Highly Stable Catalysts for the Stereospecific Polymerization of Styrene

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The synthesis of eight new catalyst precursors is described, and their catalysis of syndiospecific styrene polymerization when activated by methylaluminoxane (MAO) is compared with $IndTiCl_3$. Phenyl substitution increases polymerization activity (A) in the order $1,3\text{-}Ph_2Ind < 2\text{-}PhInd < 1\text{-}PhInd$; the opposite trend was observed for the yield (SY) of syndiotactic polystyrene (*s*-PS). The optimum polymerization temperature (T_p) is 50 °C; an increase of T_p decreases A, SY, and molecular weight (MW) of *s*-PS. Benz[*e*]$IndTiCl_3$ (**6a**) as well as the 2-methyl (**6b**) and 1,2,3-trimethyl (**11**) derivatives have been synthesized. Complexes **6a**/MAO and **6b**/MAO have exceedingly high values of $A \approx 1.8 \times 10^8$ g of PS/(mol of Ti·mol of styrene·h) for a turnover rate of 450 s^{-1}, SY over 92%, and MW $\approx 5 \times 10^5$. These parameters were only slightly lowered at $T_p = 100$ °C, indicating very thermally stable, catalytically active species. These catalyst precursors are stable in solution toward air and moisture up to 48 h and are indefinitely stable in the solid state. Though **11**/MAO has a lower A, it has a higher SY which changes to lesser degrees with increase in T_p than for either **6a** or **6b**/MAO. Attempts to make benz[*f*]indenyltrichlorotitanium have so far been unsuccessful.

Introduction

Ishihara and co-workers[1] reported in 1986 that syndiotactic polystyrene (*s*-PS) could be produced with high stereoregularity and yield under conventional conditions using an organic or inorganic titanium compound activated with methylaluminoxane (MAO).[1] There have been only a few reports[2−5] on the kinetic and mechanistic studies of this novel catalysis. In fact, *s*-PS is a new macromolecule; previously only amorphous (*a*-PS) and isotactic (*i*-PS) structures were known. Many patents have been issued to Idemitsu Kosan Co.[6] and to Dow Chemical Co.[7] for their work in this area.

(η^5-Cyclopentadienyl)trichlorotitanium ($CpTiCl_3$) was the most active precursor found by Ishihara et al.,[1] although the trivalent $CpTiCl_2$ exhibits high activity and stereospecificity as well.[1] We have been interested in elucidating the relationship of precursor structure and its catalytic behavior. The effects of methyl, phenyl, diphenylphosphino, and trimethylsilyl substituents have been reported by Kucht et al.[8] Ready et al.[9] observed that $IndTiCl_3$ is a significantly better precursor than $CpTiCl_3$.

In contrast to the modest interest in *s*-PS catalysis, there are currently intense research activities in the isospecific polymerization of propylene,[10] which is undoubtedly related to the commercial value of isotactic polypropylene (*i*-PP). The stereospecificity, activity, and molecular weight of polypropylene produced by isospecific *ansa*-zirconocene catalysts were enhanced by aromatic substituents.[11]

The central objective of this work is to introduce aromatic substituents in the design of styrene catalysts optimized for high activity, syndiospecificity, and stability as well as low probability to chain terminate, which would result in high molecular weight products.

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1996.

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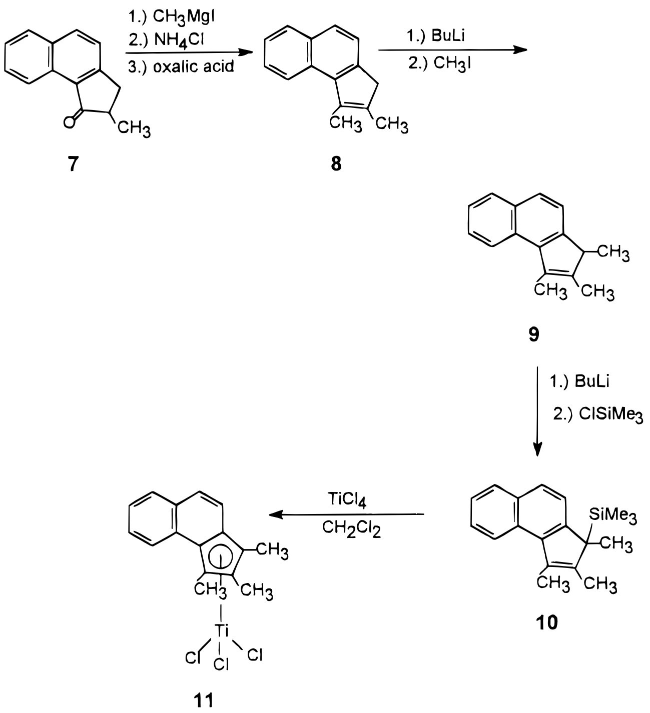
Scheme 1

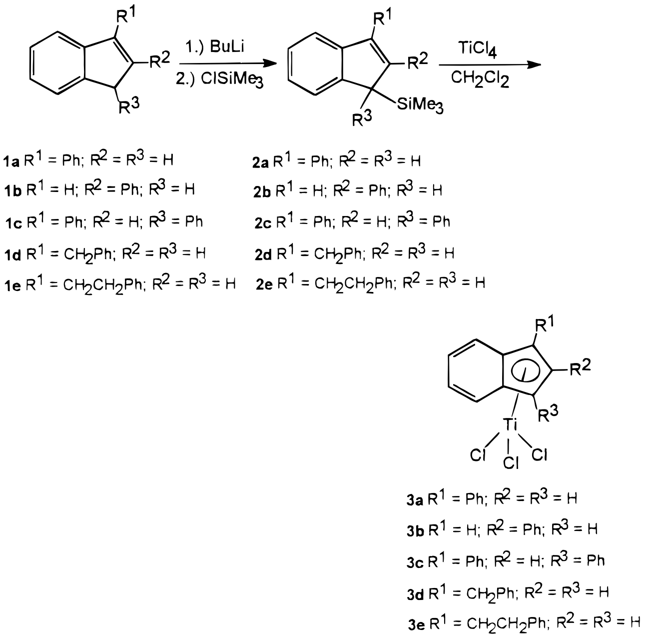


Results

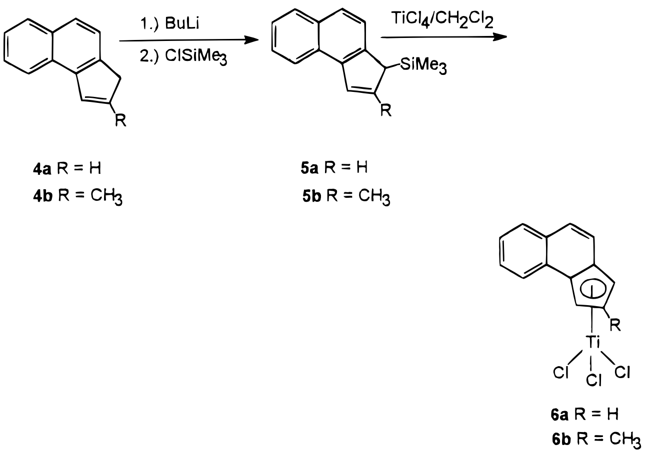
Synthesis of Catalyst Precursors. 2-Phenylindene (**1b**),[12] 1,3-diphenylindene (**1c**),[13] benz[*e*]indene (**4a**),[11a] and 2-methylbenz[*e*]indene (**4b**)[11b] were synthesized by literature procedures. 3-Phenylindene (**1a**),[12] 3-benzylindene (**1d**),[14] and 3-(2-phenylethyl)indene (**1e**)[15] were prepared by modifications of the literature methods, as described in the Experimental Section. 1,2,3-Trimethylbenz[*e*]indene (**9**) was synthesized as shown in Scheme 1. The substituted indenes were converted into the trimethylsilyl derivatives by reaction of the indene with butyllithium followed by chlorotrimethylsilane (Schemes 1−3). The corresponding titanium complexes were obtained by reaction of the substituted (trimethylsilyl)-indene derivatives with $TiCl_4$ in a dichloromethane solution (Schemes 1−3).[16]

Benz[*f*]indene (**12**) was prepared by modification[17] of a literature procedure,[18] which significantly improved the yield and decreased the reaction time (see Experimental Section). Benz[*f*]indene was readily converted into the trimethylsilyl derivative (**13**) (Scheme 4). Two attempts were made to prepare the corresponding titanium complex (**14**) (Scheme 4). The reaction between (trimethylsilyl)benz[*f*]indene and $TiCl_4$ was carried out at −78 °C in both CH_2Cl_2 and toluene. Both attempts gave a green solid, which gave no ^1H NMR spectrum and could not be recrystallized.

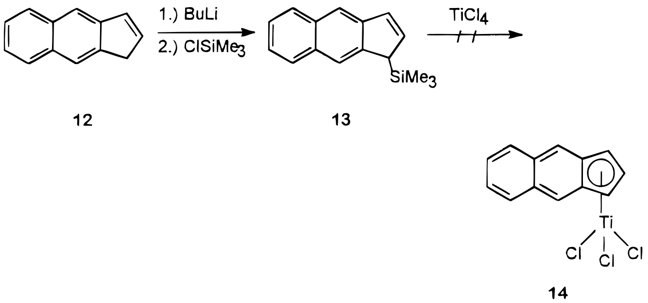
Scheme 2



Scheme 3



Scheme 4



Polymerization of Styrene. The newly synthesized catalyst precursors were examined using MAO as cocatalyst at various polymerization temperatures. The results of the phenyl-substituted precursors are summarized in Table 1, while those of the annelated precursors are found in Table 2. In general, the highest activity was obtained at 50 °C and Al:Ti = 4000:1, except for compound **3e** which was slightly more active at Al:Ti = 2000:1. At most polymerization temperatures (T_p), compounds **3a**−**c** all exhibited high activities and syndiotacticity. Molecular weights and melting points were consistent with those previously reported[3b] for *s*-PS. The reproducibility of the amount of total polymer obtained, activity, and MW is estimated at ±5%.

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Table 1. Polymerization of Styrene with Substituted $IndTiCl_3$ Compounds Activated with MAO[a]

$IndTiCl_3$ compds								
no.	R^1	R^2	R^3	T_p (°C)	$10^{-7}A^b$	s-PS^c (%)	$T_m{}^d$ (°C)	$M_w{}^e$ 10^{-5}
3[f]	H	H	H	50	3.7	98.2	270.8	7.20
				75	1.8	96.3		
				100	1.1	89.6		
3a	Ph	H	H	50	7.7	90.0	260.7	4.24
				75	3.0	91.1	260.9	1.88
				100	2.4	88.9	268.5	1.06
3b	H	H	H	50	5.2	91.3	262.5	3.23
				75	2.6	90.5	260.7	1.81
				100	2.1	87.6	259.2	1.62
3c	Ph	H	Ph	50	3.6	94.8	262.0	4.96
				75	4.1	93.5	268.0	3.42
				100	2.2	91.5	260.3	2.01
3d	CH_2Ph	H	H	50	0.2	87.2	268.3	3.23
				75	0.1	78.6	262.3	1.81
				100	0.07	66.7	261.7	1.02
3e	$H(CH_2)_2Ph$	H	H	50	1.1	88.2	267.8	4.01
				75	1.2	8.0	260.8	2.42
				100	0.6	42.7	260.9	0.95

[a] Polymerization conditions: [Ti] = 50 μM; Al/Ti = 4000:1; [styrene] = 0.88 M; time of polymerization is from 10 to 30 min depending on *A*. [b] *A* (activity) = g of PS/(mol of Ti·mol of styrene·h). [c] *s*-PS % = (g of polymer insoluble in 2-butanone)/(g of total polymer) × 100%. [d] T_m = melting point of *s*-PS. [e] Molecular weights determined by intrinsic viscosity. [f] Data were obtained from ref 9b.

Table 2. Polymerization of Styrene with Unsubstituted and Substituted $BEIndTiCl_3$ Compounds Activated with MAO[a]

$BEIndCl_3$ compds								
no.	R^1	R^2	R^3	T_p (°C)	$10^{-7}A^b$	s-PS^c (%)	$T_m{}^d$ (°C)	$10^{-5}M_w{}^e$
6a	H	H	H	50	17	92.5	270.4	5.45
				75	14	91.3	263.3	3.22
				100	10	89.0	256.8	1.28
6b	H	Me	H	50	18	92.8	275.2	4.24
				75	15	91.4	261.0	1.88
				100	7.0	90.1	258.4	1.06
11	Me	Me	Me	50	2.0	96.0	276.0	3.23
				75	2.0	97.6	275.2	1.81
				100	2.0	95.0	271.9	1.02

[a] Polymerization conditions: [Ti] = 50 μM; Al/Ti = 4000:1; [styrene] = 0.88 M; time of polymerization is from 10 to 30 min depending on *A*. [b] A (activity) = g of PS/(mol of Ti·mol of styrene·h). [c] *s*-PS % = (g of polymer insoluble in 2-butanone)/(g of total polymer) × 100%. [d] T_m = melting point of *s*-PS. [e] Molecular weights determined by intrinsic viscosity.

Discussion

$CpTiCl_3$ may be considered as the reference catalyst precursor for *s*-PS catalysis. It exhibits maximum activity $A = 1.4 \times 10^7$ g of PS/(mol of Ti·mol of styrene·h) at 50 °C.[9a] The syndiospecificity is only modest as measured by yield in weight percent of product insoluble in refluxing 2-butanone, SY = 67%.[9a] Both *A* and SY decline at higher or lower polymerization temperature (T_p). The polymerization results could be influenced significantly by one of several experimental variables, i.e. concentration of monomer, catalyst precursor, or MAO, and also by the type of solvent used.

We have studied more thoroughly a closely related system $CpTi(OBu)_3$/ MAO.[3b,c] The optimum T_p was 45 °C at which $A = 3.1 \times 10^7$ g of PS/(mol of Ti·mol of styrene·h), SY = 93%, MW of *s*-PS = 4×10^4, and $M_w/M_n = 2.8$. *A* and SY decreased at both higher and lower T_p, while MW increased with the lowering of T_p.

All the catalyst precursors in the series **3a**–**e** have high A_{max} at $T_p = 50$ °C (Table 1). Compared to $IndTiCl_3$ (**3**), the 1,3-Ph_2-substituted complex **3c** has comparable *A* and MW but slightly lower SY. There is a significant increase in A_{max} with the 2-Ph-substituted complex **3b** and an even larger increase in the case of the 1-Ph derivative **3a**, both giving *s*-PS of very high MW ((4–5) × 10^5). The trend of *A* is consistent with the aromatic substituent having an effect on the behavior of the catalyst due to the increased possible resonance stabilization. It has been shown that phenyl substituents in the 1 and/or 3 positions of indene decrease the p*K*a, stabilizing the anion formed. However, phenyl substitution in the 2 position is much less effective in stabilizing the anion due to the fact that the negative charge cannot be effectively delocalized into the phenyl ring.[19] Taking these factors into account, the increasing order of *A* of $IndTiCl_3$ < 2-$PhIndTiCl_3$ < 1-$PhIndTiCl_3$ can be rationalized. The 1,3-$Ph_2IndTiCl_3$ (**3c**)/MAO catalyst has an *A* value at 50 °C that is comparable to the unsubstituted system **3**/MAO and significantly less than catalysts derived from the monophenyl-substituted precursors **3a**,**b**. However, at $T_p = 75$ °C, **3c**/MAO is more active and produces *s*-PS having higher MW than catalysts derived from **3**, **3a**, or **3b**. These results indicate that steric problems can arise with phenyl substitution at both C-1 and C-3 but that an increase of temperature may reduce the steric effects. Also, **3c** is air stable in the solid state for prolonged periods and there was no decrease in *A* after **3c** was exposed to air for 4 weeks. This phenomenon is probably due to the steric effects which protect the metal center from decomposition (*vida infra*).

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The steric effect of phenyl substitution could also cause a reduction of stereochemical control as is evidenced by the lower SY for compounds **3a**−**c** relative to **3**. In a current mechanism for syndiospecific styrene polymerization[2,3] both the last benzyl group in the propagating chain and the styrene monomer are postulated to complex with the titanium center via multihapto interaction. Coordination of this type is thought to regulate the regio- and stereochemistry of styrene complexation and insertion. Any phenyl substituents may cause lowering of the ligand−metal interaction and consequently diminish SY.

Compounds **3d**,**e** were synthesized to investigate several effects: (1) breaking of conjugation between the indenyl ring and the phenyl substituent; (2) coordination of the phenyl substituent to titanium; (3) mobility of the substituent. The results in Table 1 show that, compared with $IndTiCl_3$, 1-($PhCH_2CH_2$)$IndTiCl_3$ (**3e**) has a third of the activity and there is another drop of a factor of 5 for 1-($PhCH_2$)$IndTiCl_3$ (**3d**). The former behaves as expected for breaking of conjugation, and the activity of **3e** is comparable to that of 1-$MeIndTiCl_3$.[9b] Steric effects as proposed above for the phenyl substituents would interfere with hapto interactions at the metal center. This effect is most pronounced for the $PhCH_2$ substituent and not as strong in the case of the $PhCH_2$-CH_2 substituent, because of the more flexible spacer unit $-CH_2CH_2-$.

A dynamic interaction between the phenyl group with titanium in **3d**,**e** cannot be entirely discounted, however. It has been shown that if a coordinating substituent is present (e.g., $-CH_2CH_2NMe_2$), polymerization of both ethylene and styrene is possible.[20] In this regard, styrene polymerization activity is much lower for **3d** than for **3e**, while ethylene polymerization activity shows the opposite trend. The catalyst **3d**/MAO exhibits a reasonably high ethylene polymerization activity of 3.4×10^5 g of PE/(mol of Ti·h), while **3e**/MAO is inactive.

All the systems in Table 1 have optimal T_p in the vicinity of 50 °C. Benz[*e*]indenyl$TiCl_3$ (BEInd$TiCl_3$, **6a**) and the 2-methyl (**6b**) and 1,2,3-trimethyl (**11**) derivatives were synthesized with the idea that annelation of the aromatic ring might improve both catalytic activity and stability. Previously, *ansa*-zirconocene studies involving benz[*e*]indene showed appreciable increases in activity and steroeselectivity over indene for propylene polymerization.[11]

BEInd$TiCl_3$/MAO has an extremely high value of A_{max} for syndiospecific styrene polymerization of 1.7×10^8 g of PS/(mol of Ti·mol of styrene·h) (Table 2). The turnover rate is 450 s^{-1}, which is truly remarkable for such a bulky monomer. Also very high are the SY (93%) and MW (5.5×10^5). These properties decline only slightly at 100 °C. The 2-MeBEInd$TiCl_3$/MAO catalyst system exhibits virtually the same A_{max} and SY as the unsubstituted system **6a**, but unexpectedly gives slightly lower MW for *s*-PS. Increasing T_p to 100 °C caused only small reductions in activity and stereospecificity. However, the lowering of MW is about the same as that observed for the indenyl systems of Table 1. The results suggest that benz[*e*]indene significantly stabilizes the active catalytic species compared to phenyl substitution on the C_5 ring. Further evidence of enhanced stability of the catalyst system 2-MeBEInd$TiCl_3$/MAO is shown in Figure 1, which is a plot of activity versus time, where time is the length of time the catalyst solution was exposed to air. The long stability and activity of the catalyst solution is suprising, since solutions of cyclopentadienyl- and indenyltrichlorotitanium complexes normally decompose readily in air (Figure 1).

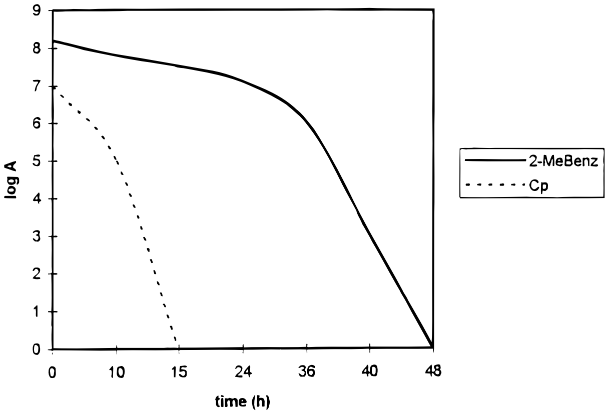

Figure 1. Log of activity versus time plot for the loss of activity of **6b** and $CpTiCl_3$ when exposed to air in a toluene solution. *A* (activity) = g of PS/(mol of Ti·mol of styrene·h); [Ti] = 50 μM; T_p = 50 °C; Al/Ti = 4000:1;[styrene] = 0.88 M; time = time catalyst precursor solution was exposed to air.

The most interesting catalyst precursor is **11** because of the temperature invariance of its polymerization activity as well as its very high stereospecificity in the T_p range investigated. The three methyl groups in **11** provide both more electron donation and steric hindrance to help stabilize it against reduction,[21] dimerization,[22] or reaction with oxygen and moisture as well as β-hydride elimination. The syndiospecificity of **11** is higher than that of **6a**,**b**, which is analogous to the behavior of (pentamethylcyclopentadienyl)trichlorotitanium versus the unsubstituted cyclopentadienyl catalyst $CpTiCl_3$.[8b]

Attempts to synthesize (benz[*f*]indenyl)trichlorotitanium (**14**) were unsuccessful. Reaction of (benz[*f*]-indenyl)lithium, derived from **12**, with chlorotrimethylsilane went as expected, forming 1-(trimethylsilyl)-benz[*f*]indene (**13**). However, when attempts were made to convert **13** into **14**, the desired product (**14**) could not be isolated.

Experimental Section

Reactions were carried out under an argon atmosphere using standard Schlenk techniques. Methylaluminoxane (MAO) was purchased from Akzo. All other reagents were purchased from Aldrich and were used without further purification. Toluene, diethyl ether, tetrahydrofuran (THF), hexane, and pentane were distilled with Na/K alloy under argon. Methylene chloride and styrene were distilled from CaH_2. ^1H NMR spectra were recorded on a Varian XL-200 or a Bruker NR-80 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA.

3-Phenylindene (1a). A modification of the procedure of Greifenstein et al.[12] was used. To a suspension of Mg turnings

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(1.85 g, 76 mmol) in 50 mL of diethyl ether was slowly added a solution of bromobenzene (11.93 g, 76 mmol) in 50 mL of the same solvent. After 30 min of reflux, 1-indanone (10 g, 76 mmol) in 20 mL of ether was added and the solution was stirred overnight. The mixture was hydrolyzed with an aqueous solution of NH_4Cl (8 g in 40 mL of H_2O). The organic phase was separated, extracted with water, and dried (Na_2SO_4), and the solvent was removed. The oily residue was dissolved in 150 mL of benzene, *p*-toluenesulfonic acid (200 mg, 1 mmol) was added, and the solution was refluxed using a Dean−Stark apparatus until separation of water subsided. The organic mixture was extracted with saturated $NaHCO_3$ and water, and dried ($MgSO_4$), and the solvent was removed. Fractional distillation (110−112 °C/ 0.1 mmHg) of the residue gave 3-phenylindene as a yellow liquid (9.7 g, 66%). ^1H NMR ($CDCl_3$): δ 7.27−7.61 (m, 9H, arom H), 6.57 (t, 1H, H-C_5(2)), 3.50 (d, 2H, CH_2).

3-Phenyl-1-(trimethylsilyl)indene (2a). To a stirred solution of **1a** (2.35 g, 12 mmol) in 50 mL of hexane was added a 1.6 M solution of butyllithium in hexane (7.6 mL, 12 mmol) at 0 °C. The mixture was stirred at 0 °C for 1 h and at room temperature for 7 h. The solvent was removed by filtration, and the solid residue was washed with pentane. Fresh hexane (50 mL) was added, and the solution was cooled to 0 °C. Chlorotrimethylsilane (1.43 g, 13.2 mmol) was added, and the mixture was stirred overnight. The mixture was filtered to remove the lithium chloride, and the solvent was removed to give **2a** (2.0 g, 63%) as a pale yellow oil. ^1H NMR ($CDCl_3$): δ 7.26−7.68 (m, 9H, arom H), 6.75 (d, 1H, H-C_5(2)), 3.68 (d, 1H, H-C_5(1)), 0.07 (s, 9H, Si−CH_3).

(1-Phenylindenyl)trichlorotitanium (3a). To a solution of **2a** (2.0 g, 7.6 mmol) in 50 mL of CH_2Cl_2 was added $TiCl_4$ (1.6 g, 8.3 mmol) at 0 °C. The mixture was warmed to room temperature and stirred overnight and the solvent removed. The solid residue was washed with pentane, 50 mL of fresh CH_2Cl_2 was added, and the solution was filtered. The filtrate was cooled to −20 °C to give **3a** (1.2 g, 46%) as purple crystals. ^1H NMR ($CDCl_3$): δ 7.47−8.20 (m, 9H, arom H), 7.38 (d, 1H, H-C_5(2)), 7.31 (dd, 1H, H-C_5(3)). Anal. Calcd for $C_{15}H_{11}Cl_3Ti$: C, 52.14; H, 3.21. Found: C, 51.93; H, 3.14.

2-Phenyl-1-(trimethylsilyl)indene (2b). 2-Phenylindene (**1b**) (1.57 g, 8.0 mmol), prepared by the procedure of Greifenstein et al.[12] [mp 162−164 °C, 67%], was dissolved in 50 mL of THF. The mixture was cooled to 0 °C, and 1.6 M butyllithium (5.1 mL, 8.0 mmol) was added. The solution was warmed to room temperature and allowed to stir for 8 h. The THF was removed, and the solid was washed with two 20-mL portions of pentane. The solid was dissolved in 50 mL of THF, chlorotrimethylsilane (0.98 g, 9.0 mmol) was added at room temperature, and the mixture was stirred overnight. The THF was removed, the residue was extracted with 50 mL of pentane, and the mixture was filtered. The pentane was removed to give **2b** (1.6 g, 74%) as a yellow oil. ^1H NMR ($CDCl_3$): δ 7.16−7.52 (m, 9H, arom H), 7.07 (s, 1H, H-C_5(3)), 4.11 (s, 1H, H-C_5(1)), −0.25 (s, 9H, Si−CH_3).

(2-Phenylindenyl)trichlorotitanium (3b). To a solution of **2b** in 50 mL of CH_2Cl_2 was added $TiCl_4$ (1.1 g, 6.0 mmol) at 0 °C. The mixture was warmed to room temperature and stirred overnight. The solvent was removed and the residue extracted with 50 mL of toluene. The extracts were filtered, and the toluene was removed. The solid residue was dissolved in 20 mL of CH_2Cl_2 and cooled to −20 °C to give **3b** (0.80 g, 39%) as a red solid. The product was dried at 70 °C in vacuo. ^1H NMR ($CDCl_3$): δ 7.45−7.96 (m, 9H, arom H), 7.27 (s, 2H, H-C_5), 5.32 (s, 0.7H, CH_2Cl_2). Anal. Calcd for $C_{15}H_{11}Cl_3Ti{\cdot}{}^1/_3CH_2Cl_2$: C, 49.27; H, 3.14. Found: C, 49.02; H, 3.18.

1,3-Diphenyl-1-(trimethylsilyl)indene (2c). Following the procedure described for **2b**, 1,3-diphenylindene (**1c**) (2.14 g, 8.0 mmol), prepared by the procedure of Miller et al.[13] [mp 82−84 °C, 75%], 1.6 M butyllithium (5.0 mL, 8.0 mmol), and chlorotrimethylsilane (0.98 g, 9.0 mmol) gave **2c** (2.1 g, 77%) as a yellow oil. ^1H NMR ($CDCl_3$): δ 7.21−7.65 (m, 14H, arom. H), 6.93 (s, 1H, H-C_5), −0.11 (s, 9H, Si−CH_3).

(1,3-Diphenylindenyl)trichlorotitanium (3c). Following the procedure described for **3a**, **2c** (2.1 g, 6.2 mmol) and $TiCl_4$ (1.2 g, 6.2 mmol) gave **3c** (0.82 g, 32%) as green crystals. ^1H NMR ($CDCl_3$): δ 7.50−8.31 (m, 14H, arom H), 7.48 (s, 1H, H-C_5). Anal. Calcd for $C_{21}H_{15}Cl_3Ti$: C, 59.82; H, 3.59. Found: C, 59.78; H, 3.63.

3-Benzylindene (1d). A solution of indene (4.7 g, 41 mmol) in 60 mL of THF was cooled to 0 °C, 1.6 M butyllithium (25.6 mL, 41 mmol) was added, and the solution was stirred for 3 h. Benzyl chloride (5.2 g, 41 mmol) was added, and the mixture was warmed to room temperature and stirred overnight. The solvent was removed, and the residue was extracted with 50 mL of hexane. Removal of the solvent followed by distillation (102 °C /0.1 mmHg) of the residue gave **1d** (3.55 g, 42%) as a yellow liquid. ^1H NMR ($CDCl_3$): δ 7.17−7.48 (m, 9H, arom H), 6.11 (t, 1H, H-C_5(2)), 3.88 (m, 2H, CH_2), 3.34 (d, 2H, H-C_5(1)).

3-Benzyl-1-(trimethylsilyl)indene (2d). Following the procedure described for **2b**, **1d** (3.55 g, 17 mmol), 1.6 M butyllithium (10.7 mL, 17 mmol), and chlorotrimethylsilane (2.1 g, 19 mmol) gave **2d** (4.0 g, 84%) as a yellow oil. ^1H NMR ($CDCl_3$): δ 7.17−7.53 (m, 9H, arom H), 6.25 (d, 1H, H-C_5(2)), 3.97 (s, 2H, CH_2), 3.42 (m, 1H, H-C_5(1)), −0.05 (s, 9H, Si−CH_3).

(3-Benzylindenyl)trichlorotitanium (3d). Following the procedure described for **3a**, **2d** (4.0 g, 14 mmol) and $TiCl_4$ (2.6 g, 14 mmol) gave **3d** (1.8 g, 36%) as purple crystals. ^1H NMR ($CDCl_3$): δ 7.25−7.83 (m, 9H, arom H), 7.14 (dd, 1H, H-C_5(2)), 6.93 (d, 1H, H-C_5(3)), 4.52 (s, 2H, CH_2). Anal. Calcd for $C_{16}H_{13}Cl_3Ti$: C, 53.45; H, 3.64. Found: C, 52.94; H, 3.80.

3-(2-Phenylethyl)indene (1e). To a suspension of Mg turnings (1.9 g, 80 mmol) in 60 mL of diethyl ether was slowly added (2-bromoethyl)benzene (14.8 g, 80 mmol). The mixture was refluxed for 1 h, 1-indanone (10 g, 80 mmol) in 20 mL of ether was added, and the solution was stirred overnight at room temperature. The mixture was hydrolyzed with aqueous NH_4Cl (8 g in 40 mL of H_2O), and the organic layer was separated. The latter was dried (Na_2SO_4) and filtered, and the solvent was removed. The residue was dissolved in 100 mL of toluene, oxalic acid (5 g) was added, and the solution refluxed for 2 h using a Dean−Stark trap to separate the H_2O formed. The mixture was washed with 10% aqueous $NaHCO_3$, dried ($MgSO_4$), and evaporated to give crude **1e**. Distillation (150 °C /0.1 mmHg) of the residue gave **1e** (11.1 g, 63%) as a yellow liquid. ^1H NMR ($CDCl_3$): δ 7.15−7.43 (m, 9H, arom H), 6.22 (m, 1H, H-C_5(2)), 3.31 (d, 2H, H-C_5(1)), 2.95−3.00 (m, 4H, CH_2CH_2).

3-(2-Phenylethyl)-1-(trimethylsilyl)indene (2e). Following the procedure described for **2b**, **1e** (3.5 g, 16 mmol), 1.6 M butyllithium (10 mL, 16 mmol), and chlorotrimethylsilane (2.0 g, 18 mmol) gave **2e** (3.86 g, 82%) as a yellow oil. ^1H NMR ($CDCl_3$): δ 7.14−7.40 (m, 9H, arom H), 6.31 (m, 1H, H-C_5(2)), 3.38 (m, 1H, H-C_5(1)), 2.98 (br s, 4H, CH_2CH_2), −0.09 (s, 9H, Si−CH_3).

(1-(2-Phenylethyl)indenyl)trichlorotitanium (3e). To a solution of **2e** (3.9 g, 13 mmol) in 50 mL of toluene was added $TiCl_4$ (2.5 g, 13 mmol) at 0 °C. The mixture was warmed to room temperature, and the solution was stirred overnight. The mixture was filtered and concentrated to half its original volume. Pentane (8 mL) was added, and the mixture was cooled to −20 °C giving **3e** (1.9 g, 39%) as a burgundy solid. ^1H NMR ($CDCl_3$): δ 7.19−7.75 (m, 9H, arom H), 7.11 (d, 1H, H-C_5), 6.82 (d, 1H, H-C_5), 3.48 (t, 2H, CH_2), 3.05 (t, 2H, CH_2). Anal. Calcd for $C_{17}H_{15}Cl_3Ti$: C, 54.66; H, 4.05. Found: C, 54.72; H, 4.07.

1-(Trimethylsilyl)benz[*e*]indene (5a). Following the procedure described for **2b**, benz[*e*]indene (**4a**) (2.0 g, 12 mmol) prepared by the procedure of Spaleck et al.,[11a] 1.6 M butyllithium (8.0 mL, 12 mmol), and chlorotrimethylsilane (1.4 g, 13 mmol) gave **5a** (2.3 g, 80%) as a yellow oil. ^1H NMR

($CDCl_3$): δ 7.44−8.25 (m, 7H, arom H and H-C_5(3)), 6.88 (dd, 1H, H-C_5(2)), 3.78 (m, 1H, H-C_5(1)), 0.02 (s, 9H, Si−CH_3).

(Benz[*e*]indenyl)trichlorotitanium (6a). Following the procedure described for **3a**, **5a** (2.3 g, 9.6 mmol) and $TiCl_4$ (1.8 g, 9.6 mmol) gave **6a** (2.2 g, 71%) as red-orange crystals. ^1H NMR ($CDCl_3$): δ 8.25−8.29 (m, 1H, arom H), 7.59−7.91 (m, 6H, arom H and H-C_5(3)), 7.26 (m, 1H, H-C_5(2)), 7.21 (m, 1H, H-C_5(1)). Anal. Calcd for $C_{13}H_9Cl_3Ti$: C, 48.87; H, 2.84; Cl, 33.29. Found: C, 48.29; H, 2.80; Cl, 32.99.

2-Methyl-1-(trimethylsilyl)benz[*e*]indene (5b). Following the procedure described for **2b**, 2-methylbenz[*e*]indene (**4b**) (6.2 g, 35 mmol) prepared by the procedure of Stehling et al.,[11b] 1.6 M butyllithium (22 mL, 35 mmol), and chlorotrimethylsilane (4.4 g, 40 mmol) gave **5b** (7.6 g, 86%) as a yellow oil. ^1H NMR ($CDCl_3$): δ 7.37−8.20 (m, 6H, arom H), 7.18 (m, 1H, H-C_5(3)), 3.58 (s, 1H, H-C_5(1)), 2.34 (d, 3H, CH_3), −0.02 (s, 9H, Si-CH_3).

(2-Methylbenz[*e*]indenyl)trichlorotitanium (6b). Following the procedure described for **3a**, **5b** (4.3 g, 17 mmol) and $TiCl_4$ (3.2 g, 17 mmol) gave **6b** (3.7 g, 65%) as red crystals. ^1H NMR ($CDCl_3$): δ 8.19−8.23 (m, 1H, arom H), 7.58−7.86 (m, 5H, arom H), 7.45 (d, 1H, H-C_5), 7.09 (d, 1H, H-C_5), 2.70 (s, 3H, CH_3). Anal. Calcd for $C_{14}H_{11}Cl_3Ti$: C, 50.42; H, 3.32. Found: C, 50.67; H, 3.39.

2,3-Dimethylbenz[*e*]indene (8). To a suspension of Mg (6.2 g, 0.26 mol) in 60 mL of diethyl ether was slowly added CH_3I (36.3 g, 0.26 mol), and the mixture was stirred for 1 h. 2-Methylbenz[*e*]indanone (**7**) (50 g, 0.26 mol), prepared by the procedure of Stehling et al.,[11b] in 20 mL of ether was added, and the solution was stirred for 8 h. The mixture was hydrolyzed with aqueous NH_4Cl (25 g in 130 mL of H_2O), and the organic layer was separated. The latter was dried (Na_2SO_4) and filtered, and the solvent was removed. The residue was dissolved in 300 mL of toluene, and 50 g of oxalic acid was added. The mixture was refluxed, using a Dean−Stark trap, until the formation of water subsided. The mixture was washed with 300 mL of 10% $NaHCO_3$ and dried ($MgSO_4$). After filtration, the solution was mixed with 40 g of silica gel and evaporated to dryness. The residue was chromatographed over 150 g of silica gel with a hexane/ethyl acetate (49:1) eluent mixture to give **8** (29.8 g, 60%) as a yellow liquid. ^1H NMR ($CDCl_3$): δ 8.48−8.51 (m, 1H, arom H), 7.35−7.90 (m, 5H, arom H), 3.43 (s, 2H, CH_2), 2.53 (d, 3H, CH_3), 2.15 (s, 3H, CH_3).

1,2,3-Trimethylbenz[*e*]indene (9). To a solution of **8** (16.73 g, 86 mmol) in 100 mL of THF was slowly added 1.6 M butyllithium (54 mL, 86 mmol) at 0 °C. The mixture was warmed to room temperature and stirred for 8 h. The solvent was removed, and the solid was washed with two 50 mL portions of pentane. THF (100 mL) was added followed by CH_3I (12.2 g, 86 mmol) and the mixture stirred for 4 h. The solvent was removed, and the solid was extracted with 50 mL of pentane. The extracts were filtered, and the solvent was removed. The residue was chromatographed over a short silica gel column using a hexane/ethyl acetate (49:1) eluent mixture to give **9** (7.6 g, 42%) as an orange oil. ^1H NMR ($CDCl_3$): δ 7.30−8.56 (m, 6H, arom H), 3.52 (m, 1H, CH), 2.08 (br s, 6H, $2 \times CH_3$), 1.42 (m, 3H, CH_3). MS (EI): *m/z* 208 (M^+, 97%), 193 ($M^+ - CH_3$, 100%), 178 ($M^+ - 2CH_3$, 20%), 163 ($M^+ - 3CH_3$, 5%).

1,2,3-Trimethyl-1-(trimethylsilyl)benz[*e*]indene (10). Following the procedure described for **2b**, **9** (2.9 g, 14 mmol), 1.6 M butyllithium (9.0 mL, 14 mmol), and chlorotrimethylsilane (1.5 g, 14 mmol) gave **10** (2.28 g, 58%) as an orange oil. ^1H NMR ($CDCl_3$): δ 7.34−8.56 (m, 6H, arom H), 2.57 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), −0.16 (s, 9H, Si−CH_3).

(1,2,3-Trimethylbenz[*e*]indenyl)trichlorotitanium (11). Following the procedure described for **3a**, **10** (2.28 g, 8.0 mmol) and $TiCl_4$ (1.5 g, 8.0 mmol) gave **11** (1.2 g, 41%) as purple crystals. ^1H NMR ($CDCl_3$): δ 8.82−8.86 (m, 1H, arom H), 7.91−8.21 (m, 5H, arom H), 3.39 (s, 3H, CH_3), 3.08 (s, 3H, CH_3), 2.92 (s, 3H, CH_3). Anal. Calcd for $C_{16}H_{15}Cl_3Ti$: C, 53.15; H, 4.18. Found: C, 52.60; H, 4.32.

Benz[*f*]indene (12). Benz[*f*]indene was synthesized by modification of the procedure of Carpino and Lin.[18] A solution of $CeCl_3$ (14.0 g, 57 mmol) in 100 mL of dry THF was stirred for 1 h. 4-Bromobenz[*f*]indan-1-one (10 g, 38 mmol), synthesized by the literature procedure, was added in 50 mL of dry THF followed by slow addition of $LiAlH_4$ (9.4 g, 0.25 mol) in 50 mL of dry THF. The mixture was refluxed for 18 h. The reaction mixture was cooled in an ice bath and quenched by slow addition of 10 mL of H_2O, 10 mL of 15% aqueous NaOH, and finally 30 mL of H_2O. The resulting suspension was filtered, and the solution was dried ($MgSO_4$). After filtration, the solvent was evaporated to give benz[f]indan-1-ol (5.6 g, 80%) as a light yellow solid having the same ^1H NMR spectrum as previously reported. The benz[f]indan-1-ol was then converted to **12** by the literature method.

1-(Trimethylsilyl)benz[*f*]indene (13). Following the procedure described for **2b**, **12** (2.32 g, 14 mmol), 1.6 M butyllithium (8.8 mL, 14 mmol), and chlorotrimethylsilane (1.6 g, 15 mmol) gave **13** as a white solid (2.0 g, 61%, mp 90−92 °C). ^1H NMR ($CDCl_3$): δ 7.33−7.85 (m, 6H, arom H), 6.76−6.99 (m, 2H, H-C2,3), 3.57 (m, 1H, CH_2), 0.00 (s, 9H, Si−CH_3).

Polymerization Procedure. A 250 mL glass pressure bottle was sealed under a nitrogen atmosphere. Freshly distilled toluene (50 mL) was added via a syringe followed by styrene (5.0 mL, 44 mmol) and the appropriate amount of methylaluminoxane (MAO). The bottle was placed in a bath at the desired polymerization temperature and stirred for 10 min. The titanium catalyst (25 μmol, 1 mL of a 2.5 mM solution) in toluene was then added, and the mixture was stirred until the desired reaction time was reached. The reaction mixture was subsequently quenched with 10% HCl in methanol, filtered, and dried in a vacuum oven at 70 °C. The polymer was then extracted with 2-butanone for 24 h in a Soxhlet extractor to remove any atactic polymer. The remaining polymer was again dried in a vacuum oven at 70 °C.

Polymer Analyses. Molecular weights were determined by intrinsic viscosity in 1,3,5-trichlorobenzene at 135 °C. Melting points were determined with a Perkin-Elmer DSC-4 system at a heating rate of 20 °C/min. The % *s*-PS was determined as the amount of polymer insoluble in 2-butanone.

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