Titanium Ester Enolate Complex Supported by a Tetradentate Bis(phenolato) Ligand: Synthesis, Structure, and Activity in Methacrylate Polymerization

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Reaction of the titanium dichloro complex containing a [OSSO]-type bis(phenolate) ligand (edtbp)$TiCl_2$ (**1**) (edtbpH_2 = (HOC_6H_2-^{t}Bu$_2$-4,6)$_2$(SCH_2CH_2S)) with 2 equiv of $AlMe_3$ produces the methylchloro complex (edtbp)TiMeCl (**2**) in 77% yield, alternatively prepared from comproportionation of **1** and the dimethyl complex (edtbp)$TiMe_2$ (**3**). The titanium ester enolate complex (edtbp)TiMe{O(^{i}PrO)C=CMe_2} (**4**) was synthesized by reaction of **2** with lithium isopropylisobutyrate, LiO(^{i}PrO)C=CMe_2, in a 1:1 molar ratio. This complex reacted with alcohols ROH (R = ^{i}Pr, Ph, Ph_3C) to give alkoxy complexes (edtbp)TiMe(OR) (**6**−**8**) and with acetone under C−C coupling to afford an aldolate complex (edtbp)TiMe($OCMe_2CMe_2CO_2{}^i$Pr) (**9**). Methyl abstraction from the neutral complexes **4**, **7**, and **9** using with $B(C_6F_5)_3$ gave the corresponding cationic species [(edtbp)Ti(OR)(THF)$_n$][$MeB(C_6F_5)_3$]. All complexes have been characterized by multinuclear NMR spectroscopy and elemental analysis. Single-crystal X-ray diffraction studies were performed for complexes **2**, **4**, and **9**. Cationic titanium enolate species initiate the polymerization of methyl methacrylate (MMA) at room temperature, producing syndiotactic-enriched poly(methyl methacrylates) (PMMAs). In the presence of the neutral enolate complex, MMA polymerization proceeds in a living fashion. The neutral titanium enolate complex **4** was found to be moderately active in *n*-butyl acrylate (*n*-BA) polymerization.

Introduction

Group 4 metallocene-mediated polymerization of alkyl methacrylate and acrylate monomers has attracted considerable attention in the recent past.[1–3] Although methyl methacrylate (MMA) polymerization by discrete group 4 metal complexes such as Cp_2MCl{O(MeO)C=CMe_2} (M = Ti, Zr), (^{i}PrO)$_3$Ti{O(MeO)C=CMe_2} and (Et_2N)$_3$Ti{O(MeO)C=CMe_2} was disclosed in the early patent literature,[3l] living polymerization of methyl methacrylate with a zirconocene-based two-component system was first reported by Collins et al. in 1992 involving the neutral complex Cp_2ZrMe{O(^{t}BuO)C=CMe_2} as initiator and a cationic complex [$Cp_2ZrMe(THF)$][BPh_4] as catalyst.[1b,c] To find a suitable model for the propagating species, various neutral and cationic group 4 metallocene ester enolate complexes have been prepared and examined for their suitability in the living polymerization of methacrylate and acrylate monomers, e.g. Cp_2ZrMe{O(^{t}BuO)C=CMe_2},[3c] [Cp_2Zr{O(^{t}BuO)C=CMe_2}(THF)]$^+$[$MeB(C_6F_5)_3$]$^-$,[3h] [(*rac*-EBI)Zr{O(^{i}PrO)C=CMe_2}(THF)]$^+$[$MeB(C_6F_5)_3$]$^-$ (EBI = ethylene-bis(indenyl)),[2h] and [(η^5-$C_5Me_4SiMe_2N^t$Bu)Ti{O(^{i}PrO)C=CMe_2}(THF)]$^+$[$MeB(C_6F_5)_3$]$^-$.[2i,3j] These systems allow to control the livingness and stereochemistry of the polymerization. However, group 4 metal enolate complexes based on nonmetallocene frameworks have not been well developed so far.[3l,4] We have recently introduced configurationally rigid titanium complexes

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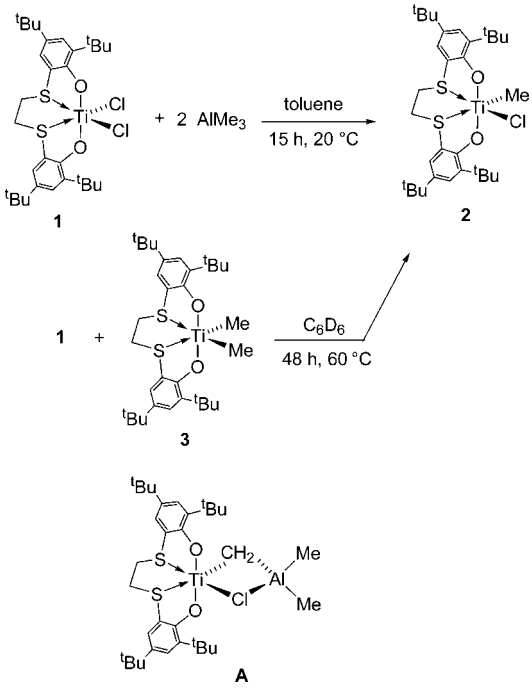
Scheme 1

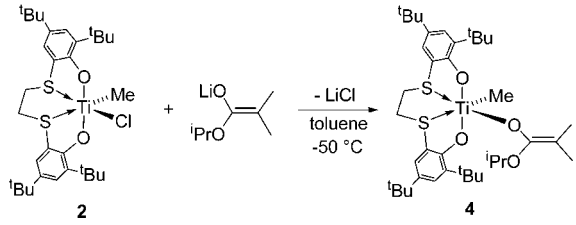


containing a linked bis(phenolato) [OSSO]-type ligand that polymerize styrene isospecifically when activated to give the corresponding alkyl cation.[5] To explore the suitability of this nonmetallocene titanium system for the controlled and stereoselective polymerization of alkyl methacrylate and acrylate monomers, we have prepared both neutral and cationic titanium enolate complexes based on this [OSSO]-type ligand and investigated their reactivity.

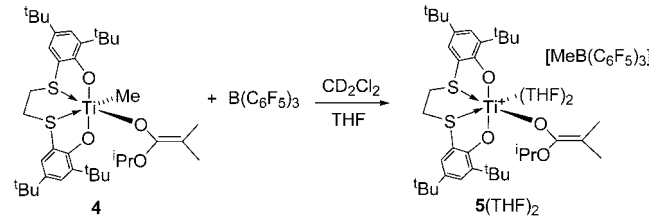
Results and Discussion

Synthesis of the Titanium Complexes. The reaction of titanium dichloro complex containing a [OSSO]-type bis(phenolate) ligand (edtbp)$TiCl_2$ (**1**) (edtbpH_2 = (HOC_6H_2-^{t}Bu_2-4,6)$_2$(SCH_2CH_2S)) with 2 equiv of $AlMe_3$ in toluene at room temperature affords the methyl chloro complex (edtbp)TiMeCl (**2**), which could be isolated as orange crystals in 77% yield. The Tebbe-type μ-methylene complex **A** was not observed even in the crude product (Scheme 1).[6] Alternatively, complex **2** could be synthesized by combining the dichloro complex **1** with the dimethyl complex **3** in C_6D_6. This reaction required higher temperatures (60 °C) to go to completion as shown by ^{1}H NMR spectroscopy. Complex **2** was characterized by elemental analysis and NMR spectroscopy. The ^{1}H NMR spectrum of **2** in C_6D_6 at room temperature exhibits an ABCD-spin system for the SCH_2CH_2S bridge (δ 2.54 (dt), 2.34 (dt), 2.21 (td), and 1.85 ppm (td)). The ^{1}H−^{13}C HMQC spectrum shows these ^{1}H NMR resonances to be correlated with two ^{13}C NMR resonances at δ 40.84 (^{1}H: δ 2.54 and 2.21 ppm) and 36.57 ppm (^{1}H: δ 2.34 and 1.85 ppm), respectively.

Scheme 2



Scheme 3



In order to investigate its activity as precursor for the methacrylate (MMA) polymerization, the synthesis of a titanium enolate complex (edtbp)TiMe{O(^{i}PrO)C=CMe_2} (**4**) was attempted.[2i] Treating **2** with 1 equiv of lithium isopropylisobutyrate, LiO(^{i}PrO)C=CMe_2, in toluene gave **4** as red crystals in 65% yield (Scheme 2). In the ^{1}H NMR spectrum of **4**, two singlets were observed at δ 2.13 and 1.82 ppm for the two =C(CH_3)$_2$ methyl groups as well as two sets of doublets at δ 1.22 and 1.18 ppm for the ^{i}PrO methyl groups. These diastereotopic groups indicate the presence of a configurationally stable, chiral [OSSO] ligand sphere at titanium. Upon addition of the electrophilic borane $B(C_6F_5)_3$ in toluene-d_8, CD_2Cl_2, or C_6D_5Br, thermally labile titanium enolate cation formed. In the presence of a Lewis base such as THF, the cationic species [(edtbp)Ti{O(^{i}PrO)C=CMe_2}(THF)$_2$]$^+$[$MeB(C_6F_5)_3$]$^-$ (**5**(THF)$_2$) could be cleanly generated and was found to be stable at room temperature at least for one day. This product, which may act as model for the key intermediate in the (edtbp)Ti-mediated polymerization of methyl methacrylate (vide infra), was characterized by ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectroscopy (Scheme 3). Notably, the ^{1}H NMR spectrum of the analogous cationic species **5** in CD_2Cl_2, generated in the presence of protio THF instead of THF-d_8, indicates the coordination of two THF molecules (^{1}H: δ 3.76 and 1.85 ppm versus ^{1}H: δ 3.40 and 1.62 ppm for free THF in CD_2Cl_2).

Reaction of the Enolate Complex (edtbp)TiMe{O(^{i}PrO)C=CMe_2} (4) with Alcohols ROH (R = ^{i}Pr, Ph, Ph_3C). During MMA polymerization acidic compounds may act as chain-transfer agent.[3i] Thus, the reaction of the enolate complex with various alcohols was examined. In an NMR experiment, 1 equiv of 2-propanol was added to the methyl enolate titanium complex **4** in C_6D_6 at room temperature. Within a few minutes, the red color of the solution faded. ^{1}H NMR spectroscopy showed the formation of the titanium methyl isopropoxy complex (edtbp)-TiMe(O^{i}Pr) (**6**), which resulted from the selective protonolysis of the Ti−O (enolate) bond with release of isopropyl isobutyrate (Scheme 4). The more acidic phenol reacted in an analogous manner to give the methyl phenolato complex (edtbp)TiMe-(OPh) (**7**) with concomitant formation of one equiv of isopropyl isobutyrate. Whereas this reaction occurred faster than the formation of the methyl isopropoxy complex **6**, enolate complex

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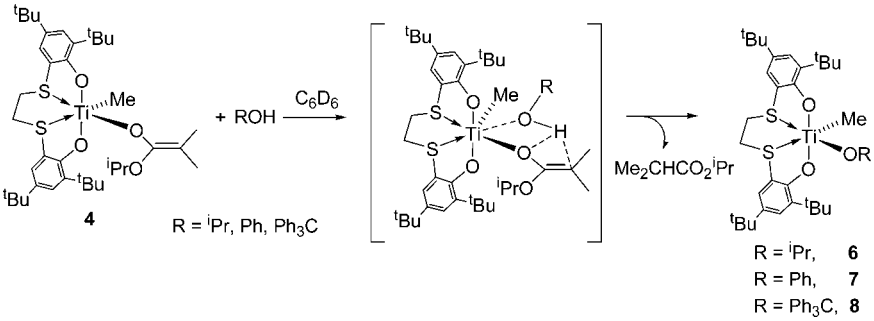
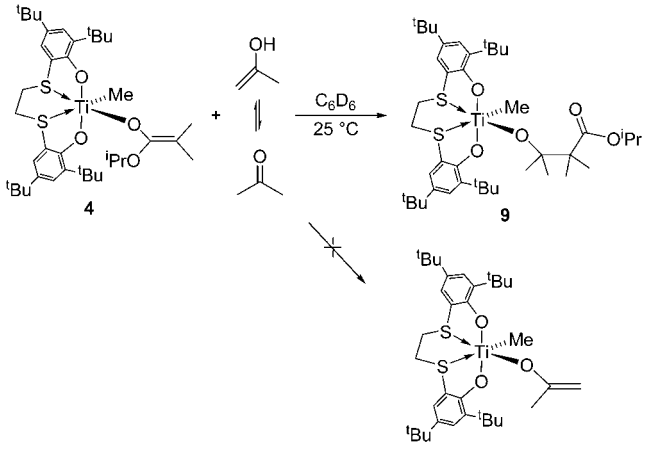
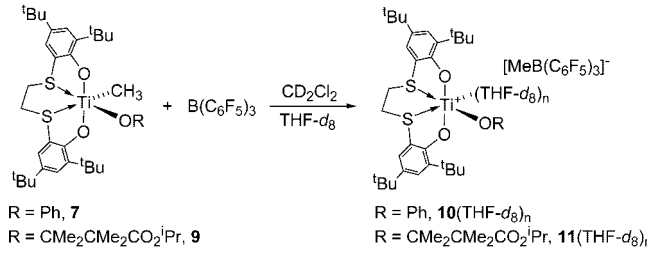
Scheme 4



Scheme 5



Scheme 6



4 reacted more slowly with the bulky trityl alcohol Ph_3COH. Monitoring the reaction by ^{1}H NMR spectroscopy showed that the conversion of **4** to (edtbp)TiMe($OCPh_3$) (**8**) was complete within 2 h at a higher temperature 60 °C. At the same time, the resonances for the ester isopropyl isobutyrate were observed. Although the rate of alcoholysis appears to correlate with the pK_A values of the alcohol (pK_A in DMSO for ^{i}PrOH: 29.3, PhOH: 18.0, Ph_3COH: 25.5), steric influence may have influence as well.[7a]

Reaction of the Enolate Complex (edtbp)TiMe{O(^{i}PrO)C=CMe$_2$} (4) with Acetone. The reaction of complex **4** with 1 equiv of enolizable acetone in C_6D_6 at room temperature quantitatively gave the aldolate-type product (edtbp)TiMe($OCMe_2CMe_2CO_2{}^iPr$) (**9**) within a few minutes (Scheme 5). Complex **9** was isolated as yellow crystals and fully characterized by 1D/2D NMR spectroscopy, elemental analysis, and single crystal X-ray analysis. Characteristic ^{1}H NMR resonances include four singlets at δ 1.78, 1.76, 1.67, and 1.63 ppm for the diastereotopic methyl groups of the $TiOC(CH_3)_2C(CH_3)_2$ group. The observed reactivity behavior confirms that enolizable acetone acts as an electrophile toward the titanium enolate complex **4** rather than as a Brönsted acid to cleave the Ti−O(enolate) bond.[1a,7b] It is notable that thermodynamically unfavorable formation of a vicinal quaternary carbon centers under equilibrium condition is observed. Reaction of the prochiral substrate acetophenone resulted in a 1:1 mixture of diastereomeric products, suggesting that the helical [OSSO] ligand framework does not exert any significant stereochemical bias during the aldol-type C−C coupling reaction.

Alkoxy Cations. The cationic complexes [(edtbp)Ti(OR)-$(THF)_n]^+[MeB(C_6F_5)_3]^-$ (R = Ph, **10**(THF-d_8)$_n$; R = $CMe_2CMe_2CO_2{}^iPr$, **11**(THF-d_8)$_n$) were cleanly generated in CD_2Cl_2 by abstracting the methyl group of **7** and **9** with 1 equiv of $B(C_6F_5)_3$ in the presence of a Lewis base such as THF (Scheme 6). The cationic species **10**(THF-d_8)$_n$ and **11**(THF-d_8)$_n$ were fully characterized by ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectroscopy and found to be stable at room temperature at least for one day. The experimental data do not suggest a rigid coordination of the carbonyl group to the titanium center in **11**(THF-d_8)$_n$. Attempts to grow crystals of this product were unsuccessful. In separate experiments, the cationic alkoxide complexes **10** and **11** were found not to initiate MMA polymerization.[3i]

X-ray Crystal Structures of 2, 4, and 9. Complexes **2**, **4**, and **9** have been characterized by single-crystal X-ray diffraction studies. The molecular structures of **2**, **4**, and **9** in the solid state as well as the selected bond lengths and bond angles are shown in Figures 1–3. Details of the crystal structure determination are given in Table 1. All of these compounds are monomeric in the solid state.

The octahedrally coordinated titanium center in complex **2** is coordinated by two *trans*-oxygen atoms, two sulfur donor atoms, and the *cis*-arranged methyl and chloro ligands (Figure 1). The (edtbp)Ti moiety adopts a C_2-symmetric helical framework. The bond angles of S1−Ti−S2 (75.17(2)°) in **2** are close to the value in the dimethyl complex **3** (74.04(2)°); the Ti−S bond distance (2.6986(8) Å and 2.6756(8) Å) in **2** is slightly shorter than in **3** (2.8056(7) Å and 2.8417(7) Å).[5e] The Ti−C bond distance (2.129(2) Å) is comparable to the values in **3** (2.077(2) Å and 2.084(2) Å).

The solid-state structure of the enolate complex **4** also features a six-coordinated titanium center with a C_2-symmetric helical (edtbp)Ti fragment (Figure 2). The O1−Ti−O2 (152.80(14)°) bond angle is slightly decreased in comparison with that of analogous (edtbp)Ti complexes, in the range of 156.7(2)−157.82(10)°,[5] indicating the generation of a rather open titanium coordination sphere. The Ti-O3 (1.798(3) Å) bond distance and Ti-O3-C32 (163.9(3)°) bond angle (close to linear) are similar to an analogous titanium enolate complex containing a linked amido-cyclopentadienyl ligand (Ti−O, 1.826(2) Å and Ti−O−C, 159.6(2)°)[2i] or a titanium amide enolate complex {(3,5-Me_2-C_6H_3)^{t}BuN}$_3$TiOC-(CH_2)NPhMe (Ti−O, 1.847(3) Å and Ti−O−C, 159.0(2)°).[8a] These observations indicate a p_π−d_π interaction between the

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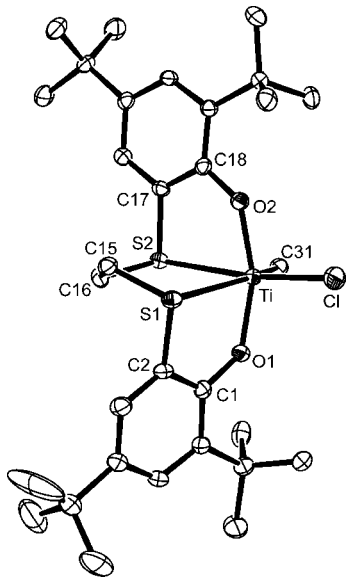

Figure 1. Molecular structure of complex (edtbp)TiMeCl (**2**) (hydrogen atoms were omitted for clarity). Selected bond lengths (Å) and angles (deg): Ti−C31, 2.129(2); Ti−Cl, 2.2893(8); Ti−O1, 1.8726(17); Ti−O2, 1.8651(17); Ti−S1, 2.6986(8); Ti−S2, 2.6756(8); O1−C1, 1.345(3); C2−S1, 1.777(2); Cl−Ti−C31, 105.32(7); O1−Ti−C31, 95.85(8); O2−Ti−C31, 93.85(8); O1−Ti−O2, 160.47(7); S1−Ti−S2, 75.17(2); S1−Ti−O1, 74.62(5).

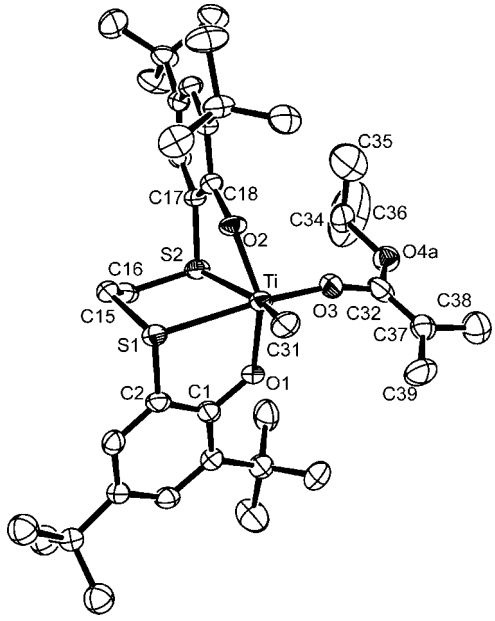

Figure 2. Molecular structure of the complex (edtbp)TiMe{O(ⁱPrO)C=CMe$_2$} (**4**) (hydrogen atoms were omitted for clarity−the disordered *tert*-butyl group and oxygen atom O4 are shown with one split position). Selected bond lengths (Å) and angles (deg): Ti−C31, 2.095(5); Ti−O1, 1.879(3); Ti−O2, 1.892(3), Ti−O3, 1.798(3); Ti−S1, 2.6389(15); Ti−S2, 2.7327(14); C32−C37, 1.334(7); C37−C38, 1.493(7); C37−C39, 1.489(7); Ti−O3−C32, 163.9(3); O3−Ti−C31, 99.72(18); O1−Ti−C31, 100.50(17); O2−Ti−C31, 95.84(17); O1−Ti−O2, 152.80(14); S1−Ti−S2, 79.28(4); C32−C37−C39, 122.1(5); C(32)−C37−C38, 122.8(5); C38−C37−C39, 115.2(5).

electron-deficient titanium center and the partly *sp*-hybridized oxygen atom.[3c,8,9] The oxygen atom O4 was found to be disordered in the solid state and refined with split positions. In each case, the sum of angles around C32 is close to 360° (O4a, 359.2° vs O4b, 357.2°). The bond length between C32 and C37 of 1.334(7) Å as well as the sum of angles around C37 agree with a C32−C37 double bond.

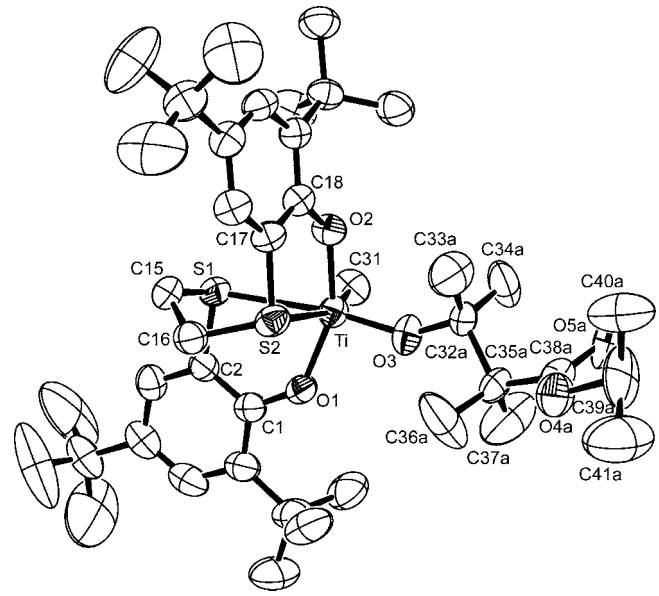

Figure 3. Molecular structure of the aldolate complex (edtbp)TiMe(OCMe$_2$CMe$_2$CO$_2$ⁱPr) (**9**) (hydrogen atoms were omitted for clarity, for the atoms of the ester alkoxy group only one the refined split positions are shown). Selected bond lengths (Å) and angles (deg): Ti−O1, 1.8815(16); Ti−O2, 1.8898(15), Ti−O3, 1.7622(16); Ti−S1, 2.7156(8); Ti−S2, 2.7227(8); Ti−C31, 2.099(2); Ti−O3−C(32a), 147.4(3); O3−Ti−C31,102.43(9); O1−Ti−C31,96.38(9); O2−Ti−C31, 95.45(8); O1−Ti−O2, 154.44(7); S1−Ti−S2 77.05(2).

The single crystal of complex (edtbp)TiMe(OCMe$_2$CMe$_2$CO$_2$ⁱPr) (**9**) was obtained from hexane at −30 °C and measured at 243 K on a CCD diffractometer due to a solid-phase transformation at 110 K, resulting in the transformation from transparent yellow crystals to a powder. The geometry around the six-coordinated titanium center is similar to that of **2** and **4** with a C_2-symmetric (edtbp)Ti moiety (Figure 3). A slightly shortened Ti−C31 bond (2.099(2) Å in **9** vs 2.129(2) Å in **2**) was found. The alkoxy group of the ester fragment (Ti(OCMe$_2$CMe$_2$CO$_2$ⁱPr) is disordered and was refined with split positions. The oxygen atom of the carbonyl group is not coordinated to the titanium center, although seven-coordination can be achieved at the titanium center within the [OSSO]-type ligand sphere, as observed in the titanium methyl cation [(edtbp)TiMe(dmpe)][MeB(C$_6$F$_5$)$_3$].[5e] The small Ti−O3−C32a bond angle (147.4(3)°) indicates a less pronounced $p_\pi-d_\pi$ Ti−O interaction as compared to that in **4**. Probably the steric crowding around the titanium center precludes the coordination of the carbonyl oxygen, a structural feature that is rather common.[8a]

MMA and *n*BA Polymerization by Titanium Enolate Complexes. Methyl methacrylate (MMA) and *n*-butyl acrylate (*n*BA) polymerization with the titanium enolate complexes **4** and **5** was investigated. Representative results are summarized in Table 2. The polymerization of MMA was carried out using various addition sequences (entries 1–7). When complex **4** was

(8) (a) Agapie, T.; Diaconescu, P. L.; Mindiola, D. J.; Cummins, C. C. *Organometallics* **2002**, *21*, 1329–1340. (b) For other examples for titanium enolate complexes, see: Curtis, M. D.; Thanedar, S.; Butler, W. M. *Organometallics* **1984**, *3*, 1855–1859. (c) Veya, P.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1993**, *12*, 4892–4898. (d) Hortmann, K.; Diebold, J.; Brintzinger, H.-H. *J. Organomet. Chem.* **1993**, *445*, 107–109.

(9) For the $p_\pi-d_\pi$ interaction in a zirconium complex, see: Collins, S.; Koene, B. E.; Ramachandran, R.; Taylor, N. J. *Organometallics* **1991**, *10*, 2092–2094.

Table 1. Crystal Data and Structure Refinement for 2, 4, and 9

	2	**4**	**9**
formula	$C_{31}H_{47}ClO_2S_2Ti$	$C_{38}H_{60}O_4S_2Ti$	$C_{41}H_{66}O_5S_2Ti$
M_r	599.16	692.88	750.96
T/K	130(2)	130(2)	243(2)
crystal size/mm	0.3 × 0.2 × 0.12	0.27 × 0.25 × 0.05	0.40 × 0.18 × 0.17
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	P-1
a/Å	15.968(3)	10.0930(11)	10.8126(10)
b/Å	12.0901(19)	15.7694(16)	13.3683(12)
c/Å	17.509(3)	25.037(2)	16.3273(15)
α/deg			105.4805(15)
β/deg	104.801(4)	100.761(3)	94.0812(16)
γ/deg			94.0877(16)
U/Å^3	3268.0(10)	3914.8(7)	2258.6(4)
Z	4	4	2
D_c/g cm^{-3}	1.218	1.176	1.104
μ/mm^{-1}	0.496	0.361	0.319
F(000)	1280	1496	812
θ range/deg	2.07 – 28.42	1.53 – 25.08	2.31 – 28.38
data collected (*hkl*)	±21, –16 to 13, –23 to 20	−12 to 11, ± 18, −28 to 29	±14, ± 17, ± 21
no. of reflns collected	26485	31518	31347
no. of independent reflns	8160	6925	11211
R_{int}	0.0552	0.1023	0.0536
final R_1, $wR_2[I > 2\sigma(I)]$	0.0512, 0.1260	0.0651, 0.1335	0.0521, 0.1091
R_1, wR_2 (all data)	0.0757, 0.1382	0.1227, 0.1689	0.1117, 0.1229
goodness of fit on F^2	1.054	0.958	0.800
$\Delta\rho_{max,\ min}$/e Å^{-3}	1.114, −0.585	0.528, −0.477	0.465, −0.243

Table 2. Polymerization of MMA and *n*BA Using the Precursors 4/E(C_6F_5)$_3$ (E = B, Al) and 5 System[a]

entry	cat.	activator	monomer	T (°C)	yield (%)	$M_{n,exp}$[b]	M_w/M_n[b]	*mm*[c]	*mr*[c]	*rr*[c]
1	**4**	$B(C_6F_5)_3$	MMA	20	<1	n.d.	n.d.	n.d.	n.d.	n.d.
2[d]	**4**	$B(C_6F_5)_3$	MMA	20	5	10 800	1.19	15	28	57
3	**4**	$B(C_6F_5)_3$·THF	MMA	20	8	12 700	1.22	9	38	53
4	**5**		MMA	20	52	16 000	2.63	12	33	55
5	**5**		MMA	60	2	n.d.	n.d.	n.d.	n.d.	n.d.
6[d]	**4**	$Al(C_6F_5)_3$	MMA	20	65	20 600	1.09	2	27	71
7[d]	**4**	2 $Al(C_6F_5)_3$	MMA	20	72	19 300	1.10	3	27	70
8	**5**		*n*BA	20	<1	n.d.	n.d.	n.d.	n.d.	n.d.
9	**4**	$B(C_6F_5)_3$·THF	*n*BA	20	<1	n.d.	n.d.	n.d.	n.d.	n.d.
10	**4**		*n*BA	20	28	112 400	2.12	19	29	52
11	**4**		*n*BA	60	15	58 100	1.96	14	30	56

[a] Polymerization conditions: solvent = 2 mL of toluene; cat. = 0.02 mmol; monomer/cat./activator = 200:1:1; polymerization time = 24 h; protocol: cat.+ activator, then MMA. [b] Determined by GPC in THF vs polystyrene standards. [c] Determined by ^{1}H NMR (PMMA) or ^{13}C NMR (P*n*BA) spectroscopy in $CDCl_3$; *mm*, *mr*, and *rr* refer to isotactic, atactic, and syndiotactic triads. [d] Protocol: cat. + MMA, then activator E(C_6F_5)$_3$.

combined in situ with the activator $B(C_6F_5)_3$ and MMA was added, no polymerization was observed (entry 1). By changing the addition sequence (entry 2) and when $B(C_6F_5)_3$·THF was used as activator (entry 3), the yield for PMMA (5–8%) only slightly improved. However, the cationic species **5** did polymerize MMA at room temperature resulting in a moderate yield of 52% PMMA (entry 4). The PMMA obtained has a molecular weight (M_n = 16 000) that is larger than the calculated one (M_n = 10 400) considering one metal center per polymer chain. The polydispersity was high, although monomodal distribution was detected. Raising the polymerization temperature to 60 °C did not improve the MMA conversion (entry 5). The obtained PMMAs have a syndiotactic microstructure (55–57% *rr*). Obviously, the higher intensity of *rr* relative to *mm* is consistent with chain-end control (either monometallic or bimetallic)[1b,c,2i,3j] rather than enantiomorphic site control,[2h] under which the last inserted MMA monomer is responsible for the stereoselectivity over the microstructure of the resultant polymer. In a separate experiment, the dimethyl complex **3** activated with $B(C_6F_5)_3$ or $B(C_6F_5)_3$·THF was shown to be inactive in the MMA polymerization. These observations suggest that the cationic titanium enolate species are active in the polymerization of MMA. However, the propagating species that contains a bis(phenolato) [OSSO]-framework are somewhat labile and follow deactivation pathways (back-biting). Upon activation with 1 or 2 equiv of $Al(C_6F_5)_3$ (entries 6 and 7), which may involve a bimetallic chain propagation fashion,[2m] complex **4** was found to give PMMAs with narrow polydispersities (1.09–1.10), albeit with moderate yield (65–72%). Notably, a mixture of the neutral complex **4** and the cationic complex **5** in 1:1 ratio, MMA polymerization was complete in less than 5 min with a living characteristic (MMA/**4**/**5** = 200:1:1, M_n = 22 200, M_w/M_n = 1.08, *rr* = 67%).

Complex **4** was also assessed for the polymerization of *n*BA containing an active α-H (entries 8–11). In contrast to MMA polymerization, the cationic titanium enolate species were totally inactive (entries 8 and 9). Notably, only the neutral precursor **4** showed a low activity toward *n*BA polymerization, giving high molecular weight P(*n*BA) with a rather low initiation efficiency (ca. 6% both at 20 °C and at 60 °C) (entries 10 and 11). The ^{13}C NMR spectra of P(*n*BA) also show a syndiotactically enriched microstructure (*rr*, 52–56%).

Conclusion

In conclusion, the readily synthesized titanium enolate complex **4** exhibits a rather high basicity/nucleophilicity in the presence of enolizable acetone resulting in a remarkable aldol-

type C−C coupling reaction. At the same time, a pronounced Lewis acidic property of the titanium center accounts for the facile protonolysis reaction with alcohols and phenols. Thus, **4** reacts with alcohols and phenol to selectively cleave the Ti−O(enolate) bond affording the alkoxy/phenoxy methyl complexes **6–8**. Although enolizable, acetone functions as an electrophile to form the structurally characterized aldolate complex **9**. Upon acitvation with a Lewis acid $E(C_6F_5)_3$ (E = B, Al), the titanium enolate complex is converted into the enolate cation that is active in MMA polymerization, producing syndiotactic-enriched PMMAs. In the light of the well controlled MMA and *n*BA polymerizations mediated by the titanium enolate precursors supported by the linked amido-cyclopentadienyl ligand,[2i,3j,k] the present results point at the suitability of group 4 nonmetallocene complexes for methacrylate and acrylate polymerization. However, the low stereoselectivity during MMA polymerization will require an improved design of the [OSSO]-type ligand, despite its certain resemblance to the EBI ligand in zirconocene catalysts.[2h]

Experimental Section

General Procedures. All experiments were carried out under purified argon using standard Schlenk techniques or a glovebox (<1 ppm O_2, 1 ppm H_2O). Toluene, pentane, diethyl ether, dichloromethane, and THF were purified from the MBraun SPS-800 system prior to use. Deuterated solvents were purchased from Aldrich and purified before use. All other chemicals were commercially available and used after appropriate purification. Complexes (edtbp)$TiCl_2$ (**1**),[5a] (edtbp)$TiMe_2$ (**3**),[5e] $LiO(^iPrO)C{=}CMe_2$,[2h] and $Al(C_6F_5)_3 \cdot 0.5C_7H_8$[10] were synthesized according to literature methods. NMR spectra were recorded on Bruker DRX 400 (^1H, 400 MHz; ^{13}C, 101 MHz) and Varian 200 spectrometers in Teflon-valved NMR tubes at 25 °C otherwise stated. ^1H and ^{13}C NMR chemical shifts were determined using residual solvent resonances and are reported vs $SiMe_4$. Assignment of signals was made from $^1H-^{13}C$ HMQC and $^1H-^{13}C$ HMBC 2D NMR experiments. Coupling constants are given in hertz. Elemental analyses were performed by the Microanalytical Laboratory of this department. Molecular weights of polymers were determined by gel permeation chromatography (GPC) at room temperature in THF and calibrated with respect to polystyrene standards. The microstructure of polymer was determined by ^1H NMR and ^{13}C NMR in $CDCl_3$.

Synthesis of (edtbp)TiMeCl (2). To a solution of (edtbp)$TiCl_2$ (0.5 g, 0.81 mmol) in toluene (20 mL) was slowly added $AlMe_3$ (0.81 mL, 2 M in hexane, 1.62 mmol) at –30 °C. The reaction mixture was warmed to room temperature and further stirred overnight. After evaporation of volatile under vacuum, the residue was recrystallized with pentane to give the orange crystals as (edtbp)TiMeCl (**2**) (0.37 g, 77%). A crystal of **2** suitable for X-ray diffraction analysis was selected. ^1H NMR ($CDCl_3$): δ 7.39 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-5-*H*), 7.36 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-5′-*H*), 7.17 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-3-*H*), 7.11 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-3′-*H*), 3.23 (dt, $^2J_{HH}$ = 13.2, $^3J_{HH}$ = 3.2 Hz, 1H, SCH_2), 3.03 (dt, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 3.2 Hz, 1H, SCH_2), 2.52 (td, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 3.2 Hz, 1H, SCH_2), 2.13 (td, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 3.2 Hz, 1H, SCH_2), 1.78 (s, 3H, TiCH_3), 1.61 (s, 9H, C(CH_3)$_3$), 1.58 (s, 9H, C(CH_3)$_3$), 1.28 (s, 9H, C(CH_3)$_3$), 1.25 (s, 9H, C(CH_3)$_3$); ^1H NMR (C_6D_6): δ 7.56 (d, ^4J = 2.4, 1 H, Ph-5-*H*), 7.52 (d, ^4J = 2.4, 1 H, Ph-5′-*H*), 7.13 (d, ^4J = 2.4, 1 H, Ph-3-*H*), 7.01 (d, ^4J = 2.4, 1 H, Ph-3′-*H*), 2.54 (dt, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 3.2 Hz, 1H, SCH_2), 2.34 (dt, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 3.2 Hz, 1H, SCH_2), 2.21 (td, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 3.2 Hz, 1H, SCH_2), 2.20 (s, 3H, TiCH_3), 1.85 (td, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 3.2 Hz, 1H, SCH_2), 1.78 (s, 9H, C(CH_3)$_3$), 1.75 (s, 9H, C(CH_3)$_3$), 1.21 (s, 9H, C(CH_3)$_3$), 1.19 (s, 9H, C(CH_3)$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 167.09 (Ph-*C*1), 166.81 (Ph-*C*1′), 144.39 (Ph-*C*6), 144.14 (Ph-*C*6′), 137.96 (Ph-*C*4), 137.06 (Ph-*C*4′), 127.08 (Ph-*C*5), 126.67 (Ph-*C*5′), 126.59 (Ph-*C*3), 126.45 (Ph-*C*3′), 120.24 (Ph-*C*2), 119.39 (Ph-*C*2′), 74.75 (Ti*C*H_3), 40.84 (S*C*H_2), 36.57 (S*C*H_2), 35.86 (*C*(CH_3)$_3$), 35.74 (*C*(CH_3)$_3$), 34.55 (*C*(CH_3)$_3$), 34.50 (*C*(CH_3)$_3$), 31.46 (C(*C*H_3)$_3$), 31.22 (C(*C*H_3)$_3$), 29.75 (C(*C*H_3)$_3$), 29.68 (C(*C*H_3)$_3$). Anal. Calcd for $C_{31}H_{47}ClO_2S_2Ti$ (599.15): C, 62.14; H, 7.91. Found: C, 62.28; H, 7.73.

Formation of 2 from (edtbp)$TiCl_2$ (1) and (edtbp)$TiMe_2$ (3). In the glovebox, a Teflon-valved NMR tube was charged with complexes (edtbp)$TiCl_2$ (10.7 mg, 0.017 mmol) and (edtbp)$TiMe_2$ (10.0 mg, 0.017 mmol), and C_6D_6 (ca. 0.5 mL) was vacuum transferred. The tube was sealed and kept at 60 °C. Periodic NMR spectroscopic monitoring revealed quantitative formation of (edtbp)TiMeCl (**2**) within 2 days. The NMR data were the same as those described above.

Synthesis of (edtbp)TiMe(O(^{i}PrO)C=CMe$_2$) (4). To a solution of **2** (0.5 g, 0.83 mmol) in toluene (30 mL) was slowly added 25 mL of a toluene solution of $LiO(^iPrO)C{=}CMe_2$ (0.114 g, 0.83 mmol) at −50 °C. The reaction mixture was warmed to room temperature and further stirred overnight. After evaporation of volatile under vacuum, the residue was recrystallized with pentane to give (edtbp)TiMe{O(^{i}PrO)C=CMe$_2$} (**4**) as red crystals (0.38 g, 65%). A crystal of **4** suitable for X-ray diffraction analysis was selected. ^1H NMR (C_6D_6): δ 7.55 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-5-*H*), 7.50 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-5′-*H*), 7.26 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-3-*H*), 7.09 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-3′-*H*), 4.85 (sept, $^3J_{HH}$ = 6.1 Hz, 1H, OC*H*(CH_3)$_2$), 2.63 (dt, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 3.2 Hz, 1H, SCH_2), 2.43 (dt, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 3.2 Hz, 1H, SCH_2), 2.30 (td, $^2J_{HH}$ = 13.5, $^3J_{HH}$ = 3.2, 1H, SCH_2), 2.13 (s, 3H, =C(CH_3)$_2$), 2.02 (td, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 3.2 Hz, 1H, SCH_2), 1.82 (s, 3H, =C(CH_3)$_2$), 1.79 (s, 3H, TiCH_3), 1.69 (s, 18H, C(CH_3)$_3$), 1.23 (s, 9H, C(CH_3)$_3$), 1.22 (d, $^3J_{HH}$ = 6.1 Hz, 3H, OCH(CH_3)$_2$), 1.19 (s, 9H, C(CH_3)$_3$), 1.18 (d, $^3J_{HH}$ = 6.1 Hz, 3H, OCH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 167.42 (Ph-*C*1), 166.72 (Ph-*C*1′), 159.70 (*C* = C(CH_3)$_2$), 143.10 (Ph-*C*6), 142.47 (Ph-*C*6′), 137.24 (Ph-*C*4), 137.22 (Ph-*C*4′), 127.26 (Ph-*C*5), 126.97 (Ph-*C*5′), 126.41 (Ph-*C*3), 126.26 (Ph-*C*3′), 119.88 (Ph-*C*2), 117.62 (Ph-*C*2′), 90.83 (=*C*(CH$_3$)$_2$), 69.44 (O*C*H(CH$_3$)$_2$), 56.26 (Ti*C*H$_3$), 40.27 (S*C*H$_2$), 36.27 (S*C*H$_2$), 35.71 (*C*(CH$_3$)$_3$), 35.60 (*C*(CH$_3$)$_3$), 34.44 (*C*(CH$_3$)$_3$), 34.37 (*C*(CH$_3$)$_3$), 31.54 (C(*C*H$_3$)$_3$), 31.53 (C(*C*H$_3$)$_3$), 29.69 (C(*C*H$_3$)$_3$), 29.67 (C(*C*H$_3$)$_3$), 22.00 (OCH(*C*H$_3$)$_2$), 21.97 (OCH(*C*H$_3$)$_2$), 18.04 (=C(*C*H$_3$)$_2$), 17.12 (=C(*C*H$_3$)$_2$). Anal. Calcd for $C_{38}H_{60}O_4S_2Ti$ (692.88): C, 65.87; H, 8.73. Found: C, 66.39; H, 9.07.

Generation of the Ion Pair [(edtbp)Ti{O(^{i}PrO)C=CMe$_2$}(THF-d_8)$_2$]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ (5(THF-d_8)$_2$). In the glovebox, a Teflon-valved NMR tube was charged with complex (edtbp)TiMe{O(^{i}PrO)C=CMe$_2$} (**4**) (10 mg, 0.014 mmol) and $B(C_6F_5)_3$ (7.4 mg, 0.014 mmol), and CD_2Cl_2 was vacuum transferred in the presence of one drop of THF-d_8 (THF free cationic species was found not stable in CD_2Cl_2 at room temperature). The tube was sealed, and NMR spectroscopy was recorded, which revealed quantitative formation of cationic species [(edtbp)Ti{O(^{i}PrO)C=CMe$_2$}(THF-d_8)$_2$]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ (**5**(THF-d_8)$_2$). ^1H NMR (CD_2Cl_2): δ 7.48 (d, $^4J_{HH}$ = 2.2 Hz, 2 H, Ph-5-*H*), 7.28 (br s, 2 H, Ph-3-*H*), 4.25 (sept, $^3J_{HH}$ = 6.1 Hz, 1H, OC*H*(CH$_3$)$_2$), 3.32 (d, $^2J_{HH}$ = 11.2 Hz, 2H, SCH_2), 2.73 (d, $^2J_{HH}$ = 11.2 Hz, 2H, SCH_2), 1.80 (s, 6H, =C(CH_3)$_2$), 1.43 (s, 18H, C(CH_3)$_3$), 1.27 (s, 18H, C(CH_3)$_3$), 1.01 (d, $^3J_{HH}$ = 6.1 Hz, 3H, OCH(CH_3)$_2$), 0.85 (d, $^3J_{HH}$ = 6.1 Hz, 3H, OCH(CH_3)$_2$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 167.43 (*C* = C(CH$_3$)$_2$), 164.50 (Ph-*C*1), 148.49 (Ph-*C*6), 145.64 (Ph-*C*4), 136.52 (Ph-*C*5), 128.16 (Ph-*C*3), 127.07 (Ph-*C*2), 102.40 (=*C*(CH$_3$)$_2$), 72.47 (O*C*H(CH$_3$)$_2$), 38.69 (S*C*H$_2$), 35.13 (*C*(CH$_3$)$_3$), 34.52 (*C*(CH$_3$)$_3$), 31.34 (C(*C*H$_3$)$_3$), 29.56 (C(*C*H$_3$)$_3$), 21.48 (OCH(*C*H$_3$)$_2$), 21.32 (OCH(*C*H$_3$)$_2$), 17.68 (=C(*C*H$_3$)$_2$). NMR data for the free anion [MeB(C$_6$F$_5$)$_3$]$^-$: ^1H

(10) Feng, S.; Roof, G. R.; Chen, E. Y.-X. *Organometallics* **2002**, *21*, 832–839.

NMR (CD_2Cl_2): δ 0.45 (br s, 3H, BCH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 148.61 (dm, $^1J_{CF}$ = 231 Hz, *o*-C_6F_5), 137.90 (dm, $^1J_{CF}$ = 231 Hz, *p*-C_6F_5), 136.63 (dm, $^1J_{CF}$ = 250 Hz, *m*-C_6F_5), 130.52 (C_{ipso}), 10.07 (br, BCH_3). ^{11}B NMR (CD_2Cl_2): δ −14.9 (s, *B*CH_3). ^{19}F NMR (CD_2Cl_2): δ –133.1 (d, $^3J_{FF}$ = 19 Hz, 6F, *o*-F), −165.3 (t, $^3J_{FF}$ = 19 Hz, 3F, *p*-F), −167.9 (m, $^3J_{FF}$ = 19 Hz, 6F, *m*-F).

Generation of Cationic Species [(edtbp)Ti{O(ⁱPrO)C=CMe₂}(THF)₂]⁺[MeB(C₆F₅)₃]⁻ (5(THF)₂). The same procedure was followed as mentioned above, using protio THF instead of THF-d_8. ^1H NMR (CD_2Cl_2): δ 7.50 (d, $^4J_{HH}$ = 2.2 Hz, 2 H, Ph-5-*H*), 7.34 (d, $^4J_{HH}$ = 2.2 Hz, 1 H, Ph-3-*H*), 7.22 (d, $^4J_{HH}$ = 2.2 Hz, 1 H, Ph-3′-*H*), 4.26 (sept, $^3J_{HH}$ = 6.1 Hz, 1H, OC*H*(CH_3)$_2$), 3.76 (m, 8H, O(CH_2CH_2)$_2$), 3.31 (d, $^2J_{HH}$ = 11.2 Hz, 2H, SCH_2), 2.74 (d, $^2J_{HH}$ = 11.2 Hz, 2H, SCH_2), 1.85 (m, 8H, O(CH_2CH_2)$_2$), 1.81 (s, 6H, =C(CH_3)$_2$), 1.46 (s, 9H, C(CH_3)$_3$), 1.42 (s, 9H, C(CH_3)$_3$), 1.29 (s, 9H, C(CH_3)$_3$), 1.28 (s, 9H, C(CH_3)$_3$), 1.02 (d, $^3J_{HH}$ = 6.1 Hz, 3H, OCH(CH_3)$_2$), 0.87 (d, $^3J_{HH}$ = 6.1 Hz, 3H, OCH(CH_3)$_2$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 167.57 (*C* = C(CH_3)$_2$), 166.38 (Ph-*C*1), 165.32 (Ph-*C*1′), 149.17 (Ph-*C*6), 146.85 (Ph-*C*6′), 137.47 (Ph-*C*4), 136.96 (Ph-*C*4′), 128.91 (Ph-*C*5), 128.35 (Ph-*C*5′), 127.92 (Ph-*C*3), 127.57 (Ph-*C*3′), 119.59 (Ph-*C*2), 117.95 (Ph-*C*2′), 102.59 (=*C*(CH_3)$_2$), 72.11 (O*C*H(CH_3)$_2$), 68.62 (O(*C*H_2CH_2)$_2$), 41.38 (S*C*H_2), 38.63 (S*C*H_2), 35.78 (*C*(CH_3)$_3$), 35.63 (*C*(CH_3)$_3$), 35.25 (*C*(CH_3)$_3$), 35.05 (*C*(CH_3)$_3$), 31.37 (C(*C*H_3)$_3$), 31.20 (C(*C*H_3)$_3$), 29.66 (C(*C*H_3)$_3$), 29.52 (C(*C*H_3)$_3$), 25.41 (O(CH_2*C*H_2)$_2$), 21.01 (OCH(*C*H_3)$_2$), 20.86 (OCH(*C*H_3)$_2$), 17.25 (=C(*C*H_3)$_2$). NMR data for the free anion $[MeB(C_6F_5)_3]^-$ were the same as those described above.

Synthesis of (edtbp)TiMe(Oⁱ Pr) (6). To a solution of (edtbp)TiMe{O(ⁱPrO)C=CMe$_2$} (**4**) (30 mg, 0.043 mmol) in C_6D_6 (ca. 0.5 mL) in a Teflon-valved NMR tube was added at room temperature isopropanol (2.6 mg, 0.043 mmol) via a microsyringe. The color of the solution quickly changed from red to yellow and NMR spectra were recorded (NMR data for the ester isopropyl isobutyrate formed. ^1H NMR (C_6D_6): δ 5.01 (sept, $^3J_{HH}$ = 6.0 Hz, 1H, OC*H*(CH_3)$_2$), 2.34 (sept, $^3J_{HH}$ = 7.0 Hz, 1H, (*O*=C)C*H*(CH_3)$_2$), 1.06 (d, $^3J_{HH}$ = 6.0 Hz, 6H, OCH(CH_3)$_2$), 1.03 (d, $^3J_{HH}$ = 7.0 Hz, 6H, (*O*=C)CH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 175.40 (*C*OOⁱPr), 66.47 (O*C*H(CH_3)$_2$), 33.83 ((CH_3)$_2$*C*HCO), 21.30 (OCH(*C*H_3)$_2$), 18.59 ((CH_3)$_2$CHCO). The conversion of **4** to **6** was virtually quantitative after 10 min. The solvent was removed under vacuum, and the residue was recrystallized with pentane to give **6** as a yellow solid (20 mg, 74%). ^1H NMR (C_6D_6): δ 7.54 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-5-*H*), 7.53 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-5′-*H*), 7.30 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-3-*H*), 7.19 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-3′-*H*), 4.90 (sept, $^3J_{HH}$ = 6.1 Hz, 1H, OC*H*(CH_3)$_2$), 2.69 (dt, $^2J_{HH}$ = 13.2, $^3J_{HH}$ = 3.2 Hz, 1H, SCH_2), 2.54 (dt, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 3.2 Hz, 1H, SCH_2), 2.33 (td, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 3.2 Hz, 1H, SCH_2), 2.07 (td, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 3.2 Hz, 1H, SCH_2), 1.73 (s, 9H, C(CH_3)$_3$), 1.71 (s, 9H, C(CH_3)$_3$), 1.59 (s, 3H, TiCH_3), 1.34 (d, $^3J_{HH}$ = 6.1 Hz, 3H, OCH(CH_3)$_2$), 1.31 (d, $^3J_{HH}$ = 6.1 Hz, 3H, OCH(CH_3)$_2$), 1.25 (s, 9H, C(CH_3)$_3$), 1.22 (s, 9H, C(CH_3)$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 167.79 (Ph-*C*1), 166.79 (Ph-*C*1′), 142.38 (Ph-*C*6), 141.59 (Ph-*C*6′), 137.37 (Ph-*C*4), 137.02 (Ph-*C*4′), 128.53 (Ph-*C*5), 128.42 (Ph-*C*5′), 126.35 (Ph-*C*3), 126.26 (Ph-*C*3′), 119.62 (Ph-*C*2), 117.08 (Ph-*C*2′), 80.14 (TiO*C*H(CH_3)$_2$), 49.00 (Ti*C*H_3), 38.94 (S*C*H_2), 36.15 (S*C*H_2), 35.81 (*C*(CH_3)$_3$), 35.75 (*C*(CH_3)$_3$), 34.52 (*C*(CH_3)$_3$), 34.44 (*C*(CH_3)$_3$), 31.74 (C(*C*H_3)$_3$), 31.62 (C(*C*H_3)$_3$), 30.00 (C(*C*H_3)$_3$), 29.61 (C(*C*H_3)$_3$), 25.67 (TiOCH(*C*H_3)$_2$). Anal. Calcd for $C_{34}H_{54}O_3S_2Ti$ (622.79): C, 65.57; H, 8.74. Found: C, 64.96; H, 8.77.

Synthesis of (edtbp)TiMe(OPh) (7). To a solution of **4** (40 mg, 0.058 mmol) in C_6D_6 (ca. 0.5 mL) in a Teflon-valved NMR tube was added at room temperature phenol (5.4 mg, 0.058 mmol). Immediately, the red solution changed to a yellow solution, and NMR spectra were recorded. The conversion of **4** to **7** was virtually quantitative after 10 min The solvent was removed under vacuum, and the residue was recrystallized with pentane to give **7** as yellow crystals (31 mg, 80%). ^1H NMR (C_6D_6): δ 7.54 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-5-*H*), 7.52 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-5′-*H*), 7.29 (dd, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 2.1 Hz, 2H, OPh-*o*-H), 7.26 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-3-*H*), 7.10 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-3′-*H*), 7.06 (dt, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 2.1 Hz, 2H, OPh-*m*-H), 7.06 (tt, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 2.1 Hz, 1H, OPh-*p*-H), 2.64 (dt, $^2J_{HH}$ = 13.2, $^3J_{HH}$ = 3.2 Hz, 1H, SCH_2), 2.45 (dt, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 3.2 Hz, 1H, SCH_2), 2.35 (td, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 3.2 Hz, 1H, SCH_2), 2.02 (td, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 3.2 Hz, 1H, SCH_2), 1.85 (s, 3H, TiCH_3), 1.68 (s, 9H, C(CH_3)$_3$), 1.62 (s, 9H, C(CH_3)$_3$), 1.22 (s, 9H, C(CH_3)$_3$), 1.20 (s, 9H, C(CH_3)$_3$); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 167.38 (Ph-*C*1), 166.84 (Ph-*C*1′), 166.38 (OPh-*ipso*-C), 143.32 (Ph-*C*6), 142.81 (Ph-*C*6′), 137.47 (Ph-*C*4), 137.40 (Ph-*C*4′), 128.90 (OPh-*m*-C), 128.53 (Ph-*C*5), 128.40 (Ph-*C*5′), 126.54 (Ph-*C*3), 126.49 (Ph-*C*3′), 121.90 (Ph-*C*2), 121.42 (OPh-*p*-C), 119.45 (Ph-*C*2′), 119.03 (OPh-*o*-C), 56.60 (Ti*C*H_3), 39.93 (S*C*H_2), 36.15 (S*C*H_2), 35.64 (*C*(CH_3)$_3$), 35.61 (*C*(CH_3)$_3$), 34.50 (*C*(CH_3)$_3$), 34.39 (*C*(CH_3)$_3$), 31.64 (C(*C*H_3)$_3$), 31.62 (C(*C*H_3)$_3$), 29.73 (C(*C*H_3)$_3$), 29.70 (C(*C*H_3)$_3$). Anal. Calcd for $C_{37}H_{52}O_3S_2Ti$ (656.8): C, 67.66; H, 7.98. Found: C, 67.74; H, 7.68.

Synthesis of (edtbp)TiMe(OCPh₃) (8). To a solution of **4** (30 mg, 0.043 mmol) in C_6D_6 (ca. 0.5 mL) in a Teflon-valved NMR tube was added at room temperature trityl alcohol (11.3 mg, 0.043 mmol). The tube was kept at 60 °C and NMR spectra were recorded. The conversion of **4** to **8** was virtually quantitative after 2 h. The solvent was removed under vacuum, and the residue was recrystallized with pentane to give **8** as brown crystals (28 mg, 78%). ^1H NMR (C_6D_6): δ 7.73 (dd, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 2.2 Hz, 6H, OCPh$_3$-*o*-H),7.54 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-5-*H*), 7.45 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-5′-*H*), 7.30 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-3-*H*), 7.12 (dt, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 2.2 Hz, 6H, OCPh$_3$-*m*-H), 7.04 (tt, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 2.2 Hz, 3H, OCPh$_3$-*p*-H), 6.92 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-3′-*H*), 2.58 (dt, $^2J_{HH}$ = 13.2, $^3J_{HH}$ = 3.2 Hz, 1H, SCH_2), 2.38 (dt, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 3.2 Hz, 1H, SCH_2), 2.17 (td, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 3.2 Hz, 1H, SCH_2), 2.03 (td, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 3.2 Hz, 1H, SCH_2), 1.66 (s, 3H, TiCH_3), 1.62 (s, 9H, C(CH_3)$_3$), 1.58 (s, 9H, C(CH_3)$_3$), 1.23 (s, 9H, C(CH_3)$_3$), 1.21 (s, 9H, C(CH_3)$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 167.42 (Ph-*C*1), 166.78 (Ph-*C*1′), 148.01 (OPh$_3$-*ipso*-C), 142.64 (Ph-*C*6), 141.79 (Ph-*C*6′), 137.16 (Ph-*C*4), 137.06 (Ph-*C*4′), 128.78 (OPh$_3$-*o*-C), 128.53 (Ph-*C*5), 128.42 (Ph-*C*5′), 127.41 (OPh$_3$-*m*-C), 126.87 (Ph-*C*3), 126.69 (OPh$_3$-*p*-C), 126.43 (Ph-*C*3′), 120.00 (Ph-*C*2), 117.61 (Ph-*C*2′), 97.50(O*C*Ph$_3$), 54.15 (Ti*C*H_3), 39.91 (S*C*H_2), 36.20 (S*C*H_2), 35.78 (*C*(CH_3)$_3$), 35.58 (*C*(CH_3)$_3$), 34.49 (*C*(CH_3)$_3$), 34.43 (*C*(CH_3)$_3$), 31.69 (C(*C*H_3)$_3$), 31.65 (C(*C*H_3)$_3$), 29.84 (C(*C*H_3)$_3$), 29.76 (C(*C*H_3)$_3$). Anal. Calcd for $C_{50}H_{62}O_3S_2Ti$ (823.02): C, 72.97; H, 7.59. Found: C, 73.20; H, 7.39.

Synthesis of (edtbp)TiMe(OCMe₂CMe₂CO₂ⁱPr) (9). To a solution of (edtbp)TiMe{O(ⁱPrO)C=CMe$_2$} (**4**) (30 mg, 0.043 mmol) in C_6D_6 (ca. 0.5 mL) in a Teflon-valved NMR tube was added acetone (2.5 mg, 0.043 mmol) via a microsyringe at room temperature. The color of the solution quickly changed from red to a yellow and NMR spectra were recorded. The conversion of **4** to **9** was virtually quantitative after 10 min. The solvent was removed under vacuum, and the residue was recrystallized from pentane to afford **9** as yellow crystals (27 mg, 83%). A crystal of **9** suitable for X-ray diffraction analysis was selected. ^1H NMR (C_6D_6): δ 7.54 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-5-*H*), 7.52 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-5′-*H*), 7.30 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-3-*H*), 7.17 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-3′-*H*), 4.93 (sept, $^3J_{HH}$ = 6.1 Hz, 1H, OC*H*(CH_3)$_2$), 2.66 (dt, $^2J_{HH}$ = 13.2, $^3J_{HH}$ = 3.2 Hz, 1H, SCH_2), 2.53 (dt, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 3.2 Hz, 1H, SCH_2), 2.25 (td, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 3.2 Hz, 1H, SCH_2), 2.07 (td, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 3.2 Hz, 1H, SCH_2), 1.78 (s, 3H, TiOC(CH_3)$_2$), 1.76 (s, 3H, TiOC(CH_3)$_2$), 1.71 (s, 9H, C(CH_3)$_3$), 1.70 (s, 9H, C(CH_3)$_3$), 1.67 (s, 3H, C(CH_3)$_2$COOⁱPr), 1.63 (s, 3H, C(CH_3)$_2$COOⁱPr), 1.56

(s, 3H, TiCH_3), 1.24 (s, 9H, C(CH_3)$_3$), 1.20 (s, 9H, C(CH_3)$_3$), 0.97 (d, $^3J_{HH}$ = 6.1 Hz, 6H, OCH(CH_3)$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 175.01 (*C*OOC(CH$_3$)$_2$), 167.66 (Ph-*C*1), 166.66 (Ph-*C*1′), 142.53 (Ph-*C*6), 141.74 (Ph-*C*6′), 137.23 (Ph-*C*4), 136.91 (Ph-*C*4′), 128.53 (Ph-*C*5), 128.41 (Ph-*C*5′), 126.90 (Ph-*C*3), 126.26 (Ph-*C*3′), 119.59 (Ph-*C*2), 116.85 (Ph-*C*2′), 89.63 (TiO*C*(CH$_3$)$_2$), 66.92 (COO*C*-(CH$_3$)$_2$), 51.40 (*C*(CH$_3$)$_2$COO^{i}Pr), 50.42 (Ti*C*H$_3$), 39.15 (S*C*H$_2$), 36.17 (S*C*H$_2$), 35.74 (*C*(CH$_3$)$_3$), 35.60 (*C*(CH$_3$)$_3$), 34.40 (*C*(CH$_3$)$_3$), 34.34 (*C*(CH$_3$)$_3$), 31.64 (C(*C*H$_3$)$_3$), 31.61 (C(*C*H$_3$)$_3$), 30.02 (C(*C*H$_3$)$_3$), 29.60 (C(*C*H$_3$)$_3$), 27.48 (TiOC(*C*H$_3$)$_2$), 21.53 (C(*C*H$_3$)$_2$COO^{i}Pr), 21.00 (COOC(*C*H$_3$)$_2$). Anal. Calcd for $C_{41}H_{66}O_5S_2Ti$ (750.96): C, 65.57; H, 8.86. Found: C, 65.35; H, 8.63.

Generation of the Ion Pair [(edtbp)Ti(OPh)(THF-d_8)$_n$]$^+$ [MeB(C$_6$F$_5$)$_3$]$^-$ (10(THF-d_8)$_n$). In the glovebox, a Teflon-valved NMR tube was charged with complex (edtbp)TiMe(OPh) (**7**) (15 mg, 0.023 mmol) and B(C_6F_5)$_3$ (11.7 mg, 0.023 mmol), and CD_2Cl_2 was vacuum transferred in the presence of one drop of THF-d_8 (THF free cationic species was found not stable in CD_2Cl_2 at room temperature). The tube was sealed and NMR spectroscopy was recorded, indicating quantitative formation of the ion pair [(edtbp)Ti(OPh)(THF-d_8)$_n$]$^+$[MeB(C_6F_5)$_3$]$^-$ (**10**·(THF-d_8)$_n$). ^{1}H NMR (CD_2Cl_2): δ 7.51 (d, $^4J_{HH}$ = 2.2 Hz, 2 H, Ph-5-*H*), 7.28 (d, $^4J_{HH}$ = 2.2 Hz, 2 H, Ph-3-*H*), 7.26 (dt, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 2.1 Hz, 2H, OPh-*m*-H), 7.09 (tt, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 2.1 Hz, 1H, OPh-*p*-H), 6.98 (dd, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 2.1 Hz, 2H, OPh-*o*-H), 3.39 (d, $^2J_{HH}$ = 11.2 Hz, 2H, SCH_2), 2.84 (d, $^2J_{HH}$ = 11.2 Hz, 2H, SCH_2), 1.47 (s, 18H, C(CH_3)$_3$), 1.29 (s, 18H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 167.42 (OPh-*ipso*-C), 165.71 (Ph-*C*1), 148.13 (Ph-*C*6), 137.28 (Ph-*C*4), 129.40 (OPh-*m*-C), 128.65 (Ph-*C*5), 127.75 (Ph-*C*3), 125.28 (OPh-*p*-C), 119.33 (Ph-*C*2), 118.78 (OPh-*o*-C), 40.28 (S*C*H$_2$), 35.37 (*C*(CH$_3$)$_3$), 34.35 (*C*(CH$_3$)$_3$), 30.84 (C(*C*H$_3$)$_3$), 29.07 (C(*C*H$_3$)$_3$). NMR data for the free anion [MeB(C_6F_5)$_3$]$^-$ were the same as those described above.

Generation of the Ion Pair [(edtbp)Ti(OCMe$_2$CMe$_2$CO$_2^i$Pr)(THF-d_8)$_n$]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ (11(THF-d_8)$_n$). In the glovebox, a Teflon-valved NMR tube was charged with complex (edtbp)-Ti(OCMe$_2$CMe$_2$CO$_2^i$Pr)Me (**9**) (10 mg, 0.013 mmol) and B(C_6F_5)$_3$ (6.8 mg, 0.013 mmol) and CD_2Cl_2 was vacuum transferred in the presence of one drop of THF-d_8 (THF free cationic species was found not stable in CD_2Cl_2 at room temperature). The tube was sealed and NMR spectroscopy was recorded, indicating quantitative formation of the ion pair [(edtbp)Ti(OCMe$_2$CMe$_2$-CO$_2^i$Pr)(THF-d_8)$_n$]$^+$[MeB(C_6F_5)$_3$]$^-$ (**11**(THF-d_8)$_n$). ^{1}H NMR (CD_2Cl_2): δ 7.46 (d, $^4J_{HH}$ = 2.2 Hz, 2 H, Ph-5-*H*), 7.26 (d, $^4J_{HH}$ = 2.2 Hz, 2 H, Ph-3-*H*), 4.90 (sept, $^3J_{HH}$ = 6.1 Hz, 1H, OC*H*(CH$_3$)$_2$), 3.31 (d, $^2J_{HH}$ = 11.2 Hz, 2H, SCH_2), 2.65 (d, $^2J_{HH}$ = 11.2 Hz, 2H, SCH_2), 1.53 (s, 3H, TiOC(CH_3)$_2$), 1.44 (s, 18H, C(CH_3)$_3$), 1.38 (s, 3H, TiOC(CH_3)$_2$), 1.27 (s, 18H, C(CH_3)$_3$), 1.26 (s, 3H, C(CH_3)$_2$ COO^{i}Pr), 1.21 (s, 3H, C(CH_3)$_2$COO^{i}Pr), 1.20 (d, $^3J_{HH}$ = 6.1 Hz, 3H, OCH(CH_3)$_2$), 1.18 (d, $^3J_{HH}$ = 6.1 Hz, 3H, OCH(CH_3)$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 174.15 (*C*OOC(CH$_3$)$_2$), 166.85 (Ph-*C*1), 147.26 (Ph-*C*6), 137.11 (Ph-*C*4), 128.39 (Ph-*C*5), 127.61 (Ph-*C*3), 118.26 (Ph-*C*2), 99.12 (TiO*C*(CH$_3$)$_2$), 68.08 (COO*C*(CH$_3$)$_2$), 50.90 (*C*(CH$_3$)$_2$COO^{i}Pr), 39.49 (S*C*H$_2$) 35.23 (*C*(CH$_3$)$_3$), 34.41 (*C*(CH$_3$)$_3$), 30.85 (C(*C*H$_3$)$_3$), 28.98 (C(*C*H$_3$)$_3$), 26.46 (TiOC(*C*H$_3$)$_2$), 21.35 (C(*C*H$_3$)$_2$COO^{i}Pr), 21.21 (COOC(*C*H$_3$)$_2$). NMR data for the free anion [MeB(C_6F_5)$_3$]$^-$ were the same as those described above.

Typical Procedure for MMA and *n*BA Polymerization. To a 20 mL flask equipped with a magnetic stirrer, containing the enolate complex (0.02 mmol) in 2 mL of toluene solvent, was introduced the proper amount of monomer. The polymerization was initiated by injection of the activator B(C_6F_5)$_3$ or Al(C_6F_5)$_3$·0.5C_7H_8 in 0.5 mL of toluene as solvent. The polymerization was carried out for a time period, then the reaction was quenched by addition of acidified methanol (3% HCl, 200 mL). The precipitated polymer was filtered and dried overnight under vacuum at 60 °C.

Crystal Structure Determination of Complexes 2, 4, and 9. X-ray diffraction measurements were performed on a Bruker AXS diffractometer with Mo Kα radiation using ω-scans. Crystal parameters and results of the structure refinements are given in Table 1 and are also available as CIF files (see the Supporting Information). Absorption corrections were carried out with the multiscan method using SADABS.[11] All structures were solved by direct methods (SHELXS-86)[12a] and refined (SHELXS-97)[12b] against all F^2 data. The crystals of **4** and **9** contain disordered groups and split positions were introduced. All nonhydrogen atoms except for those in the disordered groups were refined with anisotropic displacement parameters. Hydrogen atoms were included into calculated positions. For the graphical representation, the program ORTEP was used as implemented in the program system WinGX.[13] CCDC reference numbers 661686 (**2**), 661687 (**4**), and 661688 (**9**); these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supporting Information Available: Crystallographic data for **2**, **4**, and **9** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

OM700785C

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