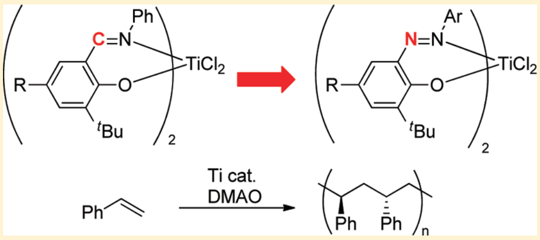
ORGANOMETALLICS
Article
pubs.acs.org/Organometallics

Bis(phenoxy-azo)titanium(IV) Complexes: Synthesis, Structure, and Catalytic Activity in Styrene Polymerization

Ryo Tanaka, Philipp Viehmann, and Stefan Hecht*

Department of Chemistry, Humboldt-Universität zu Berlin, Brook-Taylor-Straße 2, 12489 Berlin, Germany

Supporting Information



ABSTRACT: A new class of titanium(IV) complexes bearing two phenoxy-azo ligands was synthesized. The Ti−N bonds from X-ray structures were longer than those of corresponding bis(phenoxy-imine)titanium(IV) complexes, which indicates that the coordination of phenoxy-azo ligands becomes weaker on replacing the imine carbon by nitrogen. These titanium complexes were applied for the polymerization of styrene using DMAO as cocatalyst, and syndiotactic polystyrene was obtained. Premixing DMAO with the titanium complex resulted in higher activity, similar to the related bis(phenoxy-imine)titanium(IV) complexes. The coordinating azobenzene subunits did not undergo $E \rightarrow Z$ photoisomerization upon UV irradiation.

INTRODUCTION

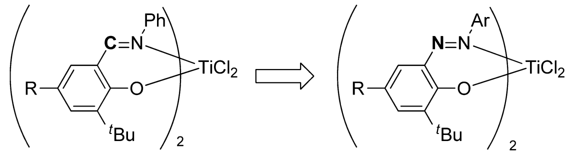
Stereoblock homopolymers often show different characteristics as compared to stereoregular polymers. For example, isotactic polypropylene containing atactic interior blocks has been reported by Coates and Waymouth to show elastic properties.[1] This particular polymer was synthesized by a titanium complex bearing freely rotating bis-indenyl ligands, which causes a change of stereoselectivity during the propagation of the polymer chain. Moreover, Po and Spera utilized a combination of a nickel and a titanium catalyst to synthesize syndiotactic polystyrene capped by isotactic polystyrene blocks.[2] In this case, the polymer chain was transferred between the two complexes, which are associated with different stereoselectivity. The two strategies outlined above do not allow for complete control over the change of stereoselectivity and, hence, exact adjustment of the ratio and average length of the individual blocks. However, synthesis of stereoblock polypropylene in a completely controlled manner was achieved by changing the ratio of activator and zirconium catalyst during the polymerization.[3] Three different polypropylenes with the same molecular weight and isotactic content yet distributed in blocks of different average length have been synthesized using this catalyst system. Furthermore, Shiono and co-workers succeeded in controlling the syndiospecificity of living propylene polymerization using an *ansa*-metallocene titanium complex by changing the reaction temperature,[4a] monomer pressure,[4b] and polarity of the solvent.[4c,d]

Stimulus-responsive catalysts are another promising way to modulate stereoselectivity during the propagation. Ideally, a stimulus, which can be precisely controlled with regard to its energy/intensity with sufficient temporal resolution, will allow the external "programming" of the catalyst system: i.e., when the catalyst is generating the type of stereoblock. Among several potential stimuli, light offers perhaps the most advantages, since it is a truly noninvasive external stimulus and allows for unprecedented control over wavelength/intensity and exposure time. Several polymerization catalysts triggered by light have been reported.[5] For example, metathesis polymerizations of alkynes and norbornenes can be initiated by photolysis of $W(CO)_6$[6] and ruthenium catalysts,[7] respectively. In all of these examples, photoexcitation was used to promote the dissociation of labile ligands and therefore to generate unsaturated, catalytically active transition-metal fragments. However, to the best of our knowledge, there has been no report of *reversible* control of catalyst activity and/or selectivity by light.[5] Thus, we were motivated to design and establish photoswitching polymerization catalyst systems by introducing photochromic azobenzene units to catalytically active transition-metal complexes. Bis(phenoxy-imine)titanium complexes, such as **1a**,**b**, are well-known for their activity in the coordination polymerization of various olefins.[8] In our first attempt to render these catalysts photoswitchable, we replaced the phenoxy-imine moiety by various phenoxy-azo units and used these new photochromic ligands to prepare the novel titanium complexes **3a**,**b** (Figure 1). Note that *o*-hydroxyazobenzene-derived complexes of group 4 metals have not been described in the literature.[9] Herein, we report the synthesis of a new class of titanium complexes, which bear phenoxy-azo ligands and their application for the polymerization of styrene.

RESULTS AND DISCUSSION

Synthesis of Bis(phenoxyazo) Titanium(IV) Complexes 3a,b. *o*-Hydroxyazobenzene ligands **2a**,**b** were synthesized by azo coupling of 2,6-di-*tert*-butylphenol and the corresponding diazonium salts in 83% and 48% yields, respectively. The reaction of 0.5 equiv of $TiCl_4$ with the sodium salts of **2a**,**b**, which were prepared by the reaction of

Received: February 27, 2012



1a (R = ^{t}Bu)
1b (R = H)

3a (R = ^{t}Bu, Ar = Ph)
3b (R = ^{t}Bu, Ar = 3,5-F$_2$-C$_6$H$_3$)

Figure 1. Design of bis(phenoxy-azo)titanium(IV) complexes.

2a,b with an excess amount of sodium hydride, gave bis(phenoxy-azo)titanium(IV) complexes **3a,b** in 72% yield, both as dark brown solids (Scheme 1). The ^{1}H NMR spectra of **3a,b** showed a single set of broad signals in the aryl region, indicating that the structures of **3a,b** are C_2 symmetric.

X-ray Structures of 3a,b. Suitable single crystals of **3a,b** were grown from CH_2Cl_2 solution by slow evaporation. Both crystals (Figure 2 and 3) showed that the *o*-hydroxyazobenzene ligand coordinates to the titanium center in such a fashion that the distant *β*-N atom engages in a Ti–N bonding interaction, thereby forming a six-membered ring. This is rather typical, as *o*-hydroxyazobenzenes are known to coordinate to metal centers by forming six-membered rings[10] and only one example of a five-membered ring has been reported.[11] The two phenoxy O atoms adopt a trans configuration, most likely to avoid steric repulsion between their *o-tert*-butyl groups, while both N donors as well as the two chlorido ligands each adopt a cis configuration. This coordination behavior is similar to that of the corresponding bis(phenoxy-imine)titanium complex **1a.**[12]

The average lengths of Ti–O bonds (Table 1) in **3a** (1.851 Å), **3b** (1.850 Å), and **1a** (1.850 Å) are almost the same, indicating that changing from an imine group to an azo group does not significantly influence the electronic properties of the phenoxide. The average lengths of the two Ti–N bonds of **3a,b** are 2.264 and 2.269 Å, respectively, which is considerably longer than that reported for **1a** (2.231 Å),[12] probably because the N atom of the azo N=N unit is more electron deficient as compared to that of an imine C=N bond. The N–Ti–N bond angles of **3a** (71.63°) and **3b** (72.76°) are significantly smaller than that of **1a** (88.33°), whereas the Cl–Ti–Cl bond angles of **3a** (107.77°) and **3b** (106.58°) are larger than that of **1a** (97.80°). The latter means that the new complexes **3a,b** exhibit rather open, i.e. sterically less congested, coordination sites under polymerization conditions.

Polymerization of Styrene using 3a,b. Styrene polymerization using either **3a** or **3b** as catalyst was investigated to compare their catalytic activity with that of the known bis(phenoxy-imine)titanium complexes. When dry methylaluminoxane (DMAO) was mixed with **3b** before the addition of styrene, the polymerization activity was greatly increased (Table 2, entries 2–4). The produced polystyrene was mainly syndiotactic, showing the same stereoselectivity for **3a,b** as for the related phenoxy-imine complex **1b.**[13] However, a small amount of isotactic sequence was also observed by ^{1}H NMR when using **3b** (entries 2 and 3), which was not obtained from **1b** and **3a** under the premix conditions (entries 1 and 5). ^{1}H NMR analysis of the mixture of **3b** and 50 equiv of DMAO in toluene-d_8 showed broad signals with a single set of downfield-shifted ligand signals, indicating that both phenoxyazo aluminum and low-oxidation-state titanium complexes were generated.[14] The observed activity was lower than that of **1b** (entries 2 and 5). The number of formed polymer chains, estimated from the M_n value of the obtained polystyrene, was smaller than the amount of the catalyst, indicating that only a fraction of the catalyst initiates chain growth and propagates

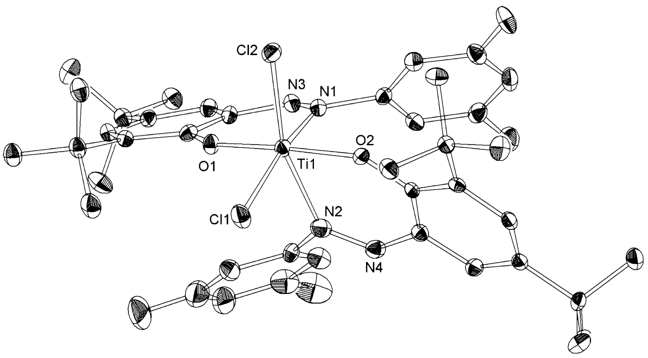


Figure 2. Crystal structure of **3a** (50% thermal ellipsoids). The minor part of the disordered moiety, CH_2Cl_2 in the crystal, and hydrogen atoms are omitted for clarity.

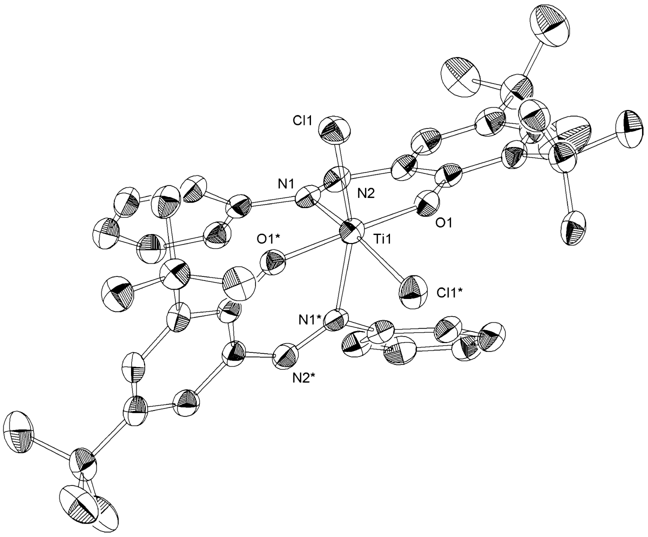
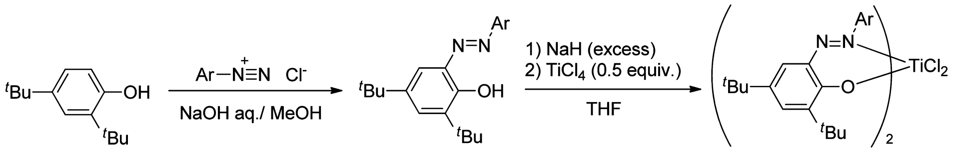


Figure 3. Crystal structure of **3b** (50% thermal ellipsoids). The minor part of the disordered moiety and hydrogen atoms are omitted for clarity. Half of the entire structure constitutes an asymmetric unit.

Scheme 1. Synthesis of Bis(phenoxy-azo)titanium(IV) Complexes 3a,b



2a (Ar = Ph, 83 %)
2b (Ar = 3,5-F$_2$-C$_6$H$_3$, 48 %)

3a (Ar = Ph, 72 %)
3b (Ar = 3,5-F$_2$-C$_6$H$_3$, 72 %)

Table 1. Selected Bond Lengths (Å) and Angles (deg) of 3a,b and 1a

	3a	3b	1a[a]
Ti−O	1.8506(16)	1.8498(18)	1.844(3)
		1.8507(19)	1.855(3)
Ti−N	2.2635(18)	2.248(2)	2.216(4)
		2.289(2)	2.245(4)
Ti−Cl	2.2873(7)	2.2639(8)	2.2744(14)
		2.2838(8)	2.2808(14)
O−Ti−O	172.83(11)	169.59(9)	165.29(14)
N−Ti−N	71.62(9)	72.75(8)	88.33(13)
Cl−Ti−Cl	107.77(4)	106.58(3)	97.79(5)

[a] Data taken from ref 12.

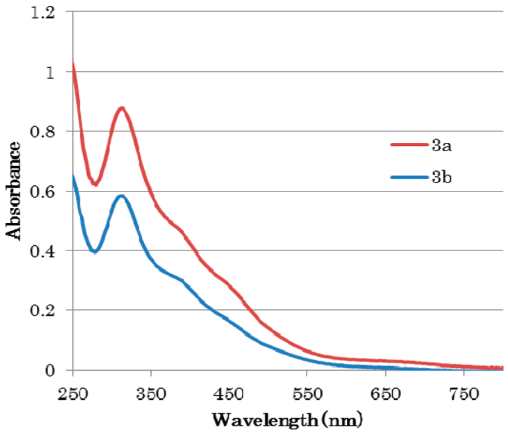


Figure 4. UV/vis absorption spectra of **3a** (5.8×10^{-5} M in CH_2Cl_2) and **3b** (4.6×10^{-5} M in CH_2Cl_2). Both spectra were taken under an Ar atmosphere in sealed cuvettes at 25 °C.

throughout the polymerization. The achieved molecular weight distributions under the premixed conditions (entries 1 and 2) are comparable with that for the bis(phenoxy-imine)titanium(IV) reference compound **1b** (entry 5).

Photochromism. After having demonstrated that complexes **3a,b** display activity for the polymerization of styrene, we investigated their ability to undergo photoinduced *E* → *Z* isomerization that should lead to potential photocontrol over the polymerization outcome. First, the UV/vis absorption of **3a,b** in dichloromethane was recorded (Figure 4). **3a,b** both showed an intense UV absorption band at 312 nm, corresponding to the characteristic $\pi \rightarrow \pi^*$ transition of the azobenzene moiety. In addition, a broad shoulder with two discernible peaks was observed in the range 370−470 nm, which are assigned to the $n \rightarrow \pi^*$ transitions of the azo groups and quinoid tautomers.[15]

Irradiation of **3a,b** with UV light (313 nm) led to no observable changes in the UV/vis spectra, indicating the inhibition of *E* → Z photoisomerization by the presence of the metal center. In the literature, there is an example of an ortho-palladated azobenzene in which the five-membered chelate complex locks the azobenzene in its *E* configuration and shuts off photoisomerization.[16] Although in our case more flexible six-membered-ring structures are being adopted, the stability of the phenoxy-azo titanium complexes seems still too high to allow for successful photoisomerization, which requires breaking of either the Ti−N or Ti−O bonds, respectively.

CONCLUSION AND OUTLOOK

A new class of bis(phenoxy-azo)titanium(IV) complexes has been synthesized and structurally characterized with the aim of investigating their ability to catalyze the polymerization of styrene. Their structures and polymerization behavior were compared to that of the known related bis(phenoxy-imine)titanium(IV) complexes. Due to its poorer σ-donating character, the N atom of the azo group forms longer Ti−N bonds, which in turn lead to a more open coordination sphere around the Ti center. The observed polymerization activity and selectivity for producing syndiotactic polystyrene are both somewhat reduced as compared to those of the imine-based systems. Unfortunately, the bis(phenoxy-azo)titanium complexes do not undergo photoinduced *E* → *Z* isomerization in their chelating azobenzene ligand frameworks. We attribute this behavior to the relatively strong Ti−N and Ti−O bonds, respectively, which need to yet cannot be broken in the course of the photoisomerization reaction. This finding suggests that photoisomerization of the azobenzene moiety will only be successful if the azo group is not coordinating, i.e. chelating, to the metal center directly but rather influences the vicinity of the active site. Although not successful, the study presented herein constitutes an important lesson on the way to design photoswitchable transition-metal catalyst systems[5] bearing photochromic azobenzene groups.

EXPERIMENTAL SECTION

General Procedures. All manipulations involving the air- and moisture-sensitive compounds were carried out by using standard Schlenk techniques under argon. All the solvents, including deuterated solvents, were distilled under argon and stored in the presence of 4A molecular sieves. The toluene solution of MAO was purchased from Sigma-Aldrich and dried under reduced pressure at 70 °C overnight. The obtained dry MAO (DMAO) was redissolved into toluene prior to use. Other materials were used as received. Column chromatography was carried out with 130−400 mesh silica gel. NMR spectra were recorded on a 300 MHz (75.6 MHz for ^{13}C) Bruker DPX 300

Table 2. Polymerization of Styrene using 3a,b/DMAO as Catalysts[a]

entry	complex	premix (min)	temp (°C)	time (h)	activity[b] (g/((mmol of Ti) h))	M_n[c]	PDI[c]	tacticity (syn/iso)[d]
1	**3a**	10	60	5	0.24	7 800	3.1	100/0
2	**3b**	10	60	1	2.1	5 700	3.6	96/4
3	**3b**	0	60	1	1.0	8 400	6.1	94/6
4	**3b**	0	20	1	trace			
5[e]	**1b**	13	60	1	16.04	101 000	2.9	100/0

[a] Conditions: 1.5 mL of toluene, 5 mL of styrene, 10 μmol of **3a,b**, 2.3 mmol of DMAO (as Al). [b] Calculated from the yield of polymer, which is insoluble in 2-butanone. [c] Determined by GPC calibrated with narrow polystyrene standards. [d] Ratio of syndiotactic and isotactic polymer determined by the integral ratio of methane signals of ^1H NMR spectra in 1,1,2,2-tetrachloroethane-d_2, referenced by isotactic polystyrene and syndiotactic polystyrene.[13] [e] Data taken from ref 13.

spectrometer at 27 °C using residual protonated solvent signals as internal standard (^{1}H NMR, δ($CDCl_3$) 7.26 ppm; ^{13}C NMR, δ($CDCl_3$) 77.0 ppm). UV/vis absorption spectra were recorded using quartz cuvettes of 1 cm path length on a Cary 50 spectrophotometer, equipped with Peltier thermostated cell holders ($\Delta T = \pm 0.05$ °C). High-resolution mass spectrometry was performed on a Thermo LTQ FT instrument (ESI) and MSI concept 1H spectrometer (EI, 70 eV ionization) as well as on a QSTARXL Applied Q-TOF instrument with a ISV of 950 V. Irradiation was performed using a LOT-Oriel 1000 W medium-pressure Xe lamp, equipped with a special cutoff filter ($\lambda_{max} > 310$ nm). GPC measurements in THF as eluent were performed on PSS columns in a WGE Dr. Bures TAU 2010 column oven, equipped with a WGE Dr. Bures Q-2010 HPLC pump, a Knauer Smartline 3800 autosampler, and WGE ETA-2020 RI-visco-detector. Calibration was done with a polystyrene calibration kit (S-L-10 LOT 79).

Preparation of Phenoxyazo Ligand 2a. Aniline (1.82 mL, 20 mmol) was dissolved in 20 mL of 1 M aqueous HCl. To this solution was slowly added $NaNO_2$ (1.38 g, 20 mmol) in water (20 mL) at 0 °C, and the mixture was stirred for 1 h. To the resulting yellow suspension was added a solution of 2,4-di-*tert*-butylphenol (4.12 g, 20 mmol) and NaOH (800 mg, 20 mmol) in MeOH (20 mL) and water (20 mL) dropwise at 0 °C, and the mixture was stirred for 15 h. The red precipitate was filtered, washed with 100 mL of water and 100 mL of MeOH, and dried under vacuum. A 5.13 g amount (83%, 16.6 mmol) of brown solid **2a** was obtained. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.70 (br s, 1H), 7.91−7.85 (m, 2H), 7.80 (d, J = 3 Hz, 1H), 7.56−7.42 (m, 4H), 1.48 (s, 9H), 1.38 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.7, 150.5, 141.5, 138.0, 137.1, 130.8 (CH), 129.5 (CH), 128.6 (CH), 127.7 (CH), 122.1 (CH), 35.5, 34.4, 31.6 (CH_3), 29.6 (CH_3). HRMS (ESI$^+$): 311.2130, calcd for $C_{20}H_{26}N_2O$ (M + H) 311.2123.

Preparation of Phenoxyazo Ligand 2b. 3,5-Difluoroaniline (1.29 g, 10 mmol) was dissolved in 10 mL of 1 M aqueous HCl. To this solution was slowly added $NaNO_2$ (690 mg, 10 mmol) in water (10 mL) at 0 °C, and the mixture was stirred for 1 h. To the resulting yellow suspension was added a solution of 2,4-di-*tert*-butylphenol (2.06 g, 10 mmol) and NaOH (400 mg, 10 mmol) in MeOH (10 mL) and water (10 mL) dropwise at 0 °C, and the mixture was stirred at room temperature for 15 h. The red precipitate was filtered, washed with 100 mL of water and 100 mL of MeOH, and dried under vacuum. A 1.63 g amount (48%, 4.8 mmol) of brown solid **2b** was obtained. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.29 (br s, 1H), 7.77 (d, J = 3 Hz, 1H), 7.50 (d, J = 2 Hz, 1H), 7.49−7.41 (m, 2H), 6.92 (tt, J = 9 Hz, 2 Hz, 1H), 1.46 (s, 9H), 1.38 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.6 (dd, $^1J_{CF}$ = 248 Hz, $^3J_{CF}$ = 14 Hz), 152.8 (t, $^3J_{CF}$ = 10 Hz), 150.8, 142.1, 138.3, 137.1, 130.0 (CH), 128.0 (CH), 105.5 (m, CH), 35.5, 34.5, 31.5 (CH_3), 29.6 (CH_3). ^{19}F NMR (282 MHz, $CDCl_3$): δ 163.6 (t, J_{HF} = 8 Hz). HRMS (ESI$^-$): 345.1776, calcd for $C_{20}H_{23}F_2N_2O$ (M − H) 345.1779.

Preparation of Titanium Complex 3a. To a solution of ligand **2a** (620 mg, 2 mmol) in THF (10 mL) was added NaH (96 mg, 4 mmol) in small portions. The resulting purple solution was stirred at room temperature for 15 min and added dropwise at −30 °C to a solution of $TiCl_4$ (0.11 mL, 1 mmol) in hexanes (5 mL). The resulting brown solution was stirred at room temperature for 15 h. The solvent was evaporated in vacuo, and the remaining brown solid was dissolved in 10 mL of CH_2Cl_2. The solution was stirred for 10 min, filtered, and evaporated. The remaining solid was washed three times with 2 mL of cold pentane. The solid was dried in vacuo, and 533 mg (72%, 0.72 mmol) of brown powder was obtained. Crystals for X-ray structure analysis were grown by slow evaporation of a CH_2Cl_2 solution. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 (br, 2H), 7.24 (br, 2H), 7.12 (br, 3H), 1.53 (s, 9H), 1.36 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.5, 147.8, 144.9, 143.0, 138.1, 134.2 (CH), 131.0 (CH), 129.0 (CH), 128.4 (CH), 123.2 (CH), 35.7, 34.6, 31.3 (CH_3), 30.0 (CH_3). HRMS (ESI$^+$): 701.3102, calcd for $C_{40}H_{50}ClN_4O_2Ti$ (M − Cl) 701.3102. Anal. Calcd for $C_{40}H_{50}Cl_2N_4O_2Ti$: C, 65.13; H, 6.83; N, 7.60. Found: C, 64.76; H, 6.79; N, 7.53.

Preparation of Titanium Complex 3b. To a solution of ligand **2b** (693 mg, 2 mmol) in THF (10 mL) was added NaH (96 mg, 4 mmol) in small portions. The resulting purple solution was stirred at room temperature for 15 min and then added dropwise at −30 °C to a solution of $TiCl_4$ (0.11 mL, 1 mmol) in hexanes (5 mL), and the resulting brown solution was stirred at room temperature for 15 h. The solvent was evaporated in vacuo, and the remaining brown solid was dissolved in 10 mL of CH_2Cl_2. The solution was stirred for 10 min, filtered, and evaporated. The remaining solid was washed three times with 2 mL of cold pentane. The solid was dried in vacuo, and 584 mg (72%, 0.72 mmol) of brown powder was obtained. Crystals for X-ray structure analysis were grown by slow evaporation of a CH_2Cl_2 solution. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (br, 1H), 7.63 (br, 1H), 6.80 (br, 2H), 6.56 (br, 1H), 1.56 (s, 9H), 1.36 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.2 ($^1J_{CF}$ = 13 Hz, $^3J_{CF}$ = 249 Hz), 156.0, 148.1, 146.0, 143.2, 138.6, 135.8 (CH), 131.1 (CH), 107.6 (CH, $^2J_{CF}$ = 24 Hz), 104.2 (CH, $^2J_{CF}$ = 24 Hz), 35.7, 34.7, 31.1 (CH_3), 30.0 (CH_3). ^{19}F NMR (282 MHz, $CDCl_3$): δ −107.1 (br) HRMS (ESI$^-$) in MeOH: 839.2615, calcd for $C_{41}H_{49}Cl_2F_4N_4O_3Ti$ ([M + MeO]$^-$) 839.2597.

Polymerization of Styrene Catalyzed by 3/DMAO. To a solution of **3a**,**b** (10 μmol) in toluene (1.5 mL) was added DMAO in toluene (0.76 mL, 2.3 mmol as Al) dropwise, and the mixture was stirred for 10 min at room temperature. To the reddish purple solution was added styrene (5.0 mL, 43.5 mmol), and this mixture was stirred at 60 °C for the appropriate time. The reaction mixture was poured into MeOH (50 mL) containing concentrated HCl (0.5 mL). The precipitated polymer was filtered, washed with MeOH, and dried. The obtained colorless solid was extracted with boiling methyl ethyl ketone (5 mL) to get rid of atactic polystyrene. The solid was filtered and dried overnight to a constant weight. The activity of **3a**,**b** was calculated from the yield of remaining polymer (12 and 21 mg, respectively). The isotactic/syndiotactic polymer ratio was analyzed by ^{1}H NMR.

X-ray Crystallography. Crystals were transferred to the respective diffractometers and cooled to 100 K by a stream of cold N_2 gas. In order to increase the signal to noise ratio for the diffracted intensities, a data collection strategy involving ψ scans and multiple ω scans at different ψ values and constant φ was employed. The resulting high-redundancy intensity data were averaged using the programs SADABS (Sheldrick/Bruker-AXS, 2005) and SCALEPACK (Otwinowski, 1997). $R_{int} = \sum|F_o^2 - F_o^2(\text{mean})|/\sum[F_o^2]$, R1 $= \sum||F_o| - |F_c||/\sum|F_o|$ and wR2 $= \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. Structures were solved using direct methods (SHELXS-97) and refined by least-squares (SHELXL-97) on F_o^2 (both programs from G. Sheldrick, University of Göttingen, 1997).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files, tables, and figures giving details of the X-ray structures and characterization data of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: sh@chemie.hu-berlin.de.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Generous support by the German Research Foundation (DFG via SPP 1179 and SFB 658) and JSPS research fellowships for young scientists are gratefully acknowledged. BASF AG, Bayer Industry Services, and Sasol Germany are thanked for generous donations of chemicals.

REFERENCES

(1) Coates, G. W.; Waymouth, R. M. *Science* **1995**, *267*, 217.

(2) Po, R.; Spera, S. *Polym. J.* **2010**, *42*, 416.

(3) Harney, M. B.; Zhang, Y.; Sita, L. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 2400.

(4) (a) Cai, Z.; Nakayma, Y.; Shiono, T. *Macromol. Res.* **2010**, *18*, 737. (b) Cai, Z.; Nakayma, Y.; Shiono, T. *Macromolcules* **2008**, *41*, 6596. (c) Cai, Z.; Nakayma, Y.; Shiono, T. *Kinet. Catal.* **2006**, *47*, 274. (d) Nishii, K.; Matsumae, T.; Dare, E. O.; Shiono, T.; Ikeda, T. *Macromol. Rapid Commun.* **2004**, *25*, 1029.

(5) For a recent review, see: Stoll, R. S.; Hecht, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 5054.

(6) Landon, S. J.; Shulman, P. M.; Geoffrey, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 6739.

(7) (a) Karlen, T.; Ludi, A.; Mühlebach, A.; Bernhard, P.; Pharisa, C. *J. Polym. Sci., Part A* **1995**, *33*, 1665. (b) Stumpf, A. W.; Saive, E.; Demonceau, A.; Noels, A. F. *J. Chem. Soc., Chem. Commun.* **1995**, 1127. (c) Hafner, A.; Mühlebach, A.; van der Schaaf, P. A. *Angew. Chem., Int. Ed.* **1997**, *36*, 2121. (d) Delaude, L.; Szypa, M.; Demonccau, A.; Noels, A. F. *Adv. Synth. Catal.* **2002**, *344*, 749. (e) Wang, D.; Wurst, K.; Knolle, W.; Decker, U.; Prager, L.; Naumov, S.; Buchmeiser, M. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 3267. (f) Keitz, B. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **2009**, *131*, 2038.

(8) For reviews of group 4 phenoxyimine catalysts, see: (a) Makio, H.; Fujita, T. *Acc. Chem. Res.* **2009**, *42*, 1532. (b) Makio, H.; Terao, H.; Iwashita, A.; Fujita, T. *Chem. Rev.* **2011**, *111*, 2363.

(9) For a notable yet not related exception, see: Ludwig, E.; Hefele, H.; Schilde, U.; Uhlemann, E. *Z. Anorg. Allg. Chem.* **1994**, *620*, 346.

(10) (a) Ueno, K. *J. Am. Chem. Soc.* **1957**, *79*, 3066. (b) Mahapatra, A. K.; Bandyopadhyay, D.; Bandyopadhyay, P.; Chakravorty, A. *Inorg. Chem.* **1986**, *25*, 2214. (c) Schröder, D. L.; Keim, W.; Zuideveld, M. A.; Mecking, S. *Macromolecules* **2002**, *35*, 6071. (d) Groux, L. F.; Weiss, T.; Reddy, D. N.; Chase, P. A.; Piers, W. E.; Ziegler, T.; Parvez, M.; Benet-Buchholz, J. *J. Am. Chem. Soc.* **2005**, *127*, 1854. (e) Kogan, V. A.; Lyubchenko, S. N.; Shcherbakov, I. N.; Ionov, A. M.; Tkachev, V. V.; Shilov, G. V.; Aldoshin, S. M. *Russ. J. Coord. Chem.* **2005**, *31*, 533. (f) Yoshino, J.; Furuta, A.; Kambe, T.; Itoi, H.; Kano, N.; Kawashima, T.; Ito, Y.; Asashima, M. *Chem. Eur. J.* **2010**, *16*, 5026.

(11) Basuli, F.; Peng, S.-M.; Bhattacharya, S. *Polyhedron* **1998**, *18*, 391.

(12) Tuian, J.; Hustad, P. D.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 5134.

(13) Michiue, K.; Onda, M.; Tanaka, H.; Makio, H.; Mitani, M.; Fujita, T. *Macromolecules* **2008**, *41*, 6289.

(14) Makio, H.; Fujita, T. *Macromol. Symp.* **2004**, *213*, 221.

(15) Wu, L. P.; Suenaga, Y.; Kuroda-Sowa, T.; Maekawa, M.; Furuichi, K.; Munakata, M. *Inorg. Chim. Acta* **1996**, *248*, 147.

(16) Ghose, B. N.; Lasisi, X. M. *Synth. React. Inorg. Met.-Org. Chem.* **1986**, *16*, 1121.