Articles

(Fluorenyl)titanium Triisopropoxide and Bis(fluorenyl)titanium Diisopropoxide: A Facile Synthesis, Molecular Structure, and Catalytic Activity in Styrene Polymerization

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$[(\eta^1\text{-Flu})Ti(\mu\text{-O}^iPr)(O^iPr)_2]_2$ (**1**) and $(\eta^1\text{-Flu})(\eta^5\text{-Flu})Ti(O^iPr)_2$ (**2**) were easily prepared from FluLi and $ClTi(^iPrO)_3$ and demonstrated a remarkable thermal stability in comparison with known (fluorenyl)titanium complexes. Both complexes were characterized by X-ray analysis and temperature-dependent NMR spectroscopy. In combination with methylaluminoxane, both compounds are highly efficient initiators for styrene polymerization, producing highly syndiotactic polymers.

Introduction

(Fluorenyl)titanium(IV) trichlorides and bis(fluorenyl)titanium(IV) dichlorides are known to be unstable, in contrast to amido(fluorenyl)titanium dichlorides of "constrained" structure[1] and bis(fluorenyl)zirconium dichlorides.[2] Furthermore, the very preparation of compounds having an "unsupported" (fluorenyl)titanium fragment is usually considered impossible because of two main factors: a small tendency of the five-membered ring of the fluorenyl moiety to form an aromatic system[3] and the tendency of Ti(IV) toward reduction to Ti(III) or Ti(II), which thereby promotes the oxidation of aromatic π-anions to the corresponding radicals[4] and thus makes an additional contribution to the (fluorenyl)titanium template instability. Indeed, only one stable half-sandwich complex comprising a π-coordinated Flu−Ti^{IV} template, [9-((2,2,6,6-tetramethylpiperidino)borane)fluorenyl]titanium trichloride, has been structurally characterized.[5]

However, taking into account the practical significance of half-sandwich (cyclopentadienyl)- and (indenyl)-titanium(IV) complexes as catalysts for syndiotactic styrene polymerization,[6] the synthesis of stable (fluorenyl)titanium complexes might be of great interest for catalysis.

Previously, some of us reported attempts to prepare various mono(fluorenyl)titanium trichlorides starting from $Flu'SnMe_3$ ($Flu' = C_{13}H_9$, 9-Et-$C_{13}H_9$, 9-$SiMe_3$-$C_{13}H_9$) and $TiCl_4$.[7] As expected, the above complexes were stable in solution only below −20 °C and their rapid thermal decomposition afforded $TiCl_3$ and bifluorenes in quantitative yield. However, $Flu'TiMe_3$ species were stable in solution up to 0 °C.[8] It has also been

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[1] (a) Dias, H. V. R.; Wang, Z.; Bott, S. G. *J. Organomet. Chem.* **1996**, *508*, 91. (b) Hagihara, H.; Shiono, T.; Ikeda, T. *Macromolecules* **1998**, *31*, 3184. (c) Dias, H. V. R.; Wang, Z. *J. Organomet. Chem.* **1997**, *539*, 77. (d) Putzer, M. A.; Lachicotte, R. J.; Baran, G. C. *Inorg. Chem. Commun.* **1999**, *2*, 319.

[2] (a) Alt, H. G.; Samuel, E. *Chem. Soc. Rev.* **1998**, *27*, 323−329 and references therein. (b) Atwood, J. L.; Razavi, A. *J. Am. Chem. Soc.* **1993**, *115*, 7529. (c) Kowala, C.; Wailes, P. C.; Weigold, H.; Wunderlich, J. A. *J. Chem. Soc., Chem. Commun.* **1974**, 993.

[3] Alt, H. G. *Russ. Chem. Bull. (Engl. Transl.)* **1995**, *44*, 1.

[4] Fritze, C.; Erker, G.; Fröhlich, R. *J. Organomet. Chem.* **1995**, *501*, 41.

[5] Helm, S.; Nöth, H. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1331.

[6] For the most comprehensive reports see: (a) Ready, T. E.; Gurge, R.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1998**, *17*, 5236 and references therein. (b) Tomotsu, N.; Ishijara, N.; Newman, T. H.; Malanga, M. T. *J. Mol. Catal. A: Chem.* **1998**, *128*, 167 and references therein.

[7] Knjazhanski, S. Ya.; Moreno, G.; Cadenas, G.; Belsky, V. K.; Bulychev, B. M. *Tetrahedron* **1999**, *55*, 1639.

[8] Unreported data from our laboratory. Red solutions of $Flu'TiCl_3$ (prepared as described in ref 6) were treated in situ with 3 equiv of MeMgI at −40 °C. The change of the solution color to yellow and the precipitation of inorganic salts were observed over the course of 20 min. Heating the solutions to 0 °C immediately led to their darkening and then to the appearance of a metallic mirror on the inside surface of the reaction flask.

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mentioned by Alt that Flu_2ZrMe_2 is more stable than Flu_2ZrCl_2.[3] Thus, the question is whether this instability is an inherent feature of the (fluorenyl)titanium fragment or might be affected, at least in part, by the electronic properties of auxiliary ligands.

Obviously, the only way to prepare stable (fluorenyl)titanium(IV) compounds is to diminish somehow the reduction potential of the Ti(IV)/Ti(III) pair or, in other words, to augment the electronic density on the metal center. This goal can be achieved from two sides: by use of auxiliary ligands on the Ti atom more electron donating than methyl or Cl ligands, for example, OR or NR_2, or by use of fluorenyl ligands substituted with electron donor groups such as alkyl, alkoxy, silyloxy, amino, etc. The first way looks more attractive synthetically, taking into account the commercial availability of $ClTi(^iPrO)_3$. The use of this reagent in organometallic synthesis has been widely reported by Chien and Rausch.[9] Thus, we explored this synthetic route in applications for (fluorenyl)titanium and report here a facile synthesis and crystal and molecular structure as well as catalytic applications of the first stable (fluorenyl)titanium(IV) compounds containing no heteroatom or bridging group attached to the "flap" carbon atom of a fluorenyl ligand: $[(\eta^1\text{-Flu})Ti(^iPrO)_2(\mu\text{-}^iPrO)]_2$ (**1**) and $(\eta^1\text{-Flu})(\eta^5\text{-Flu})Ti(^iPrO)_2$ (**2**) (Flu = C_9H_{13}).

Results and Discussion

Preparation of 1 and 2. Haf-sandwich derivatives of early transition metals are usually prepared from silylated or stannylated cyclopentadienes (or its analogues) and the corresponding metal halogenides.[10] However, $ClTi(^iPrO)_3$ does not react either with $FluSiMe_3$ or with $FluSnMe_3$ for days in such solvents as methylene dichloride, toluene, or diethyl ether. Reaction mixtures in CD_2Cl_2 and toluene-d_8 were monitored by ^1H NMR for 5 days, and no reactions were observed.

We made an attempt to prepare $FluTi(O^iPr)_3$ (**1**) starting from fluorenyllithium. It was found that reaction between equimolar amounts of FluLi and $Ti(O^iPr)_3Cl$ in ether leads to formation of two main products, the desired $FluTi(O^iPr)_3$ (**1**) and the bis(fluorenyl) derivative $Flu_2Ti(O^iPr)_2$ (**2**) in yields of 28% and 32%, correspondingly (eq 1). Even a 2-fold excess of $Ti(O^iPr)_3Cl$ did not suppress the formation of **2** in considerable amount. Changing the solvent from ether to hexane leads to the selective formation of **1** in acceptable yield (85%). Note that only the etherate of FluLi permits the selective preparation of compound **1**. A reaction in hexane between $Ti(^iPrO)_3Cl$ and (fluorenyl)lithium prepared in the absence of ether gives only dark amorphous products. This phenomenon can be explained by the fact that a substance of the composition FluLi exists in the form of a dimer[11] and thus demonstrates a reaction ability different from that of the monomeric (fluorenyl)lithium etherate.

$$FluLi\cdot Et_2O + Ti(O^iPr)_3Cl \xrightarrow[Et_2O/hexane]{} \underset{\mathbf{1}}{FluTi(O^iPr)_3} + \underset{\mathbf{2}}{Flu_2Ti(O^iPr)_2} \quad (1)$$

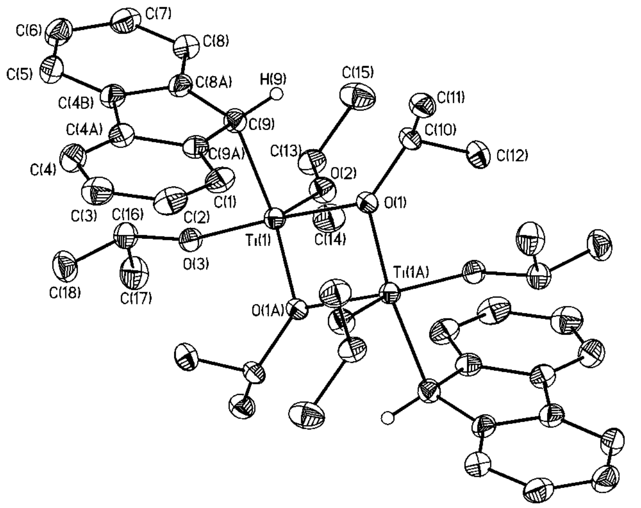

Figure 1. General view of the complex **1** and numbering scheme. All hydrogen atoms with the exception of H(9) are omitted for clarity.

$FluTi(^iPrO)_3$ (**1**) is very soluble in all common solvents and is thermally stable under an inert atmosphere up to 100 °C. In the presence of even small amounts of oxygen, the dark orange crystals of **1** are slowly covered with a white crust of bifluorene (as analyzed by ^1H NMR). The formation of bifluorene (instead of fluorene) implies radical breakage of the $(\eta^1\text{-Flu})-Ti$ bond. Sunlight exposure causes **1** to degrade slowly to give a green solution containing bifluorene and $Ti(^iPrO)_3$. The bifluorenyl derivative **2** is significantly more stable to the sunlight and to oxygen. Its solubility, however, is poorer than that of **1**. The complex **2** is practically insoluble in aliphatic solvents, slightly soluble in toluene, and slightly more soluble in THF and CH_2Cl_2.

Molecular Structure of 1 and 2. X-ray diffraction reveals that the complex **1** is a centrosymmetric dimer where titanium atoms are coordinated by two terminal and two bridged isopropoxy groups and one η^1-fluorenyl ligand (Figure 1). The coordination sphere of titanium is a trigonal bipyramid with O(1) and O(3) in axial positions. The mononuclear complex **2** comprises a pseudo-tetrahedral titanium atom surrounded by one η^1-fluorenyl and one η^5-fluorenyl ligand and two terminal O^iPr groups (Figure 2). Structural data for (fluorenyl)titanium compounds are limited to $[t\text{-BuNSiMe}_2\text{-Flu}]TiCl_2$;[1d] thus, **1** and **2** represent the first structurally characterized (η^1-fluorenyl)titanium complexes. The important bond lengths and angles for **1** and **2** are collected in Table 1. The experimental conditions and crystallographic data are listed in Table 2.

Despite the obvious distinction of the titanium coordination sphere the essential features of η^1-bonded fluorenyl ligands in **1** and **2** are practically identical. The only notable difference is the widening of Ti(1)C(9)H(9) in **1** (104°) in comparison with 92° in **2**. This

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[9] (a) Kucht, A.; Kucht, H.; Barry, S.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1993**, *12*, 3075. (b) Blais, M. S.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1998**, *17*, 3775. (c) Flores, J. C.; Ready, T. E.; Chien, J. C. W.; Rausch, M. D. *J. Organomet. Chem.* **1998**, *562*, 11.

[10] (a) Cardoso, A. M.; Clark, R. J. H.; Moorhouse, S. *J. Chem. Soc., Dalton Trans.* **1980**, 1156. (b) Lund, E. C.; Livinghouse, T. *Organometallics* **1990**, *9*, 2426. (c) Llinas, G. H.; Mena, M.; Palacios, F.; Royo, P.; Serrano, R. *J. Organomet. Chem.* **1988**, *340*, 37. (d) Royo, B.; Royo, P.; Cadenas, L. M. *J. Organomet. Chem.* **1998**, *551*, 293.

[11] Üffing, C.; Köppe, R.; Schnöckel, H. *Organometallics* **1998**, *17*, 3512.

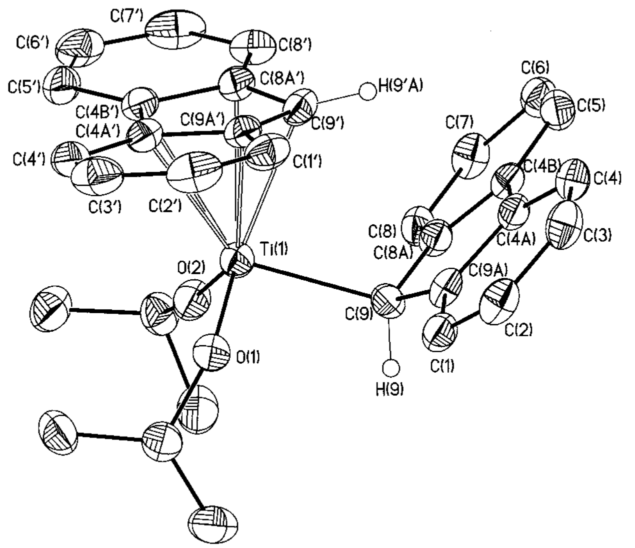

Figure 2. General view of the complex **2** and numbering scheme. All hydrogen atoms with the exception of H(9) and H(9′) are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in 1 and 2

		2	
	1	η^1-fluorenyl	η^5-fluorenyl
Ti(1)−C(9)	2.199(2)	2.198(2)	2.320(3)
Ti(1)−C(4A′)			2.482(2)
Ti(1)−C(4B′)			2.523(3)
Ti(1)−C(8A′)			2.462(3)
Ti(1)−C(9A′)			2.430(2)
Ti(1)−O(1)	2.108(1)	1.783(2)	
Ti(1)−O(1)a	1.985(1)		
Ti(1)−O(2)	1.787(2)	1.757(2)	
Ti(1)−O(3)	1.777(1)		
Ti(1)-X[b])			2.122
C(4)−C(4A)	1.391(3)	1.391(3)	1.421(3)
C(4A)-C(4B)	1.465(3)	1.461(3)	1.444(3)
C(4A)-C(9A)	1.428(3)	1.410(3)	1.423(3)
C(4B)-C(8A)	1.412(3)	1.412(3)	1.427(3)
C(8A)-C(9)	1.479(3)	1.476(3)	1.425(3)
C(9)−C(9A)	1.482(3)	1.473(3)	1.417(3)
O(1)−Ti(1)−O(1A)	72.09(6)		
O(1)−Ti(1)O(2)	88.76(7)	107.52(8)	
O(1)Ti(1)−O(3)	169.44(7)		
O(1A)[a]−Ti(1)O(2)	121.42(7)		
O(1A)[a]Ti(1)−O(3)	100.41(6)		
O(2)−Ti(1)−O(3)	101.62(7)		
O(1)−Ti(1)−C(9)	86.12(7)	96.77(8)	
O(1A)−Ti(1)−C(9)	126.73(8)		
O(2)−Ti(1)−C(9)	92.88(7)	96.37(9)	
O(3)−Ti(1)−C(9)	105.48(8)		
Ti(1)−O(1)−Ti(1A)[a]	107.91(6)		
C(9A)−C(9)−C(8A)	104.2(2)	104.4(2)	108.0(2)
C(9)−C(8A)−C(4B)	110.2(2)	109.4(2)	108.3(2)
C(8A)−C(4B)−C(4A)	108.1(2)	108.0(2)	107.1(2)
C(4B)−C(4A)−C(9A)	107.7(2)	107.9(2)	107.8(2)
C(4A)−C(9A)−C(9)	109.5(2)	109.7(2)	108.2(2)

[a] The atom is obtained from the base one by symmetry transformation. [b] X denotes the center of the five-membered ring of the fluorenyl ligand.

Table 2. Crystallographic Data for Complexes 1 and 2

	1	**2**
mol formula	$C_{44}H_{58}O_6Ti_2$	$C_{32}H_{32}O_2Ti$
fw	778.70	496.48
color, shape	yellow, cubic	violet, prism
dimens (mm)	0.35 × 0.35 × 0.35	0.35 × 0.30 × 0.20
diffractometer	SMART 1000 CCD	
temp (K)	110	
cryst syst	orthorhombic	monoclinic
space group	*Pbca*	$P2_1/n$
a (Å)	11.959(2)	12.373(2)
b (Å)	16.271(3)	14.641(2)
c (Å)	21.310(3)	14.139(2)
β (deg)		90.011(4).
V (Å^3)	4147(1)	2561.3(7)
Z	4	4
F(000)	1656	1048
ρ_{calcd} (g cm^{-3})	1.247	1.288
radiation, λ(Mo Kα) (Å)	0.710 72	
linear abs coeff, μ (cm^{-1})	4.30	3.61
T_{min}/T_{max}	0.894/0.956	0.783/0.964
scan type	ω scan with 0.3° step in ω and 10 s exposure per frame	
θ range (deg)	1.91−8.99	2.00−8.06
completeness of data set (%)	99.8	98.1
no of measd rflns	19 432	11 709
no. of unique rflns	5500 (R(int) = 0.0399)	6107 (R(int) = 0.0351)
no. of rflns with $I > 2\sigma(I)$	3893	3593
no. of params	351	444
final $R(F_{hkl})$: R1	0.0600	0.0525
wR2	0.1618	0.1057
GOF	1.107	1.116
ρ_{max}/ρ_{min} (e Å^{-3})	0.862/−0.363	0.606/−0.442

suggests a more covalent character of the Ti−C(9) bond in **1** than in **2**. The distances of Ti−C σ-bonds in **1** and **2** are notably shorter than those in $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}C_5H_5)_2$ (2.33 Å).[12] Despite the different ligand hapticities, C(9) atoms in all three fluorenyls deviate 0.09−0.12 Å from the mean plane of the rest of the atoms. The titanium−η^5-fluorenyl bond in **2** is somewhat distorted toward C(9), with the ring slippage being 0.22 Å. All other bond lengths and angles in **1** and **2**, including those formed with O^{i}Pr, are as expected for such complexes.

Temperature-Dependent NMR Experiments with 1 and 2. Both complexes have structures considered necessary to account for the temperature-dependent NMR spectra in solution. Only one set of resonances from two different fluorenyl ligands was observed in the NMR spectra of **2**, which suggests a fast exchange in hapticity between the two fluorenyl moieties. However, lowering the temperature did not cause any significant change in the spectra (in toluene, tetrahydrofuran, and methylene dichlorid), besides some broadening of the signals. The resonances seem to coalesce at −100 °C, but very low sample concentration and the prevalence of resonances from impurities at this temperature do not let us make a definitive conclusion.

A broad, nonresolved resonance from −OC*H* in the proton spectra of **1** (in cyclohexane-d_{12} and, to a lesser extent, in toluene-d_8 and tetrahydrofuran-d_8) at room temperature suggests rapid exchange between terminal and bridged alkoxy groups. Both ^{1}H and ^{13}C NMR spectra of **1** do not change when the samples are heated to 100 °C. It can be concluded, therefore, that **1** maintains the dimeric structure and the ligand hapticity in solution, even at elevated temperature. Lowering the temperature to −95 °C allows us to observe two broad resonances from −OC*H* protons at 4.73 and 3.08 ppm (Table 4) in the ratio 1:2, which correspond to the bridging and terminal isopropoxy groups, respectively.

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(12) Calderon, J. L.; Cotton, F. A.; DeBoer, B. G.; Takats, J. *J. Am. Chem. Soc*, **1971**, *93*, 3592.

Table 3. Conditions and Results of Styrene Polymerization with Initiators 1−4[a]

run	cat.	pt, min	t,[c] min	yield, g	$10^{-6}A$[d]	$10^{-3}M_n$	M_w/M_n	SY,[e] %
1	**1**	0.17	30	1.22	1.22	170.6	1.90	>99
2	**1**	1	30	0.81	0.81			
3	**1**	0.17	15	0.98	1.96	95.8	2.02	
4	**2**	0.17	30	3.07	3.07	184.3	2.17	>99
5	**2**	1	30	2.58	2.58			
6	**2**	0.17	15	2.42	4.84	110.0	2.33	
7	**3**	0.17	30	0.33	0.33			
8	**3**	5	30	0.85	0.85	471.5	2.24	95
9	**3**	5	15	0.41	0.82			
10	**4**	0.17	30	0.99	0.99			
11	**4**	5	30	1.43	1.43	360.0	2.15	98
12	**4**	5	15	0.75	1.50			

[a] Conditions: toluene 30 mL (total volume), styrene 10 mL (9.1 g), MMAO-3A 1.86 M toluene solution, Al/Ti = 500, polymerization temperature 50 °C, [cat.] = 50 μmol/L. [b] Preactivation time. [c] Polymerization time. [d] Activity, in g of PS/((M of cat.) h). [e] Percent of 2-butanone-insoluble fraction.

In addition, a doublet from the methyl groups is split into four broad overlapped peaks, indicating hindered rotation of the ^{i}OPr groups at −95 °C.

Styrene Polymerization with 1 and 2. In the past decade an impressive amount of titanium half-sandwich complexes of the common formula $LTiX_3$ (L = cyclopentadienyl- and indenyl-based ligands, X = Cl, F, Me, CH_2Ph, OMe, OPh, O^{i}Pr, OBu, NMe_2) have been reported as initiators for syndiotactic styrene polymerization, and (pentamethylcyclopentadienyl)titanium derivatives have been the most frequently used in this process.[6] The syndiotactic polystyrene (sPS) has usually contained a part of atactic polymer provided from some undefined nonstereospecific catalytic species formed upon the activation of a titanium(IV) compound with MAO.[14] A discussion about the nature of catalytic species (Ti^{3+} or Ti^{4+} or maybe both of them) is still continuing.[6a,15] There have also been controversial reports regarding the influence of the macroligand (cyclopentadienyls and indenyls) on the catalytic activity.[6b] A reason for this controversy may be associated with different polymerization conditions used by different research groups.

We tested both **1** and **2** in combination with MMAO-3A in styrene polymerization.[16] To compare the catalytic behavior of these novel (fluorenyl)titanium compounds with their analogues containing cyclopentadienyl and indenyl ligands, we synthesized $(C_5Me_5)Ti(O^iPr)_3$ (**3**) and $(C_9H_7)Ti(O^iPr)_3$ (**4**) in accord with eq 1.[17] Thus, we had an opportunity to observe the influence of a macroligand on the catalyst performance under similar experimental conditions. The polymerization conditions and polymer properties are listed in Table 3.

Whereas a preactivation time is required for **3** and, to a lesser extent, for **4**, the activation of **1** and **2** is instantaneous. This fact indicates that the differences in catalytic activities, which follow the order **3** < **4** < **1** < **2**, is associated, at least in part, with different catalyst efficiencies (amount of active species related to the precatalyst amount) or, in other words, with different tendencies toward Ti(IV)→Ti(III) reduction. The increase of the metal center acidity in the same order makes another contribution to the activity increment. The decrease of the polymer molecular weight in the opposite order is also associated with the difference in the metal center acidities.

The amount of 2-butanone-soluble atactic fraction diminishes in the order **3** > **4** > **1**, **2** and goes to near zero in the case of the (fluorenyl)titanium precursors. It indicates that the activation of **1** and **2** with MAO does not lead to the formation of nonstereospecific active species.

In contrast to the catalysts **3** and **4,** the catalytic activities of the initiators **1** and **2** decrease significantly after a short preactivation time in the absence of the monomer (compare runs 1 and 2 and runs 4 and 5) and even in the course of polymerization (compare runs 1 and 3 and runs 4 and 6). This effect may be associated with the active species decomposition due to ring slippage rearrangements.

In contrast to titanocenes (bridged and nonbridged), which have shown much less catalytic activity in the syndiotactic styrene polymerization than half-sandwich titanium complexes,[6b] the bis(fluorenyl)titanium complex **2** displayed the highest activity among the initiators tested. It may be related either to easy homolytic breaking of the Ti−(η^1-fluorenyl) bond in **2** upon the reaction with MAO to produce Ti(III) species or to the relatively high kinetic stability of the Ti−(η^5-fluorenyl) moiety upon activation of **2** with MAO.

Finally, **1** and **2** were tested in the polymerization of propene. In contrast to **3**, which has been claimed to produce high-molecular-weight atactic polypropylene,[18] neither **1** nor **2** showed catalytic activity in this process.

Experimental Section

General Considerations. All operations were performed under argon by using standard Schlenk techniques or under vacuum using sealed glass “equipped-with-everything” systems. Fluorene and BuLi (1.6 M solution in hexanes) were used as purchased (Aldrich). $ClTi(^iPrO)_3$ (Aldrich) was distilled under vacuum before use. MMAO-3A (Akzo Nobel, solution in heptane) was heated under vacuum at 50 °C to remove solvent and residual $AlMe_3$, and the oily residue was dissolved in toluene to give a 1.86 M solution. Toluene, benzene, pentane, hexanes, and 2,2,4-trimethylpentane were all washed with H_2SO_4, washed five times with wateand then were dried over $CaCl_2$, further refluxed over $LiAlH_4$ for 3 h, distilled, refluxed over Na/K alloy for 12 h, and finally distilled before use. CH_2Cl_2 was twice refluxed for 3 h and distilled over P_2O_5. Diethyl ether was distilled with $LiAlH_4$, refluxed over Na/K alloy for 6 h, and distilled before use. Styrene was washed twice with a 5% aqueous solution of KOH and five times with water, was then dried over Na_2SO_4 for 2 h and over CaH_2 for 4 days, and was distilled with solid methylaluminoxane (Witco) under

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(13) The total content of fluorene and bifluorene in the samples is ca. 1%, which does not interfere with the observation of the resonances from the main products at 20 °C.

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(15) (a) Minieri, G.; Corradini, P.; Zambelli, A.; Guerra, G.; Cavallo, L. *Macromolecules* **2001**, *34*, 2459. (b) Minieri, G.; Corradini, P.; Zambelli, A.; Guerra, G.; Cavallo, L. *Macromolecules* **2001**, *34*, 5379.

(16) Some data dealing with catalytic behavior of **1** have been reported in: Knjazhanski, S. Ya.; Cadenas, G.; Moreno G.; Zamora, M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1999**, *40*(2), 831.

(17) To our knowledge, there have been no reliable reports on the preparation and characterization of **3** and **4**. Compound **3** has been mentioned in: Campbell, R. E., Jr.; Hefner, J. G. PCT Int. Appl. WO8810275 (to Dow Chemical Co.). The compound was generated in situ by treatment of $(C_5Me_5)TiCl_3$ with 2-propanol. Our approach allows preparing both compounds easily in analytically pure form.

(18) Wu, Q.; Lin, S.; Zhu, F. Chinese Pat. Appl. 1269367.

Table 4. NMR Data for 1 and 2 (δ (J in Hz), 20 °C)

	aromatic	H9/C9	OCH<	Me
	Compound **1**			
cyclohexane-d_{12}	7.75 d, $J_{H-H} = 7.2$, 2H; 7.58 d, $J_{H-H} = 7.2$, 2H; 7.20 tr, $J_{H-H} = 7.2$, 2H; 7.10 tr, $J_{H-H} = 7.2$, 2H	4.94 s, 1H	4.32 br, $J_{H-H} = 6.2$, 3H	1.05 br, $J_{H-H} = 6.2$, 18H
	144.4; 138.2; 124.7; 123.8; 122.2; 118.9	82.9	76.5	25.8
toluene-d_8	7.87 d, $J_{H-H} = 7.4$, 2H; 7.76 d, $J_{H-H} = 9\ 2$, 2H; 7.35 d tr, $J_{H-H} = 7.4, 1.8$, 2H; 7.23 d tr, $J_{H-H} = 9.2, 1.8$, 2H	5.08 s, 1H	4.22 br hept, $J_{H-H} = 6.2$, 3H	1.00 br d. $J_{H-H} = 6.2$, 18H
	145.3; 138.9; 125.6; 124.6; 123.3; 120.1	83.1	78.2	26.5
toluene-d_8, −95 °C	7.95 br, 2H; 7.80 br, 2H; 7.60 br, 1H; 7.41 br, 3H	5.24 br s, 1H	4.73 br, 1H; 3.08 br, 2H	1.22; 1.12; 1.05; 0.93, 18 H
	145.0; 139.2; 125.6; 124.6; 122.7 br; 120.0 br	84.0 br	79.2 br; 74.9 br	25.5; 23.5; 22.7
THF-d_8	7.83 d, $J_{H-H} = 7.2$, 2H; 7.62 d, $J_{H-H} = 9.0$, 2H; 7.23 d tr, $J_{H-H} = 7.2, 1.5$, 2H; 7.13 d tr, $J_{H-H} = 9.0, 1.5$, 2H	4.97 s, 1H	4.33 br hept. $J_{H-H} = 6.2$, 3H	1.08 br d, $J_{H-H} = 6.2$, 18H
	145.3; 138.9; 125.6; 124.6; 123.3; 120.1	82.2	78.2	26.5
	Compound **2**			
CD_2Cl_2	7.94 m, 4H; 7.22 (m, 8H); 6.79 (m, 4H)	4.48 s, 2H	4.29 hept, $J_{H-H} = 6.1$, 2H	1.09 d, $J_{H-H} = 6.1$, 12H
	139.1; 129.1; 125.8; 124.8; 123.3; 120.9	88.2	79.6	26.2
THF-d_8	7.98 m, 4H; 7.18 m, 8H; 6.79 m, 4H	4.45 s, 2H	4.29 hept, $J_{H-H} = 6.2$, 2H	1.09 d, $J_{H-H} = 6.2$, 12H
	139.1; 129.1; 125.8; 124.8; 123.3; 120.9	88.2	79.6	26.2

reduced pressure before use. Deuterated benzene, toluene, cyclohexane, and tetrahydrofuran were stored over Na/K alloy for weeks in flasks with a high-vacuum Teflon valve-to-glass seal. CD_2Cl_2 was stored in the same way over a brilliant surface of sodium. Samples for NMR studies were prepared in sealed tubes or in tubes with PTFE valves (Aldrich). Deuterated solvents were condensed under reduced pressure directly into NMR tubes.

Equipment. NMR spectra were recorded on a JEOL Eclipse-300 spectrometer (300 MHz). Size exclusion chromatographic analyses were run on a Waters 150-C chromatograph in 1,2,4-trichlorobenzene at 135 °C. The molecular weights of polymers were determined using polystyrene standards. Elemental analysis was performed on a Perkin-Elmer Series II CHNS/O Analyzer 2400. The samples for elemental analysis were sealed into a tin foil in a glovebox. Analysis for titanium was done using a Varian SpectrAA-250plus atomic absorption spectrometer.

Polymerization Procedure. Styrene. A 100 mL reaction flask equipped with magnetic stirrer was charged under argon with 10 mL of styrene and 29 mL of toluene. The flask was cooled to −10 °C, and argon was removed under vacuum. The flask was heated afterward to 50 °C. A 2 μmol amount of catalyst in 1 mL of a 1.86 M toluene solution of MMAO-3A was quickly added with a syringe. The polymerizations were stopped with acidified 2-propanol. The polymers (fine powder) were washed with MeOH/HCl and then with methanol to neutral pH and were dried at 80 °C for 24 h.

Propene. The polymerizations were performed in a Parr 5103 glass-jacketed reactor equipped with a pressure buret. The reaction conditions were as follows: toluene, 3 atm propene pressure, 70 °C, $C_{cat} = 10\ \mu$mol/L, MMAO-3A/Ti = 500, 5000, 10 000.

X-ray Crystallography. The crystallographic data for complexes **1** and **2** are summarized in Table 2. Due to the proximity of all angles in **2** to 90° the choice of crystal system was done on the basis of the detailed analysis of R_{int} values and systematic absence of all possible variants. All attempts to describe the crystal as a twin (monoclinic, which emulates orthorhombic) did not lead to any change in discrepancy factors as well as the standard deviations and residual Fourier electron density synthesis. Structures were solved by direct methods and refined by full-matrix least squares against F^2 in the anisotropic (H atoms isotropic) approximation using the SHELXTL-97 pakage. All hydrogen atoms in **1** and **2** were located from the electron density difference synthesis and were included in the refinement in isotropic approximations. A crystal of **1** suitable for X-ray experiments was obtained by storing a hexane solution at 0 °C. A crystal of **2** suitable for X-ray experiments was obtained by storing a saturated CH_2Cl_2 solution at −20 °C.

Interaction between (Fluorenyl)lithium and $ClTi(^iPrO)_3$. In Diethyl Ether. A solution of $ClTi(^iPrO)_3$ (2.6 g, 10 mmol) in 10 mL of diethyl ether was added at −80 °C to a suspension of (fluorenyl)lithium in 60 mL of diethyl ether prepared from fluorene (1.83 g, 11 mmol) and 6.3 mL of 1.6 M BuLi in hexane (10 mmol). The resulting mixture turned dark red immediately, and a bright red solid precipitated. The mixture was warmed to room temperature and was stirred for 2 h. A reddish yellow solution was separated from a red crystalline precipitate. The solution was evaporated, and the residue was extracted three times with 50 mL of hot hexane. The resulting solution was concentrated to 25 mL and was stored at −30 °C for 2 days. The yellow crystalline solid was collected, washed twice with cooled pentane, and dried under vacuum to give 1.09 g (28%) of **1**. Anal. Found: C, 67.91; H, 7.55; Ti, 12.0. Calcd for $C_{22}H_{30}O_3Ti$: C, 67.69; H, 7.75; Ti, 12.27.

The red precipitate was recrystallized from dichloromethane to give 1.60 g (32%) of **2**. Anal. Found: C, 77.09; H, 6.55; Ti, 9.5. Calcd for $C_{32}H_{32}O_2Ti$: C, 77.42; H, 6.50; Ti, 9.65.

In Hexane. A 6.3 mL portion of a 1.6 M hexane solution of *n*-BuLi (10 mmol) was slowly added with stirring to a fluorene solution (1.83 g, 11 mmol) in 60 mL of Et_2O at 0 °C. The resulting mixture was heated to room temperature and was stirred for 24 h. The solvent was removed under vacuum. The resulting lemon yellow solid was suspended in 80 mL of hexane and then was mixed with 3.38 g of $ClTi(OiPr)_3$ (13 mmol) at −60 °C. The reaction mixture was stirred for 1 h at −60 °C, and then it was allowed warmed to ambient temperature. The resulting yellowish brown suspension was filtered. The filtrate was concentrated to 25 mL and was stored at −30 °C for 2 days. Yellow crystals were separated by decantation, washed twice with cooled pentane, and dried under vacuum to afford 4.31 g (85%) of **1**.

$(C_5Me_5)Ti(O^iPr)_3$ (3). A 14 mmol portion of C_5Me_5Li (Aldrich) was suspended in pentane (60 mL). Diethyl ether (1 mL) was added, and the mixture was stirred until the solid had dissolved completely. This solution was added slowly to a solution of $ClTi(^iPrO)_3$ in pentane (14 mmol in 20 mL) at −40 °C; the mixture was warmed to room temperature, was stirred for 1 h, and was then filtered. The light green solution was concentrated to 20 mL, was cooled to −95 °C, and was maintained at this temperature for 4 h. *Note*: no product precipitation occurs at higher temperature. The liquid was removed through a cannula with a paper filter into a second flask. The pentane was recondensed back via cannula from the second flask to the solid remaining in the first flask at −95 °C. The suspension was stirred for 20 min at this temperature, and the liquid was removed in a similar way. The light yellow powder was dried under vacuum at 50 °C for 2 h. A 4.14 g amount (82%) of **3** was obtained. Anal. Found: C, 63.59; H, 10.81; Ti, 13.1. Calcd for $C_{19}H_{38}O_3Ti$: C, 63.32; H, 10.63; Ti, 13.29. ^1H NMR (20 °C, C_6D_6, δ): 4.63 hept, J_{H-H} = 6.0 Hz, 3H; 2.03 s, 15H; 1.19 d, J_{H-H} = 6.0 Hz, 18H. ^{13}C NMR (20 °C, C_6D_6, δ): 121.7; 75.25; 27.2; 11.85.

$(C_9H_7)Ti(O^iPr)_3$ (4). (Indenyl)lithium was prepared from indene (Aldrich) and BuLi in hexanes at room temperature. The formed solid was washed three times with hexanes and dried under vacuum at 50 °C for 4 h. A 15 mmol portion of IndLi was dissolved in diethyl ether (60 mL) to obtain a colorless solution, which was added slowly to a solution of $ClTi(^iPrO)_3$ in pentane (15 mmol in 40 mL) at −40 °C. The mixture was stirred at this temperature for 30 min, was then warmed to room temperature, and was stirred for an additional 30 min. The solvents were removed under reduced pressure. The residual red-orange oil was dissolved in 60 mL of pentane, the solution was filtered, and the solvent was removed under reduced pressure at 50 °C. A 5.05 g amount of a red-orange oil was obtained. Said oil contains ∼95% of **IV**, as determined by ^1H NMR. Cooling the pentane solution of this oil at −95 °C for 4 h led to the formation of an orange ice under a supernatant solution. The liquid was removed through a cannula with a paper filter. The residue, which melted at ∼−80 °C, was dried under vacuum at 50 °C for 4 h. According to the ^1H NMR analysis, the resultant red-orange oil had the same purity that the oil obtained before the low-temperature crystallization. Anal. Found: C, 63.97; H, 8.55; Ti, 13.8. Calcd for $C_{18}H_{28}O_3Ti$: C, 63.53; H, 8.29; Ti, 14.07. ^1H NMR (20 °C, C_6D_6, δ): 7.50 dd, J_{H-H} = 6.3, 3.0 Hz, 2H; 6.98 dd, J_{H-H} = 6.3, 3.0 Hz, 2H; 6.54 tr, J_{H-H} = 3.3 Hz, 1H; 6.29 d, J_{H-H} = 3.3 Hz, 2H; 4.41 hept, J_{H-H} = 6.0 Hz, 3H; 1.03 d, J_{H-H} = 6.0 Hz, 18H. ^{13}C NMR (20 °C, C_6D_6, δ): 135.8; 124.5; 123.9; 100.9; 77.87; 26.5.

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Supporting Information Available: Tables giving details of crystal structure determinations, atomic coordinates, isotropic and anisotropic displacement parameters, and bond lengths and angles of complexes **1** and **2**; these data are also available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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