-*tert*-butyl-6-(2-hydroxycyclohexylamino)-4-methylphenol (2.60 g, 9.39 mmol) in 40 mL of Et_2O was added 0.61 mL (9.39 mmol) of CH_3SO_3H, after which the mixture was stirred for 30 min at room temperature. After the dropwise addition of 0.63 mL (9.48 mmol) of $ClSO_3H$, the reaction mixture was stirred for 10 h at room temperature.

(40) Polymerization experiments with **7a**, **9b**, and **10a** gave less than 5 mg of poly(1-hexene) after workup. Conditions: **10a** (1.25 μmol) was activated with MAO (Al:Ti = 1500) in 5 mL of 1-hexene and 7.5 mL of toluene at 40 °C; dimethyl complexes of **7a** and **9b** (10 μmol) were activated with $B(C_6F_5)_3$ (1−2 equiv) in 5 mL of 1-hexene at room temperature; the reaction time was 2 h.

(41) Pastor, S. D.; Denney, D. Z. *J. Heterocycl. Chem.* **1988**, *25*, 681–683.
(42) Waltman, A. W.; Grubbs, R. H. *Organometallics* **2004**, *23*, 3105–3107.
(43) Christoffers, J.; Schulze, Y.; Pickardt, J. *Tetrahedron* **2001**, *57*, 1765–1769.

A large amount of white precipitate had formed during the reaction. The solvent was removed under reduced pressure, and 30 mL of a 20% NaOH solution was added. The mixture was refluxed for 10 h and neutralized with a saturated $NaHCO_3$ solution, and the product was extracted with diethyl ether. The combined organic layers were dried over $MgSO_4$, and the solvent was removed to give 1.85 g (76%) of a green solid. ^{1}H NMR: δ 1.06−1.35 (m, 3H, C_6H_{10} CH), 1.39 (s, 9H, $C(CH_3)_3$), 1.67 (m, 2H, C_6H_{10} CH), 1.73−1.82 (m, 2H, C_6H_{10} CH), 1.98 (m, 1H, C_6H_{10} CH), 2.26 (s, 3H, CH_3), 2.31 (m, 1H, C_6H_{10} CH), 2.98 (m, 1H, CHO), 3.91 (m, 1H, CHN), 6.80 (s, 1 H, C_6H_2), 6.86 (s, 1H, C_6H_2). $^{13}C\{^1H\}$ NMR: δ 21.00 (CH_3), 24.02 (C_6H_{10} CH_2), 25.91 (C_6H_{10} CH_2), 29.45 (C(CH_3)$_3$), 31.41 (C_6H_{10} CH_2), 34.49 ($C(CH_3)_3$), 36.09 (C_6H_{10} CH_2), 63.79 (CHO), 65.53 (CHN), 122.82 (C_6H_2 CH), 123.99 (C_6H_2 CH), 127.60 (C_6H_2), 131.43 (C_6H_2), 135.07 (C_6H_2), 149.31 (C_6H_2). Anal. Calcd for $C_{17}H_{25}NO$: C, 78.72; H, 9.71; N, 5.40. Found: C, 77.32; H, 8.61; N, 5.20.

Bis(phenol) 1a. A mixture of 1.85 g (7.1 mmol) of 6-*tert*-butyl-8-methyl-2,3,4,4a,10,10a-hexahydrophenoxazine, 1.4 g (7.1 mmol) of 2-*tert*-butyl-6-mercapto-4-methylphenol, and 290 mg (7.1 mmol) of NaOH in 30 mL of ethanol was refluxed for 5 h. After cooling to room temperature, the resulting green solution was dried in vacuo. The residue was neutralized with a saturated NH_4Cl solution and extracted with diethyl ether. The organic layers were combined and dried over $MgSO_4$, and the solvent was removed under reduced pressure to give the crude product, which was recrystallized from *n*-hexane to give 2.00 g (62%) of a white solid. ^{1}H NMR: δ 1.05−1.55 (m, 4H, C_6H_{10} CH, overlap with $C(CH_3)_3$ signals), 1.39 (s, 9H, $C(CH_3)_3$), 1.42 (s, 9H, $C(CH_3)_3$), 1.67 (m, 2H, C_6H_{10} CH), 2.13 (m, 2H, C_6H_{10} CH), 2.26 (s, 6H, CH_3), 2.68 (m, 1H, CHS), 2.83 (m, 1H, C_6H_{10} CHN), 6.68 (s, 1H, C_6H_2), 6.83 (s, 1H, C_6H_2), 7.11 (d, $^4J_{HH}$ = 2 Hz, 1H, C_6H_2), 7.20 (d, $^4J_{HH}$ = 2 Hz, 1H, C_6H_2). $^{13}C\{^1H\}$ NMR: δ 20.61 (CH_3), 21.06 (CH_3), 24.37 (C_6H_{10} CH_2), 26.21 (C_6H_{10} CH_2), 29.44 (C(CH_3)$_3$), 29.66 (C(CH_3)$_3$), 32.75 (C_6H_{10} CH_2), 33.63 (C_6H_{10} CH_2), 34.54 ($C(CH_3)_3$), 34.93 ($C(CH_3)_3$), 55.67 (CHS), 59.44 (CHN), 116.82 (C_6H_2), 121.09 (C_6H_2 CH), 122.75 (C_6H_2 CH), 128.06 (C_6H_2), 128.34 (C_6H_2), 129.83 (C_6H_2 CH), 132.70 (C_6H_2), 134.88 (C_6H_2 CH), 135.97 (C_6H_2), 147.31 (C_6H_2), 154.14 (C_6H_2). HRMS. Calcd for $C_{28}H_{41}NO_2S$: *m*/*z* 455.2858. Found: *m*/*z* 455.2853. Mp: 115.2−115.8 °C. Anal. Calcd for $C_{28}H_{41}NO_2S$: C, 73.80; H, 9.07; N, 3.07. Found: C, 74.17; H, 9.30; N, 3.10.

Bis(phenol) 1b. This compound was prepared in the same manner as that of bis(phenol) **1a**. ^{1}H NMR: δ 1.10−1.55 (m, 4H, C_6H_{10} CH, overlap with $C(CH_3)_3$ signals), 1.30 (s, 9H, $C(CH_3)_3$), 1.31 (s, 9H, $C(CH_3)_3$), 1.42 (s, 9H, $C(CH_3)_3$), 1.44 (s, 9H, $C(CH_3)_3$), 1.70 (m, 2H, C_6H_{10} CH), 2.18 (m, 2H, C_6H_{10} CH), 2.68 (m, 1H, CHS), 2.81 (m, 1H, C_6H_{10} CHN), 6.90 (d, $^4J_{HH}$ = 2 Hz, 1H, C_6H_2), 7.10 (d, $^4J_{HH}$ = 2 Hz, 1H, C_6H_2), 7.35 (d, $^4J_{HH}$ = 2.5 Hz, 1H, C_6H_2), 7.40 (d, $^4J_{HH}$ = 2.5 Hz, 1H, C_6H_2). $^{13}C\{^1H\}$ NMR: δ 24.55 (C_6H_{10} CH_2), 26.20 (C_6H_{10} CH_2), 29.53 (C(CH_3)$_3$), 29.71 (C(CH_3)$_3$), 31.57 (C(CH_3)$_3$), 31.69 (C(CH_3)$_3$), 33.07 (C_6H_{10} CH_2), 33.91 (C_6H_{10} CH_2), 34.25 ($C(CH_3)_3$), 34.31 ($C(CH_3)_3$), 34.93 ($C(CH_3)_3$), 35.26 ($C(CH_3)_3$), 56.11 (CHS), 60.44 (CHN), 117.07 (C_6H_2), 118.44 (C_6H_2 CH), 119.65 (C_6H_2 CH), 126.16 (C_6H_2 CH), 131.34 (C_6H_2 CH), 131.84 (C_6H_2), 135.44 (C_6H_2), 141.36 (C_6H_2), 141.76 (C_6H_2), 147.48 (C_6H_2), 153.88 (C_6H_2). HRMS. Calcd for $C_{34}H_{53}NO_2S$: *m*/*z* 539.3797. Found: *m*/*z* 539.3795. Mp: 161−163 °C. Anal. Calcd for $C_{34}H_{53}NO_2S$: C, 75.64; H, 9.90; N, 2.59. Found: C, 75.88; H, 9.99; N, 2.51.

Bis(phenol) 2a. Bis(phenol) **1a** (4.55 g, 10.0 mmol) was dissolved in 30 mL of HCO_2H (some Et_2O or CH_2Cl_2 was added to keep the mixture solution clear), and an excess of solid $NaBH_4$ was added. The reaction was stirred at room temperature for 12 h and was monitored by thin-layer chromatography. After the reaction was complete, water was added to the reaction mixture, the product was extracted with Et_2O, and the combined organic phase was dried over $MgSO_4$. The solvent was removed under reduced pressure to give the crude product, which was recrystallized from Et_2O/MeOH to give 4.32 g (92%) of a white solid. ^{1}H NMR: δ 1.25−1.55 (m, 2H, C_6H_{10} CH, overlap with $C(CH_3)_3$ signals), 1.39 (s, 9H, $C(CH_3)_3$), 1.45 (s, 9H, $C(CH_3)_3$), 1.63 (m, 1H, C_6H_{10} CH), 1.73 (m, 1H, C_6H_{10} CH), 1.95 (m, 1H, C_6H_{10} CH), 2.03 (m, 1H, C_6H_{10} CH), 2.23 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.64 (m, 1H, CHS, partial overlap with NCH_3), 2.67 (s, 3H, NCH_3), 2.97 (m, 1H, CHN), 6.86 (s, 1H, C_6H_2), 6.93 (s, 1H, C_6H_2), 7.08 (s, 1H, C_6H_2), 7.21 (s, 1H, C_6H_2). $^{13}C\{^1H\}$ NMR: δ 20.63 (CH_3), 21.15 (CH_3), 24.90 (C_6H_{10} CH_2), 25.47 (C_6H_{10} CH_2), 26.08 (C_6H_{10} CH_2), 29.38 (C(CH_3)$_3$), 29.53 (C(CH_3)$_3$), 33.34 (C_6H_{10} CH_2), 34.78 ($C(CH_3)_3$), 34.87 (NCH_3), 52.35 (CHS), 66.17 (CHN), 117.25 (C_6H_2), 122.61 (C_6H_2), 124.17 (C_6H_2), 126.75 (C_6H_2), 128.41 (C_6H_2 CH), 129.59 (C_6H_2 CH), 134.67 (C_6H_2 CH), 135.50 (C_6H_2), 135.67 (C_6H_2 CH), 137.71 (C_6H_2), 148.82 (C_6H_2), 154.00 (C_6H_2). HRMS. Calcd for $C_{29}H_{43}NO_2S$: *m*/*z* 469.3015. Found: *m*/*z* 469.3013. Mp: 140.6−141.4 °C. Anal. Calcd for $C_{29}H_{43}NO_2S$: C, 74.15; H, 9.23; N, 2.98. Found: C, 74.27; H, 9.63; N, 3.02.

Bis(phenol) 2b. This compound was prepared in the same manner as that of bis(phenol) **2a**, starting from 1.08 g (1.95 mmol) of bis(phenol) **1b** in 15 mL of HCO_2H to give 0.86 g (78%) of a white solid. ^{1}H NMR: δ 1.15 (m, 2H, C_6H_{10} CH), 1.25−1.55 (m, 2H, C_6H_{10} CH, overlap with $C(CH_3)_3$ signals), 1.28 (s, 9H, $C(CH_3)_3$), 1.31 (s, 9H, $C(CH_3)_3$), 1.41 (s, 9H, $C(CH_3)_3$), 1.46 (s, 9H, $C(CH_3)_3$), 1.65 (m, 1H, C_6H_{10} CH), 1.75 (m, 1H, C_6H_{10} CH), 1.98 (m, 2H, C_6H_{10} CH), 2.62−2.75 (m, 1H, CHS, overlap with NCH_3), 2.70 (s, 3H, NCH_3), 2.98 (m, 1H, CHN), 7.06 (d, $^4J_{HH}$ = 2 Hz, 1H, C_6H_2), 7.16 (d, $^4J_{HH}$ = 2 Hz, 1H, C_6H_2), 7.32 (d, $^4J_{HH}$ = 2.5 Hz, 1H, C_6H_2), 7.38 (d, $^4J_{HH}$ = 2.5 Hz, 1H, C_6H_2). $^{13}C\{^1H\}$ NMR: δ 24.95 (C_6H_{10} CH_2), 25.54 (C_6H_{10} CH_2), 26.11 (C_6H_{10} CH_2), 29.46 (C(CH_3)$_3$), 29.65 (C(CH_3)$_3$), 31.55 (C(CH_3)$_3$), 31.71 (C(CH_3)$_3$), 33.63 (C_6H_{10} CH_2), 34.25 ($C(CH_3)_3$), 34.41 ($C(CH_3)_3$), 35.12 ($C(CH_3)_3$), 35.19 (NCH_3), 52.20 (CHS), 66.38 (CHN), 117.07 (C_6H_2), 118.74 (C_6H_2), 120.50 (C_6H_2), 125.91 (C_6H_2 CH), 131.46 (C_6H_2 CH), 134.90 (C_6H_2), 135.15 (C_6H_2 CH), 137.07 (C_6H_2), 140.28 (C_6H_2), 141.85 (C_6H_2 CH), 148.63 (C_6H_2), 153.80 (C_6H_2). HRMS. Calcd for $C_{35}H_{55}NO_2S$: *m*/*z* 553.3954. Found: *m*/*z* 553.3955. Mp: 144.1−144.9 °C. Anal. Calcd for $C_{35}H_{55}NO_2S$: C, 75.90; H, 10.01; N, 2.53. Found: C, 76.10; H, 9.64; N, 2.45.

2-(2-Aminocyclohexylthio)-4,6-di-*tert*-butylphenol. A mixture of 2,4-di-*tert*-butyl-6-mercaptophenol (23.8 g, 100 mmol) and 7-azabicyclo[4.1.0]heptane (9.7 g, 100 mmol) in 50 mL of methanol was refluxed for 5 h. The solvent was removed under reduced pressure to give a viscous residue, which was recrystallized from *n*-hexane to give 29.5 g (88%) of a white solid. ^{1}H NMR: δ 1.12−1.26 (m, 3H, C_6H_{10} CH), 1.29 (s, 9H, $C(CH_3)_3$), 1.37−1.46 (m, 1H, C_6H_{10} CH, overlap with $C(CH_3)_3$), 1.42 (s, 9H, $C(CH_3)_3$), 1.68 (m, 2H, C_6H_{10} CH), 1.98 (m, 1H, C_6H_{10} CH), 2.14 (m, 1H. C_6H_{10} CH), 2.31−2.45 (m, 2H, C_6H_{10} CHX), 7.33 (m, 2H, C_6H_2). $^{13}C\{^1H\}$ NMR: δ 25.10 (C_6H_{10} CH_2), 26.48 (C_6H_{10} CH_2), 29.55 (C(CH_3)$_3$), 31.56 (C(CH_3)$_3$), 34.12 ($C(CH_3)_3$), 34.16 (C_6H_{10} CH_2), 35.25 ($C(CH_3)_3$), 37.63 (C_6H_{10} CH_2), 53.90 (CHS), 56.98 (CHN), 117.00 (C_6H_2), 125.73 (C_6H_2 CH), 132.36 (C_6H_2 CH), 136.00 (C_6H_2), 140.92 (C_6H_2), 155.51 (C_6H_2). Anal. Calcd for $C_{20}H_{33}NOS$: C, 71.59; H, 9.91; N, 4.17. Found: C, 71.51; H, 9.76; N, 4.10.

Bis(phenol) 3. A mixture of 2-(2-aminocyclohexylthio)-4,6-di-*tert*-butylphenol (11.36 g, 33.9 mmol) and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (8.0 g, 33.9 mmol) in 80 mL of methanol was refluxed for 5 h. A yellow solid formed during the reaction. The mixture was subsequently cooled to room temperature, and 8.2 g (47%) of a yellow solid was collected. ^{1}H NMR: δ 1.20−1.55 (m, 3H, C_6H_{10} CH, overlap with $C(CH_3)_3$ signals), 1.27 (s, 9H, $C(CH_3)_3$), 1.32 (s, 9H, $C(CH_3)_3$), 1.36 (s, 9H, $C(CH_3)_3$), 1.46 (s, 9H, $C(CH_3)_3$), 1.62 (m, 1H, C_6H_{10} CH), 1.76 (m, 2H, C_6H_{10} CH), 1.86 (m, 1H, C_6H_{10} CH), 2.13 (m, 1H, C_6H_{10} CH),

2.95 (m, 1H, CHS), 3.07 (m, 1H, C_6H_{10} CHN), 7.14 (d, $^4J_{HH}$ = 2.5 Hz, 1H, C_6H_2), 7.27 (m, 2H, C_6H_2), 7.41 (d, $^4J_{HH}$ = 2.5 Hz, 1H, C_6H_2), 8.40 (s, 1H, HC=N). ^{13}C NMR: δ 24.18 (C_6H_{10} CH_2), 25.78 (C_6H_{10} CH_2), 29.39 (C(CH_3)$_3$), 29.50 (C(CH_3)$_3$), 31.49 (C(CH_3)$_3$), 31.53 (C(CH_3)$_3$), 32.77 (C_6H_{10} CH_2), 34.14 (C(CH$_3$)$_3$), 34.21 (C(CH$_3$)$_3$), 35.06 (C(CH$_3$)$_3$), 35.15 (C(CH$_3$)$_3$), 35.26 (C_6H_{10} CH_2), 53.93 (CHS), 71.43 (C_6H_{10} CHN), 116.58 (C_6H_2), 117.77 (C_6H_2), 125.84 (C_6H_2 CH), 126.09 (C_6H_2 CH), 127.23 (C_6H_2 CH), 131.30 (C_6H_2 CH), 134.93 (C_6H_2), 136.83 (C_6H_2), 140.15 (C_6H_2), 141.55 (C_6H_2), 153.51 (C_6H_2), 158.11 (C_6H_2), 165.76 (N=C). HRMS. Calcd for $C_{35}H_{53}NO_2S$: m/z 551.3797. Found: m/z 551.3799. Mp: 133.4−133.9 °C. Anal. Calcd for $C_{35}H_{53}NO_2S$: C, 76.19; H, 9.68; N, 2.54. Found: C, 76.27; H, 9.24; N, 2.47.

Bis(phenol) 4. A solution of **3** (2.2 g, 4.0 mmol) was dissolved in a mixture of diethyl ether and MeOH. Solid $NaBH_4$ (760 mg, 20 mmol) was added slowly in small portions. The color of the reaction mixture changed from yellow to colorless after the reaction mixture was stirred overnight at room temperature. Water (30 mL) was added to precipitate a solid, which was collected, washed with cold MeOH, and dried in vacuo to give 2.1 g (95%) of a white solid. ^{1}H NMR: δ 1.21−1.47 (m, 4H, C_6H_{10} CH, overlap with C(CH_3)$_3$ signals), 1.30 (s, 9H, C(CH_3)$_3$) 1.31 (s, 9H, C(CH_3)$_3$), 1.40 (s, 9H, C(CH_3)$_3$), 1.44 (s, 9H, C(CH_3)$_3$), 1.72 (m, 2H, C_6H_{10} CH), 2.07 (m, 1H, C_6H_{10} CH,), 2.30 (m, 1H, C_6H_{10} CH), 2.49 (m, 1H, CHS), 2.72 (m, 1H, C_6H_{10} CHN), 3.89 (d, $^1J_{HH}$ = 12.8 Hz, 1H, NCH_2), 4.12 (d, $^1J_{HH}$ = 12.8 Hz, 1H, NCH_2), 6.95 (d, $^4J_{HH}$ = 2 Hz, 1H, C_6H_2), 7.27 (m, 2H, C_6H_2), 7.33 (d, $^4J_{HH}$ = 2 Hz, 1H, C_6H_2). ^{13}C NMR: δ 24.35 (C_6H_{10} CH_2), 25.96 (C_6H_{10} CH_2), 29.43 (C(CH_3)$_3$), 29.70 (C(CH_3)$_3$), 31.57 (C(CH_3)$_3$), 31.69 (C(CH_3)$_3$), 33.23 (C_6H_{10} CH_2), 34.18 (C(CH$_3$)$_3$), 34.26 (C(CH$_3$)$_3$), 34.95 (C(CH$_3$)$_3$), 35.19 (C(CH$_3$)$_3$), 50.31 (NCH_2), 54.04 (CHS), 59.43 (C_6H_{10} CHN), 115.72 (C_6H_2), 122.57 (C_6H_2), 123.25 (C_6H_2 CH), 126.15 (C_6H_2 CH), 131.34 (C_6H_2 CH), 135.32 (C_6H_2), 136.39 (C_6H_2), 140.80 (C_6H_2), 141.96 (C_6H_2), 153.90 (C_6H_2), 154.30 (C_6H_2). HRMS. Calcd for $C_{35}H_{55}NO_2S$: m/z 553.3954. Found: m/z 553.3962. Mp: 135−137 °C. Anal. Calcd for $C_{35}H_{55}NO_2S$: C, 75.90; H, 10.01, N, 2.53. Found: C, 76.18, H, 10.03, N, 2.55.

Complex 5a. A solution of **1a** (455 mg, 1.0 mmol) in 10 mL of toluene was cooled to −30 °C, after which 110 μL (190 mg, 1.0 mmol) of neat titanium tetrachloride was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 2 h. The solvent was removed under reduced pressure, after which the residue was washed twice with pentane (5 mL) and dried in vacuo to give 530 mg (93%) of a red powder. ^{1}H NMR: δ 0.91 (s, 9H, C(CH_3)$_3$), 1.24−1.35 (m, 1H, C_6H_{10} CH), 1.40 (s, 9H, C(CH_3)$_3$), 1.43−1.57 (m, 2H, C_6H_{10} CH), 1.69 (m, 1H, C_6H_{10} CH), 1.85 (m, 1H C_6H_{10} CH), 1.93 (m, 1H, C_6H_{10} CH), 2.19 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.38 (m, 1H, C_6H_{10} CH), 2.75 (m, 1H, C_6H_{10} CH), 2.89 (m, 1H, CHS), 4.00 (m, 1H, C_6H_{10} CHN), 5.22 (d, $^3J_{HH}$ = 10.8 Hz, 1H, NH), 6.60 (s, 1H, C_6H_2), 6.87 (s, 1H, C_6H_2), 7.00 (d, $^4J_{HH}$ = 2 Hz, 1H, C_6H_2), 7.04 (d, $^4J_{HH}$ = 2 Hz, 1H, C_6H_2). ^{13}C{^{1}H} NMR: δ 20.92 (CH_3), 21.37 (CH_3), 24.25 (C_6H_{10} CH_2), 25.97 (C_6H_{10} CH_2), 28.79 (C(CH_3)$_3$), 29.63 (C(CH_3)$_3$), 32.44 (C_6H_{10} CH_2), 34.71 (C(CH$_3$)$_3$), 34.86 (C(CH$_3$)$_3$), 36.53 (C_6H_{10} CH_2), 59.69 (CHS), 61.1 (CHN), 117.3 (C_6H_2 CH), 118.25 (C_6H_2), 125.21 (C_6H_2 CH), 130.69 (C_6H_2 CH), 131.90 (C_6H_2), 132.44 (C_6H_2), 132.52 (C_6H_2 CH), 134.95 (C_6H_2), 136.30 (C_6H_2), 137.52 (C_6H_2), 157.30 (C_6H_2, 166.12 (C_6H_2). Anal. Calcd for $C_{28}H_{39}Cl_2NO_2STi \cdot 0.25C_7H_8$: C, 60.00; H, 6.94; N, 2.35. Found: C, 59.86; H, 7.33; N, 2.31.

Complex 5b. A solution of **1b** (1.08 g, 2.0 mmol) in 10 mL of toluene was cooled to −30 °C, and 220 μL (380 mg, 2.0 mmol) of neat titanium tetrachloride was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 5 h. The solvent was removed under reduced pressure, and the residue was washed twice with pentane (10 mL) and dried in vacuo to give 1.25 g (95%) of a red powder. ^{1}H NMR: δ 0.91 (s, 9H, C(CH_3)$_3$), 1.21 (s, 9H, C(CH_3)$_3$), 1.25−1.35 (m, 1H, C_6H_{10} CH, overlap with C(CH_3)$_3$), 1.29 (s, 9H, C(CH_3)$_3$), 1.42 (s, 9H, C(CH_3)$_3$), 1.45−1.68 (m, 3H, C_6H_{10} CH), 1.84−1.95 (m, 2H, C_6H_{10} CH), 2.38 (m, 1H, C_6H_{10} CH), 2.77 (m, 1H, C_6H_{10} CH), 2.88 (m, 1H, CHS), 3.98 (m, 1H, C_6H_{10} CHN), 5.24 (d, $^3J_{HH}$ = 10.8 Hz, 1H, NH), 6.85 (m, 1H, C_6H_2), 7.15 (m, 1H, C_6H_2, overlapping), 7.16 (m, $^4J_{HH}$ = 2.3 Hz, 1H, C_6H_2), 7.27 (m, $^4J_{HH}$ = 2.3 Hz, 1H, C_6H_2). ^{13}C{^{1}H} NMR: δ 24.24 (C_6H_{10} CH_2), 26.04 (C_6H_{10} CH_2), 28.87 (C(CH_3)$_3$), 29.67 (C(CH_3)$_3$), 31.46 (C(CH_3)$_3$), 31.53 (C(CH_3)$_3$), 32.39 (C_6H_{10} CH_2), 34.59 (C(CH$_3$)$_3$), 34.73 (C(CH$_3$)$_3$), 35.00 (C(CH$_3$)$_3$), 35.10 (C(CH$_3$)$_3$), 36.93 (C_6H_{10} CH_2), 59.68 (CHS), 61.40 (CHN), 113.77 (C_6H_2 CH), 117.81 (C_6H_2), 121.7 (C_6H_2 CH), 126.96 (C_6H_2 CH), 129.28 (C_6H_2 CH), 134.51 (C_6H_2), 135.61 (C_6H_2), 137.26 (C_6H_2), 145.27 (C_6H_2), 145.89 (C_6H_2), 157.07 (C_6H_2), 165.93 (C_6H_2). Anal. Calcd for $C_{34}H_{51}Cl_2NO_2STi$: C, 62.19; H, 7.83; N, 2.13. Found: C, 62.20; H, 7.84; N, 2.08.

Complex 6a. A solution of **1a** (455 mg, 1.0 mmol) in 10 mL of toluene was cooled to −40 °C, after which 300 μL (287 mg, 1.0 mmol) of neat titanium tetra(isopropoxide) was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 6 h. The solvent was removed under reduced pressure (96% crude yield), and the residue was recrystallized from isopropyl alcohol at −30 °C to give a yellow powder in 29% yield. ^{1}H NMR: δ 0.99 (d, $^3J_{HH}$ = 6 Hz, 3H, CH-(CH_3)$_2$), 1.07 (d, $^3J_{HH}$ = 6 Hz, 3H, CH(CH_3)$_2$), 1.12 (d, $^3J_{HH}$ = 6 Hz, 3H, CH(CH_3)$_2$), 1.14 (d, $^3J_{HH}$ = 6 Hz, 3H, CH(CH_3)$_2$), 1.23−1.38 (m, 2H, C_6H_{10} CH), 1.41 (s, 9H, C(CH_3)$_3$), 1.42 (s, 9H, C(CH_3)$_3$), 1.50−1.68 (m, 3H, C_6H_{10} CH), 1.73 (m, 1H, C_6H_{10} CH), 1.88−2.01 (m, 2H, C_6H_{10} CH), 2.23 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.53 (m, 1H, CHS), 2.89 (m, 1H, C_6H_{10} CHN), 4.28 (d, $^3J_{HH}$ = 3.5 Hz, 1H, NH), 4.55 (septet, $^3J_{HH}$ = 6 Hz, 1H, CH(CH$_3$)$_2$), 4.68 (septet, $^3J_{HH}$ = 6 Hz, 1H, CH(CH$_3$)$_2$), 6.66 (s, 1H, C_6H_2), 6.93 (m, 2H, C_6H_2), 7.10 (d, $^4J_{HH}$ = 2 Hz, 1H, C_6H_2). ^{13}C{^{1}H} NMR: δ 20.74 (CH_3), 21.05 (CH_3), 24.41 (C_6H_{10} CH_2), 25.14 (C_6H_{10} CH_2), 25.79 (CH(CH_3)$_2$), 25.83 (CH(CH_3)$_2$), 29.22 (C(CH_3)$_3$), 29.31 (C(CH_3)$_3$), 31.17 (C_6H_{10} CH_2), 32.75 (C_6H_{10} CH_2), 34.66 (C(CH$_3$)$_3$), 34.95 (C(CH$_3$)$_3$), 49.58 (CHS), 61.94 (C_6H_{10} CHN), 77.63 (CH(CH$_3$)$_2$), 78.5 (CH-(CH$_3$)$_2$), 114.51 (C_6H_2), 123.33 (C_6H_2), 125.92 (C_6H_2), 125.99 (C_6H_2), 128.22 (C_6H_2), 129.03 (C_6H_2), 129.89 (C_6H_2), 134.01 (C_6H_2), 135.98 (C_6H_2), 136.83 (C_6H_2), 162.23 (C_6H_2), 167.80 (C_6H_2). Anal. Calcd for $C_{34}H_{53}NO_4STi \cdot C_5H_{12}$: C, 67.70; H, 9.47; N, 2.02. Found: C, 68.03; H, 9.61; N, 2.27.

Complex 7a. A solution of **2a** (469 mg 1.0 mmol) in 10 mL toluene was cooled to −30 °C, after which 110 μL (190 mg, 1.0 mmol) of neat titanium tetrachloride was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 4 h. A large amount of red precipitate had formed during the reaction. The precipitate was separated by filtration, washed twice with toluene (5 mL), and dried in vacuo to give 525 mg (90%) of a red powder. ^{1}H NMR: δ 0.83−0.96 (m, 1H, C_6H_{10} CH), 1.07 (m, 1H, C_6H_{10} CH), 1.23−1.33 (m, 2H, C_6H_{10} CH), 1.45 (s, 9H, C(CH_3)$_3$), 1.51 (s, 9H, C(CH_3)$_3$), 1.64 (m, 1H, C_6H_{10} CH), 1.72 (m, 1H, C_6H_{10} CH), 2.11 (m, 1H, C_6H_{10} CH), 2.24 (m, 1H, C_6H_{10} CH), 2.29 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.77 (m, 2H, C_6H_{10} CHX), 3.21 (s, 3H, NCH_3), 6.71 (d, $^4J_{HH}$ = 2 Hz, 1H, C_6H_2), 7.01 (m, 2H, C_6H_2), 7.22 (d, $^4J_{HH}$ = 2 Hz, 1H, C_6H_2). ^{13}C{^{1}H} NMR: δ 0.93 (CH_3), 21.40 (CH_3), 24.04 (C_6H_{10} CH_2), 25.38 (C_6H_{10} CH_2), 26.62 (C_6H_{10} CH_2), 29.46 (C(CH_3)$_3$), 29.69 (C(CH_3)$_3$), 31.69 (C_6H_{10} CH_2), 34.81 (C(CH$_3$)$_3$), 35.15 (C(CH$_3$)$_3$), 47.63 (NCH_3), 52.91 (CHS), 70.9 (CHN), 117.19 (C_6H_2), 123.42 (C_6H_2 CH), 127.10 (C_6H_2 CH), 128.69 (C_6H_2), 130.32 (C_6H_2), 131.22 (C_6H_2 CH), 133.62 (C_6H_2 CH), 136.15 (C_6H_2), 136.69 (C_6H_2), 136.94 (C_6H_2), 159.37 (C_6H_2), 167.45 (C_6H_2). Anal. Calcd for $C_{29}H_{41}Cl_2NO_2STi$: C, 59.39; H, 7.05; N, 2.39. Found: C, 59.86; H, 7.33; N, 2.31.

Complex 7b. A solution of **2b** (1.16 g, 2.0 mmol) in 10 mL of toluene was cooled to −30 °C, after which 220 μL of neat

titanium tetrachloride (380 mg, 2.0 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 5 h. The solvent was removed under reduced pressure, after which the residue was washed twice with pentane (10 mL) and dried in vacuo to give 1.30 g (97%) of a red powder. ^{1}H NMR: δ 0.83−0.94 (m, 1H, C_6H_{10} CH), 1.06 (m, 1H, C_6H_{10} CH), 1.23−1.45 (m, 2H, C_6H_{10} CH, overlap with $C(CH_3)_3$ signals), 1.28 (s, 9H, $C(CH_3)_3$), 1.30 (s, 9H, $C(CH_3)_3$), 1.47 (s, 9H, $C(CH_3)_3$), 1.53 (s, 9H, $C(CH_3)_3$), 1.64, (m, 1H, C_6H_{10} CH), 1.72 (m, 1H, C_6H_{10} CH), 2.12 (m, 1H, C_6H_{10} CH), 2.27 (m, 1H, C_6H_{10} CH), 2.77 (m, 2H, C_6H_{10} CH(X)), 3.23 (s, 3H, NCH_3), 6.88 (d, $^4J_{HH}$ = 2.3 Hz, 1H, C_6H_2), 7.17 (d, $^4J_{HH}$ = 2.3 Hz, 1H, C_6H_2), 7.23 (d, $^4J_{HH}$ = 2.3 Hz, 1H, C_6H_2), 7.45 (d, $^4J_{HH}$ = 2.3 Hz, 1H, C_6H_2). ^{13}C NMR: δ 24.21 (C_6H_{10} CH_2), 25.51 (C_6H_{10} CH_2), 26.68 (C_6H_{10} CH_2), 29.51 ($C(CH_3)_3$), 29.72 ($C(CH_3)_3$), 31.49 ($C(CH_3)_3$), 31.60 ($C(CH_3)_3$), 31.63 (C_6H_{10} CH_2), 34.49 ($C(CH_3)_3$), 34.55 ($C(CH_3)_3$), 35.07 ($C(CH_3)_3$), 35.43 ($C(CH_3)_3$), 47.56 (NCH_3), 52.82 (CHS), 70.85 (CHN), 116.95 (C_6H_2), 119.86 (C_6H_2 CH), 123.18 (C_6H_2 CH), 127.40 (C_6H_2 CH), 130.31 (C_6H_2 CH), 135.32 (C_6H_2), 136.28 (C_6H_2), 136.47 (C_6H_2), 142.04 (C_6H_2), 143.60 (C_6H_2), 159.07 (C_6H_2), 167.16 (C_6H_2). Anal. Calcd for $C_{35}H_{53}Cl_2NO_2STi \cdot HCl$: C, 59.45; H, 7.70; N, 1.98. Found: C, 59.31; H, 7.81; N, 1.90.

Complex 8a. A solution of **2a** (469 mg, 1.0 mmol) in 10 mL of toluene was cooled to −40 °C, after which 300 μL of neat titanium tetra(isopropoxide) (287 mg, 1.0 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 6 h. The solvent was removed under reduced pressure (98% crude yield), and the residue was dissolved in 2 mL of dry pentane. Upon standing at room temperature, a yellow precipitate formed, which was collected, washed twice with cold pentane (5 mL), and dried in vacuo to give a yellow product in 25% yield. ^{1}H NMR: δ 0.82 (d, $^3J_{HH}$ = 6 Hz, 3H, $CH(CH_3)_2$), 0.92 (d, $^3J_{HH}$ = 6 Hz, 3H, $CH(CH_3)_2$), 0.97−1.06 (m, 1H, C_6H_{10} CH, overlap with $CH(CH_3)_2$ signals), 1.02 (d, $^3J_{HH}$=6 Hz, 3H, $CH(CH_3)_2$, overlap with C_6H_{10} CH and $CH(CH_3)_2$), 1.03 (d, $^3J_{HH}$ = 6 Hz, 3H, $CH(CH_3)_2$), 1.23−1.36 (m, 2H, C_6H_{10} CH), 1.42 (s, 9H, $C(CH_3)_3$), 1.43 (s, 9H, $C(CH_3)_3$), 1.57−1.72 (m, 3H, C_6H_{10} CH), 2.05 (m, 1H, C_6H_{10} CH), 2.25 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.38−2.52 (m, 2H, C_6H_{10} CH), 2.68 (m, 1H, CHN), 2.84 (s, 3H, NCH_3), 4.43 (septet, $^3J_{HH}$ = 6 Hz, 1H, $CH(CH_3)_2$), 4.62 (septet, $^3J_{HH}$ = 6 Hz, 1H, $CH(CH_3)_2$), 6.73 (d, $^4J_{HH}$ = 2.0 Hz, 1H, C_6H_2), 6.88 (d, $^4J_{HH}$ = 2.0 Hz, 1H, C_6H_2), 7.08 (d, $^4J_{HH}$ = 2.3 Hz, 1H, C_6H_2), 7.13 (d, $^4J_{HH}$=2.3 Hz, 1H, C_6H_2). ^{13}C{^{1}H} NMR: δ 20.67 (CH_3), 21.29 (CH_3), 24.49 (C_6H_{10} CH_2), 24.71 (C_6H_{10} CH_2), 25.27 (CH $(CH_3)_2$), 25.41 (CH$(CH_3)_2$), 25.73 (CH$(CH_3)_2$) 25.75 (CH $(CH_3)_2$), 26.04 (C_6H_{10} CH_2), 29.31 ($C(CH_3)_3$), 29.50 (C $(CH_3)_3$), 34.56 (NCH_3), 34.75 ($C(CH_3)_3$), 35.06 ($C(CH_3)_3$), 35.56 (C_6H_{10} CH_2), 59.23 (CHS), 70.19 (CHN), 78.03 (CH-$(CH_3)_2$), 79.05 (CH$(CH_3)_2$), 118.19 (C_6H_2 CH), 123.53 (C_6H_2), 123.68 (C_6H_2), 124.43 (C_6H_2 CH), 125.02 (C_6H_2), 129.36 (C_6H_2 CH), 130.99 (C_6H_2 CH), 134.96 (C_6H_2), 136.44 (C_6H_2), 142.08 (C_6H_2), 157.99 (C_6H_2), 164.77 (C_6H_2). Anal. Calcd for $C_{35}H_{55}NO_4STi$: C, 66.33; H, 8.75; N, 2.21. Found: C, 65.88; H, 8.74; N, 2.14.

Complexes 9a and 9b. A solution of **3** (551 mg 1.0 mmol) in 10 mL of toluene was cooled to −30 °C, after which 110 μL (190 mg, 1.0 mmol) of neat titanium tetrachloride was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 6 h. The solvent was removed under reduced pressure, and the residue was washed twice with pentane (5 mL) and dried in vacuo to give 636 mg (95%) of a red powder (a 3:5 mixture of two isomers). ^{1}H NMR (major isomer **9b**): δ 1.17 (m, 1H, C_6H_{10} CH), 1.23−1.52 (m, 2H, C_6H_{10} CH, overlap with $C(CH_3)_3$ signals), 1.28 (s, 9H, $C(CH_3)_3$), 1.31 (s, 9H, $C(CH_3)_3$), 1.33 (s, 9H, $C(CH_3)_3$), 1.55 (s, 9H, $C(CH_3)_3$), 1.63 (m, 1H, C6H10 CH), 1.92 (m, 2H, C_6H_{10} CH), 2.41 (m, 2H, C_6H_{10} CH), 3.31 (m, 1H, CHS), 3.47 (m, 1H, C_6H_{10} CHN), 7.21 (d, $^4J_{HH}$ = 2.3 Hz, 1H, C_6H_2), 7.35 (d, $^4J_{HH}$ = 2.3 Hz, 1H, C_6H_2), 7.36 (d, $^4J_{HH}$ = 2.3 Hz, 1H, C_6H_2), 7.65 (d, $^4J_{HH}$ = 2.3 Hz, 1H, C_6H_2), 8.32 (d, $^3J_{HH}$ = 2 Hz, 1H, CH=N). ^{13}C NMR: δ 23.75 (C_6H_{10} CH_2), 25.89 (C_6H_{10} CH_2), 29.47 ($C(CH_3)_3$), 29.58 ($C(CH_3)_3$), 31.1 (C_6H_{10} CH), 31.37 ($C(CH_3)_3$), 31.40 (C_6H_{10} CH), 31.50 ($C(CH_3)_3$), 34.59 ($C(CH_3)_3$), 34.63 ($C(CH_3)_3$), 35.20 ($C(CH_3)_3$), 35.28 ($C(CH_3)_3$), 54.92 (CHS), 67.84 ($C(CH_3)_3$ CHN), 117.41 (C_6H_2), 125.07 (C_6H_2), 126.94 (C_6H_2 CH), 129.22 (C_6H_2 CH), 130.20 (C_6H_2 CH), 130.88 (C_6H_2 CH), 135.94 (C_6H_2), 136.59 (C_6H_2), 145.08 (C_6H_2), 145.30 (C_6H_2), 158.65 (C_6H_2), 161.00 (C=N), 166.56 (C_6H_2). Anal. Calcd for $C_{35}H_{51}Cl_2NO_2STi$: C, 62.87; H, 7.69; N, 2.09. Found: C, 62.69; H, 8.11; N, 2.00.

Complexes 10a and 10b. A solution of **4** (553 mg, 1.0 mmol) in 10 mL of toluene was cooled to −30 °C, after which 110 μL (190 mg, 1.0 mmol) of neat titanium tetrachloride was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 6 h. The solvent was removed under reduced pressure, and the residue was washed twice with pentane (5 mL) and dried in vacuo to give 610 mg (91%) of a red powder (a mixture of two isomers in a ratio of ca. 1:1). Separation of **10a** and **10b** was possible by crystal picking after recrystallization from toluene at room temperature. Single crystals suitable for X-ray crystallography of **10a** (red plates) and **10b** (red blocks) were obtained from the same crop. ^{1}H NMR (isomer **10a**): δ 0.81−0.97 (m, 3H, C_6H_{10} CH), 1.25 (s, 9H, $C(CH_3)_3$), 1.32 (s, 9H, $C(CH_3)_3$), 1.49−1.92 (m, 4H, C_6H_{10} CH, overlap with $C(CH_3)_3$ signals), 1.50 (s, 9H, $C(CH_3)_3$), 1.56 (s, 9H, $C(CH_3)_3$), 1.97 (m, 1H, C_6H_{10} CH), 2.21 (m, 1H, CHS), 2.74 (m, 1H, C_6H_{10} CHN), 3.93 (dd, $^2J_{HH}$ = 13.8 Hz, $^3J_{HH}$ = 1.3 Hz, 1H, NCH_2), 4.03 (m, 1H, NH), 4.60 (dd, $^2J_{HH}$ = 13.8 Hz, $^3J_{HH}$ = 3.5 Hz, 1H, NCH_2), 7.01 (d, $^4J_{HH}$ = 2.3 Hz, 1H, C_6H_2), 7.05 (m, $^4J_{HH}$ = 2.3 Hz, 1H, C_6H_2), 7.36 (d, $^4J_{HH}$ = 2.3 Hz, 1H, C_6H_2), 7.37 (d, $^4J_{HH}$ = 2.3 Hz, 1H, C_6H_2). ^{13}C{^{1}H} NMR (isomer **10a**): δ 24.24 (C_6H_{10} CH_2), 25.57 (C_6H_{10} CH_2), 29.52 ($C(CH_3)_3$), 30.22 ($C(CH_3)_3$), 30.96 (C_6H_{10} CH_2), 31.12 (C_6H_{10} CH_2), 31.49 ($C(CH_3)_3$), 31.61 ($C(CH_3)_3$), 34.37 ($C(CH_3)_3$), 34.62 ($C(CH_3)_3$), 35.16 ($C(CH_3)_3$), 35.34 ($C(CH_3)_3$), 47.53 (NCH_2), 54.43 (CHS), 61.98 (C_6H_{10} CHN), 115.77 (C_6H_2), 124.23 (C_6H_2 CH), 125.29 (C_6H_2), 127.15 (C_6H_2), 128.22 (C_6H_2 CH), 129.03 (C_6H_2 CH), 129.85 (C_6H_2 CH), 135.94 (C_6H_2), 136.9 (C_6H_2), 142.83 (C_6H_2), 145.16 (C_6H_2), 159.70 (C_6H_2), 166.66 (C_6H_2). ^{1}H NMR (isomer **10b**): δ 1.07−1.50 (m, 4H, C_6H_{10} CH, overlap with $C(CH_3)_3$ signals), 1.30 (s, 9H, $C(CH_3)_3$), 1.31 (s, 9H, $C(CH_3)_3$), 1.36 (s, 9H, $C(CH_3)_3$), 1.55 (s, 9H, $C(CH_3)_3$), 1.86 (m, 2H, $C(CH_3)_3$ CH), 2.32−2.38 (m, 1H, C_6H_{10} CH), 2.49 (m, 1H, CHS), 2.64 (m, 1H, C_6H_{10} CH), 3.27 (m, 1H, NH), 3.51 (m, 1H, C_6H_{10} CHN), 3.84 (d, J_{HH} = 12 Hz, 1H, NCH_2), 4.21 (t, J_{HH} = 12 Hz, 1H, NCH_2), 7.00 (d, $^4J_{HH}$ = 2.3 Hz, 1H, C_6H_2), 7.18 (d, $^4J_{HH}$ = 2.3 Hz, 1H, C_6H_2), 7.35 (d, $^4J_{HH}$ = 2.3 Hz, 1H, C_6H_2), 7.40 (d, $^4J_{HH}$ = 2.3 Hz, 1H, C_6H_2). ^{13}C{^{1}H} NMR (isomer **10b**): δ 24.12 (C_6H_{10} CH_2), 26.03 (C_6H_{10} CH_2), 29.84 ($C(CH_3)_3$), 30.10 ($C(CH_3)_3$), 31.51 ($C(CH_3)_3$), 31.56 ($C(CH_3)_3$), 31.63 (C_6H_{10} CH_2), 32.82 (C_6H_{10} CH_2), 34.62 ($C(CH_3)_3$), 34.65 ($C(CH_3)_3$), 35.26 ($C(CH_3)_3$), 35.34 ($C(CH_3)_3$), 51.10 (NCH_2), 55.47 (CHS), 62.90 (C_6H_{10} CHN), 117.72 (C_6H_2), 123.81 (C_6H_2 CH), 124.58 (C_6H_2 CH), 126.35 (C_6H_2), 127.09 (C_6H_2 CH), 130.16 (C_6H_2 CH), 135.78 (C_6H_2), 135.91 (C_6H_2), 145.28 (C_6H_2), 145.32 (C_6H_2), 160.34 (C_6H_2), 165.65 (C_6H_2). Anal. Calcd for $C_{35}H_{53}Cl_2NO_2STi \cdot 0.5C_7H_8$: C, 64.52; H, 8.02; N, 1.95. Found: C, 64.69; H, 8.27; N, 1.91.

General Polymerization Procedure. To a 100 mL Schlenk flask were added 7.5 mL of toluene, 5 mL of styrene, and 1.25 mL of MAO, after which the mixture was stirred at 40 °C for 15 min before polymerization was initiated by adding 1.25 μmol of catalyst precursor in 0.5 mL of toluene. The polymerization was allowed to run for 2 h, after which the run was aborted by addition of 1 mL of isopropyl alcohol. The mixture was stirred for 10 min and then poured into acidified methanol (150 mL).

Table 2. Crystallographic Data for **5b**, **7b**, **8a**, and **9b**

compound	**5b**	**7b**·$2CH_2Cl_2$	**8a**	**9b**·1.5 C_7H_8
empirical formula	$C_{34}H_{51}Cl_2NO_2STi$	$C_{37}H_{57}Cl_6NO_2STi$	$C_{35}H_{55}NO_4STi$	$C_{45}\cdot 5H_{63}Cl_2NO_2STi$
M_r	656.62	840.50	633.76	806.83
crystal size (mm^3)	$0.17 \times 0.06 \times 0.02$	$0.48 \times 0.38 \times 0.12$	$0.27 \times 0.22 \times 0.05$	$0.29 \times 0.13 \times 0.12$
cryst syst	monoclinic	orthorhombic	monoclinic	triclinic
space group	$P2_1/c$	*Pbcn*	$P2_1/n$	$P\bar{1}$
a (Å)	16.406(2)	9.4683(18)	11.5417(12)	10.390(2)
b (Å)	14.6793(18)	18.311(4)	16.1424(17)	11.539(2)
c (Å)	15.8086(19)	24.477(5)	18.5544(19)	18.850 (4)
α (deg)	90	90	90	91.811(4)
β (deg)	107.390(5)	90	96.864(3)	104.850(4)
γ (deg)	90	90	90	95.667(4)
V ($Å^3$)	3633.1(8)	4243.7(15)	3432.1(6)	2170.0(7)
Z	4	4	4	2
D_{calc} (g cm^{-3})	1.200	1.316	1.227	1.235
T (K)	123(2)	130(2)	130(2)	130(2)
μ(Mo Kα) (mm^{-1})	0.469	0.660	0.347	0.405
F(000)	1400	1768	1368	862
θ range (deg)	2.55−25.12	1.66−28.35	2.18−28.35	2.04−28.33
reflns collected	31333	42001	39150	29712
indep reflns (R_{int})	5850 (0.1408)	5305 (0.0501)	8560 (0.0989)	10744 (0.0722)
max and min transmn	0.9907 and 0.9246	0.9250 and 0.7423	0.9829 and 0.9121	0.9530 and 0.8916
data/restraints/param	5850/0/386	5305/0/239	8560/0/371	10 744/0/502
GOF on F^2	1.062	1.157	1.019	0.979
R1, wR2 [$I > 2\sigma(I)$]	0.0737, 0.1604	0.0882, 0.2215	0.0725, 0.1482	0.0540, 0.1205
R1, wR2 (all data)	0.1223, 0.1945	0.1029, 0.2349	0.1108, 0.1655	0.0909, 0.1358
largest diff peak/hole (e $Å^{-3}$)	0.507/−0.446	1.1497/−1.048	0.704/−0.489	0.477/−0.362

The obtained polymer was filtered and washed twice with methanol and the residue was dried to constant weight at 60 °C under vacuum.

X-ray Crystallography. Crystals of **5b**, **9b**, **10a**, and **10b** suitable for X-ray analysis were obtained by slow evaporation of a toluene solution at room temperature; crystals of **8a** were obtained from a toluene solution at −20 °C, and crystals of **7b** were obtained from a dichloromethane solution at −20 °C. X-ray diffraction measurements were performed on a Bruker AXS SMART CCD diffractometer with Mo Kα radiation (0.710 73 Å) using *ω* scans. The data reductions as well as absorption corrections based on multiple and symmetry-equivalent measurements were carried out using *SADABS*[44a] (**5b**, **7b**, **8a**, and **9b**) or *MULABS* as implemented in the program system *PLATON*[44b] (**10a** and **10b**). All structures were solved by direct methods and Fourier difference methods (*SIR-92*)[44c] and refined (*SHELXS-97*)[44d] against all F_o^2 data with hydrogen atoms riding in calculated positions. Crystal parameters and the results of structure refinements for **5b**, **7b**, **8a**, and **9b** are given in Table 2; data for **10a** and **10b** are given in Table S1 of the Supporting Information. The unit cell of **10a** contains two crystallographically independent molecules. Compounds **7b**, **9b**, **10a**, and **10b** contain cocrystallized solvent molecules, which are disordered in **7b** and **9b**. In the crystal structures of **7b** and **8a** the sulfur and *N*-methyl positions are disordered; **8a** and **10b** show disorder in one of the arene moieties. Disordered positions were refined with fractional occupancy. For the graphical representation, the program *ORTEP* was used as implemented in the program system *WinGX*.[44e] Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre under the following numbers: CCDC 730702 (**5b**), 730703 (**7b**), 730704 (**8a**), 730705 (**9b**), 730706 (**10a**), and 730707 (**10b**). Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (http://www.ccdc.cam.ac.uk, fax (+44)1223-336-033, e-mail deposit@ccdc.cam.ac.uk).

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Supporting Information Available: X-ray structures of **10a** and **10b** and CIF files for **5b**, **7b**, **8a**, **9b**, **10a**, and **10b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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