Preparation and Characterization of Half-Sandwich (Pentamethylcyclopentadienyl)(triflato)titanium(IV) Complexes: Solid-State Structural Motifs and Catalysis Studies

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Dedicated to Professor *Dieter Seebach* on the occasion of his 65th birthday in recognition of his seminal contributions to synthetic organic chemistry

Half-sandwich (pentamethylcyclopentadienyl)(triflato)titanium(IV) complexes of the type [Ti(Cp*)-(TfO)$_2$X] (X = MeO (**1**), Me (**2**), 2,4,6-Me$_3$C$_6$H$_2$O (**5**)) or [Ti(Cp*)(*o*-OC$_6$H$_4$O)(TfO)] (**7**) were readily synthesized *via* methathesis of the corresponding chloride complexes with silver triflate (Cp* = (η^5-1,2,3,4,5-pentamethylcyclopenta-2,4-dien-1-yl)). In addition, the complex **3** with X = OH was prepared by controlled hydrolysis of **2**. The solid-state structures of these new complexes were determined by single-crystal X-ray-diffraction techniques. Three different structural motifs were identified; **1**, **2**, **3**, and **7** are dimeric, while **5** is monomeric. The complexes were screened for their ability to stereospecifically polymerize styrene under homogeneous conditions. In the absence of activators, such as MAO (methylaluminoxane), **1** and **2** readily catalyzed the formation of atactic polystyrene; a strong dependence on the steric size of X was noted. In the presence of MAO, all of the complexes showed high activity and strong preference for the synthesis of syndiotactic polystyrene that was superior to that of [TiCl$_3$(Cp*)]/MAO.

1. Introduction. – The catalytic polymerization of α-olefins by homogeneous early transition metal complex/cocatalyst systems has enjoyed a renaissance and is an area of burgeoning research [1]^1). Current evidence points to the formation of cationic complexes or tight ion pairs as the catalytically relevant species [3]. *Marks* and co-workers [4], among others [5], have elegantly demonstrated how the complex interplay between the nature of the metal ion, the identity of the alkyl and ancillary ligands, and the choice of cocatalyst affect the efficacy of the polymerization catalyst.

While the use of half-sandwich (cyclopentadienyl) and (indenyl)titanium(IV) complexes with chloro, alkoxo, aryloxo, and alkyl ligands for the stereoregular polymerization of styrene [6] and other α-olefins [7] [8] has been well-studied, there are relatively few reports dealing with analogues containing the weakly coordinating triflato (CF$_3$SO$_3^-$ = TfO = (trifluoromethanesulfonato-κO)) ligand [7a] [7b] [9]. In a preliminary communication, we reported that half-sandwich (η^5-1,2,3,4,5-pentamethylcyclopenta-2,4-dien-1-yl) (triflato) titanium(IV) complexes [Ti(Cp*)(TfO)$_2$X] show excellent promise for the syndiotactic polymerization of styrene in the presence of methylaluminoxane (MAO) [9]. In this paper, we describe in detail the synthesis, structural characterization, and catalytic studies of these novel compounds.

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^{1}) Entire issues of periodicals have been devoted to current reports in this area of research [2].

2. Results and Discussion. – *Synthesis and NMR Spectroscopic Characterization of the Triflato Complexes.* Complexes **1**, **2**, **5**, and **7** could be prepared in modest to excellent yields by treatment of $[TiCl_2(Cp^*)X]$ (X = MeO (for **1**), Me (for **2**), 2,4,6-$Me_3C_6H_2O$ (for **5**)) or of $[TiCl(Cp^*)(o\text{-}OC_6H_4O)]$ (for **7**) with AgOTf in Et_2O with protection from ambient light (*Scheme*, *a*). The reactions were generally fast and were accompanied by precipitation of AgCl. Spectroscopically pure product was obtained after filtration and concentration. Complex **3** was obtained by controlled hydrolysis of methyl complex **2** (*Scheme*, *b*). We note that $[Ti(Cp^*)(2,6\text{-}{}^iPr_2C_6H_3O)(TfO)_2]$ has been synthesized similarly by reaction of AgOTf with $[TiCl_2(Cp^*)(2,6\text{-}{}^iPr_2C_6H_3O]$ in CH_2Cl_2 [7a,b].

Scheme. *Preparation of the Titanium Triflate Complexes*

a) $$[TiCl_n(Cp^*)X] + n\,AgOTf \xrightarrow{Et_2O} [Ti(Cp^*)(OTf)_nX] + n\,AgCl$$

1 $n = 2$, X = MeO
2 $n = 2$, X = Me
5 $n = 2$, X = 2,4,6-$Me_3C_6H_2O$
7 $n = 1$, X = o-C_6H_4O

b) $$\mathbf{2} + H_2O \xrightarrow{Et_2O} \underset{\mathbf{3}}{[Ti(Cp^*)(OH)(OTf)_2]} + CH_4$$

The new complexes were moisture-sensitive, but generally thermally stable. The methyl complex **2** showed some decomposition during X-ray data collection. ^{19}F-NMR Spectra of the bis-triflato complexes **1**, **2**, and **5** in $CDCl_3$ solution showed only one resonance for the triflato ligands, even though the solid-state structures of **1** and **2** are dimeric, with inequivalent terminal and bridging triflato ligands (*vide infra*). Apparently, there is a rapid dynamic exchange involving terminal and bridging sites, perhaps through an equilibrium between monomeric and dimeric structures for **1** and **2** in $CDCl_3$ solution. On the other hand, the ^{19}F-NMR spectrum of **3** contained two resonances, assigned to bridging and terminal triflato ligands, in accord with its solid-state structure (*vide infra*). The significantly lower solubility of **3** in $CDCl_3$ is consistent with a maintenance of the dimeric structure in solution.

The ^1H- and ^{13}C-NMR spectra of the triflato complexes were generally unexceptional. A single $^{13}CF_3$ resonance for the triflato ligands of **1**, **2**, **5**, and **7** was observed (*q* at 119–120 ppm $^1J(C,F) = 316$ Hz). No triflato signal was detectable in the ^{13}C-NMR spectrum of **3**; this result is not surprising, due to the low solubility of **3**, coupled with the inequivalence of the TfO ligands in a dimeric structure. Notably, the $^{13}CH_3$-Ti resonance for **2** (98.0 ppm) was shifted significantly downfield from that for $[TiCl_2(Cp^*)(Me)]$ (79.3 ppm). A similar but smaller downfield shift was observed for the $^{13}CH_3O$-Ti resonance of **1** (70.1 ppm) *vs.* that of $[TiCl_2(Cp^*)(MeO)]$ (67.1 ppm). These deshielding effects may be attributed to the strong electron withdrawal by the TfO ligands.

Structural Studies. The solid-state structures of **1** and **2** are of a similar structural type in that both are crystallographically enforced centrosymmetric dimers,

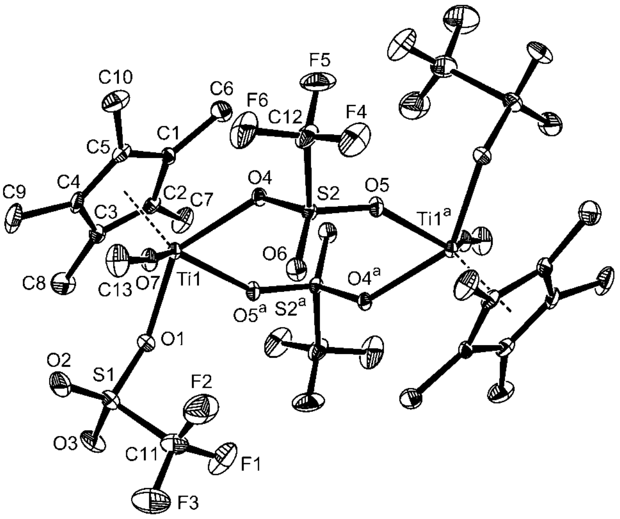

Fig. 1. *Molecular structure and atom-numbering scheme for* **1**. Atoms labeled with 'a' are related to unlabeled atoms by the transformation $(1.5-x, 0.5-y, -z)$. The molecular structure and atom-numbering scheme for **2** are essentially the same, except that the MeO ligand of **1** (O(7) and C(13)) is replaced with a Me ligand (C(13)) directly bonded to Ti(1). H-Atoms on the Cp* ligand are omitted for clarity.

$[\mathrm{Ti(Cp^*)(TfO)(\mu\text{-}TfO)X}]_2$, where X = MeO (**1**) and Me (**2**) (*Fig. 1*). Each Ti-center is pseudo-five-coordinate, including two (μ-TfO-κO:$\kappa O'$) interactions and one terminal TfO′-κO ligand. The coordination spheres are completed with an η^5-Cp* ligand and a monodentate ligand (MeO for **1**; Me for **2**) to give an approximate four-legged piano-stool geometry about each Ti-atom.

Selected bond lengths and angles for the coordination sphere of **1** are collected in *Table 1*. For **1**, the atoms O(1), O(4), O(5a), and O(7) are coplanar to ±0.073 Å, with the Ti-atom 0.72 Å above this plane towards the Cp* ring. The distance between Ti-atoms in the dimer is 5.678(2) Å. The two (μ-TfO-κO:$\kappa O'$) ligands, along with the two Ti-atoms in the dimer, form an eight-membered ring with a chair conformation (*Fig. 1*). The Ti−O bond lengths to the bridging ligands are very nearly the same. By contrast, the only other structurally characterized Ti-complex with two bridging TfO ligands, $[\mathrm{Ti_2(^{t}BuO)_2(\mu\text{-}O)(\mu\text{-}TfO)_2(H_2O)_2}]$ [10], has unsymmetrical bonding interactions, with Ti−(μ-TfO) bond lengths of 2.059(4) and 2.225(4) Å. Curiously, the average of these two bond lengths for the latter nonmetallocene complex is approximately the value observed for the Ti−(μ-TfO) bond lengths in **1**.

The Ti-to-ring-centroid distance for **1** is within the usual range observed for mono(Cp*)titanium complexes [7a][11][12]. Likewise, the Ti−O bond length for the TfO-κO ligand is quite typical for (triflato)titanium interactions in a variety of metallocene and nonmetallocene complexes [10][13–20]. The remainder of the structural features for the TfO-κO ligands resemble those reported for the free anion [21]. The S(1)−O(2) and S(1)−O(3) bond lengths of 1.415(6) and 1.420(6) Å are comparable to the mean distance of 1.43 Å for the three S−O bonds of the free anion.

Table 1. *Selected Bond Lengths* [Å] *and Angles* [°] *for* **1** *and* **2**

	1	**2**		**1**	**2**
Ti(1)···centroid[a])	2.042(6)	2.026(12)	Ti(1)−X[b])	1.734(4)	2.085(14)
Ti(1)−O(1)	2.039(4)	1.991(8)	Ti(1)−O(5a)[c])	2.142(4)	2.143(9)
Ti(1)−O(4)	2.164(3)	2.081(8)			
O(1)−Ti(1)−O(4)	140.6(2)	140.9(4)	X[b])−Ti(1)−O(5a)[c])	131.2(2)	133.0(4)
O(1)−Ti(1)−X[b])	91.3(2)	86.8(5)	X[b])−Ti(1)···centroid[a])	117.4(2)	111.6(5)
O(1)−Ti(1)−O(5a)[c])	75.4(2)	80.2(4)	O(5a)−Ti(1)···centroid[a])[c])	111.4(2)	115.4(5)
O(1)−Ti(1)···centroid[a])	108.3(2)	109.7(5)	Ti(1)−O(1)−S(1)	141.4(3)	136.2(6)
O(4)−Ti(1)−X[b])	87.1(2)	85.2(4)	Ti(1)−O(4)−S(2)	130.9(2)	160.1(6)
O(4)−Ti(1)−O(5a)[c])	76.3(1)	77.8(3)	Ti(1)−O(5a)−S(2a)[c])	149.1(2)	143.0(7)
O(4)−Ti(1)···centroid[a])	107.3(2)	108.8(5)	Ti(1)−O(7)−C(13)	170.8(4)	–

[a]) Centroid refers to the ring centroid of the Cp* ligand. [b]) X is O(7) for **1** and C(13) for **2**. [c]) Symmetry transformations ($1.5-x$, $0.5-y$, $-z$) and ($2.0-x$, $-y$, $1.0-z$) for **1** and **2**, respectively.

The S(1)−O(1) distance (1.471(4) Å), involving the O-atom bonded to Ti, is slightly longer in accord with other metal complexes containing TfO-*κO* ligands [22]. The Ti−O(7) bond length for the terminal MeO ligand is within normal range for terminal alkoxytitanium interactions [23]. It is comparable to Ti−O bond lengths found for isopropoxy ligands in other triflato complexes of titanium [15] and the MeO−Ti distance in cationic $[TiBr_2(MeO)(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})]^+$ [24], but considerably shorter than terminal MeO−Ti bond distances in more electron-rich clusters [25]. The large Ti(1)−O(7)−C(13) angle of 170.8(4)° is indicative of nearly sp O-hybridization. *Van Koten* and co-workers have noted that the increase in s character for the alkoxy donor O-atom correlates well with the increased *Lewis* acidity at titanium as the number of coordinated TfO ligands is increased [16].

Since, as noted above, the structure of **2** is analogous to that of **1** with replacement of the terminal MeO ligand with a Me ligand (*Fig. 1*) and, since **2** decomposed somewhat during data collection, we will limit the discussion of this structure. Selected bond lengths and angles for the coordination sphere of **2** are collected in *Table 1*. For **2**, the atoms O(1), O(4), O(5a), and C(13) are coplanar to ±0.087 Å, with the Ti-atom 0.75 Å above this plane towards the Cp* ring. The Ti-atoms in the dimer are 5.633(4) Å distant from each other across the chair-like eight-membered ring formed by the two (*μ*-TfO-*κO*:*κO′*) ligands. While most of the bonding parameters for **2** are unexceptional and similar to those found for **1**, bonding of the Ti-atom to the bridging ligands in **2** is somewhat unsymmetrical. We note that both symmetrically and unsymmetrically bonded (*μ*-sulfonato-*κO*:*κO′*) bridging ligands have been observed for relevant earlier d-block and f-block transition-metal complexes having a doubly bridging bis-sulfonato eight-membered ring [10][26].

For **3**, which contains the small, electron-rich OH ligand, a second structural type emerges in the solid state, namely $[Ti(Cp^*)(TfO)(\mu\text{-}TfO)(\mu\text{-}OH)]_2$. The general structure of **3** is related to those found in a series of dimeric fluorotitanium(IV) complexes, $[Ti(Cp^*)F(\mu\text{-}F)(\mu\text{-}L)]_2$ ($L = CF_3CO_2$, $C_6F_5CO_2$, Ph_2PO_2, $4\text{-}MeC_6H_4SO_3$), reported by *Roesky* and co-workers [27]. For **3**, the Ti-atoms of the dimer are bridged by two OH ligands, as well as two (μ-TfO-κO:$\kappa O'$) ligands, and can be considered to be pseudo six-coordinate (*Fig. 2*). The coordination geometry is best described as distorted octahedral, with the Cp*-ring centroid and O(7) occupying axial positions on Ti(1) (see *Table 2* for selected bond lengths and bond angles). The O(1), O(4), O(5a), and O(7a) atoms, coplanar to ±0.032 Å, are bent away from the Cp* ligand; this plane is very nearly parallel to the Cp* ring (dihedral angle of 2.9(2)°). The Ti-atom is 0.48 Å above this plane towards Cp* and is somewhat more distant on average from this ligand than was found for **1** and **2**.

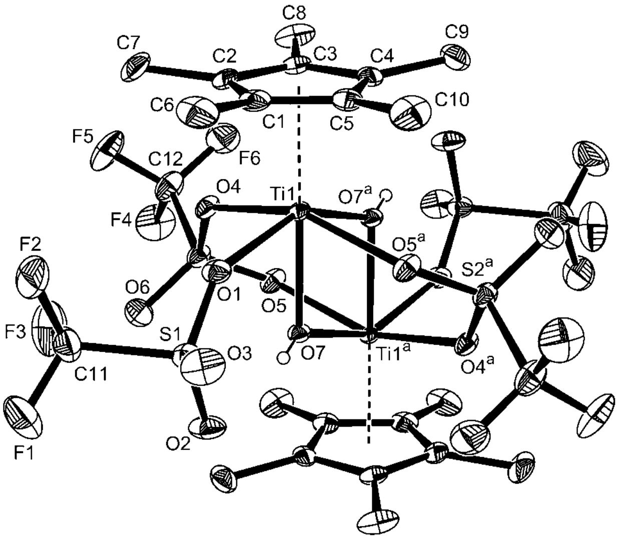

Fig. 2. *Molecular structure and atom-numbering scheme for* **3**. Atoms labeled with 'a' are related to unlabeled atoms by the transformation ($-x$, $-y$, $2.0-z$). H-atoms are omitted for clarity.

The two interlocking rings formed by the bridging ligands bring the Ti-atoms of **3** much closer together at 3.277(1) Å than was found in dimeric **1** and **2**. The eight-membered ring involving the bridging TfO ligands adopts a very flattened chair conformation with nearly symmetrical bonding to Ti. On the other hand, the four-membered ring involving the bridging OH ligands is rhomboidal, with one short and one long Ti–(μ-OH) bond. The Ti–(μ-OH) bonds are longer than terminal Ti–OH bonds (typically 1.85–1.88 Å) [28], but bracket the values found for the bridging OH ligands in $[Ti_3(Cp)_3(\mu\text{-}HCOO)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$ [29], and are at the limits of the range found for typical Ti–(μ-alkoxy) bonds (1.91–2.12 Å) [25b][30]. The Ti–(TfO-κO) bond is somewhat longer than those found in **1** and **2**, but still within normal range [10][13–20]; other structural features of the terminal triflato ligand are as expected, including a slightly longer S(1)–O(1) bond.

Table 2. *Selected Bond Lengths* [Å] *and Angles* [°] *for* **3**

Ti(1)···centroid a)	2.108(4)	Ti(1)–O(1)	2.071(3)
Ti(1)–O(4)	2.125(2)	Ti(1)–O(7)	2.116(3)
Ti(1)–O(5a) b)	2.145(2)	Ti(1)–O(7a)	1.911(2)
O(1)–Ti(1)···centroid a)	101.3(2)	O(1)–Ti(1)–O(4)	91.5(1)
O(1)–Ti(1)–O(7)	78.9(1)	O(1)–Ti(1)–O(5a) b)	88.4(1)
O(1)–Ti(1)–O(7a) b)	150.0(1)	O(4)–Ti(1)···centroid a)	101.5(2)
O(4)–Ti(1)–O(7)	77.7(1)	O(4)–Ti(1)–O(5a)	155.1(1)
O(4)–Ti(1)–O(7a) b)	85.2(1)	O(7)–Ti(1)···centroid a)	179.1(2)
O(7)–Ti(1)–O(5a) b)	77.8(1)	O(7)–Ti(1)–O(7a) b)	71.2(1)
O(5a)–Ti(1)···centroid a) b)	103.0(2)	O(5a)–Ti(1)–O(7a) b)	82.5(1)
O(7a)–Ti(1)···centroid a) b)	108.6(2)	Ti(1)–O(1)–S(1)	147.4(2)
Ti(1)–O(4)–S(2)	129.8(2)	Ti(1)–O(7)–Ti(1a) b)	108.8(1)
Ti(1)–O(5a)–S(2a) b)	125.9(1)	O(4)–S(2)–O(5)	113.0(1)

a) Centroid refers to the ring centroid of the Cp* ligand. b) Symmetry transformation ($-x$, $-y$, $2.0-z$).

For **5**, a third structural type emerges, namely monomeric [Ti(Cp*)(2,4,6-$Me_3C_6H_2O$)$(TfO)_2$]. For comparison, we also crystallized [$TiCl_2$(Cp*)(2,4,6-$Me_3C_6H_2O$)] (**4**). Both **4** and **5** are pseudo-four-coordinate, three-legged-piano-stool complexes (*Figs. 3* and *4*). The plane defined by the basal atoms Cl(1), Cl(2), and O(1) in **4** is nearly parallel to the Cp* best plane (dihedral angle 2.5(1)°), while the benzene ring of the phenolato ligand is nearly parallel to both of these planes (dihedral angle 9.4(1)° to the former, 6.9(1)° to the latter plane). The bonding parameters for **4** (*Table 3*) are, not surprisingly, almost identical to those for [$TiCl_2$(Cp*)(2,4-$Me_2C_6H_3O$)] [11] and are comparable to those observed in similar [$TiCl_2$(Cp^R)(ArO)] complexes (Cp^R = Cp or Cp*; ArO = a general phenolato ligand) [7a][12].

Table 3. *Selected Bond Lengths* [Å] *and Angles* [°] *for* **4**

Ti(1)···centroid a)	2.030(7)	Ti(1)–Cl(1)	2.262(2)
Ti(1)–Cl(2)	2.269(2)	Ti(1)–O(1)	1.781(4)
Cl(1)–Ti(1)···centroid a)	113.4(2)	Cl(1)–Ti(1)–Cl(2)	103.2(1)
Cl(1)–Ti(1)–O(1)	102.0(1)	Cl(2)–Ti(1)···centroid a)	114.4(2)
Cl(2)–Ti(1)–O(1)	101.6(1)	O(1)–Ti(1)···centroid a)	120.1(3)
Ti(1)–O(1)–C(11)	162.1(4)		

a) Centroid refers to the ring centroid of the Cp* ligand.

The structure of **5** bears many similarities to that of **4**, even though the triflato ligands are sterically larger than chloro ligands. Apparently, the phenolato ligand in **5**, substituted at the 2- and 6-positions, is sterically encumbered enough to prevent bridging either by triflato ligands or by the phenolato O-atom. The plane defined by the atoms O(1), O(4), and O(7) is essentially parallel to the Cp* best plane (dihedral angle 0.5(3)°); the benzene ring of the phenolato ligand makes a dihedral angle of 14.2(3)° to

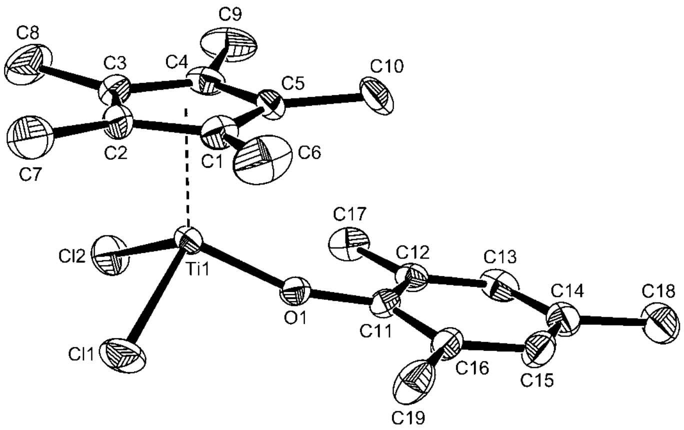

Fig. 3. *Molecular structure and atom-numbering scheme for* **4**. H-atoms are omitted for clarity.

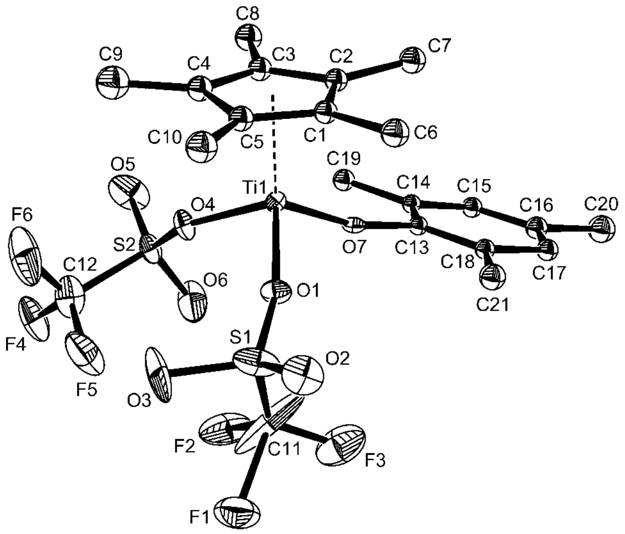

Fig. 4. *Molecular structure and atom-numbering scheme for* **5**. H-atoms are omitted for clarity.

each of these two planes. The crystals of **5** were of only fair quality and there is slight disorder in one of the triflato ligands that could not be modeled adequately; to the extent that the larger standard deviations allow, we can say that bonding parameters within the coordination sphere (*Table 4*) are in the expected ranges, with the possible exception of the Ti–(TfO-κO) bond lengths. The terminal Ti–(TfO-κO) bonds have nearly identical values of *ca.* 1.94(1) Å and are significantly shorter than those observed for other Ti–(TfO-κO) bonds in the present study and for related Ti-complexes [10] [13–20]. We note that the Ti–O–S angles in **5** are quite obtuse, perhaps signifying a greater π-bonding interaction to the Ti-center.

Table 4. *Selected Bond Lengths* [Å] *and Angles* [°] *for* **5**

Ti(1)···centroid[a])	2.003(11)	Ti(1)−O(1)	1.938(11)
Ti(1)−O(4)	1.940(9)	Ti(1)−O(7)	1.779(9)
O(1)−Ti(1)···centroid[a])	114.2(7)	O(1)−Ti(1)−O(4)	100.2(4)
O(1)−Ti(1)−O(7)	102.1(4)	O(4)−Ti(1)···centroid[a])	113.1(7)
O(4)−Ti(1)−O(7)	105.9(4)	O(7)−Ti(1)···centroid[a])	119.1(7)
Ti(1)−O(1)−S(1)	167.1(7)	Ti(1)−O(4)−S(2)	151.6(7)
Ti(1)−O(7)−C(13)	165.5(7)		

[a]) Centroid refers to the ring centroid of the Cp* ligand.

Complex **7** is of a different sort, in that only one triflato ligand per Ti-atom is required to satisfy charge considerations because of the presence of the dianionic catecholato (=benzene-1,2-diolato) ligand. Crystals of a Et_2O solvate of **7** revealed that the organometallic portion of the unit-cell consists of centrosymmetric dimers of formula $[Ti(Cp^*)\{\mu\text{-}(o\text{-}OC_6H_4O\text{-}\kappa O^1{:}\kappa O^1,\kappa O^2)\}(TfO)]_2$ (*Fig. 5*). The Ti-centers are pseudo-five-coordinate; the geometry is best described as distorted four-legged piano stool about each Ti-atom (*Table 5*).

Table 5. *Selected Bond Lengths* [Å] *and Angles* [°] *for* **7** · Et_2O

Ti(1)···centroid[a])	2.053(3)	Ti(1)−O(1)	2.077(3)
Ti(1)−O(2)	1.888(3)	Ti(1)−O(3)	2.040(3)
Ti(1)−O(1a)	2.024(3)		
O(1)−Ti(1)···centroid[a])	110.8(1)	O(1)−Ti(1)−O(2)	77.8(1)
O(1)−Ti(1)−O(3)	139.1(1)	O(1)−Ti(1)−O(1a)	71.5(1)
O(2)−Ti(1)···centroid[a])	112.5(1)	O(2)−Ti(1)−O(3)	87.8(1)
O(2)−Ti(1)−O(1a)	127.6(1)	O(3)−Ti(1)···centroid[a])	110.1(1)
O(3)−Ti(1)−O(1a)	88.6(1)	O(1a)−Ti(1)···centroid[a])	117.7(1)
Ti(1)−O(1)−Ti(1a)	108.5(1)	Ti(1)−O(1)−C(11)	111.5(2)
Ti(1)−O(2)−C(16)	118.2(2)	Ti(1)−O(3)−S(1)	137.0(2)

[a]) Centroid refers to the ring centroid of the Cp* ligand. [b]) Symmetry transformation (2.0 − *x*, − *y*, 1.0 − *z*).

Interestingly, the catecholato ligands act as chelate ligands, while one donor O-atom from each catecholato ligand also provides a bridging interaction with the other Ti atom of the dimer. The four-membered ring involving the bridges is nearly a rhombus, with bond lengths similar to those found for the anionic dimer $[Ti(dtbc)_2(Hdtbc)]_2^{2-}$ [31], where H_2dtbc is 3,5-di(*tert*-butyl)catechol, and a nearly identical distance between Ti atoms (3.328(2) Å for **7** *vs.* 3.326(1) Å for the dianionic complex). The catecholato chelate ring in **7** is unsymmetrical due to the bridging interaction at O(1). The Ti(1)−O(2) bond length is somewhat shorter than previously observed for terminal titanium−catecholato bonds [31], probably due to the poorly electron-donating triflato ligand; it is nearly 0.2 Å shorter than Ti(1)−O(1). The Ti−(TfO-*κO*) bond length, as well as the remainder of the structural features of the terminal triflato ligand, are comparable to other complexes in this study and in the literature [10][13–20].

Catalysis Studies. Our principal focus on the catalytic activity of these half-sandwich (triflato)titanium complexes was their ability to promote the syndiotactic polymer-

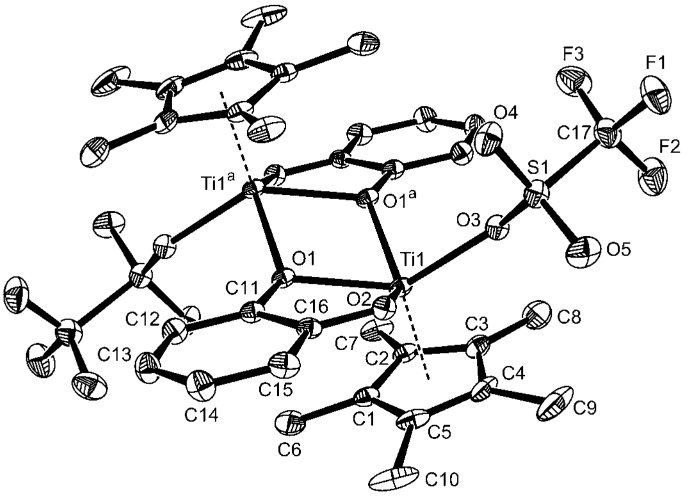

Fig. 5. *Molecular structure and atom-numbering scheme for* **7**. Atoms labeled with 'a' are related to unlabeled atoms by the transformation $(2.0-x, -y, 1.0-z)$. H-atoms are omitted for clarity.

ization of styrene. One of our major objectives was to prepare complexes for which an activator, such as methylaluminoxane (MAO), would not be required to obtain this result. Studies to estimate an appropriate complex/styrene ratio were effected at room temperature with the methyl-ligated derivative **2**. No polymer was obtained for reactions in which the complex concentration was less than 0.20 mol-%. While a very small amount of polystyrene (PS) was obtained at 0.20 mol-%, we found that a concentration of 0.40 mol-% was satisfactory for producing sufficient polymer for further tests. Activity for the catalysts was determined as the weight in grams of polystyrene obtained (g PS) divided by the product (mol of Ti catalyst) · (mol of styrene) · (time in h) [32]. We note that comparison of polymerization results from different research groups is usually not practical, due to differences in polymerization conditions. Complex **2** was also utilized to optimize reaction temperature. At a Ti-complex concentration of 0.40 mol-%, we observed that polymerization activity increased up to 50° and decreased at higher temperatures, presumably due to catalyst decomposition or deactivation of catalyst sites [32d]. The relative mol mass of the PS, as determined from viscosity measurements, decreased at higher temperatures, suggesting that chain-transfer reactions were becoming more important.

Results of polymerization of styrene by the (triflato)titanium complexes in the absence of MAO are collected in *Table 6*. The results clearly indicate a remarkable effect of increasing steric bulk on polymerization activity. The 2,4,6-trimethylphenolato-ligated derivative **5** gave essentially no polymer product, even at 0.80 mol-% concentration. The OH-ligated derivative **3** also showed poor activity; this result can be explained by the *retention* of a dimeric structure in solution in the absence of an activator, in accord with the ^{19}F-NMR spectrum of **3** (*vide supra*). Presumably, the catalytic activities of **1** and **2** can be attributed to the probable presence of monomer (in equilibrium with dimer) in solution, as indicated by the presence of only one ^{19}F-NMR signal (*vide supra*). Unfortunately, extraction with butan-2-one indicated that only *atactic* PS (APS) was produced in all cases, so we turned our attentions to polymerizations in the presence of MAO.

Table 6. *Polymerization of Styrene by Titanium Complexes* **1**–**3** *and* **5** *without MAO*

	Activity[a]) · 10^5
1	0.82[b])
2	0.44[b])
3	0.054[b])
5	0[c])

[a]) Activity = (g PS)/(mol Ti complex)(mol styrene)(h). [b]) 0.40 mol-% of Ti-complex rel. to monomer, 50°, 3 h. [c]) 0.80 mol-% of Ti-complex rel. to monomer, 50°, 3 h

Polymerization conditions with MAO were adapted from reported procedures [33], as well as from our own studies on the effect of time on activity of the catalysts. The latter studies were performed with the MeO- and Me-ligated complexes **1** and **2**, respectively. Activity generally decreased at longer times, presumably due to deactivation of active centers and/or occlusion of catalyst sites in the precipitating polymer. The optimum reaction time for comparisons was determined to be 2 h; subsequent polymerizations with all of the (triflato)titanium complexes in the presence of MAO were then performed over 2-h time periods.

Results for the polymerization runs are summarized in *Table 7*. For comparison purposes, polymerizations utilizing [$TiCl_3(Cp^*)$] (**8**) and [$TiCl_2(Cp)_2$] (**9**) are included. The combination of the (triflato)titanium complexes with MAO produced largely syndiotactic polystyrene (SPS), as determined by the butan-2-one extraction method. NMR Spectra of the butan-2-one-insoluble fractions displayed the characteristic *quint.* and *t* resonances at 1.9 and 1.4 ppm, respectively, in the ^1H-NMR spectrum [34], with the resonance of the *rrrr* pentad of the *ipso*-C-atom of the benzene ring appearing at 145.1 ppm in the ^{13}C-NMR spectrum.

Table 7. *Polymerization of Styrene with Titanium Complexes* **1**–**3**, **5**, *and* **7**–**9** *in the Presence of MAO*[a])

	% SPS[b])	Activity[c]) · 10^5	T_m[d])	M_r[e]) · 10^5
1	95.9	5.32	263	1.60
2	96.1	5.29	263	1.68
3	95.8	7.29	267	1.96
5	94.7	5.00	263	1.96
7	94.5	3.80	261	1.36
8	89.6	1.69	263	0.84
9	52.3	0.25	246	0.094

[a]) Styrene/MAO/Ti complex 6000 : 500 : 1. [b]) Butan-2-one-insoluble fraction. [c]) Activity = (g PS)/(mol Ti complex)(mol styrene)(h). [d]) Melting point T_m [°] by differential-scanning-calorimetry (DSC) measurement. [e]) Relative molar mass M_r by gel-permeation-chromatography (GPC) measurement.

The triflato catalysts showed a 5–7% improvement in stereoselectivity over the chloro complex **8** and marked superiority over titanocene **9**. Interestingly, stereoselectivity within the series of triflato complexes was not appreciably affected by the nature of the ancillary ligands. The activity of **7** was somewhat less than the other (triflato)titanium complexes, perhaps because it is somewhat less *Lewis* acidic (only one triflato ligand per Ti-atom) or because the dimer structure persists in the presence of MAO. Melting points of the isolated, butan-2-one-insoluble polymers generated by our triflato catalysts were generally found to be *ca.* 260°, which are consistent with those reported for SPS [32][34]. The lower melting point observed for the polymer obtained in the presence of **9**/MAO could be an indication of a loss of stereocontrol in that polymerization.

3. Conclusions. – Half-sandwich (pentamethylcyclopentadienyl)(triflato) titanium(IV) complexes of the type [Ti(Cp*)(TfO)$_2$X] (X = MeO (**1**), Me (**2**), 2,4,6-Me$_3$C$_6$H$_2$O (**5**)) or [Ti(Cp*)(*o*-OC$_6$H$_4$O)(TfO)] (**7**) are readily prepared *via* metathesis of the corresponding chloro complexes with silver triflate. In addition, the complex **3** with X = OH is readily available by controlled hydrolysis of **2**. Single-crystal X-ray-diffraction analysis of **1**–**3** and **5** reveal three different solid-state structural types for the highly *Lewis* acidic [Ti(Cp*)(TfO)$_2$X] complexes. Complexes **1** and **2** are dimeric, possessing two (μ-TfO-κO:$\kappa O'$) ligands. Complex **3** is also dimeric; however, it possesses two bridging OH ligands, as well as two (μ-TfO-κO:$\kappa O'$) ligands. Presumably the smaller OH ligand allows these additional interactions. Although **1**–**3** are dimeric in the solid-state, room-temperature ^{19}F-NMR spectroscopy suggests that the dimer structure persists only for **3** in solution and that a rapid dimer-monomer equilibrium exists for **1** and **2**. On the other hand, **5** is monomeric in the solid-state; here the sterically large 2,4,6-Me$_3$C$_6$H$_2$O$^-$ phenolato ligand prevents dimerization from occurring. Complex **7** is also dimeric, containing two [μ-(*o*-OC$_6$H$_4$O-κO^1:κO^1,κO^2)]$^{2-}$ catecholato ligands.

The triflato complexes were examined for catalytic activity in the syndiospecific polymerization of styrene. In the absence of activators, [Ti(Cp*)(TfO)$_2$X] produced only atactic polystyrene (APS). Marked dependences of activity on the steric size of X and the presumed availability of a monomeric structure in solution were observed. Thus, **5**, which contains the bulky 2,4,6-Me$_3$C$_6$H$_2$O$^-$ ligand, showed no catalytic activity; polymerizations with **3** were sluggish, probably due to the presence of little or no monomeric complex in solution. On the other hand, all the triflate complexes, including **7**, had excellent activity for the polymerization of styrene *in the presence* of MAO. Nearly all the PS formed was syndiotactic, as determined by NMR and IR spectroscopies and melting points. Comparisons to [TiCl$_3$(Cp*)]/MAO (**8**/MAO), a catalyst commonly used for the preparation of SPS, showed that the more highly *Lewis* acidic triflato complexes **1**–**3**, **5**, and **7** have a slightly higher (5–7%) preference for formation of SPS than **8**, and are 2.5–4.5 times more active under the conditions that we employed. In addition, the triflato complexes are vastly superior to [TiCl$_2$(Cp)$_2$]/MAO for the synthesis of SPS.

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Experimental Part

1. *General.* Unless otherwise noted, all manipulations were performed *via* standard *Schlenk*-type methods or in a N_2-filled *Vacuum-Atmospheres* glovebox with an efficient recirculating atmosphere-purification system. Solvents were purified by standard methods and freshly distilled under N_2 from either sodium/benzophenone ketyl (= oxidodiphenylmethyl) (Et_2O, THF, toluene) or sodium/benzophenone/diglyme (pentane, hexane). All reactions involving silver triflate (AgOTf; *Aldrich*) were protected from ambient light. Reagent-grade styrene was washed with 10% NaOH soln., then H_2O, dried ($MgSO_4$), and finally distilled at 25°/8 Torr and stored over CaH_2. The purified styrene was freshly distilled a second time immediately prior to use in the polymerization studies. Methylaluminoxane (MAO; $[\text{-Al(Me)O-}]_n$) was obtained from *Aldrich Chemical Co.* as a 10% soln. in toluene.

NMR Spectra: Samples (*ca.* 5–15 mg of complex/1 ml of $CDCl_3$) were prepared in the glovebox by direct addition of $CDCl_3$ to the isolated, solid Ti-complexes; $CDCl_3$ was dried over molecular sieves, degassed, and stored under N_2 in the glovebox; *Varian Gemini-300-NMR* spectrometer at 300 (^{1}H), 75.46 (^{13}C), and 282.3 MHz (^{19}F); δ(H) and δ(C) referenced to the residual signals of the $CDCl_3$ solvent (δ(H) 7.24, δ(C) 77.00; rel. to $SiMe_4$), δ(F) referenced to C_6F_6 (δ(F) −162.9, rel. to $CFCl_3$). Elemental analyses were performed by *M-H-W Laboratories* (Phoenix, AZ).

2. *Polymer Analyses.* Polymer samples were continuously extracted with butan-2-one under reflux in a *Soxhlet* extractor. Polymers were dried in a vacuum oven for 24 h at 100°/1 Torr. ^{1}H- and ^{13}C-NMR Spectra: in $CDCl_2CDCl_2$ at 100°; sample concentrations of 25–35 mg polymer/ml solvent; δ rel. to the residual signals of $CDCl_2CDCl_2$ (δ(H) 5.98, δ(C) 73.70). IR Spectra: KBr pellets, *Perkin-Elmer 18-PC-FT-IR* spectrometer; in cm^{-1}. DSC Data: *DuPont DSC-2910* instrument; 5–10 mg of sample; temp. range 25–300°; heating rate 20°/min and 40°/min for the first and second scans, resp.; melting points (T_m) from the peak maximum temp. Molecular-mass (M_r) determinations: *via* either viscosity measurements in an *Ostwald* viscometer with toluene as solvent at 25° or gel-permeation chromatography (GPC) with THF (35°) in a *Waters* instrument with DRI detector and an *Ultrastyragel* column; the M_r were determined with the Trisec software; calibration curve with a narrow molecular-mass polystyrene sample.

3. *Triflato Complexes. [Ti(Cp*)(MeO)(TfO)(μ-TfO)]₂* (**1**). A mixture of $[TiCl_2(Cp^*)(MeO)]$ [11] (0.10 g, 0.35 mmol) and AgOTf (0.18 g, 0.70 mmol) in Et_2O (25 ml) was stirred at r.t. for 1 h and then filtered through glass wool. The red-orange filtrate was concentrated to 5 ml and layered with pentane (15 ml). Cooling to −45° afforded dark red crystals of **1** (0.16 g, 86%) suitable for X-ray-diffraction studies. ^{1}H-NMR ($CDCl_3$): 4.48 (*s*, MeO); 2.30 (*s*, Me_5C_5). ^{13}C-NMR ($CDCl_3$): 137.0 (Me_5C_5), 118.8 (*q*, ^1J(C,F) = 316, CF_3); 70.1 (MeO); 12.3 (Me_5C_5). ^{19}F-NMR ($CDCl_3$): −77.17 (*s*, CF_3).

$[Ti(Cp^*)(Me)(TfO)(\mu\text{-}TfO)]_2$ (**2**). A mixture of $[TiCl_2(Cp^*)(Me)]$ [35] (0.10 g, 0.37 mmol) and AgOTf (0.19 g, 0.74 mmol) in Et_2O (25 ml) was stirred at r.t. for 1 h and then filtered through glass wool. The red filtrate was concentrated to 5 ml and layered with pentane (15 ml). Cooling to −37° afforded dark red crystals of **2** (0.13 g, 70%) suitable for X-ray-diffraction studies. ^{1}H-NMR ($CDCl_3$): 2.21 (*s*, Me_5C_5); 1.84 (*s*, Me-Ti). ^{13}C-NMR ($CDCl_3$): 137.5 (Me_5C_5); 118.8 (*q*, ^1J(C,F) = 316, CF_3); 98.0 (Me-Ti); 13.1 (Me_5C_5). ^{19}F-NMR ($CDCl_3$): −76.63 (*s*, CF_3).

$[Ti(Cp^*)(\mu\text{-}OH)(TfO)(\mu\text{-}TfO)]_2$ (**3**). A soln. of **2** (0.31 g, 0.31 mmol) in Et_2O (50 ml) was treated with a soln. of H_2O (0.010 ml, 0.61 mmol) in Et_2O (5 ml). After stirring at r.t. for 3 h, the volatiles were evaporated. The residue was washed with pentane and dried *in vacuo* to give blackish-red microcrystals of **3** (0.28 g, 90%). Single crystals suitable for X-ray-diffraction studies were obtained by layering pentane over a Et_2O soln. of **3** at −35°. ^{1}H-NMR ($CDCl_3$): 2.16 (*s*, Me_5C_5). ^{13}C-NMR ($CDCl_3$): 142.6 (Me_5C_5); 12.9 (Me_5C_5). ^{19}F-NMR ($CDCl_3$): −76.25 (*s*, TfO); −77.32 (*s*, *μ*-TfO). Anal. calc. for $C_{24}H_{32}F_{12}O_{14}S_4Ti_2$: C 28.93, H 3.24; found: C 28.77, H 3.55.

$TiCl_2(Cp^*)(2,4,6\text{-}Me_3C_6H_2O)]$ (**4**). A soln. of 2,4,6-trimethylphenol (0.24 g, 1.7 mmol) and Et_3N (0.24 ml, 1.7 mmol) in Et_2O (10 ml) was added to a stirred mixture of $[TiCl_3(Cp^*)]$ [36] (0.50 g, 1.7 mmol) in Et_2O (40 ml). The mixture was stirred at r.t. for 22 h and then filtered through glass wool. The filtrate was concentrated *in vacuo* until crystals of the product began to appear and was then cooled to 0°. Removal of the mother liquor and washing with cold hexane afforded orange-red crystals of **4** (0.30 g, 45%) suitable for X-ray-diffraction studies. ^{1}H-NMR ($CDCl_3$): 6.74 (*s*, $Me_3C_6H_2$); 2.22 (br. *s*, $Me_3C_6H_2$); 2.19 (*s*, Me_5C_5). ^{13}C-NMR ($CDCl_3$): 160.1 (C_{ipso}); 133.0 (C_p); 132.3 (Me_5C_5); 128.7 (C_m); 128.4 (C_o); 20.8 (*p*-Me); 17.2 (*o*-Me); 13.1 (Me_5C_5). Anal. calc. for $C_{19}H_{26}Cl_2OTi$: C 58.63, H 6.73; found: C 58.73, H 6.98.

$[Ti(Cp^*)(2,4,6\text{-}Me_3C_6H_2O)(TfO)_2]$ (**5**). A mixture of **4** (0.10 g, 0.25 mmol) and AgOTf (0.13 g, 0.51 mmol) in Et_2O (35 ml) was stirred at r.t. for 1 h and then filtered through glass wool. The dark red filtrate was

concentrated to 5 ml and layered with pentane (15 ml). Cooling to $-45°$ afforded dark red crystals of **5** (0.080 g, 40%) suitable for X-ray-diffraction studies. ^{1}H-NMR (CDCl$_3$): 6.82 (*s*, Me$_3$C$_6$*H*$_2$); 2.31 (*s*, *Me*$_5$C$_5$); 2.26 (*s*, *p*-Me); 2.23 (*s*, 2 *o*-Me). ^{13}C-NMR (CDCl$_3$): 161.6 (C_{ipso}); 138.6 (Me$_5$*C*$_5$); 135.2 (C_p); 129.4 (C_m); 128.9 (C_o); 118.8 (*q*, ^1J(C,F) = 316, CF$_3$); 20.9 (*p*-Me); 17.1 (*o*-Me); 12.7 (*Me*$_5$C$_5$). ^{19}F-NMR (CDCl$_3$): -76.78 (*s*, CF$_3$).

[TiCl(Cp)(*o*-OC$_6$H$_4$O)]* (**6**). Catechol (0.10 g, 0.91 mmol) was added to a soln. of [TiCl(Cp*)(Me)$_2$] [37] (0.22 g, 0.89 mmol) in Et$_2$O (55 ml). After stirring for 21 h, all volatiles were evaporated, providing dark red-orange, microcrystalline **6** (0.27 g, 92%). ^{1}H-NMR (CDCl$_3$): 7.28 (*m*, 2 H_m); 6.93 (*m*, 2 H_o); 1.82 (*s*, 1 *Me*$_5$C$_5$). ^{13}C-NMR (CDCl$_3$): 157.7 (C_{ipso}); 134.9 (Me$_5$*C*$_5$); 121.1 (C_o), 117.3 (C_m), 12.3 (*Me*$_5$C$_5$).

[Ti(Cp){μ-(*o*-OC$_6$H$_4$O-κO^1:κO^1,κO^2)}(TfO)]$_2$* (**7**). A mixture of **6** (0.079 g, 0.24 mmol) and AgOTf (0.09 g, 0.3 mmol) in Et$_2$O (40 ml) was stirred at r.t. for 1 h and then filtered through glass wool. Evaporation provided brownish-red microcrystals of **7** (0.13 g, 97%). Single crystals of **7** · Et$_2$O suitable for X-ray-diffraction studies were obtained by layering pentane over a Et$_2$O soln. of **7** at $-37°$. ^{1}H-NMR (CDCl$_3$): 7.17 (*m*, 2 H_o); 7.09 (*m*, 2 H_m); 1.79 (*s*, *Me*$_5$C$_5$). ^{13}C-NMR (CDCl$_3$): 157.3 (C_{ipso}); 138.3 (Me$_5$*C*$_5$); 122.7 (C_o); 120.0 (*q*, ^1J(C,F) = 316, CF$_3$); 117.2 (C_m); 11.9 (*Me*$_5$C$_5$). ^{19}F-NMR (CDCl$_3$): -76.85 (*s*, CF$_3$).

4. *X-Ray Crystallography.* Unless otherwise noted above, crystals suitable for X-ray-diffraction studies were obtained by layering pentane (10–15 ml) over an Et$_2$O soln. (3–5 ml) of the complex in a *Schlenk* tube. The mixture was cooled to 0° and subsequently, at a rate of $-10°$/day, to the desired temp. in an acetone bath. Temp. control of the bath was accomplished with a *Neslab Cryocool* unit. Well-formed single crystals were isolated in the glovebox and placed in quartz capillary tubes (0.7 mm diameter, 80 mm length, 1/100 mm wall thickness; *Charles Supper & Co.*). The capillary tubes were sealed temporarily with degassed silicone grease (*Dow Corning*), taken out of the glovebox, and flame-sealed with the end holding the crystal cooled in a bed of crushed dry ice.

Unit-cell parameters were determined from 20 to 25 well-centered, intense reflections in the range $15° \leq 2\theta \leq 25°$. A *Siemens(Bruker)-R3m* diffractometer in the $\omega/2\theta$ mode (for **1**, **4**, and **5**) or $\theta/2\theta$ mode (for **2**, **3**, and **7** · Et$_2$O) with variable scan speed (3–20° min^{-1}) and graphite monochromated Mo*Kα* radiation (λ 0.71073 Å) was used to collect the intensity data at r.t. No decay was observed over the course of the data collections, except for **2**. For this compound, *ca.* 20% decrease in intensity was observed during the two-day collection period, and intensities were corrected by scaling on the standards. For crystals of each compound, data were corrected for background, attenuators, *Lorentz* and polarization effects in the usual fashion, but not for absorption [38].

Structure solutions and full-matrix least-squares refinements were accomplished with the SHELXTL PC package of programs [39]. Heavy atoms were located *via Patterson* maps for **1** and **2**, while direct methods were employed for **3**–**5** and **7** · Et$_2$O. Atomic scattering factors were from [40]. All non-H-atoms were refined anisotropically, except for **5** and **7** · Et$_2$O. For **5**, only heteroatoms and the C-atoms of the triflato ligands were refined anisotropically, due to a paucity of data. Disorder in the vicinity of the triflato ligand containing S(1) and C(11) in **5** was apparent from difference *Fourier* maps, as evinced by the appearance of the larger difference peaks here; due to the relatively small number of observed data and due to the predominance of site occupancy by one conformer over the other, we did not attempt to model the disorder. In the case of **7** · Et$_2$O, the Et$_2$O solvate molecule was disordered with O(6) situated on an inversion center. The geometry of this solvate molecule was restrained with O–C and C–C distances initially set to 1.38 and 1.54 Å, resp., and the site occupancies of the disordered C(α) atom, C(19), set at 0.50 for each of two positions. Subsequent refinement (O(6) and C(18) anisotropically and the disordered positions of C(19) isotropically), resulted in final O(6)–C(19) and O(6)–C(19′) distances of 1.28(5) and 1.30(9) Å, while the C(19)–C(18) and C(19′)–C(18) distances were both 1.30(6) Å. H-atom positions were calculated geometrically, fixed at a C–H distance of 0.96 Å, and not refined, with two exceptions. For **3**, the H-atom for the bridging OH ligand was located and refined. For **7** · Et$_2$O, the H-atoms of the disordered Et$_2$O solvate molecule were not set, nor were they located. Crystal data and further data-collection parameters for the studied complexes are summarized in *Table 8*.

Crystallographic data (excluding structure factors) for structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as deposition Nos. CCDC-184582 (**1**), CCDC-184583 (**2**), CCDC-184584 (**3**), CCDC-184585 (**4**), CCDC-184586 (**5**), and CCDC-184587 (**7** · Et$_2$O). Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ UK (fax: + 44(1223) 336 033; e-mail: deposit@ccdc.cam.ac.uk).

5. *Polymerizations without MAO.* Unless otherwise noted, polymerizations were effected by a slight modification of reported procedures [32].

5.1. *Optimization of Complex/Styrene Ratio.* A soln. of **2** (10–20 mM) in toluene was prepared. To each of five *Schlenk* flasks was added the appropriate amount of Ti-complex soln. to give ultimately 0.050, 0.10, 0.20, 0.40, and 0.80 mol-% of complex/styrene. Toluene was added to the flask to bring the total soln. volume to 50 ml.

Table 8. *Crystallographic Data and Parameters for* **1**–**5**, *and* **7** · *Et₂O*

	1	**2**	**3**	**4**	**5**	**7** · Et_2O
Formula	$C_{26}H_{36}F_{12}O_{14}S_4Ti_2$	$C_{26}H_{36}F_{12}O_{12}S_4Ti_2$	$C_{24}H_{32}F_{12}O_{14}S_4Ti_2$	$C_{19}H_{26}Cl_2OTi$	$C_{21}H_{26}F_6O_7S_2Ti$	$C_{34}H_{38}F_6O_{10}S_2Ti_2 \cdot C_5H_{10}O$
M_r	1024.6	992.6	996.6	389.2	616.4	996.6
Crystal color, habit	orange prism	dark brown plate	dark brown prism	red needle	dark orange plate	brown plate
Crystal dimensions [mm]	0.20 × 0.30 × 0.50	0.20 × 0.20 × 0.40	0.30 × 0.35 × 0.50	0.25 × 0.25 × 0.60	0.15 × 0.30 × 0.50	0.16 × 0.40 × 0.60
Crystal system	monoclinic	triclinictriclinic	orthorhombic	monoclinic	monoclinic	
Space group	*C*2/*c*	*P*-1	*P*-1	*Pbca*	*C*2/*c*	$P2_1/c$
a [Å]	15.274(4)	8.949(4)	9.773(3)	7.305(2)	16.879(5)	12.546(3)
b [Å]	11.882(4)	9.181(4)	10.340(2)	16.755(5)	12.906(5)	11.845(3)
c [Å]	22.975(8)	13.558(8)	11.554(3)	32.338(7)	25.931(11)	15.657(3)
α [deg]	90	82.91(4)	64.71(2)	90	90	90
β [deg]	101.51(3)	72.93(4)	67.65(2)	90	103.10(3)	109.95(2)
γ [deg]	90	71.77(4)	69.03(2)	90	90	90
V [Å^3]	4085(2)	1010.9(9)	949.4(5)	3958(2)	5502(4)	2187.1(9)
Z	4	1	1	8	8	2
D_{calc} [g cm^{-3}]	1.666	1.630	1.743	1.306	1.488	1.450
μ (Mo$K\alpha$) [cm^{-1}]	7.09	7.10	7.60	7.04	5.41	5.41
F(000)	2080	504	504	1632	2528	988
2θ max [deg]	45.0	45.0	55.0	50.0	45.0	45.0
Reflections collected	2802	2763	4612	3531	2943	3000
Independent reflections	2661 ($R_{int} = 0.65\%$)	2604 ($R_{int} = 4.25\%$)	4349 ($R_{int} = 0.44\%$)	3483 ($R_{int} = 0.87\%$)	2841 ($R_{int} = 0.82\%$)	2845 ($R_{int} = 0.87\%$)
Observed reflections	1589 ($F > 6.0\sigma(F)$)	1527 ($F > 6.0\sigma(F)$)	3224 ($F > 6.0\sigma(F)$)	1774 ($F > 4.0\sigma(F)$)	1422 ($F > 4.0\sigma(F)$)	1757 ($F > 6.0\sigma(F)$)
Largest difference peak [eÅ^{-3}]	0.32	1.64	0.61	0.36	0.51	0.39
Largest difference hole [eÅ^{-3}]	– 0.26	– 1.10	– 0.75	– 0.33	– 0.38	– 0.33
No. of parameters	262	253	257	208	239	269
R [a])	0.0388	0.1158	0.0503	0.0586	0.0910	0.0550
wR [a])	0.0432	0.1663	0.0681	0.0627	0.1112	0.0743
GOF[b])	1.21	1.93	1.29	1.62	1.76	1.39

[a]) $R = \Sigma / / F_o| - |\Sigma F_c / / \Sigma F_o|$; $wR = [\Sigma w(F_o,| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o) + g^*(F_o)^2$; $g = 0.0005$ for **1** and **4**, 0.006 for **2**, and 0.002 for **3**, **5**, and **7** · Et_2O.

[b]) $GOF = [\Sigma w(F_o,| - |F_c|)^2/(NO - NV)]^{1/2}$, where *NO* is the number of observations and *NV* is the number of variables.

After stirring for 5 min at r.t., styrene (5.0 ml, 44 mmol) was added, and the mixture was stirred for another 3 h. The reaction was quenched by the addition of MeOH (40 ml). The mixture was poured into acidified MeOH (47 ml of MeOH/3 ml of conc. HCl soln.) and diluted with additional MeOH to 1 l. The precipitated polystyrene (PS) was separated by filtration, dried *in vacuo* as described above, and weighed. The dried PS was continuously extracted with boiling butan-2-one for 24 h. No insoluble fraction was obtained. The soluble fraction (reprecipitated by addition of MeOH), was again dried, and reported as atactic PS (APS).

5.2. *Optimization of Reaction Temperature.* To each of five *Schlenk* flasks was added the appropriate amount of Ti complex soln. to give ultimately 0.40 mol-% of complex/styrene, as well as toluene (35 ml). A flask was placed in each of five baths maintained at 0, 25, 50, 75, and 90°, resp. Styrene (5.0 ml, 44 mmol) was added, and the mixture was stirred for 3 h. Workup and isolation of the PS proceeded as described in *5.1.* Again, only APS was isolated.

5.3. *General Polymerization Method.* Based on styrene, 0.40 or 0.80 mol-% of complex was used to effect polymerization of styrene by the Ti-complexes in the absence of MAO. To the appropriate amount of Ti-complex dissolved in toluene (12 ml) was added styrene (5.0 ml, 44 mmol). The mixture was stirred at r.t. for 5 min, then at 50° for 2 h. Workup and isolation proceeded as described in *5.1.*, except that the reaction was quenched with a lesser amount of MeOH (20 ml) and the mixture was diluted, after acidification, with additional MeOH to a final volume of 200 ml. Only APS was isolated.

6. *Polymerizations with MAO.* Unless otherwise noted, all polymerization reactions were performed under conditions similar to those in the literature [32], with a styrene/MAO/Ti-complex ratio of 6000:500:1 [33]. General procedures follow.

6.1. *Optimization of Reaction Time.* Ti-Complexes **1** and **2** were utilized for these experiments. To a *Schlenk* flask containing the appropriate amount of complex and MAO, toluene (35 ml) was added. Styrene (15 ml, 44 mmol) was added, and the mixture was placed in an oil bath at 50°. Aliquots (10 ml) were taken after 0.5, 1, 2, 3, 4, and 5 h. Workup of each aliquot proceeded by addition to MeOH (25 ml), followed by stirring for 5 min. Acidified MeOH (47 ml of MeOH/3 ml of conc. HCl soln.) was added, followed by dilution to 200 ml with MeOH. The precipitated PS was separated by filtration, then dried, and weighed. The PS was continuously extracted in the usual manner. Both the insoluble portion and the soluble fraction (reprecipitated by addition of MeOH) of PS were dried in the usual way. The weight of syndiotactic polystyrene (SPS) was obtained from the butan-2-one-insoluble portion, while the weight of atactic PS was derived from the soluble fraction.

6.2. *General Polymerization Method.* To a stirred soln. of MAO in toluene (5 ml) was added a soln. of the appropriate amount of Ti-complex in toluene (7 ml). The mixture was stirred for 9 min, and then styrene (5.0 ml, 44 mmol) was added. The mixture was stirred for 5 min after the addition, then at 50° for 2 h. Workup proceeded as described in *6.1*, except that the reaction was quenched with less MeOH (20 ml). ^{1}H-NMR of SPS ($CDCl_2CDCl_2$): 7.08 (*m*); 6.59 (*dd*); 1.91 (*quint.*); 1.40 (*t*). ^{13}C-NMR of SPS ($CDCl_2CDCl_2$): 145.1; 127.5; 125.2; 44.0; 40.8. IR of SPS: 1069, 537. ^{1}H-NMR of APS ($CDCl_2CDCl_2$): br. resonances in the regions of δ 7.0 and 1.5. IR of APS: 1077 (br.).

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