

Ca-Mediated Styrene Polymerization: Tacticity Control by Ligand Design

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New heteroleptic benzylcalcium complexes with modified fluorenyl ligands were prepared which include a complex with a chelating dimethylamino substituent, [9-(2-Me₂N-ethyl)fluorenyl][2-Me₂N- α -Me₃Si-benzyl]Ca (**4**), and a series of complexes with bulky substituents like *t*Bu-, Ph(Me)₂C-, Me(Ph)₂C- and Me(4-*t*BuC₆H₄)₂C- in the 2- and 7-positions of the fluorenyl ligand (complexes **5** through **9**, respectively). Crystal structures of **4**, [(2,7-*t*Bu-9-Me₃Si-fluorenyl)(2-Me₂N-benzyl)Ca]₂ (**5**) and [2,7-Ph(Me)₂C-9-Me₃Si-fluorenyl][2-Me₂N- α -Me₃Si-benzyl]Ca·THF (**6**) show that modification of the fluorenyl ligand hardly affects the coordination mode of the benzylic ligand. Also, in solution all compounds are of

heteroleptic nature and it was shown that fluorenyl modifications hardly affect the barriers for inversion at the chiral benzylic carbon atom [18.7(2)–19.2(2) kcal/mol]. Complex **4** does not initiate styrene polymerization, which underscores the importance of a free coordination site at calcium. Complexes **5–9** initiate styrene polymerization, and the syndiotacticity of the obtained polymers increases with the bulkiness of the substituents on the fluorenyl ligands. Syndiotacticities up to *r* = 95 % (*rr* = 90 %) were obtained.

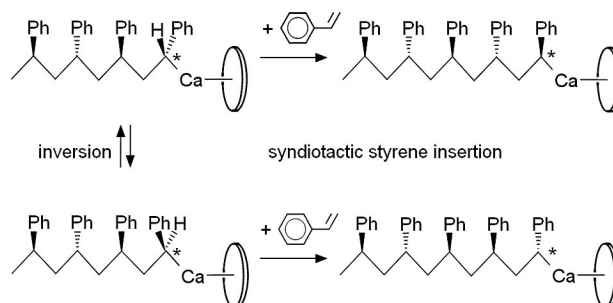
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Introduction

Syndiotactic polystyrene is a relatively young polymeric material^[1,2] which receives much industrial as well as academic interest.^[3–9] Its many advantageous properties,^[10,11] which include a high melting point (273 °C), fast crystallization rate, high modulus, low density, low dielectric constant and excellent solvent resistance, have led to its successful application as a specialty polymer.^[12]

We recently introduced a new class of polymerization initiators based on calcium which produced syndiotactic polystyrene by a chain-end-controlled monomer insertion (Scheme 1).^[13–14] The initial catalyst systems consist of a polymerization-active benzyl group and a passive spectator ligand (generally a fluorenyl ligand). The monomeric (**1**)^[14] and more active dimeric (**2**)^[15] forms are well-defined complexes which have been structurally characterized by X-ray diffraction.

These initiators, which can be regarded as a cross-breed between organolithium initiators and cationic Ti^{III} half-sandwich catalysts,^[2,6] combine the advantages of a living polymerization with those of a stereoselective polymerization. Syndiotactic polystyrene, however, was only obtained for polymerization in neat styrene. This is due to the predominant ionicity and inherent weakness of the Ca–C bond, which allows for inversion of the chiral chain-end. The ratio between insertion and inversion rates, which can



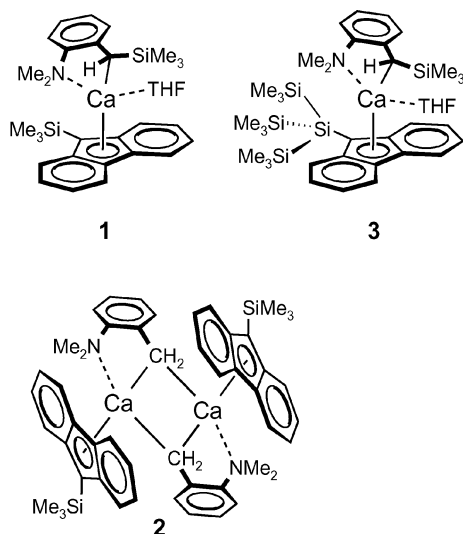
Scheme 1.

be controlled by monomer concentration,^[14] thus controls the tacticity of the polymer (Scheme 1).

A slight improvement in stereoregularity could also be achieved by lowering the polymerization temperature.^[14] Despite continuous efforts however, no significant improvement was obtained by variation of the spectator ligand. Earlier attempts to increase the syndiospecificity in styrene polymerization were based on increasing the steric bulk of the spectator ligand; that is, our initial catalyst (**1**) was modified by the introduction of a bulky hypersilyl substituent (**3**).^[16] This would enforce a stronger interaction between the chiral polymer chain-end and the incoming monomer, and thus improve stereocontrol. The bulkier catalyst **3**, however, gave polystyrene of very similar tacticity but much shorter chain length. It was reasoned that the use of bulky substituents did not only result in improved communication between polymer and monomer, but also led to more stereoerrors by retarding monomer insertion and thus allowing inversion of the chiral chain-end.

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In a further attempt to understand the factors that govern the stereoselectivity in calcium-mediated styrene polymerizations, we prepared a series of new benzylcalcium catalysts with modified fluorenyl ligands.

Results and Discussion

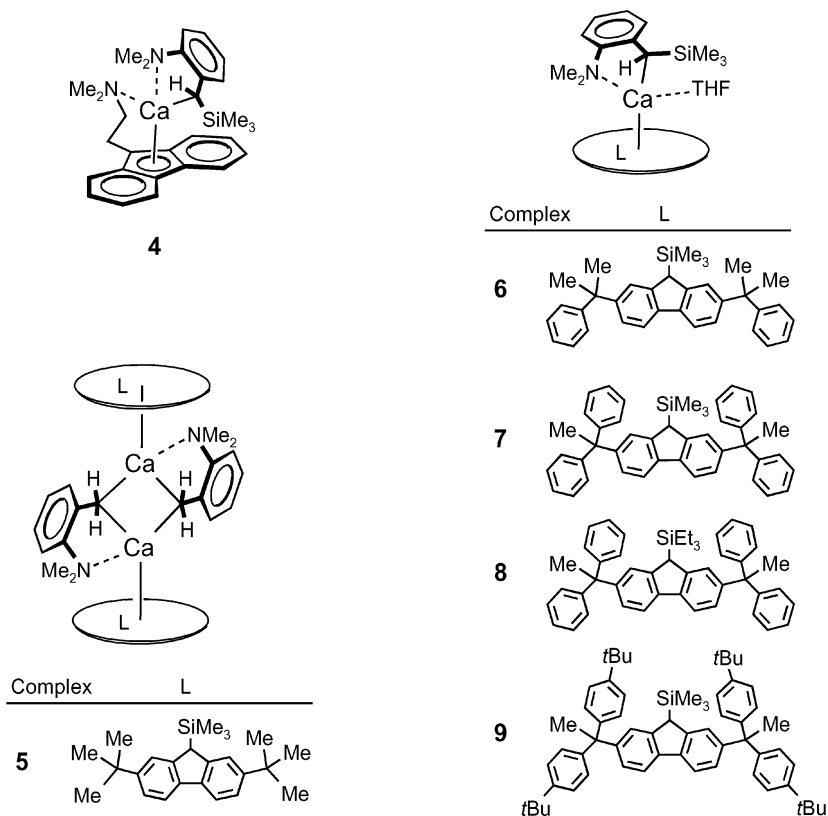
1. Syntheses and Structures of Modified Heteroleptic Benzylcalcium Complexes

In order to investigate the importance of the metal's coordination sphere in the polymerization reaction, a fluorene

ligand with a potential chelating dimethylamino substituent was prepared. Deprotonation by $(o\text{-Me}_2\text{N-}\alpha\text{-Me}_3\text{Si-benzyl})_2\text{Ca}\cdot(\text{THF})_2$ gave the heteroleptic benzylcalcium complex **4**.

Furthermore, the influence of steric bulk in remote positions was investigated by the introduction of large substituents in the 2- and 7-positions of the fluorenyl ligand. Several 2,7-disubstituted fluorene ligands were prepared and converted into heteroleptic benzylcalcium catalysts. In one instance, this was done by reacting the substituted fluorene with $(o\text{-Me}_2\text{N-benzyl})_2\text{Ca}$, in which case a dimeric benzylcalcium complex was typically formed (**5**).^[15] In other cases, reaction with $(o\text{-Me}_2\text{N-}\alpha\text{-Me}_3\text{Si-benzyl})_2\text{Ca}\cdot(\text{THF})_2$ gave monomeric benzylcalcium initiators (**6–9**). We were able to obtain crystal structures of **4** as well as representative dimeric and monomeric benzylcalcium complexes (**5** and **6**).

The heteroleptic benzylcalcium complex **4** crystallizes with two independent, but geometrically similar, molecules in the asymmetric unit (Figure 1). The fluorenyl rings coordinate in a slightly distorted η^5 -fashion in which the Ca–C bond lengths vary between 2.630(3) and 2.782(3) Å. The average Ca–C(fluorenyl) bond of 2.710(3) Å is slightly shorter than that observed in **1** [2.743(3) Å]. Likewise, the C,N-bidentate benzyl ligand in **4** [Ca–C1 2.504(3) Å; Ca–N2 2.463 Å] is coordinated in a similar fashion to that in **1** [Ca–C 2.506(2) Å; Ca–N 2.466(2) Å]. Whereas the coordination sphere of Ca in **1** is saturated by an additional THF ligand, complex **4** crystallizes solvent-free with intramolecular coordination of the Me₂N arm.



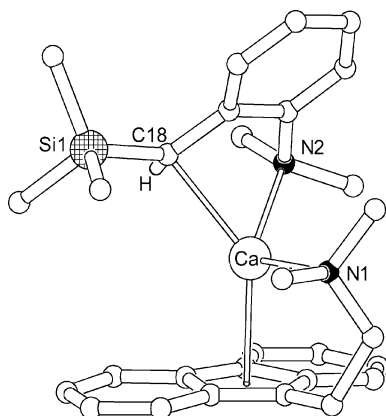


Figure 1. Crystal structure of **4**. Only one of the two crystallographically independent, but very similar, molecules is shown. Except for the benzylic hydrogen, all hydrogen atoms have been omitted for clarity. Average selected bond lengths [Å] and angles [°]: Ca–C18 2.508(3), Ca–N1 2.487(2), Ca–N2 2.460(2); Ca–C(fluorenyl): 2.630(3), 2.658(3), 2.727(3), 2.739(3), 2.782(3); C18–Ca–N1 113.6(1), C18–Ca–N2 71.4(1), N1–Ca–N2 112.0(1).

The heteroleptic complex **5** (Figure 2) crystallizes as a crystallographically C_2 -symmetric dimer with symmetrically bridging benzyl ligands and terminal fluorenyl ligands. Its crystal structure is very much comparable to that of dimeric **2** in which the 2- and 7-positions of the fluorenyl ring are not substituted. The fluorenyl ring in **5** coordinates to Ca in η^5 -fashion with Ca–C bond lengths in the range of 2.698(2) to 2.800(2) Å. The average Ca–C bond length of 2.750(2) Å is equal to that in **2** [2.750(3) Å]. Also, both symmetrically bridging benzyl anions are bound very similarly; the Ca–C17 [2.572(2) Å] and Ca–N1 [2.568(2) Å] bond lengths in **5** are equal to those in **2** [2.561(3) Å and 2.569(3) Å, respectively] within standard deviation. The bulky *t*Bu substituents in the 2- and 7-positions therefore do not affect the bonding of ligands to Ca.

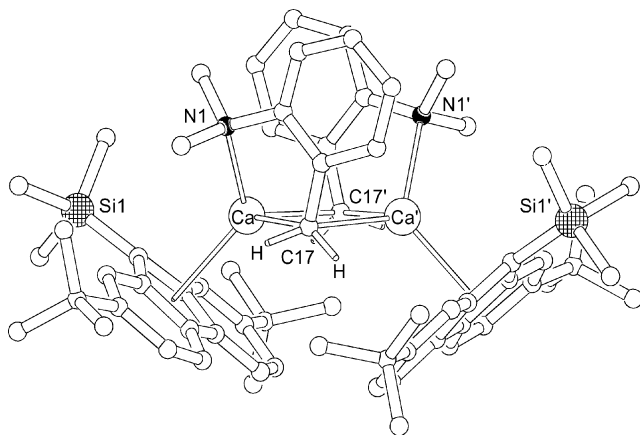


Figure 2. Crystal structure of **5**. Except for the benzylic hydrogen atoms, all hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ca–C17 2.572(2), Ca–C17' 2.572(2), Ca–N1 2.568(2); Ca–C(fluorenyl): 2.698(2), 2.705(2), 2.749(2), 2.796(2), 2.800(2); Ca...Ca' 3.5074(6), C17–Ca–C17' 93.95(6), C17–Ca–N1 68.08(5), C17'–Ca–N1 120.08(5).

The heteroleptic benzylcalcium complex **6** (Figure 3) crystallizes similarly to complex **1**. The fluorenyl–Ca coordination geometry is slightly distorted from η^5 -coordination. The Ca–C bond lengths range from 2.631(2) to 2.843(2) Å. The average Ca–C(fluorenyl) bond length of 2.734(2) Å compares well to that observed in **1** [2.743(3) Å]. Also, the *C,N*-bidentate benzyl ligand in **6** binds similarly; the Ca–C [2.517(3) Å] and Ca–N [2.496(2) Å] bond lengths for the *C,N*-bidentate benzyl ligand are only slightly longer than those in **1** [Ca–C: 2.506(2) Å; Ca–N: 2.466(2) Å, respectively]. In addition, the Ca–O(THF) bonds are very similar [**6**: 2.331(2) Å; **1**: 2.307(2) Å]. Therefore, the coordination geometry around Ca is hardly influenced by the large Ph(Me)₂C substituents in the 2- and 7-positions of the fluorenyl ring.

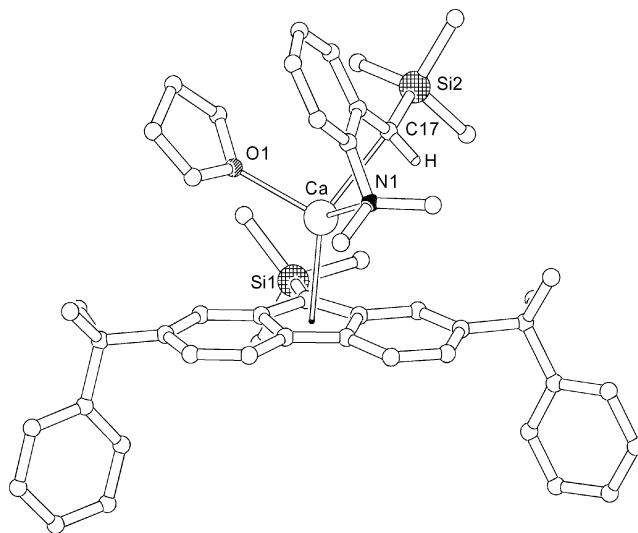


Figure 3. Crystal structure of **6**. Except for the benzylic hydrogen, all hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ca–C17 2.517(3), Ca–N1 2.496(2), Ca–O1 2.331(2); Ca–C(fluorenyl): 2.631(2), 2.647(2), 2.768(2), 2.779(2), 2.843(2); C17–Ca–N1 70.95(8), C17–Ca–O1 99.63(8), N1–Ca–O1 113.37(6).

The complexes dissolve well in aromatic solvents (except for dimer **5** which shows lower solubility), and their heteroleptic solid-state structures are retained in solution. The monomeric complexes with the chiral *o*-Me₂N- α -Me₃Si-benzyl ligand (**4** and **6–9**) display fluorenyl ligands with diastereotopic sides at room temperature. Fast exchange by inversion at the chiral benzylic carbon atom can be accomplished by heating the sample or by the addition of THF; both processes have been discussed previously.^[14] For some of the complexes, an activation barrier for this inversion process could be determined. These values for **4** [$T_{\text{coal}} = 105^\circ\text{C}$, $\Delta G^\ddagger = 19.2(2)$ kcal/mol] and **6** [$T_{\text{coal}} = 85^\circ\text{C}$, $\Delta G^\ddagger = 18.7(2)$ kcal/mol] are, within standard deviation, equal to that measured for **1** [$T_{\text{coal}} = 90^\circ\text{C}$, $\Delta G^\ddagger = 18.8(2)$ kcal/mol]. Therefore, like in the crystal structures, the bonding of the benzyl ligands to calcium is neither affected by the replacement of THF in **1** by a chelating arm, nor by the introduction of bulky substituents in the 2- and 7-positions of the fluorenyl ring.

The benzylcalcium complex **5** is also a heteroleptic dimer in benzene solution. Proof of its dimeric nature comes from the unusual ^1H NMR chemical shifts for the aromatic ring protons. The ^1H NMR spectra of anionic benzyl species generally show a high-field triplet, characteristic for the aromatic ring proton in the *para*-position with respect to the benzylic carbon.^[17,18] For **5**, the most high-field aromatic signal is a doublet at $\delta = 5.81$ ppm, which can be assigned to a proton in the *meta*-position with respect to the benzylic carbon. This anomaly can be explained by the anisotropy effect caused by ring currents^[19] in a nearby aryl ring: the *meta*-H is positioned in the shielding cone of the neighbouring ring. Similar observations for the analogous complex **2** have been discussed extensively.^[15]

In conclusion, neither the introduction of an intramolecularly coordinating amine ligand, nor substitution of the fluorenyl ligand in the 2- and 7-positions, changes the structures of heteroleptic benzylcalcium complexes **1** and **2**. In fact, the structures and all bond lengths remain surprisingly equal. The compositions of these complexes in solution are basically similar to those in the solid state, and modification of the fluorenyl ligands does not affect the dynamic behaviour of these complexes significantly.

2. Styrene Polymerization with Modified Heteroleptic Benzylcalcium Complexes

Complex **4**, the benzylcalcium complex with a fluorenyl ligand containing a chelating amine arm, was found to be completely inactive as an initiator in styrene polymerization. Whereas dissociation of the THF ligand in initiator **1** generates a free site for monomer coordination, the strongly bound intramolecular Me_2N substituent in **4** effectively kills the reactivity of this benzylcalcium complex towards styrene. This underscores the importance of precoordination of the styrene monomer in the insertion step. Effective benzylcalcium catalysts should therefore have a relatively open coordination sphere around the calcium metal. This observation is in line with the fact that large bulky groups in the 9-position, that is, close to the metal, substantially retard monomer insertion.^[16] Therefore, modification of the fluorenyl spectator ligand in the periphery instead of close to the metal coordination site was pursued.

All of the heteroleptic complexes **5** through **9** were found to be active in styrene polymerization. Polymerizations were generally run under two different sets of conditions: a) polymerization of a 10% solution of styrene in cyclohexane at 50 °C and b) polymerization of neat styrene at 20 °C. All polymers showed a unimodal MW distribution with poly-dispersion-indexes (*D*) between 2 and 3 and a Gold distribution,^[20,21] that is, tailing in the low molecular weight range (Table 1). The latter is typical of heteroleptic benzylcalcium initiators and is, as we have shown before, related to a slow initiation by the stabilized carbanion rather than to chain termination.^[13–16] These rather broad molecular weight distributions, however, hinder the syntheses of well-defined block-copolymers.

The tacticity of all polymers was analyzed by ^{13}C NMR spectroscopy, and tacticities were calculated using Bernoulli statistics based on the new heptade assignment we recently reported.^[22] Figure 4a shows the ^{13}C NMR signals for the C_{ipso} atom in the phenyl rings of the different polystyrenes obtained in solution at 50 °C. Under these conditions, polymer produced by initiator **1** is essentially atactic (the signals in the *mr* and *rr* regions are only slightly high relative to those from an atactic polymer produced by an alkyl lithium initiator). Polymer obtained with initiator **5**, that is, an initiator with additional *t*Bu groups in the 2- and 7-positions of the fluorenyl ring, showed a noticeable increase in syndiotacticity ($r = 87\%$). The ^{13}C NMR signal for the C_{ipso} atom merely consists of four singlets which represent the *rrrrrr* heptade and the three erroneous heptades formed after a single stereochemically wrong insertion (*mrrrrr*, *rmrrrr* and *rrmrrr*). Substitution of the *t*Bu groups for the more bulky $\text{Ph}(\text{Me})_2\text{C}$ substituents (**6**) again leads to improvement of the polymer's syndiotacticity; the largest signal is that of the *rrrrrr* heptade ($r = 88\%$). Further increase of steric bulk by the introduction of $(\text{Ph})_2\text{MeC}$ substituents (**7**) gave a polymer of 92% syndiotacticity in diads. Subsequent increase of steric bulk by substitution of the Me_3Si group for Et_3Si (**8**) or by additional *t*Bu substituents on the Ph rings (**9**) gave no significant improvement of the tacticity.

Spurred by the advantageous effect of steric bulk on the syndioselectivity of styrene polymerization in solution, we

Table 1. Styrene polymerization with initiators **1**, **5–9**.

Initiator	<i>T</i> [°C]	[<i>m</i>] ^[a] [mol L ^{−1}]	<i>t</i> [min]	<i>M_n</i> [g mol ^{−1}]	<i>D</i>	<i>rr</i> [%]	<i>r</i> [%]
1 ^[14]	50	0.10	45	1.115×10^5	2.306	<50	<70
5	50	0.10	45	1.449×10^5	2.549	76	87
6	50	0.10	60	2.014×10^5	1.947	77	88
7	50	0.10	60	1.515×10^5	2.394	85	92
8	50	0.10	50	2.377×10^5	2.377	85	92
9	50	0.10	45	2.440×10^5	2.030	85	92
1 ^[14]	20	neat	60	0.960×10^5	2.350	79	89
5	20	neat	40	2.213×10^5	2.570	83	91
6	20	neat	45	1.235×10^5	2.265	85	92
7	20	neat	60	1.302×10^5	2.635	86	93
8	20	neat	95	3.022×10^5	2.134	88	94
9	20	neat	50	1.506×10^5	2.984	88	94
9	−20	neat	3840 ^[b]	1.870×10^5	4.293	91	95

[a] Concentration of monomer in cyclohexane. [b] 64 h.

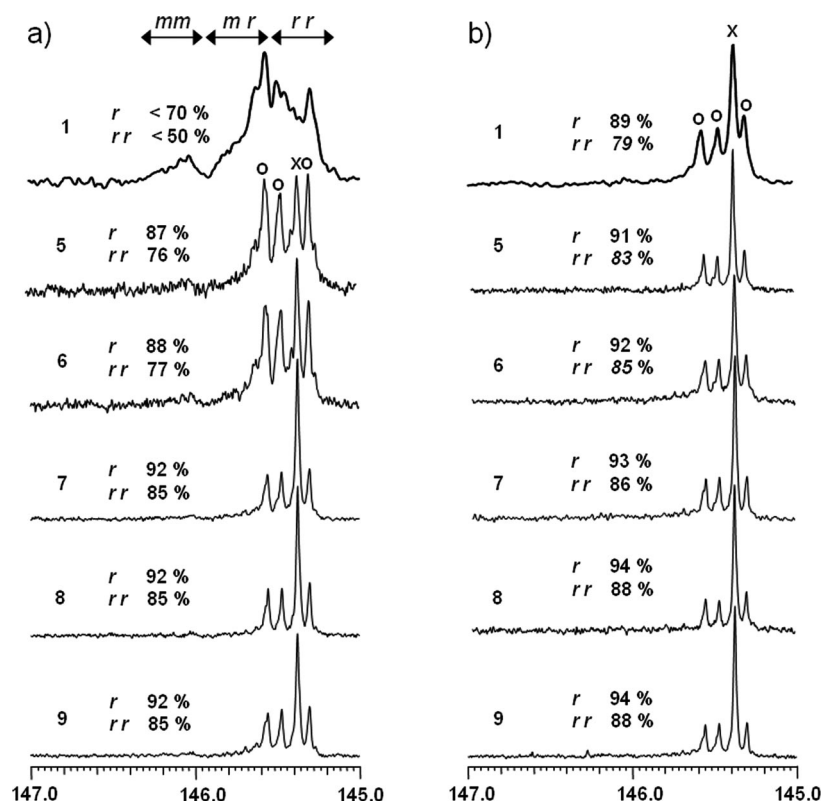


Figure 4. ^{13}C NMR signals of the phenyl C_{ipso} atom in the polystyrene materials ($[\text{D}_2]$ tetrachloroethane, $T = 100\text{ }^\circ\text{C}$). a) Polymers obtained with the various initiators 1, 5–9; 10% styrene solutions in cyclohexane; 50 °C. b) Polymers obtained with the various initiators 1, 5–9; 100% styrene; 20 °C. The syndiotactic $rrrrrr$ heptade is marked by $\times$, and the error heptades mr , rrr and $rrrr$ by $\circ$.

also performed polymerization studies in pure styrene (Figure 4b). Polymers obtained under these conditions generally show much higher syndiotacticities than the polymers produced by polymerization in solution.^[14–16] This is partly due to a temperature effect (for polymerizations in solution, improved syndiotacticity is also observed at lower temperature; Figure 5), but is also related to a higher ratio of the insertion to inversion rates on account of the higher monomer concentration (Scheme 1). The positive effect of increasing steric bulk in the 2- and 7-positions of the fluorenyl ring on the syndiotacticity of the polymer is also noticeable for polymerizations in neat styrene. It is, however, less extreme than that observed for polymerizations in solution. The most syndiotactic polymer was obtained with the most bulky calcium initiator 9 at $-20\text{ }^\circ\text{C}$ ($r = 95\%$, $rr = 90\%$); however, rather slow polymerization and a broad molecular weight distribution were observed (Table 1).

The data for polymerization in solution in particular show a clear increase in stereoselectivity upon increase in the steric bulk of the substituents in the periphery of the ligand system. The reason for this trend is unclear. Figure 6 shows space-filling models of fluorenyl–Ca units containing differently substituted ligand systems. It is evident from the structural studies (vide supra) that substitution in the 2- and 7-positions of the fluorenyl ligand has a negligible effect on the coordination sphere of the Ca^{2+} ion. It can only be speculated that the sterically large groups at the sides of

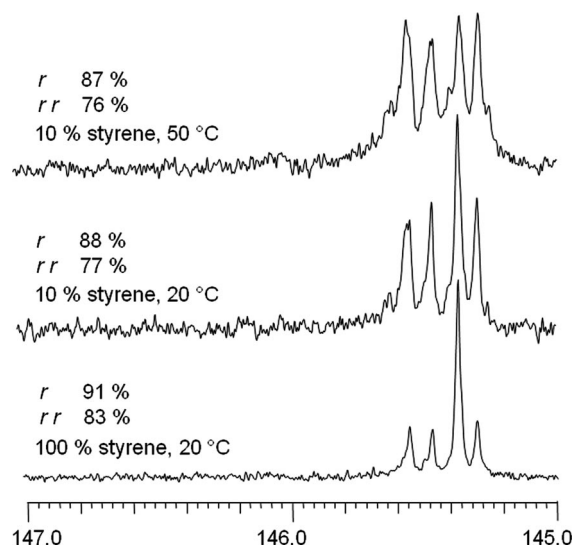


Figure 5. ^{13}C NMR signals of the phenyl C_{ipso} atom in the polystyrene materials ($[\text{D}_2]$ tetrachloroethane, $T = 100\text{ }^\circ\text{C}$) obtained with initiator 5 under various conditions.

the fluorenyl ligand restrict the dynamic behaviour of the polymer chain attached to calcium. Reducing the degrees of freedom of the polymer chain and the coordinated styrene would lead to a higher selectivity in the insertion step.

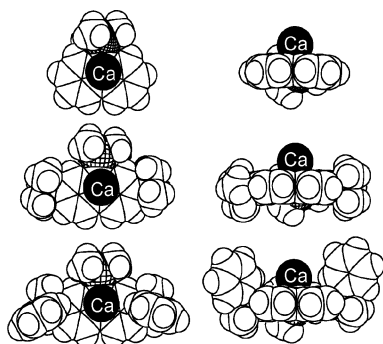


Figure 6. Space-filling models of the fluorenyl–Ca unit with increasing steric bulk of the fluorenyl ligand (top to bottom) as in the initiators **1**, **5** and **6**. Left: view perpendicular to the fluorenyl plane. Right: view along the fluorenyl plane.

Conclusions

Replacing the THF ligand in **1** with an intramolecular chelating amine ligand does not affect the coordination of the *o*-Me₂N-*α*-Me₃Si-benzyl ligand. Also, the introduction of bulky substituents in the 2- and 7-positions of the fluorenyl ligand has no influence on ligand coordination to the metal. In all cases, very similar fluorenyl–Ca and benzyl–Ca coordination geometries are observed.

The composition and structures of the benzylcalcium complexes **4–9** in solution (benzene, toluene) are similar to those observed in the solid state; that is, the Schlenk equilibria lie completely towards the heteroleptic side, and the chiral benzylic carbon is configurationally stable on the NMR time scale (the fluorenyl ligands show diastereotopic sides). Also, the dynamic inversion of the chiral benzylic carbon at higher temperatures is not affected by the ligand modifications.

On the other hand, a significant effect of fluorenyl ligand modifications was observed on the polymerization of styrene. First of all, substitution of THF in **1** for an intramolecularly coordinated Me₂N substituent effectively kills the reactivity of this benzylcalcium complex towards styrene. Apparently, the strongly bound chelate arm prevents the formation of a free coordination site, which effectively blocks the polymerization reaction. Secondly, an increase in the steric bulk of the substituents in the periphery of the fluorenyl ligand resulted in greater syndioselectivity in styrene polymerization.

These are important observations from which it can be deduced that these benzylcalcium complexes likely function as single-site catalysts in which precoordination of the monomer and subsequent insertion are the key steps in styrene polymerization. These new initiators allow syndioselective styrene polymerization not only in neat styrene, but also in solution. The broad molecular weight distributions, however, disable syntheses of well-defined block-copolymers.

Experimental Section

General Comments: All experiments were carried out under argon using predried solvents and Schlenk techniques. The following starting materials were prepared according to literature: [(2-Me₂N-*α*-Me₃Si-benzyl)]₂Ca·(THF)₂,^[13] [9-(2-dimethylamino)ethyl]fluorene,^[23] 2,7-di-*tert*-butylfluorene^[24] and 2,7-bis(1-methyl-1-phenylethyl)fluorene.^[25] Me₃SiCl was freed from HCl by distillation from dry *N,N*-diethylaniline. Other reagents were commercially available and used as received. NMR spectra were recorded with Bruker DPX300 and DRX500 machines.

Synthesis of 2,7-Bis(1,1-diphenylethyl)fluorene: 2,7-Dibenzoylfluorene was prepared according to a modified literature procedure.^[25] A mixture of fluorene (10.0 g, 60.2 mmol), benzoic acid (16.0 g, 131 mmol) and polyphosphoric acid (200 g) was heated to 140 °C in a conical flask for 50 h. The cooled mixture was treated carefully with ice/water and, in later stages, with a hot aqueous potassium hydroxide solution. The heated suspension was filtered, and the residue dissolved in toluene. After aqueous workup and drying of the organic layer, the solution was concentrated and 2,7-dibenzoylfluorene precipitated at room temperature (10.7 g, 48%), m.p. 193 °C. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 8.01 (s, 2 H, fluorenyl), 7.96–7.82 (m, 8 H, Ar), 7.62–7.58 (m, 2 H, Ar), 7.51–7.46 (m, 4 H, Ar), 4.04 (s, 2 H, CH₂) ppm. ¹³C{¹H} NMR (300 MHz, CDCl₃): δ = 196.6 (C=O), 144.5, 144.2, 137.9, 136.9, 132.3, 130.0, 129.7, 128.3, 126.9, 120.4, 36.9 (CH₂) ppm. C₂₇H₁₈O₂ (374.4): calcd. C 86.61, H 4.85; found C 86.62, H 4.81.

A twofold excess of phenylmagnesium bromide (14.5 g, 80.0 mmol) was added to a solution of 2,7-dibenzoylfluorene (7.80 g, 20.8 mmol) in toluene (100 mL) and was heated at reflux for 4 h. After hydrolysis with 2 N HCl and extraction with toluene, the organic layer was dried. 2,7-Bis(hydroxydiphenylmethyl)fluorene was crystallized from a concentrated solution at –22 °C (7.35 g, 67%), m.p. 253 °C. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 7.63 (d, ³J_{H,H} = 8.0 Hz, 2 H, fluorenyl), 7.41 (s, 2 H, fluorenyl), 7.32–7.18 (m, 22 H, Ar), 3.74 (s, 2 H, CH₂), 2.78 (s, 2 H, OH) ppm. ¹³C{¹H} NMR (300 MHz, CDCl₃): δ = 147.4, 146.1, 143.8, 140.8, 128.3, 128.3, 127.6, 127.3, 124.9, 119.6, 82.6 (COH), 37.5 (CH₂) ppm. C₃₉H₃₀O₂ (530.7): calcd. C 88.27, H 5.70; found C 88.26, H 5.90.

To a suspension of 2,7-bis(hydroxydiphenylmethyl)fluorene (7.35 g, 13.8 mmol) in toluene (100 mL) and acetic acid (0.2 mL) was added a trimethylaluminum solution (2.0 M in toluene, 35 mL, 70.0 mmol). After being heated at reflux for 4 h, the mixture was poured into ice/water. The remaining product was dissolved in concentrated hydrochloric acid (20 mL), and the aqueous layer was extracted with dichloromethane. The organic solution was dried, and the solvent was removed. 2,7-Bis(1,1-diphenylethyl)fluorene was obtained as a white solid product (5.75 g, 79%), m.p. 217 °C. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 7.60 (d, ³J_{H,H} = 8.1 Hz, 2 H, fluorenyl), 7.25–6.88 (m, 24 H, Ar), 3.71 (s, 2 H, CH₂), 2.22 (s, 6 H, CH₃) ppm. ¹³C{¹H} NMR (300 MHz, CDCl₃): δ = 149.8, 148.2, 143.7, 139.8, 129.3, 128.3, 128.1, 126.4, 125.8, 119.5, 53.1 [(CCH₃)₂], 37.6 (CH₂), 31.2 (CH₃) ppm. C₄₁H₃₄ (526.7): calcd. C 93.49, H 6.51; found C 93.16, H 6.45.

Synthesis of 2,7-Bis[1,1-bis(4'-*tert*-butylphenyl)ethyl]fluorene: The first intermediate, 2,7-bis(4'-*t*Bu-benzoyl)fluorene, was prepared analogously to 2,7-dibenzoylfluorene (vide supra). After quenching the reaction with water and aqueous potassium hydroxide, the residue was extracted with dichloromethane, dried and isolated by removal of the solvent. Crystallization from acetone at –27 °C gave 2,7-bis(4'-*t*Bu-benzoyl)fluorene (26.8 g, 43%) as a white solid, m.p. 251 °C. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 8.05 (s, 2 H, fluorenyl),

enyl), 7.96–7.88 (m, 4 H, fluorenyl), 7.81 (d, $^3J_{\text{H,H}} = 8.1$ Hz, 4 H, Ar), 7.53 (d, $^3J_{\text{H,H}} = 8.3$ Hz, 4 H, Ar), 4.05 (s, 2 H, CH₂), 1.39 (s, 18 H, CH₃) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, CDCl₃): $\delta = 197.0$ (C=O), 156.9, 145.2, 144.9, 138.0, 135.8, 130.8, 130.3, 127.6, 126.0, 121.1, 37.7 (CH₂), 35.9 (CCH₃), 31.9 (CH₃) ppm. C₃₅H₃₄O₂ (486.6): calcd. C 86.38, H 7.04; found C 85.99, H 7.18.

A twofold excess of 4-*t*Bu-phenylmagnesium bromide (19.9 g, 84.0 mmol) was added to a solution of 2,7-bis(4'-*t*Bu-benzoyl)fluorene (10.0 g, 20.5 mmol) in toluene (100 mL), and was heated at reflux for 6.5 h. After the reaction mixture was hydrolyzed with 2 N HCl, extracted with diethyl ether and dried, the solvent was removed. 2,7-Bis[hydroxybis(4'-*t*Bu-phenyl)methyl]fluorene crystallized from hexane at room temperature as a white solid (11.5 g, 74%), m.p. 249 °C. ^1H NMR (300 MHz, CDCl₃, 25 °C): $\delta = 7.56$ (d, $^3J_{\text{H,H}} = 8.0$ Hz, 2 H, fluorenyl), 7.43 (s, 2 H, fluorenyl), 7.26–7.08 (m, 18 H, Ar), 3.73 (s, 2 H, CH₂), 2.72 (br s, 2 H, OH), 1.23 (s, 36 H, CH₃) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, CDCl₃): $\delta = 150.0$, 145.8, 144.2, 143.3, 140.3, 127.6, 126.8, 124.8, 124.4, 119.0, 81.9 (COH), 37.7 (CH₂), 34.5 [C(CH₃)₃], 31.3 [C(CH₃)₃] ppm. C₅₅H₆₂O₂ (755.1): calcd. C 87.49, H 8.28; found C 87.07, H 7.97.

To a suspension of 2,7-bis[hydroxybis(4'-*t*Bu-phenyl)methyl]fluorene (4.80 g, 6.36 mmol) in toluene (100 mL) and acetic acid (0.2 mL) was added a trimethylaluminum solution (2.0 M in toluene, 12.5 mL, 25.0 mmol). After heating the mixture for 5 h, the solution was poured into ice/water. After aqueous workup and drying of the organic layer, the solvent was removed. 2,7-Bis[1,1-bis(4'-*t*Bu-phenyl)ethyl]fluorene was obtained as a white solid after washing with hexane (3.92 g, 82%), m.p. 311 °C. ^1H NMR (300 MHz, CDCl₃, 25 °C): $\delta = 7.54$ (d, $^3J_{\text{H,H}} = 8.1$ Hz, 2 H, fluorenyl), 7.23–7.18 (m, 10 H, Ar), 7.01–6.95 (m, 10 H, Ar), 3.69 (s, 2 H, CH₂), 2.13 (s, 6 H, CH₃), 1.24 (s, 36 H, CH₃) ppm. ^{13}C NMR (^1H) (300 MHz, CDCl₃): $\delta = 148.4$, 148.1, 146.4, 143.1, 139.2, 128.3, 127.6, 125.2, 124.6, 118.8, 51.8 (CCH₃), 37.1 (CH₂), 34.3 [C(CH₃)₃], 31.4 [C(CH₃)₃], 30.6 (CCH₃) ppm. C₅₇H₆₆ (751.1): calcd. C 91.14, H 8.86; found C 90.61, H 8.78.

Synthesis of 2,7-Di-*tert*-butyl-9-(trimethylsilyl)fluorene: *n*-Butyllithium (2.5 M in hexane, 12.0 mL, 30.0 mmol) was added to a pre-cooled (–70 °C), stirred solution of 2,7-di-*tert*-butylfluorene^[24] (7.70 g, 27.7 mmol) in THF (50 mL). The solution was slowly warmed to –10 °C and stirred for 30 min at this temperature, then cooled again to –70 °C, and chlorotrimethylsilane (4.1 mL, 32.2 mmol) was added. The cooling bath was removed, and the solution was stirred at room temperature for 24 h. After aqueous workup, the solvent was removed under vacuum, and colourless needles were recovered (8.65 g, 89%), m.p. 145 °C. ^1H NMR (300 MHz, CDCl₃, 25 °C): $\delta = 7.74$ (d, $^3J_{\text{H,H}} = 8.0$ Hz, 2 H, fluorenyl), 7.53 (s, 2 H, fluorenyl), 7.38 (d, $^3J_{\text{H,H}} = 8.0$ Hz, 2 H, fluorenyl), 3.83 (s, 1 H, CH), 1.42 (s, 18 H, CH₃), –0.04 (s, 9 H, Me₃Si) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, CDCl₃): $\delta = 148.6$, 145.6, 137.9, 122.2, 121.0, 119.0, 42.5 (CH₂), 34.8 [C(CH₃)₃], 31.7 [C(CH₃)₃], –2.60 (Me₃Si) ppm. C₂₄H₃₄Si (350.6): calcd. C 82.22, H 9.77; found C 81.82, H 9.94.

Synthesis of 2,7-Bis(1-methyl-1-phenylethyl)-9-(trimethylsilyl)fluorene: This compound was synthesized according to the preparation of 2,7-bis(*t*Bu)-9-Me₃Si-fluorene. Colourless needles crystallized from acetone at –28 °C (72%), m.p. 122 °C. ^1H NMR (300 MHz, CDCl₃, 25 °C): $\delta = 7.71$ (d, $^3J_{\text{H,H}} = 7.9$ Hz, 2 H, fluorenyl), 7.32–7.15 (m, 14 H, Ar), 3.71 (s, 1 H, CH), 1.77 (s, 6 H, CH₃), 1.75 (s, 6 H, CH₃), –0.23 (s, 9 H, Me₃Si) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, CDCl₃): $\delta = 151.3$, 148.4, 145.6, 137.8, 127.9, 126.8, 125.5, 123.7, 122.9, 119.0, 43.1 [(CCH₃)₂], 42.5 [(CCH₃)₂], 31.1 (CH₃), 30.8

(CH₃), –2.81 (Me₃Si) ppm. C₃₄H₃₈Si (474.8): calcd. C 86.02, H 8.07; found C 85.96, H 7.94.

Synthesis of 2,7-Bis(1,1-diphenylethyl)-9-Me₃Si-fluorene: This compound was synthesized according to the preparation of 2,7-bis(*t*Bu)-9-Me₃Si-fluorene. A white solid precipitated from acetone at –28 °C (88%), m.p. 143 °C. ^1H NMR (300 MHz, CDCl₃, 25 °C): $\delta = 7.63$ (d, $^3J_{\text{H,H}} = 7.4$ Hz, 2 H, fluorenyl), 7.25–7.03 (m, 24 H, Ar), 3.57 (s, 1 H, CH), 2.18 (s, 6 H, CH₃), –0.40 (s, 9 H, Me₃Si) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, CDCl₃): $\delta = 149.6$, 146.9, 145.6, 138.0, 128.8, 127.8, 125.9, 125.7, 124.9, 119.1, 52.7 (CCH₃), 42.7 (CH), 30.7 (CH₃), –2.84 (Me₃Si) ppm. C₄₄H₄₂Si (598.9): calcd. C 88.24, H 7.07; found C 87.38, H 7.22.

Synthesis of 2,7-Bis[1,1-bis(4'-*t*Bu-phenyl)ethyl]-9-Me₃Si-fluorene: This compound was synthesized according to the preparation of 2,7-bis(*t*Bu)-9-Me₃Si-fluorene. A white solid precipitated from toluene at –28 °C (79%), m.p. 247 °C. ^1H NMR (300 MHz, CDCl₃, 25 °C): $\delta = 7.62$ (d, $^3J_{\text{H,H}} = 8.1$ Hz, 2 H, fluorenyl), 7.21–6.90 (m, 20 H, Ar), 3.51 (s, 1 H, CH), 2.14 (s, 6 H, CCH₃), 1.22 [s, 36 H, C(CH₃)₃], –0.48 (s, 9 H, Me₃Si) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, CDCl₃): $\delta = 148.4$, 147.4, 146.6, 145.4, 137.9, 128.3, 125.4, 125.2, 124.6, 118.9, 51.8 (CCH₃), 42.5 (CH), 34.3 [C(CH₃)₃], 31.4 [C(CH₃)₃], 30.4 (CCH₃), –2.75 (Me₃Si) ppm. C₆₀H₇₄Si (823.3): calcd. C 87.53, H 9.06; found C 87.28, H 9.02.

Synthesis of 2,7-Bis(1,1-diphenylethyl)-9-Et₃Si-fluorene: *n*-Butyllithium (2.45 M in hexane, 1.88 mL, 4.61 mmol) was added to a pre-cooled (–70 °C), stirred solution of 2,7-bis(1,1-diphenylethyl)fluorene (2.20 g, 4.18 mmol) in THF (50 mL). After being slowly heated to –10 °C and stirred over a period of 30 min at this temperature, the solution was re-cooled (–70 °C), and chlorotriethylsilane (0.78 mL, 4.66 mmol) was added. The cooling bath was removed, and the solution was stirred at room temperature for 20 h. After aqueous workup, the solvent was removed. 2,7-Bis(1,1-diphenylethyl)-9-Et₃Si-fluorene precipitated from acetone at –28 °C as a pale yellow solid (2.26 g, 84%), m.p. 103 °C. ^1H NMR (300 MHz, CDCl₃, 25 °C): $\delta = 7.65$ (d, $^3J_{\text{H,H}} = 8.1$ Hz, 2 H, fluorenyl), 7.21–7.00 (m, 22 H, Ar), 6.93 (s, 2 H, fluorenyl), 3.69 (s, 1 H, CH), 2.17 (s, 6 H, CH₃), 0.51 [t, 9 H, Si(CH₂CH₃)₃], 0.08 [q, 6 H, Si(CH₂CH₃)₃] ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, C₆D₆): $\delta = 150.6$, 150.3, 147.8, 146.6, 139.2, 126.7, 126.7, 126.5, 126.1, 120.1, 53.5 (CCH₃), 39.8 (CH), 31.3 (CH₃), 8.00 [Si(CH₂CH₃)₃], 3.00 [Si(CH₂CH₃)₃]. C₄₇H₄₈Si (641.0): calcd. C 88.07, H 7.55; found C 87.88, H 7.34.

Synthesis of 4: A solution of [9-(2-dimethylamino)ethyl]fluorene^[23] (734 mg, 3.09 mmol) and [(2-Me₂N- α -Me₃Si-benzyl)]₂Ca·(THF)₂^[13] (1.87 g, 3.13 mmol) in toluene (20 mL) was heated to 85 °C over a period of 5 h. All volatiles were removed, and the product was dried under vacuum to yield complex **4** with one molecule of THF. Drying of this product under vacuum over a period of 30 min (90 °C, 1 Torr) and cooling a toluene solution thereof to –30 °C gave yellow-orange plates of **4** (1.09 g, 73%) which are only soluble in hot benzene. NMR spectroscopic data are given for **4** with one equivalent of THF; m.p. 132 °C. ^1H NMR (300 MHz, C₆D₆, 25 °C): $\delta = 8.33$ (d, $^3J_{\text{H,H}} = 8.1$ Hz, 1 H, fluorenyl), 8.23 (d, $^3J_{\text{H,H}} = 8.0$ Hz, 1 H, fluorenyl), 7.69 (d, $^3J_{\text{H,H}} = 8.3$ Hz, 1 H, fluorenyl), 7.56 (t, $^3J_{\text{H,H}} = 8.1$ Hz, 1 H, fluorenyl), 7.45 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 1 H, fluorenyl), 7.29–7.22 (m, 2 H, fluorenyl), 7.10–6.99 (m, 2 H, Ar and fluorenyl), 6.80 (t, $^3J_{\text{H,H}} = 7.1$ Hz, 1 H, Ar), 6.35 (d, $^3J_{\text{H,H}} = 7.0$ Hz, 1 H, Ar), 6.25 (t, $^3J_{\text{H,H}} = 7.1$ Hz, 1 H, Ar), 3.13–3.09 (m, 2 H, CH₂), 2.89 (br., 4 H, THF), 2.84–2.76 (m, 1 H, CH₂), 2.30–2.19 (m, 1 H, CH₂), 2.15–1.72 (br., 6 H, NCH₃), 1.65 (s, 6 H, NCH₃), 1.22 (br., 4 H, THF), 0.41 (s, 9 H, Me₃Si), 0.14 (s, 1 H, CH) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, C₆D₆, 25 °C): $\delta = 147.8$,

135.6, 132.3, 131.4, 126.5 (benzyl), 124.5, 124.1, 123.5, 123.3, 122.1, 122.0 (benzyl), 119.6, 118.6, 118.4, 116.9, 116.8, 114.7 (benzyl), 112.5 (benzyl), 91.7 (C9), 68.1 (THF), 63.2, 61.3, 44.8, 44.7, 25.3 (THF), 22.8, 22.3, 2.8 (Me₃Si) ppm.

Synthesis of 5: A solution of 2,7-bis(*t*Bu)-9-Me₃Si-fluorene (475 mg, 1.35 mmol) and [(2-Me₂N-benzyl)]₂Ca^[15] (469 mg, 1.52 mmol) in benzene (10 mL) was heated to 60 °C over a period of 2.5 h. Slow cooling of the reaction mixture to room temperature gave large yellow crystals of **5** (537 mg, 76%), m.p. 151 °C (dec.). ¹H NMR (500 MHz, C₆D₆/[D₈]THF, 25 °C): δ = 7.85 (s, 2 H, fluorenyl), 7.74 (d, ³J_{H,H} = 8.2 Hz, 2 H, fluorenyl), 6.85 (d, ³J_{H,H} = 8.2 Hz, 2 H, fluorenyl), 6.34 (t, ³J_{H,H} = 7.8 Hz, 1 H, benzyl), 6.31–6.21 (m, 2 H, benzyl), 5.80 (t, ³J_{H,H} = 6.4 Hz, 1 H, benzyl), 2.04 (s, 6 H, NCH₃), 1.52 (br s, 2 H, CH₂), 1.33 (s, 18 H, CH₃), 0.44 (s, 9 H, Me₃Si) ppm. ¹H NMR (500 MHz, C₆D₆, 25 °C): δ = 8.52 (d, ³J_{H,H} = 8.6 Hz, 1 H, fluorenyl), 8.47 (d, ³J_{H,H} = 8.6 Hz, 1 H, fluorenyl), 8.25 (s, 1 H, fluorenyl), 8.05 (s, 1 H, fluorenyl), 7.47 (d, ³J_{H,H} = 8.5 Hz, 1 H, fluorenyl), 7.39 (d, ³J_{H,H} = 8.2 Hz, 1 H, fluorenyl), 6.67 (t, ³J_{H,H} = 7.3 Hz, 1 H, benzyl), 6.10 (t, ³J_{H,H} = 6.9 Hz, 1 H, benzyl), 5.85 (d, ³J_{H,H} = 7.8 Hz, 1 H, benzyl), 5.81 (d, ³J_{H,H} = 7.2 Hz, 1 H, benzyl), 1.78 (s, 3 H, NCH₃), 1.51 (s, 9 H, CH₃), 1.42 (s, 9 H, CH₃), 1.24 (s, 3 H, NCH₃), 0.73 (s, 9 H, Me₃Si), –0.55 (d, ²J_{H,H} = 11.8 Hz, 1 H, CH₂), –0.96 (d, ²J_{H,H} = 11.7 Hz, 1 H, CH₂) ppm. ¹³C{¹H} NMR (500 MHz, C₆D₆/[D₈]THF, 25 °C): δ = 148.0, 143.5, 143.3, 136.9, 125.4 (benzyl), 123.0, 122.3 (benzyl), 120.1, 117.9 (benzyl), 116.1, 112.8, 110.0 (benzyl), 85.2 (C-9), 43.3 [N(CH₃)₂], 40.9 (CH₂), 34.8 [C(CH₃)₃], 32.1 [C(CH₃)₃], 2.39 (Me₃Si) ppm.

Synthesis of 6: A mixture of 2,7-bis(1-methyl-1-phenylethyl)-9-Me₃Si-fluorene (315 mg, 664 μmol) and [(2-Me₂N-*α*-Me₃Si-benzyl)]₂Ca·(THF)₂^[13] (417 mg, 698 μmol) in THF (4.0 mL) was stirred for 2.5 h at 60 °C. The solvent was removed under vacuum, and the remaining orange product was dissolved in warm hexane (4 mL). Cooling the solution to room temperature yielded yellow crystals (410 mg, 80%), m.p. 132 °C (dec.). ¹H NMR (500 MHz, C₆D₆, 25 °C): δ = 8.15 (s, 1 H, fluorenyl), 8.00 (s, 1 H, fluorenyl), 7.89 (d, ³J_{H,H} = 8.5 Hz, 1 H, fluorenyl), 7.79 (d, ³J_{H,H} = 8.5 Hz, 1 H, fluorenyl), 7.41 (d, ³J_{H,H} = 7.5 Hz, 2 H, Ar), 7.34 (d, ³J_{H,H} = 7.5 Hz, 2 H, Ar), 7.22–6.91 (m, 8 H, Ar), 6.86 (d, ³J_{H,H} = 8.5 Hz, 1 H, benzyl), 6.67 (t, ³J_{H,H} = 7.1 Hz, 1 H, benzyl), 6.32 (d, ³J_{H,H} = 7.6 Hz, 1 H, benzyl), 6.19 (t, ³J_{H,H} = 7.1 Hz, 1 H, benzyl), 2.63 (br., 4 H, THF), 1.96 (s, 3 H, CH₃), 1.87 (s, 3 H, CH₃), 1.85 (s, 3 H, NCH₃), 1.84 (s, 3 H, NCH₃), 1.79 (s, 6 H, CH₃), 0.95 (br., 4 H, THF), 0.64 (s, 9 H, Me₃Si-fluorenyl), 0.51 (s, 1 H, CH), 0.45 (s, 9 H, Me₃Si-benzyl) ppm. ¹³C{¹H} NMR (500 MHz, C₆D₆, 25 °C): δ = 151.4, 151.2, 147.2, 146.1, 145.6, 141.6, 141.4, 136.1, 128.3, 127.3, 127.2, 125.9, 125.9, 125.5 (benzyl), 123.9 (benzyl), 121.4, 121.3, 121.2, 121.0, 119.2 (benzyl), 118.2, 118.2, 118.0, 117.6, 113.1 (benzyl), 87.9 (C-9), 68.5 (THF), 44.8 (NCH₃), 44.4 (CH), 43.6 [C(CH₃)₂], 43.4 [C(CH₃)₂], 41.5 (NCH₃), 31.4 (CH₃), 31.3 (CH₃), 30.9 (CH₃), 30.7 (CH₃), 24.9 (THF), 2.71 (Me₃Si-fluorenyl), 2.48 (Me₃Si-benzyl) ppm.

Synthesis of 7: A solution of 2,7-bis(1,1-diphenylethyl)-9-Me₃Si-fluorene (242 mg, 404 μmol) and [(2-Me₂N-*α*-Me₃Si-benzyl)]₂Ca·(THF)₂^[13] (245 mg, 410 μmol) in THF (3.0 mL) was stirred for 2.5 h at 60 °C. After removing the solvent under vacuum, the remaining product was washed with hexane (2 mL) and dried in vacuo. Repeating this procedure resulted in a yellow product (307 mg, 83%), m.p. 202 °C (dec.). ¹H NMR (500 MHz, C₆D₆, 25 °C): δ = 8.02 (d, ³J_{H,H} = 8.6 Hz, 1 H, fluorenyl), 7.95 (d, ³J_{H,H} = 8.6 Hz, 1 H, fluorenyl), 7.61 (s, 1 H, fluorenyl), 7.52 (s, 1 H, fluorenyl), 7.33–6.96 (m, 23 H, Ar), 6.69 (t, ³J_{H,H} = 7.3 Hz, 1 H,

benzyl), 6.30 (d, ³J_{H,H} = 7.1 Hz, 1 H, benzyl), 6.17 (t, ³J_{H,H} = 7.2 Hz, 1 H, benzyl), 2.61 (br., 4 H, THF), 2.26 (s, 3 H, CH₃), 2.23 (s, 3 H, CH₃), 1.87 (s, 3 H, NCH₃), 1.81 (s, 3 H, NCH₃), 0.97 (br., 4 H, THF), 0.45 (s, 1 H, CH), 0.34 (s, 9 H, Me₃Si-fluorenyl), 0.24 (s, 9 H, Me₃Si-benzyl) ppm. ¹³C{¹H} NMR (500 MHz, C₆D₆, 25 °C): δ = 150.6, 150.2, 150.2, 150.1, 147.3, 144.4, 143.7, 141.4, 141.2, 129.4, 129.4, 129.3, 129.2, 129.2, 128.3, 128.1, 128.1, 128.0, 126.5, 126.2, 126.2, 126.1, 126.0, 124.5, 121.7 (benzyl), 121.5, 121.5, 121.3, 121.2 (benzyl), 119.3, 118.7 (benzyl), 113.0 (benzyl), 88.9 (C-9), 68.6 (THF), 53.4 (CCH₃), 53.2 (CCH₃), 44.8 (CH), 44.6 (NCH₃), 41.5 (NCH₃), 30.9 (CH₃), 30.3 (CH₃), 25.0 (THF), 2.56 (Me₃Si-fluorenyl), 2.19 (Me₃Si-benzyl) ppm.

Synthesis of 8: As complex **8** is highly soluble even in cold hexane, it was synthesized in situ by reacting 2,7-bis(1,1-diphenylethyl)-9-Et₃Si-fluorene with [(2-Me₂N-*α*-Me₃Si-benzyl)]₂Ca·(THF)₂ (1.05 equiv.) in C₆D₆. Stirring the orange solution for 50 h at 70 °C led to quantitative formation of the heteroleptic complex **8** which, because of its extreme solubility, could not be freed from 2-Me₂N-*α*-Me₃Si-toluene by washing procedures. It was therefore used in solution for further polymerization experiments. The product has been fully characterized by 2D NMR methods. ¹H NMR (500 MHz, C₆D₆, 25 °C): δ = 7.93 (d, ³J_{H,H} = 8.5 Hz, 1 H, fluorenyl), 7.87 (d, ³J_{H,H} = 8.5 Hz, 1 H, fluorenyl), 7.58 (s, 1 H, fluorenyl), 7.43 (s, 1 H, fluorenyl), 7.22–6.83 (m, 23 H, Ar), 6.58 (t, ³J_{H,H} = 7.5 Hz, 1 H, benzyl), 6.23 (d, ³J_{H,H} = 7.0 Hz, 1 H, benzyl), 6.10 (t, ³J_{H,H} = 7.5 Hz, 1 H, benzyl), 2.52 (br., 4 H, THF), 2.21 (s, 3 H, CH₃), 2.16 (s, 3 H, CH₃), 1.80 [s, 6 H, N(CH₃)₂], 0.83–0.74 [m, 15 H, Si(CH₂CH₃)₃], 0.29 (s, 1 H, CH), 0.27 (s, 9 H, Me₃Si) ppm. ¹³C{¹H} NMR (500 MHz, C₆D₆, 25 °C): δ = 150.6, 150.3, 150.2, 150.1, 147.3, 144.5, 143.6, 142.0, 141.8, 130.1, 129.4, 129.4, 129.3, 129.0, 128.2, 128.1, 128.1, 128.0, 126.4 (benzyl), 126.2, 126.1, 125.4, 124.4 (benzyl), 123.9, 122.1, 121.6, 121.5, 121.4, 121.4, 121.2, 119.4, 119.1 (benzyl), 118.5, 113.0 (benzyl), 86.5 (C-9), 68.6 (THF), 53.4 (CCH₃), 53.2 (CCH₃), 45.0 (CH), 44.4 (NCH₃), 41.7 (NCH₃), 30.8 (CH₃), 30.2 (CH₃), 25.0 (THF), 8.50 [Si(CH₂CH₃)₃], 6.40 [Si(CH₂CH₃)₃], 2.58 (Me₃Si-benzyl) ppm.

Synthesis of 9: As complex **9** is highly soluble even in cold hexane, it was synthesized in situ with a procedure similar to that for **8**. The orange solution of **9** prepared in situ was used for further polymerization experiments. ¹H NMR (500 MHz, C₆D₆, 25 °C): δ = 7.97 (d, ³J_{H,H} = 8.5 Hz, 1 H, fluorenyl), 7.91 (d, ³J_{H,H} = 9.0 Hz, 1 H, fluorenyl), 7.43 (s, 1 H, fluorenyl), 7.36 (s, 1 H, fluorenyl), 7.22–6.82 (m, 19 H, Ar), 6.57 (t, ³J_{H,H} = 7.0 Hz, 1 H, benzyl), 6.27 (d, ³J_{H,H} = 6.5 Hz, 1 H, benzyl), 6.10 (t, ³J_{H,H} = 6.5 Hz, 1 H, benzyl), 2.70 (br., 4 H, THF), 2.26 (s, 3 H, CH₃), 2.24 (s, 3 H, CH₃), 1.90 (s, 6 H, NCH₃), 1.81 (s, 6 H, NCH₃), 1.19 [s, 9 H, C(CH₃)₃], 1.16 [s, 9 H, C(CH₃)₃], 1.15 [s, 9 H, C(CH₃)₃], 1.13 [s, 9 H, C(CH₃)₃], 1.00 (br., 4 H, THF), 0.40 (s, 1 H, CH), 0.28 (s, 9 H, Me₃Si-benzyl), 0.12 (s, 9 H, Me₃Si-fluorenyl) ppm. ¹³C{¹H} NMR (500 MHz, C₆D₆, 25 °C): δ = 148.6, 148.6, 147.7, 147.4, 147.3, 147.2, 147.0, 144.9, 144.6, 141.3, 141.1, 129.2, 129.1, 129.1, 129.0, 126.5 (benzyl), 125.0, 125.0, 124.5 (benzyl), 121.7, 121.5, 121.2, 121.1, 119.3, 119.3 (benzyl), 118.8, 113.0 (benzyl), 88.7 (C-9), 68.6 (THF), 52.6 (CCH₃), 52.5 (CCH₃), 44.8 (CH), 44.4 (NCH₃), 41.5 (NCH₃), 34.5 [C(CH₃)₃], 34.4 [C(CH₃)₃], 31.5 [C(CH₃)₃], 30.5 (CCH₃), 30.1 (CCH₃), 25.1 (THF), 2.70 (Me₃Si-fluorenyl), 2.22 (Me₃Si-benzyl) ppm.

Styrene Polymerization: Polymerizations of styrene were performed in a thermostatted 100 mL stainless steel Büchi reactor at normal pressure either in cyclohexane (1 M styrene solution, 1 mM catalyst, 50 °C) or in pure styrene (1 mM catalyst, 20 °C). In a typical polymerization experiment, the reactor was loaded with dry cyclohex-

Table 2. Crystal data for the compounds **4**, **5** and **6**.

Compound	4	5	6
Formula	C ₅₈ H ₇₆ Ca ₂ N ₄ Si ₂ ·C ₇ H ₈	C ₆₆ H ₉₀ Ca ₂ N ₂ Si ₂	C ₅₀ H ₆₅ CaNOSi ₂
MW	1057.70	1047.74	792.29
Size [mm]	0.7 × 0.7 × 0.2	0.5 × 0.4 × 0.3	0.5 × 0.4 × 0.3
Crystal system	monoclinic	monoclinic	triclinic
Space group	Cc	C2/c	P $\bar{1}$
<i>a</i> [Å]	10.6545(8)	17.271(1)	10.9274(4)
<i>b</i> [Å]	43.504(4)	15.677(1)	16.0377(5)
<i>c</i> [Å]	12.9522(9)	23.585(1)	16.3604(6)
<i>a</i>	90	90	110.334(2)
<i>β</i>	96.288(6)	110.099(1)	94.677(2)
<i>γ</i>	90	90	97.161(2)
<i>V</i> [Å ³]	5967.4(8)	5996.7(7)	2643.4(2)
<i>Z</i>	4	4	4
<i>ρ</i> [g cm ⁻³]	1.177	1.161	1.103
<i>μ</i> (Mo-K α) [mm ⁻¹]	0.273	0.270	0.195
<i>T</i> [°C]	−120	−90	−90
<i>θ</i> (max.)	25.1	29.3	27.5
Reflections total, unique	8146, 5571	127637, 8205	159543, 12019
<i>R</i> _{int}	0.017	0.068	0.077
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	5061	6476	9479
Parameter	966	331	500
<i>R</i> ₁	0.028	0.051	0.065
<i>wR</i> ₂	0.072	0.139	0.155
GOF	1.04	1.10	1.08
Max./min. residual electron density [e Å ⁻³]	−0.30/0.26	−0.60/0.74	−0.46/0.36

ane (90 mL, dried with CaH₂ and distilled from *n*BuLi) and dry styrene (11.5 mL, ca. 100 mmol, freshly distilled from CaH₂ and stored over alox pearls). A solution of the initiator (0.1 mmol) in benzene (1.0 mL) was added through a port. The usual appearance of a red colour and a slight increase in temperature (1–3 °C) indicated that the polymerization started immediately. After a polymerization time of 45–60 min, the mixture was quenched with oxygen-free methanol. Evaporation of all solvents yielded the polymer in quantitative yields. Polymerization in neat styrene should only be carried out at temperatures ≤20 °C, should be monitored continuously and should be quenched when temperatures exceed 25 °C. The polymers were analyzed by GPC and high temperature ¹H and ¹³C NMR (solvent: [D₂]tetrachloroethane). The tacticity of the polymer was checked by analyzing the ¹³C NMR signal for the C_{ipso} in the phenyl ring.^[22]

Crystal Structures: Crystal diffraction data were measured on Enraf–Nonius CAD4 and Siemens SMART CCD diffractometers. All crystal structures were solved with SHELXS-97^[26] and refined with SHELXL-97.^[27] PLATON^[28] was used for geometry calculations and graphics. Crystal data are given in Table 2.) The space group for **4** was checked with the ADSYM procedure incorporated in the program PLATON. No additional symmetry was found, and therefore the true space group is Cc. The Flack parameter was refined to 0.00(2). Crystals of **6** contain one equivalent of hexane in the asymmetric unit. This molecule was extensively disordered and treated with the SQUEEZE procedure^[29] incorporated in PLATON.

CCDC-646400 (compound **4**), -646401 (compound **5**), and -646402 (compound **6**) contain the supplementary crystallographic data for this paper. 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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