[1-(2-Phenylethyl)-2,3,4,5-tetramethylcyclopentadienyl]titanium Compounds. Synthesis and Their Use for the Syndiospecific Polymerization of Styrene

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A series of monocyclopentadienyltitanium complexes containing the 1-(2-phenylethyl)-2,3,4,5-tetramethylcyclopentadienyl ligand ($C_5Me_4CH_2CH_2Ph$) have been synthesized and characterized. The reaction of $C_5Me_4(SiMe_3)CH_2CH_2Ph$ (**2**) with $TiCl_4$ was used to synthesized the trichloro complex $(C_5Me_4CH_2CH_2Ph)TiCl_3$ (**3**), the molecular structure of which was confirmed by an X-ray diffraction study. Compound **3** was further converted into $(C_5Me_4CH_2CH_2Ph)TiMe_3$ (**4**). Reaction of the latter with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ was almost quantitative to give the "cationic" compound $[(C_5Me_4CH_2CH_2Ph)TiMe_2]^+[B(C_6F_5)_4]^-$ (**5**). Complex **5** was thermally unstable in solution and very moisture sensitive. Compound **4** was readily hydrolyzed to $[(C_5Me_4CH_2CH_2Ph)TiMe_2]_2(\mu\text{-}O)$ (**6**) upon recrystallization in wet pentane. Structural data indicate intramolecular coordination of the phenyl group to titanium in compound **5**, whereas there are no such indications for **3**, **4**, or **6**. The catalytic performance for styrene polymerization of **3** activated with methylaluminoxane (MAO) has been compared with the nonsubstituted reference compound $(C_5Me_5)TiCl_3$ (**7**). Complex **5**, prepared *in situ* by reacting **4** with $[Ph_3C][B(C_6F_5)_4]$, has also been found to be active for the syndiospecific polymerization of styrene. The polymerization data for **3** and **5** lead to the tentative suggestion that the active species is in equilibrium between two states, one with and one without intramolecular phenyl coordination to Ti. These findings would be consistent with postulated multihapto coordination of styrene by both the vinylic double bond and the aromatic ring to the metal center during the catalytic process.

Introduction

Ishihara and co-workers found that organotitanium compounds activated with methylaluminoxane (MAO) catalyze syndiospecific polymerization of styrene at temperatures above 25 °C.[1] This finding, together with other studies in this field, has led to the conclusion that half-sandwich titanium chloride or alkoxide compounds containing η^5-C_5H_5, η^5-C_5Me_5, η^5-C_5Me_4H, or η^5-C_9H_7 ligands are among the favored precursors.[1−3] The isolation of metallocenium species (Cp_2M^+R)[4] by reacting alkylmetallocenes with a strong Lewis acidic salt of a noncoordinating anion (e.g., $[Ph_3C]^+[B(C_6F_5)_4]^-$), and their use in the polymerization of ethylene and propylene,[5] have led to the acceptance of a catalytically active metallocenium species.[4,6] This idea has recently been applied to group 4 monocyclopentadienyl compounds and several "cationic" complexes of the types $[CpMR_2]^+$ and $[CpMR_2L]^+$ have been reported.[7] Some of the complexes were successfully used for the syndiospecific polymerization of styrene and other α-olefins.[8] The formation of this type of active species by the action of MAO on half-sandwich metallocenes is anticipated, although other proposed species cannot be ruled out.[2b,2c,9] In compounds of the type $[CpMR_2L]^+$ (L = η^6-toluene, η^n-styrene, η^n-benzyl; M = Ti, Zr, Hf),

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the multihapto coordination of the phenyl ring has been demonstrated in solution as well as in the solid state.[7]

Recently, there is interest in the study of substituted cyclopentadienylmetal complexes containing a terminal donor group in the side chain.[10] Coordination of the pendant Lewis base to a metal center has been described for several half-sandwich compounds. Yanlong et al. have demonstrated chelation of the pendant ligand in ($C_5H_4CH_2CH_2OMe$)$TiCl_3$ by X-ray studies.[11] We have also recently reported the synthesis of ($C_5H_4CH_2CH_2NMe_2$)$TiCl_3$ and ($C_5Me_4CH_2CH_2NMe_2$)$TiCl_3$ and obtained structural and Ziegler−Natta polymerization data. Intramolecular coordination of nitrogen to titanium was proposed in these complexes.[12] This Lewis acid−base interaction occurs between the lone pair of electrons on nitrogen and the doubly degenerate LUMO of e symmetry (basically metal-$d_{x^2-y^2}$ and -d_{xy} in character) extended along a plane parallel to the cyclopentadienyl ring in $CpTiCl_3$.[13] During the course of the present work, X-ray diffraction evidence for a Ti−N interaction was obtained for the related *N*-pyrrolidinyl analog [$C_5H_4CH_2CH_2N(CH_2)_4$]$TiCl_3$.[10h]

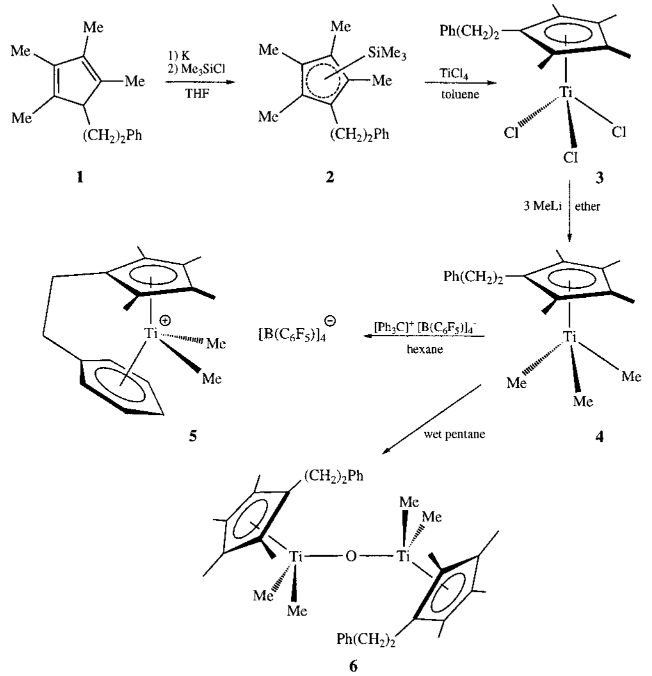
The principal objective of this work was to synthesize similar compounds where the basic group on the substituted cyclopentadienyl ligand was a π-electron system such as in $[C_5Me_4CH_2CH_2Ph]^-$ (**1**$^-$) and to investigate the Ti−Ph interactions. Okuda et al. have shown[14] chelation of the vinyl π-electron system to the metal in the case of the $(C_5Me_4CH_2CH_2CH{=}CH_2)^-$ ligand.

We describe here the synthesis of new precursors for the preparation of organometallic compounds $C_5Me_4(H)CH_2CH_2Ph$ (**1**) and $C_5Me_4(SiMe_3)CH_2CH_2Ph$ (**2**), the titanium complexes ($C_5Me_4CH_2CH_2Ph$)$TiCl_3$ (**3**), ($C_5Me_4CH_2CH_2Ph$)$TiMe_3$ (**4**), “cationic” $[(C_5Me_4CH_2CH_2Ph)TiMe_2]^+[B(C_6F_5)_4]^-$ (**5**), and the hydrolysis product of **4** $[(C_5Me_4CH_2CH_2Ph)TiMe_2]_2(\mu\text{-}O)$ (**6**), as well as olefin polymerization catalysis of **3** in comparison with the reference compound (C_5Me_5)$TiCl_3$ (**7**) and **5**, obtained by *in situ* reaction of **4** with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$. Results of a single-crystal X-ray diffraction study on **3** are also presented and discussed.

Results and Discussion

Synthesis. NMR and analytical data for **1**−**5** are given in the Experimental Section. Only selected data will be presented for this discussion.

Scheme 1



Compound **1** was prepared using a procedure similar to that reported by Okuda for $C_5Me_4(H)CH_2CH_2CH{=}CH_2$[15] and was isolated as a golden-yellow liquid in good yield. Its ^{1}H-NMR spectrum is consistent with a mixture of several isomers, and follows the pattern found for $C_5Me_4(H)CH_2CH_2NMe_2$.[16]

The stepwise reaction of **1** with K metal and subsequent treatment of the resulting potassium salt with Me_3SiCl in THF afforded the silyl derivative **2** as a light-sensitive yellow liquid (Scheme 1). Examination of the ^{1}H-NMR spectrum of **2** reveals the fluxional behavior of the Me_3Si group around the C_5 core of the ring by sigmatropic shifting of the ring C−Si bond. The latter is in agreement with earlier findings for $C_5Me_5(SiMe_3)$ or $C_5Me_4(SiMe_3)CH_2CH_2NMe_2$.[17] In these spectra, the $C_5Me_4(SiMe_3)$ fragment is represented by a broad singlet at high field for protons of the Me_3Si group and a broad singlet for the protons of the methyl groups on the ring. The other fragment (i.e., $-CH_2CH_2Ph$) is observed as two multiplets for the ethylenic side chain and a multiplet at low field for the aromatic protons.

Addition of 1 equiv of **2** to a solution of $TiCl_4$ in toluene, followed by workup of the reaction mixture, gave complex **3** as fairly air-stable red crystals (Scheme 1). In its ^{1}H-NMR spectrum in either C_6D_6 or $CDCl_3$, the methyl protons on the five-membered ring appear as two singlets, and the ethylene bridge as two distinct triplets, where the one at higher field is assigned to $-CH_2Ph$ by $^1H-^1H$ decoupling. The aromatic protons on the phenyl ring gave a doublet for the *ortho* protons at higher field than a multiplet for the *para* and *meta* ones. The ^{13}C-NMR spectrum of **3** in $CDCl_3$ shows all the expected peaks with chemical shifts and spin-spin coupling constants in the normal range.

It is well-known that the *ortho* protons of an η^6-arene (e.g., η^6-toluene) coordinated to an electronically unsat-

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Table 1. ^{1}H and ^{13}C NMR Data for the Phenyl Group in Compounds 3−5

^{1}H-NMR (ppm)

	δ			
assgnt (δ)	**3**[a]	**4**[b]	**5**[c]	Δδ[d]
ortho-H[f]	7.02	7.16	7.03	−0.13
meta-H[g]	7.20−7.27[e]	7.27	8.35	+1.08
para-H[g]		7.19	8.51	+1.32

^{13}C-NMR (ppm/Hz)

	$\delta/^1J_{CH}$			
assgnt	**3**[a]	**4**[a]	**5**[c]	$\Delta\delta/\Delta^1J_{CH}$[d]
ipso-C	140.2	141.7	145.3	+3.6/-
ortho-C	128.5/159	128.3/159	137.6/175	+9.3/+16
meta-C	128.6/157	128.6/156	125.8/168	−2.8/+12
para-C	126.5/158	126.0/159	130.9/175	+4.9/+16

[a] $CDCl_3$, 25 °C. [b] CD_2Cl_2, 25 °C. [c] CD_2Cl_2, −50 °C. [d] $\Delta\delta = \delta(\mathbf{5}) - \delta(\mathbf{4})$; $\Delta J = J(\mathbf{5}) - J(\mathbf{4})$. [e] Multiplet. [f] Doublet. [g] Triplet.

urated group 4 compound are shifted in ^{1}H-NMR to lower field with respect to the *ortho* protons on the free arene.[7,18] In contrast, for benzyl complexes the electronic unsaturation is very often relieved *via* η^n-benzyl interactions ($n = 1-3$), resulting in a shift of the *ortho* protons to higher field.[19] The study of the aromatic region for **3** (see Table 1 and Experimental Section) leads to the conclusion that coordination of the phenyl ring to the titanium center is very unlikely in solution. There is also no coordination in the solid state as shown by X-ray diffraction studies, since the phenyl ring is located far away from the metal (*vide infra*).

As mentioned before, in compounds like ($C_5R_4CH_2CH_2Y$)$TiCl_3$ (Y = $-N(CH_2)_{4,5}$, R = H;[10h] Y = −OMe, R = H;[11] Y = $-NMe_2$, R = H, Me[12]), the Y function is intramolecularly coordinated to titanium. The different result found for **3** could be related to the fact that the phenyl group is a weaker base compared to the N- and O-containing ligands and also possibly to steric effects.

A peralkylation reaction of **3** with MeLi in pentane at low temperature led to a thermally-stable moisture-sensitive yellow crystalline solid, characterized as the trimethyl compound **4** (Scheme 1). The ^{1}H-NMR spectrum of **4** is fairly similar to the spectrum observed for **3**, with the addition of an intense singlet for the methyl protons attached to titanium. In different deuterated solvents, the resonance for the CH_2CH_2 backbone follows an AA′BB′ splitting pattern, and the low-field region is better resolved. Thus, from higher to lower field a doublet, a triplet and another triplet are recorded for the *ortho*, *para*, and *meta* protons, respectively (see Table 1 and Experimental Section). As in the case of compound **3**, neither ^{1}H- nor ^{13}C-NMR data of **4** indicate any Ti−Ph interaction.

Addition of $[Ph_3C]^+[B(C_6F_5)_4]^-$ to a hexane suspension of **4** at −40 °C, followed by slow warming to room temperature, afforded the "cationic" compound $[(C_5Me_4CH_2CH_2Ph)TiMe_2]^+[B(C_6F_5)_4]^-$ (**5**) as a mustard-yellow solid in almost quantitative yield (Scheme 1). The Ph_3CMe byproduct was isolated (97% yield) spectroscopically pure from the mother liquor of this reaction. Compound **5** is insoluble in hexanes or aromatic solvents and very soluble in dichloromethane. It is highly air-sensitive but thermally stable at room temperature as a solid. However, solutions of **5** in dichloromethane readily decompose above 0 °C in less than 15 min. For the $C_5Me_4CH_2CH_2$-fragment, both ^{1}H- and ^{13}C-NMR spectroscopic data of **5** are very similar to the data found for **3** and **4**. For instance, compared with its precursor **4**, the ^{1}H-NMR spectrum of **5** in CD_2Cl_2 shows the same splitting pattern for this group, and almost all resonances are shifted to slightly lower field (*ca.* 0.2 ppm)—shifts expected for a more electron-deficient metal center in **5**. However, the Ti−Me singlet is shifted 0.4 ppm to higher field. This change can only be attributed to an anisotropic effect due to the proximity of the phenyl and the $TiMe_2$ groups in **5**. Other interesting features in the ^{1}H- and ^{13}C-NMR spectra of **5** are the chemical shift and $^1J_{CH}$ observed for the C_6H_5 group. Thus, again compared with its precursor **4**, the two triplets for the *meta*- and *para*-protons appear shifted to lower field (Δδ *ca.* 1.1 and 1.3 ppm, respectively), whereas the doublet for the *ortho*-protons is shifted slightly to higher field (see Table 1). Even more significant are the field shifts (Δδ from *ca.* −3 up to +9 ppm) for the C_6-ring carbons relative to the comparable values in **4**, together with increasing of the $^1J_{CH}$ (Δ^1J_{CH} = 12−16 Hz) for the *ortho*- *meta*-, and *para*-carbons (see Table 1). These differences indicate an important change in the electronic environment of the phenyl group in **5** compared to **4**. Similar observations have been made in "cationic" compounds of the type $[CpMR_2L]^+$ (M = Ti, Zr, Hf; L = η^6-arene), where arene multihapto coordination to the metal has been demonstrated in solution,[7] as well as in the solid state.[7c−e,g] Therefore, we propose an η^n-coordinate phenyl group (most likely η^6) in compound **5**. Besides, NMR experiments at different concentrations and temperatures (never above −10 °C to avoid thermal decomposition) show the phenyl group in **5** to be intramolecularly coordinated to Ti and strongly bound as it does not exchange in dichloromethane. The steric relief relative to **3** or **4**, together with the stronger Lewis acidity of the $Ti(IV)^+$ center in **5**, facilitate the Ti−Ph intramolecular coordination in the latter, conferring to the cation in *ansa*-titanocenium character (16-electron complex).

Recrystallization in wet pentane of a sample of the trimethyl compound **4**, led to the isolation of the μ-oxo compound **6** as a thermally-stable, moisture-sensitive pale-yellow microcrystalline solid (Scheme 1). Complexes such as $C_5Me_5TiMe_3$ have been found to be very moisture sensitive,[20] and the formation of **6** results from the hydrolysis of **4**. This oxo compound has been characterized by elemental analyses and ^{1}H-NMR. The ^{1}H-NMR spectrum of **6** in C_6D_6 shows the Ti−Me protons at 1.06 ppm with an integral ratio 1:1 compared to any of the two C_5M_4 signals. In this case, the ethylenic side chain is recorded as a complicated multiplet (δ 2.50−2.73) and the aromatic protons on the phenyl ring grouped in a singlet multiplet (δ 7.00−7.19).

Structure of ($C_5Me_4CH_2CH_2Ph$)$TiCl_3$ (3). Single crystals of **3** were obtained by recrystallization from a dichloromethane/toluene mixture at −20 °C. Figure 1 gives an ORTEP view of the structure of **3** together with

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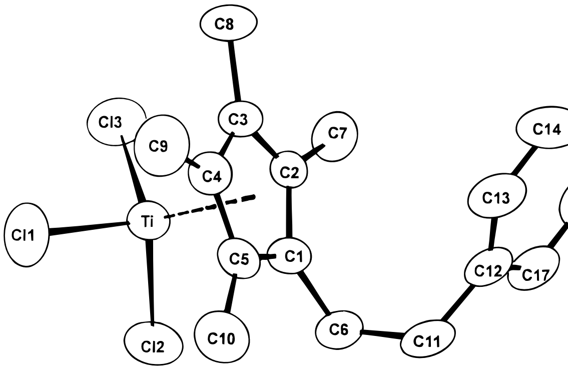

Figure 1. Structure of $(C_5Me_4CH_2CH_2Ph)TiCl_3$ (**3**), showing the atomic numbering scheme.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 3[a]

Bond Lengths			
Ti–Cl(1)	2.221(2)	Ti–Cl(3)	2.245(2)
Ti–Cl(2)	2.241(2)	Ti–Cp	2.011(3)
Bond Angles			
Cl(1)–Ti–Cl(2)	102.7(1)	Cl(1)–Ti–Cp	115.8(1)
Cl(1)–Ti–Cl(3)	103.9(1)	Cl(2)–Ti–Cp	115.4(1)
Cl(2)–Ti–Cl(3)	102.1(1)	Cl(3)–Ti–Cp	115.1(1)

[a] Cp is the center of the cyclopentadienyl ring.

the atom labeling, while Table 2 presents selected bond distance and angle data for the coordination geometry of the titanium atom. The metal center and phenyl group are located at opposite faces of the cyclopentadienyl ring. The geometry around Ti, as defined by the centroid of the five-membered ring and the Cl atoms, is roughly tetrahedral, the angles from the centroid to the Cl atoms being much larger (average 115.4(1)°) than the angles between the Cl atoms (average 102.9(1)°). The Ti–Cl(1) bond distance is slightly shorter (*ca.* 0.02 Å) than the other Ti–Cl separations, and there is a small spread in the Ti–C(ring) distances. The substitution of the benzyl group at C(6) causes no apparent distortion of the $C_5Me_4(CH_2-)$ group, which has local 5-fold symmetry to within the standard deviations. The average C–C distance in the ring is 1.413(7) Å, while the average exocyclic distance to carbons C(6) to C(10) is 1.501(7) Å.

Polymerization Catalysis. The $C_5Me_5TiCl_3$ (**7**)/MAO catalyst system has previously been found to be highly active and syndiospecific for the polymerization of styrene.[1b,3c] Table 3 summarizes the results obtained with both **3**/MAO and **7**/MAO under several polymerization conditions. The data show differences in activity (A) as well as syndioselectivity and the effect of T_p on them.

The maximum polymerization activities for **7**/MAO and **3**/MAO were found at $T_p = 70$ °C. Both the *A* value and yield of *s*-PS are lower at 90 °C, which could be due to decomposition of the titanium complexes. The polymerization activities at 25 °C are only one-tenth of those at 50 °C for both catalyst systems. The *A* values over the entire temperature range were about 2–3 times smaller for **3**/MAO than **7**/MAO, whereas they produce the same % *s*-PS (see Table 3).

Zambelli et al. have established that the mechanism of syndiospecific styrene polymerization in the presence of half-sandwich titanium catalysts is a polyinsertion of the monomer, the regiospecificity is secondary, and the addition to the double bond is *cis*.[21] They propose that the active species is similar to **a** (Scheme 2) with the addition of one η^2 coordinated styrene through the vinylic double bond.[9b,21b] In this model they also propose the η^n coordination of the phenyl group of the last inserted monomer, which accounts for the formation of a benzyl-type growing chain due to 2,1-insertions. The lowering in *A* observed for **3**/MAO compared to **7**/MAO could be merely due to the steric hindrance of the cyclopentadienyl ligand. However, another reasonable interpretation, derived from Zambelli's mechanism,[9b,21b] could be the formation of intermediate **b** (Scheme 2), which leads to a *cis*-secondary mode for the migratory insertion. This intermediate bears a multihapto coordination of styrene, by both the vinylic double bond and the aromatic ring and of the benzyl group of the last inserted monomer as well.[2b] This proposed mechanism is supported by recent X-ray molecular structures obtained for group 4 monocyclopentadienyl cationic complexes[7d,e] as well as the isolation of compound **5** in this work. The geometric requirement for the multihapto interactions is not met by a group 4 metal with bis(cyclopentadienyl) ligands, thus they are not suited for syndiospecific styrene polymerization. That is also the case for species **c** (Scheme 3) which has a pseudometallocene character.

Therefore, we tentatively suggest that the active species derived from **3** is in equilibrium between two states, one with (**c** in Scheme 3) and one without (**a** in Scheme 3) intramolecular phenyl coordination to Ti. Species **a** polymerizes styrene proceeding through multihapto coordination of the monomer as shown in Scheme 2, whereas the Ph–Ti interaction in species **c** blocks the monomer coordination. As a result, starting with the same concentration of precursors **3** and **7**, the concentration of active species formed from them is greater for the latter.

Table 4 summarizes the results for **3**/MAO in the polymerization of ethylene. It has an *A* value of about 3×10^6 g polymer/$(mol_{Ti} \cdot [C_2H_4] \cdot h)$, which is much greater than $CpTiCl_3$/MAO.[12] $(C_5H_4CH_2CH_2NMe_2)TiCl_3$/MAO has *A* for ethylene comparable to **3**/MAO, where for the former intramolecular coordination of the amino group has also been proposed.[12a]

Table 5 summarizes the results obtained by **5**, prepared *in situ* by reacting **4** with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$, in the polymerization of ethylene and styrene. It is noteworthy that this catalytic system was inactive for either monomer in the absence of triisobutylaluminum (TIBA) (runs 10, 12, and 15). However, the presence of a sufficient amount of TIBA (1 mM for ethylene, run 11; 5 mM for styrene, runs 14 and 17) to scavenge any monomer or solvent impurities led to the formation of the corresponding polymers. The increase of *A*(ethylene) compared to **3**/MAO (run 11, Table 5 vs run 9, Table 4) could be understood as a result of a looser ion-pair interaction of the active species (*e.g.*, **c** in Scheme 3) with $[B(C_6F_5)_4]^-$ compared to MAO, which might even shift the equilibrium depicted in Scheme 3 to the metallocene-like **c**-species. However, *A*(styrene) compared to **3**/MAO (runs 14 and 17, Table 5 vs runs 4 and 5, Table 3) is comparable or slightly lower, and both catalyst systems produce the same % *s*-PS. For **7**/MAO

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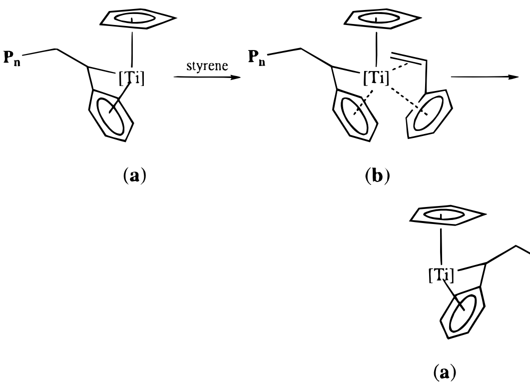
[21] (a) Reference 2b. (b) Longo, P.; Proto, A.; Zambelli, A. *Macromol. Chem. Phys.* **1995**, *196*, 3015 and references therein.

Table 3. Styrene Polymerization Catalyzed by 3 or 7/MAO[a]

				$(C_5Me_5)TiCl_3$ (**7**)				$[C_5Me_4(CH_2CH_2Ph)]TiCl_3$ (**3**)			
run no.	[Ti] (μM)	Al/Ti	*T*p (°C)	yield (g)	$A^b \times 10^{-6}$	% *s*-PS[c]	T_m (°C)	yield (g)	$A^b \times 10^{-6}$	% *s*-PS[c]	T_m (°C)
1	25	2000	25					0.016	0.29	56	
2	50	2000	25					0.028	0.26	68	
3	50	4000	25	0.058	1.07	88		0.044	0.40	86	
4	50	4000	50	0.698	12.8	89	271.1 273.2	0.441	4.06	90	260.3 268.3
5	50	4000	70	0.932	17.1	95	269.1 271.4	0.899	8.27	95	258.8 263.4
6	50	4000	90	0.701	12.9	92		0.580	5.33	80	

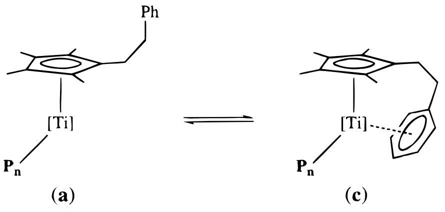
[a] Polymerization conditions: volume, 50 mL toluene + 5 mL styrene; $t_p = 0.5$ h for **7** and 1 h for **3**. [b] g of bulk polymer/($mol_{Ti} \times mol_{styrene} \times$ h). [c] % *s*-PS = (g of 2-butanone insoluble polymer/g of bulk polymer) × 100.

Scheme 2



[Ti] represents the metal fragment of the active species

Scheme 3



[Ti] represents the metal fragment of the active species

Table 4. Ethylene Polymerization Catalyzed by 3/MAO[a]

run no.	Al/Ti	T_p (°C)	yield(g)	$A^b \times 10^{-6}$	T_m (°C)	$M_w \times 10^{-4}$
7	2000	20	0.164	2.12	136.8	5.3
8	4000	20	0.290	3.75	137.3	3.4
9	4000	50	0.147	2.56	136.5	1.4

[a] Polymerization conditions: volume, 50 mL toluene; [Ti] = 50 μM; $t_p = 5$ min; $P_{C_2H_4} = 15$ psig, $[C_2H_4]_{(20\ °C)} = 0.37$ M, $[C_2H_4]_{(50\ °C)} = 0.28$ M. [b] g of polymer/($mol_{Ti} \times [C_2H_4] \times$ h).

compared to the $Cp^*TiMe_3/[Ph_3C][B(C_6F_5)_4]$ catalytic system, a higher *A*(styrene) and the same syndiospecificity has been previously observed.[3c] The discrepancy in the trend of *A* for the current case could be explained if the positive effect of a weaker counterion association is compensated by the above mentioned shift of the equilibrium in Scheme 3 to the **c** species, which we suggest not to be active vs styrene.

Experimental Section

All operations were performed under an argon atmosphere using Schlenk or drybox techniques. Argon was deoxygenated with activated BTS catalyst and dried with molecular sieves and P_2O_5. Solvents were purified as described elsewhere.[22] (2-Bromoethyl)benzene were purchased from Fluka and other chemicals from Aldrich, unless otherwise stated. $[Ph_3C]^+[B(C_6F_5)_4]^-$ was prepared according to a literature procedure.[5a] NMR spectra were recorded on Varian Unity 500+ (^{1}H-NMR, 500 MHz; ^{13}C-NMR, 125 MHz) and Varian XL 200 NMR spectrometers. Chemical shifts (δ) are reported in ppm referenced to TMS. Elemental analyses were performed by the University of Massachusetts or University of Alcalá Microanalytical Laboratories. Styrene was purified by distillation from calcium hydride under reduced pressure and stored at −25 °C under argon in darkness. Polymerization grade ethylene was dried and purified by passing it through a Matheson Gas Purifier (Model 6436). Methylaluminoxane (MAO) was purchased from Akzo. The procedures used to polymerize styrene[3] and ethylene[5b,23] have been previously given in detail. A Perkin-Elmer DSC-4 Thermoanalytic instrument was used to obtain DSC melting endotherms. Polyethylene molecular weight determinations were made by viscosity measurements in decalin at 135 °C.

1-(2-Phenylethyl)-2,3,4,5-tetramethylcyclopentadiene (1). (2-Bromoethyl)benzene (11.10 g, 60 mmol) was added dropwise to an excess of magnesium turnings (1.70 g, 70 mmol) in diethyl ether (50 mL) at room temperature. The reaction mixture was subsequently heated at reflux for 1 h. After cooling, the Grignard reagent was reacted *in situ* by the slow addition of *cis*, *trans*-2,3,4,5-tetramethyl-2-cyclopentenone (8.30 g, 60 mmol) at room temperature. The reaction mixture was then heated at reflux for 2 h, quenched by addition of 150 g of ice, treated with concentrated HCl (40 mL), and stirred for 2 h. The organic layer was collected and the aqueous layer extracted with diethyl ether (4 × 50 mL). The combined organic extracts were washed with a 10% aqueous solution of $NaHCO_3$ (4 × 60 mL) and a saturated aqueous solution of NaCl (2 × 50 mL), before being dried over $MgSO_4$. After filtration, the volatiles were removed under vacuum to give a brownish liquid, which was distilled (111−112 °C at 10^{-3} mmHg) to afford pure **1** as a yellow-golden liquid. Yield: 8.78 g (65%). Anal. Calcd for $C_{17}H_{22}$: C, 90.20; H, 9.80. Found: C, 90.38; H, 9.81. ^{1}H-NMR ($CDCl_3$): δ 0.99 (d, *J* = 8.4 Hz, C_5*Me*$_4$H), 1.04 (d, *J* = 8.6 Hz, C_5*Me*$_4$H), 1.63, 1.72, 1.77 and 1.83 (major) (4 s, ring-Me on sp^2 carbons)[12H]; 2.04 (m, 1H, C_5Me_4*H*); 2.48 (m, 2H, C*H*$_2$Ph); 2.61−2.68 (m, 2H, C*H*$_2$); 7.14−7.27 (m, 5H, *Ph*).

[1-(2-Phenylethyl)-2,3,4,5-tetramethylcyclopentadienyl]trimethylsilane (2). A reaction of $C_5Me_4(H)CH_2CH_2Ph$ (**1**) (3.15 g, 13.9 mmol) with potassium metal (0.42 g, 13.9 mmol) was carried out in refluxing THF (50 mL) over night. Removal of the solvent under reduced pressure afforded a white potassium salt which was washed with pentane (50 mL), dried, redissolved in THF (50 mL), and reacted with Me_3SiCl (1.51 g, 13.9 mmol) at 0 °C. After stirring for 5 h the THF was evaporated and the residue was extracted with pentane (2 × 40 mL). The silyl derivative **2** was isolated as an analytically pure yellow-golden liquid by simple removal of the solvent from

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Table 5. Ethylene or Styrene Polymerization Catalyzed by 4/Cocatalyst[a]

run no.	monomer[b]	T_p (°C)	t_p (min)	cocatalyst	Al/Ti	yield (g)	$A^c \times 10^{-6}$	% *s*-PS[d]
10	ethylene	50	60	$[Ph_3C]^+[B(C_6F_5)_4]^-$	0	0		
11	ethylene	50	1[e]	$[Ph_3C]^+[B(C_6F_5)_4]^-$/TIBA	20	0.331	28.8	
12	styrene	50	60	$[Ph_3C]^+[B(C_6F_5)_4]^-$	0	0		
13	styrene	50	60	$[Ph_3C]^+[B(C_6F_5)_4]^-$/TIBA	20	0		
14	styrene	50	60	$[Ph_3C]^+[B(C_6F_5)_4]^-$/TIBA	100	0.435	4.00	92
15	styrene	70	60	$[Ph_3C]^+[B(C_6F_5)_4]^-$	0	0		
16	styrene	70	60	$[Ph_3C]^+[B(C_6F_5)_4]^-$/TIBA	20	0		
17	styrene	70	60	$[Ph_3C]^+[B(C_6F_5)_4]^-$/TIBA	100	0.543	4.99	96

[a] Polymerization conditions: volume, 50 mL toluene; [Ti] = 50 μM; ratio $[Ph_3C][B(C_6F_5)_4]/Ti = 1$. [b] For runs 10 and 11, $P_{C_2H_4} = 15$ psig, $[C_2H_4]_{(50\ °C)} = 0.28$ M. For runs 12−17, 5 mL of styrene. [c] *A* vs ethylene; see note *b* of Table 4; *A* vs styrene; see note *b* of Table 3. [d] See note *c* of Table 3. [e] The polymer produced stops the stirring of the polymerization mixtures in less than 1 min.

Table 6. Crystal Data and Structure Refinement for 3

Diffractometer	Enraf-Nonius CAD-4
empirical formula	$C_{17}H_{21}Cl_3Ti$
fw	379.61
temp	293(2) K
wavelength	0.710 73 Å; monochromated Mo Kα
cryst system	monoclinic
space group	$P2_1/a$
a (Å)	15.114(2)
b (Å)	7.212(4)
c (Å)	17.131(4)
β(deg)	102.45(2)
V (Å^3)	1823.4(11)
Z	4
D_{calcd} (g cm^{-1})	1.383
abs coeff (cm^{-1})	9.00
abs corr	empirical; ψ scans
F(000)	784
cryst size (mm)	0.3 × 0.55 × 0.2
2θ range (deg)	5−44; $\omega/2\theta$ scans
index ranges	$0 \le h \le 15$, $0 \le k \le 7$, $-17 \le l \le 17$
reflcns collcd	2073
indepdt reflcns	2073 [$R_{int} = 0.0000$]
refinement method	full-matrix least-squares on F^2
data/restraints/params	2073/0/194
goodness of fit on F^2	1.105
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0387$, w$R_2 = 0.0895$ on 1409 data
R indices (all data)	$R_1 = 0.0809$, w$R_2 = 0.1123$
largest diff peak and hole (e·Å^{-3})	0.227 and −0.254

the combined extracts. Yield: 3.40 g (82%). Anal. Calcd for $C_{20}H_{30}Si$: C, 80.46; H, 10.13. Found: C, 80.46; H, 10.30. ^{1}H-NMR ($CDCl_3$, 25 °C): δ −0.15 (s, 9H, $Si\mathit{Me}_3$); 1.81 (br s, 8 Hz, 12H, $C_5\mathit{Me}_4$); 2.05 (m, 2H, $C\mathit{H}_2Ph$); 2.50 (m, 2H, $C\mathit{H}_2$); 7.21 (br s, 8 Hz, *Ph*).

[1-(2-Phenylethyl)-2,3,4,5-tetramethylcyclopentadienyl]trichlorotitanium (3). A solution of **2** (3.38 g, 11.3 mmol) in toluene (20 mL) was slowly added to a second solution of $TiCl_4$ (2.14 g, 11.3 mmol) in toluene (80 mL) at −78 °C. After the addition was completed the mixture was allowed to warm to room temperature and stirred overnight. A small amount of sticky red precipitate was filtered from the bright red solution. Evaporation of the solvent afforded crude **3**, which was washed with pentane (2 × 40 mL), recrystallized from CH_2Cl_2/toluene, and collected in two crops as air-stable red needles. Yield: 2.52 g (59%). Anal. Calcd for $C_{17}H_{21}Cl_3Ti$: C, 53.79; H, 5.58. Found: C, 54.23; H, 5.39. ^{1}H-NMR ($CDCl_3$, 25 °C): δ 2.18 (s, 6H, $C_5\mathit{Me}_4$); 2.36 (s, 6H, $C_5\mathit{Me}_4$); 2.73 (t, 2H, *J* = 7.5 Hz, $C\mathit{H}_2Ph$); 3.16 (t, 2H, *J* = 7.5 Hz, $C\mathit{H}_2$); 7.02 (d, 2H, *o-Ph*); 7.20−7.27 (m, 3H, *m-* and *p-Ph*). ^{1}H-NMR (C_6D_6, 25 °C): δ 1.81 (s, 6H, $C_5\mathit{Me}_4$); 1.90 (s, 6H, $C_5\mathit{Me}_4$); 2.31 (t, 2H, *J* = 7.5 Hz, $C\mathit{H}_2Ph$); 2.92 (t, 2H, *J* = 7.5 Hz, $C\mathit{H}_2$); 6.71 (d, 2H, *o-Ph*); 6.97−7.05 (m, 3H, *m-* and *p-Ph*). ^{13}C-NMR ($CDCl_3$, 25 °C): δ 14.13 ($C_5\mathit{Me}_4$, $^1J_{CH} = 128.8$ Hz); 14.31 ($C_5\mathit{Me}_4$, $^1J_{CH} = 129.0$ Hz); 31.38 ($\mathit{C}H_2$, $^1J_{CH} = 130.9$ Hz); 35.90 ($\mathit{C}H_2Ph$, $^1J_{CH} = 128.4$ Hz); 126.47 (*p-Ph*, $^1J_{CH} = 158.0$ Hz); 128.51 (*o-Ph*, $^1J_{CH} = 159.0$ Hz); 128.59 (*m-Ph*, $^1J_{CH} = 157.3$ Hz); 137.78 (*ipso*-C_5Me_4); 138.00 and 140.10 (C_5Me_4); 140.22 (*ipso-Ph*).

[1-(2-Phenylethyl)-2,3,4,5-tetramethylcyclopentadienyl]trimethyltitanium (4). A solution of MeLi·LiBr (6.0 mL, 1.7 M in diethyl ether) was slowly added to a suspension of compound **3** (1.10 g, 2.9 mmol) in pentane (50 mL) at −40 °C. When the addition was completed the mixture was gradually (1 h) warmed to room temperature, and the resulting yellow solution filtered from a white precipitate. Vacuum distillation of the solvent gave a yellow microcrystalline solid which was recrystallized in pentane, producing a yellow crystalline solid characterized as the trimethyl compound **4**. Yield: 0.81 g (88%). Anal. Calcd for $C_{20}H_{30}Ti$: C, 75.46; H, 9.50. Found: C, 75.08; H, 9.42. ^{1}H-NMR ($CDCl_3$, 25 °C): δ 0.71 (s, 9H, Ti−*Me*); 1.86 (s, 6H, $C_5\mathit{Me}_4$); 1.94 (s, 6H, $C_5\mathit{Me}_4$); 2.56−2.60 (m, $2H_{AA'}$, $C\mathit{H}_2Ph$); 2.74−2.78 (m, $2H_{BB'}$, $C\mathit{H}_2$); 7.16 (d, 2H, *o-Ph*); 7.19 (t, 1H, *p-Ph*); 7.27 (t, 2H, *m-Ph*). ^{1}H-NMR (C_6D_6, 25 °C): δ 1.01 (s, 9H, Ti−*Me*); 1.66 (s, 6H, $C_5\mathit{Me}_4$); 1.74 (s, 6H, $C_5\mathit{Me}_4$); 2.48−2.52 (m, $2H_{AA'}$, $C\mathit{H}_2Ph$); 2.60−2.64 (m, $2H_{BB'}$, $C\mathit{H}_2$); 6.99 (d, 2H, *o-Ph*); 7.07 (t, 1H, *p-Ph*); 7.13 (t, 2H, *m-Ph*). ^{1}H-NMR (CD_2Cl_2, 25 °C): δ 0.71 (s, 9H, Ti−*Me*); 1.86 (s, 6H, $C_5\mathit{Me}_4$); 1.95 (s, 6H, $C_5\mathit{Me}_4$); 2.57−2.61 (m, $2H_{AA'}$, $C\mathit{H}_2Ph$); 2.74−2.78 (m, $2H_{BB'}$, $C\mathit{H}_2$); 7.16 (d, 2H, *o-Ph*); 7.19 (t, 1H, *p-Ph*); 7.27 (t, 2H, *m-Ph*). ^{13}C-NMR ($CDCl_3$, 25 °C): δ 11.81 ($C_5\mathit{Me}_4$, $^1J_{CH} = 126.0$ Hz); 12.01 ($C_5\mathit{Me}_4$, $^1J_{CH} = 126.0$ Hz); 29.66 ($\mathit{C}H_2$, $^1J_{CH} = 126.6$ Hz); 36.93 ($\mathit{C}H_2Ph$, $^1J_{CH} = 127.0$ Hz); 60.90 (Ti−*Me*; $^1J_{CH} = 118.7$ Hz); 122.25 (C_5Me_4); 124.98 (*ipso*-C_5Me_4); 125.96 (*p-Ph*, $^1J_{CH} = 159.5$ Hz); 128.32 (*o-Ph*, $^1J_{CH} = 159.4$ Hz); 128.57 (*m-Ph*, $^1J_{CH} = 155.5$ Hz); 141.76 (*ipso-Ph*).

ansa-{η^5:η^n:**[1-(2-Phenylethyl)-2,3,4,5-tetramethylcyclopentadienyl]dimethyltitanium(IV)**} **Tetrakis(pentafluorophenyl)borate (5).** To a mixture of compound **4** (0.32 g, 1.0 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (0.92 g, 1.0 mmol) as solids, hexane (20 mL) was added at −40 °C. The resulting suspension was warmed to room temperature and stirred for 1 h. The solvent was then decanted, and the solid washed with toluene (2 × 10 mL) and pentane (2 × 10 mL). The Ph_3CMe byproduct was obtained spectroscopically pure from the combined mother-liquor and extracts (0.25 g, 97% yield). The product of this reaction was isolated as a very air-sensitive mustard-yellow powder, and characterized as compound **5**. This salt was found to be soluble in chlorinated solvents, and thermally unstable in solution. Yield: 0.93 g (95%). Anal. Calcd for $C_{43}H_{27}BF_{20}Ti$: C, 52.58; H, 2.77. Found: C, 53.08; H, 3.29. ^{1}H-NMR (CD_2Cl_2, −50 °C): δ 0.27 (s, 6H, Ti−*Me*); 1.85 (s, 6H, $C_5\mathit{Me}_4$); 2.13 (s, 6H, $C_5\mathit{Me}_4$); 2.80 (t, $2H_{AA'}$, $C\mathit{H}_2Ph$); 3.03 (t, $2H_{BB'}$, $C\mathit{H}_2$); 7.03 (d, 2H, *o-Ph*); 8.35 (t, 1H, *p-Ph*); 8.51 (t, 2H, *m-Ph*). ^{13}C-NMR (CD_2Cl_2, −50 °C): δ 12.25 ($C_5\mathit{Me}_4$, $^1J_{CH} = 127.2$ Hz); 12.39 ($C_5\mathit{Me}_4$, $^1J_{CH} = 127.4$ Hz); 24.50 ($\mathit{C}H_2$, $^1J_{CH} = 130.1$ Hz); 33.99 ($\mathit{C}H_2Ph$, $^1J_{CH} = 131.8$ Hz); 64.05 (Ti−*Me*; $^1J_{CH} = 125.0$ Hz); 125.84 (*m-Ph*, $^1J_{CH} = 168.1$ Hz); 127.06 (C_5Me_4); 127.52 (*ipso*-C_5Me_4); 130.87 (*p-Ph*, $^1J_{CH} = 175.3$ Hz); 131.90 (C_5Me_4); 137.63 (*o-Ph*, $^1J_{CH} = 174.5$ Hz); 145.27 (*ipso-Ph*). ^{13}C-NMR data for C_6F_5 of $[B(C_6F_5)_4]^-$: 122−123 (br m, *ipso*-C), 135.3 (br, d, $^1J_{CF} = 229.7$ Hz, *o*-C), 137.1 (br d, $^1J_{CF} = 235.5$ Hz, *m*-C), 147.0 (br d, $^1J_{CF} = 243.5$ Hz, *p*-C).

Isolation of {[1-(2-Phenylethyl)-2,3,4,5-tetramethylcyclopentadienyl]dimethyltitanium}(μ-oxo) (6). A sample of compound **4** (0.70 g, 1.8 mmol) was dissolved in wet pentane. Concentration of the resulting yellow solution to *ca*. 10 mL and cooling at −78 °C overnight gave a yellow solid which was recrystallized in dry pentane, producing a pale yellow microcrystalline solid characterized as the μ-oxo compound **6**. Yield: 0.28 g (49%). Anal. Calcd for $C_{38}H_{54}OTi_2$: C, 73.30; H, 8.74. Found: C, 72.83; H, 9.01. ^{1}H-NMR (C_6D_6, 25 °C): δ 1.06 (s, 12H, Ti−*Me*); 1.71 (s, 12H, C_5Me_4); 1.79 (s, 12H, C_5Me_4); 2.50−2.73 (m, 8H, CH_2CH_2); 7.00−7.19 (m, 10H, *Ph*).

X-ray Structure Determination. The details of the X-ray data collection, lattice parameters, and physical properties of the crystal of **3** are summarized in Table 6. Lattice parameters were determined for a crystal mounted in a Lindemann glass capillary from 25 reflections in the range $18° > 2\theta > 26°$. The reflection data were corrected for Lorentz and polarization factors and an empirical absorption correction based on ψ scans. Five standard reflections monitored during the data collection showed no significant change in intensity. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 using all 2073 independent reflections in the SHELX-TL set of programs.[24] The final residuals (based on *F*) for the 1409 reflections with $I \geq 2\sigma(I)$ are $R = 0.039$ and $R_w = 0.089$. Hydrogen atoms based on riding model were included. Neutral atom scattering factors for non-hydrogen atoms were taken from ref 25, while that tabulated by Stewart et al. was used for hydrogen.[26] Corrections for anomalous dispersion were included.[27]

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Supporting Information Available: Tables S1−S4, listing complete crystallographic information for ($C_5Me_4CH_2CH_2$-Ph)$TiCl_3$, including atomic coordinates, anisotropic thermal parameters, H coordinates, and complete bond distances and angles (4 pages). Ordering information is given on any current masthead page.

OM960475S

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