# Dimeric Benzylcalcium Complexes: Influence of THF in Stereoselective Styrene Polymerization

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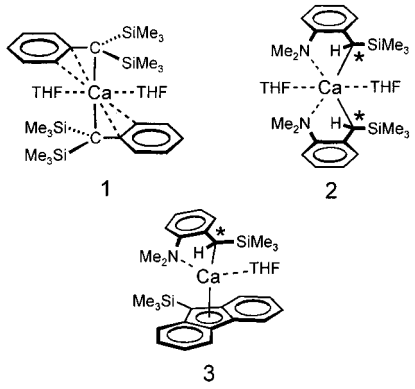
Two dimeric benzylcalcium complexes were prepared and structurally characterized by single-crystal X-ray diffraction: {($Me_3Si$-fluorenyl)[*o*-(dimethylamino)benzyl]Ca}$_2$ (**6**) and {($EtMe_4Cp$)[*o*-(dimethylamino)benzyl]Ca}$_2$ (**8**). Both complexes show a core of $Ca^{2+}$ ions that are symmetrically bridged by benzyl anions. Fluorenyl or cyclopentadienyl ligands are bonded in terminal positions. The $Me_2N$ groups coordinate each on a different $Ca^{2+}$ ion. Their dimeric nature is preserved in apolar solvents (benzene, toluene), and addition of THF results in cleavage of the dimer in THF-solvated monomers. The THF-free dimeric benzylcalcium complex **6** initiates the living polymerization of styrene. Polymers enriched in syndiotactic sequences are obtained (ca. 85% *r*-diads). Addition of equimolar amounts of THF (Ca/THF ratio is 1:1) does not disturb the stereocontrol in the polymerization reaction. A Ca/THF ratio of 1:4, however, significantly impairs the stereocontrol. We propose an insertion step that proceeds with a high degree of syndiotactic selectivity and an inversion mechanism that racemizes the chiral chain-ends. Excess THF increases the rates of inversion of the chiral carbanionic chain-ends, thus destroying the stereoregularity in the polymer chain.



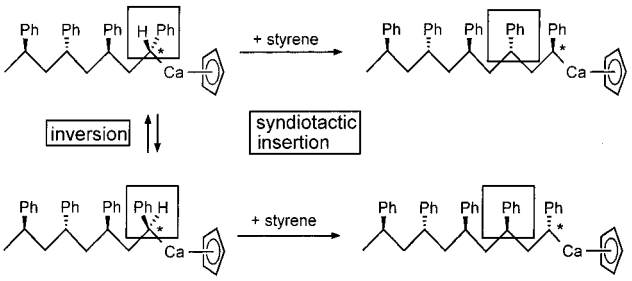
## Introduction

We recently published the structures of the first homoleptic (**1**, **2**)[1] and heteroleptic (**3**)[2] benzylcalcium compounds. The complexes **2** and **3** initiate the anionic living polymerization of styrene.




The heteroleptic benzylcalcium compound (**3**) is isovalent with $CpTi^{III}Me^+$, a species proposed to be active in the highly syndiotactic polymerization of styrene.[3] The polystyrene obtained with the heteroleptic benzylcalcium initiator (**3**) under standard polymerization conditions (10% styrene in cyclohexane at 50 °C) is only slightly enriched in syndiotactic sequences. However, the syndiotacticity of the material can be increased considerably by increasing the monomer concentration: polymerization in pure styrene yields a polymer with 85% *r*-diads and 76% *rr*-triads.[2]

**Scheme 1**




We propose a polymerization mechanism in which monomer insertion proceeds with a high degree of tacticity (Scheme 1). Errors in the stereoregularity of the polymer chain are likely due to inversion of the chiral carbanionic chain-end. Inversion of carbanionic centers, which is well-established for highly ionic organolithium compounds,[4] has also been observed in the benzylcalcium initiators **2** and **3**. The ratio between the rates of monomer insertion and chain-end inversion determines the extent of stereoregularity of the polystyrene. An increase in the monomer concentration accelerates the insertion rate, while leaving the inversion rate largely unaffected.

Dynamic NMR experiments show that the barrier for inversion of the chiral benzylic carbanion in **3** ($\Delta G^{\ddagger}$(80 °C, toluene) = 18.8 kcal/mol) is concentration

(1) (a) Feil, F.; Harder, S. *Organometallics* **2000**, *19*, 5010. (b) Harder, S.; Feil, F.; Weeber, A. *Organometallics* **2001**, *20*, 1044.

(2) Harder, S.; Feil, F.; Knoll, K. *Angew. Chem.* **2001**, *113*, 4391; *Angew. Chem., Int. Ed.* **2001**, *40*, 4261.

(3) (a) Ishihara, N.; Seimiya, T.; Kuramoto, M.; Uoi, M. *Macromolecules* **1986**, *19*, 2464. (b) Zambelli, A.; Pellecchia, C.; Oliva, L.; Longo, P.; Grassi, A. *Makromol. Chem.* **1991**, *192*, 223.

(4) (a) Hoffmann, R. W.; Rühl, T.; Chemla, F.; Zahneisen, T. *Liebigs Ann. Chem.* **1992**, 719. (b) Hoffmann, R. K.; Dress, R. P.; Ruhland, T.; Wenzel, A. *Chem. Ber.* **1995**, *128*, 861. (c) Fraenkel, G.; Duncan, J. H.; Martin, K.; Wang, J. *J. Am. Chem. Soc.* **1999**, *121*, 10538.

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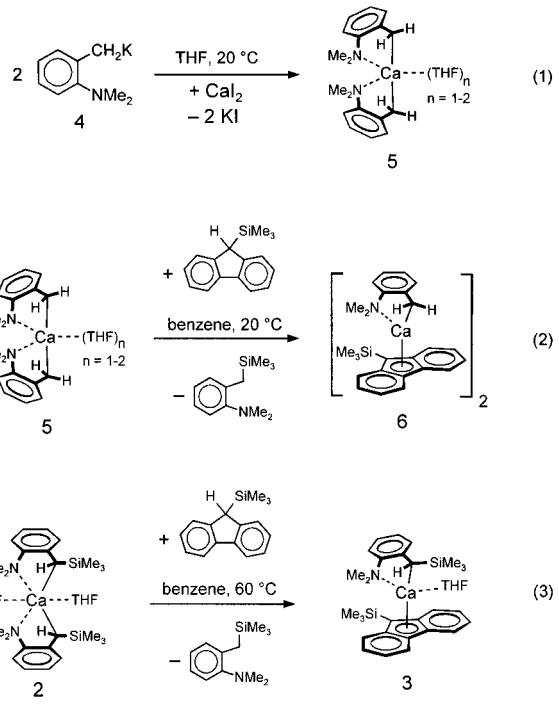



(1) (2) (3)

4 5 6 2 3



independent and can be considerably lowered by addition of a few equivalents of THF (**3** + 5 equiv of THF: $\Delta G^{\ddagger}$(20 °C, toluene) = 15.4 kcal/mol). We propose two pathways for inversion of the chiral carbanion in **3** (Scheme 2): (i) a dissociative pathway in which the Ca−C bond is broken[5] and (ii) a THF-assisted pathway in which a free THF molecule coordinates to Ca, thus facilitating cleavage of the Ca−C bond.

The presence of THF could also have a substantial influence on the configurational stability of chiral polystyryl chain-ends bonded to $Ca^{2+}$. Small amounts of THF will accelerate inversion of the chain-ends, resulting in less tacticity control in the polymer obtained. The use of THF-free benzylcalcium initiators could substantially improve the syndiotacticity of the polystyrene. Attempts to free the homoleptic (**2**) and heteroleptic (**3**) benzylcalcium complexes from their coordinated THF ligands were dissatisfying: the severe conditions needed led to partial decomposition of the benzylcalcium complexes.

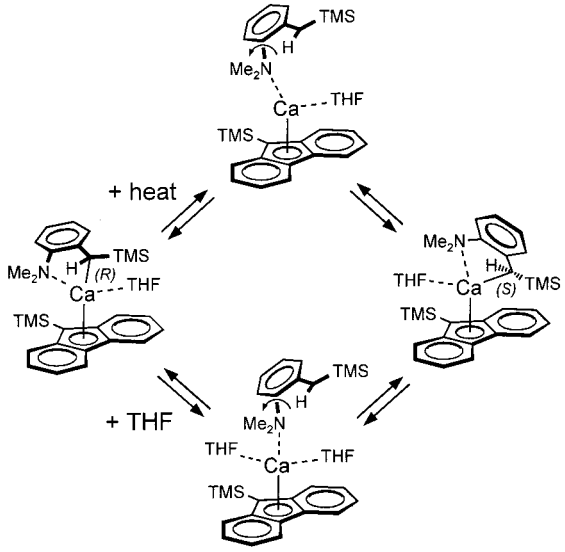
Here we describe the syntheses of heteroleptic THF-free complexes that are dimeric in the solid state and in solution and discuss the influence of THF on the stereoselectivity of the styrene polymerization.

## Results and Discussion

**Syntheses.** Deprotonation of *o*-(dimethylamino)toluene with a BuLi/KOR superbase quantitatively yielded *o*-(dimethylamino)benzylpotassium (**4**). In contrast to benzylpotassium, which smoothly reacts with THF at 0 °C,[6] the dimethylamino-substituted benzylpotassium complex is relatively stable in THF at room temperature.[7]

Reaction of *o*-(dimethylamino)benzylpotassium with anhydrous $CaI_2$ results in the $Me_3Si$-free analogue of **2** (eq 1). The homoleptic benzylcalcium compound **5** shows

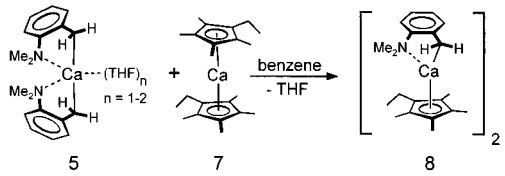
**Scheme 2**




a much higher reactivity toward $Me_3Si$-fluorene (eq 2) than the $Me_3Si$-stabilized analogue **2** (eq 3), which only reacts slowly after heating to 60 °C. Both benzyl carbanions in **5** can react with $Me_3Si$-fluorene, although the second benzyl carbanion reacts markedly slower and only at higher temperature (60 °C). In the $Me_3Si$-stabilized benzylcalcium complex **2**, only the first benzyl carbanion reacts with $Me_3Si$-fluorene.

A $^1$H NMR spectrum of the reaction product **6** is in accordance with a THF-free heteroleptic benzylcalcium species. Even crystallization of **6** in the presence of several equivalents of THF resulted in a THF-free product. A crystal structure determination of **6** reveals a dimeric species in the solid state.

Another dimeric benzylcalcium complex was obtained by the disproportionation reaction of $(Me_4EtCp)_2Ca$ (**7**) and [*o*-(dimethylamino)benzyl]$_2$calcium·THF (**5**) (eq 4). The Schlenk equilibrium is completely at the heteroleptic side, and the product crystallizes as a THF-free dimer.




(4)

5 7 8

**Crystal Structures.** The crystal structure of **6** shows a dimeric aggregate (Figure 1) in which the $Ca^{2+}$ ions are bridged by the small benzylic $CH_2$ groups in a more or less symmetrical fashion: the Ca−C bonds vary from 2.537(3) to 2.571(3) Å and are only slightly longer than the benzylic C−Ca bond in **3** (2.501(2) and 2.510(2) Å).[2] The bridging benzyl groups in **6** display hybridizations very close to sp$^3$: the sums of the valence angles at the benzylic carbons are 329(2)° and 331(2)°. The $Me_2N$ groups coordinate each on a different $Ca^{2+}$ ion (Ca−N

(5) Also cleavage of the N−Ca bond with subsequent inversion at N is observed: $\Delta G^{\ddagger}$(60 °C, toluene) = 17.9(1) kcal/mol.

(6) Hoffmann, D.; Bauer, W.; Hampel; F.; van Eikema Hommes, N. J. R.; Schleyer, P. von R.; Otto, P.; Pieper, U.; Stalke, D.; Wright, D. S.; Snaith, R. *J. Am. Chem. Soc.* **1994**, *116*, 528.

(7) A solution of *o*-(dimethylamino)benzylpotassium in THF-$d_8$ shows 15% decomposition after 24 h at room temperature. At 60 °C the decomposition is complete after 3 h, showing α-monodeuterated *o*-(dimethylamino)toluene as the product.

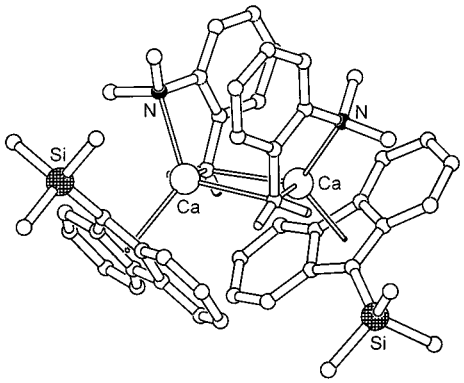



**Figure 1.** Molecular structure of the dimer {($Me_3Si$-fluorenyl)[*o*-(dimethylamino)benzyl]Ca}$_2$ (**6**); only the benzylic hydrogens are shown.

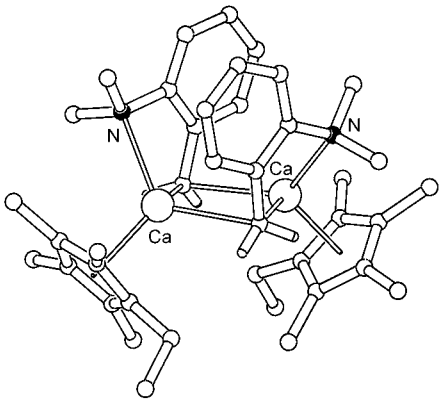



**Figure 2.** Molecular structure of the dimer {($EtMe_4Cp$)-[*o*-(dimethylamino)benzyl]Ca}$_2$ (**8**); only the benzylic hydrogens are shown.

distances: 2.558(2) and 2.579(3) Å). The benzyl anions are situated at the same side of the $Ca_2C_2$ plane. This alignment makes the core of the dimer pseudo $C_2$-symmetric. The terminal $Me_3Si$-fluorenyl anions break this symmetry and are bonded to Ca in different orientations. Both $Me_3Si$-fluorenyl ligands, however, show a coordination mode similar to that observed in the crystal structure of **3**;[2] that is, the $\eta^5$-coordination is slightly distorted toward an allylic coordination. The Ca metal is slipped toward the Si-substituted carbon which shows the shortest Ca−C bond (Figure 1, left fluorenyl ligand: Ca−C = 2.695(3), 2.736(3), 2.798(3), 2.823(3), 2.741(3) Å; right fluorenyl ligand: Ca−C = 2.674(2), 2.688(3), 2.765(3), 2.817, 2.765(3) Å). The dimer **6** represents the first example of benzyl anions bridging $Ca^{2+}$ ions. The much smaller $CH_2$ group enables the bridging of the two $Ca^{2+}$ centers. The large benzylic ($Me_3Si$)CH group in **3** cannot take part in bridging for sterical reasons. Complex **3** therefore crystallizes as a monomeric species in which open coordination sites are filled with a THF ligand.

The crystal structure of complex **8** shows a dimeric structure very similar to **6** (Figure 2), i.e. a dimer with bridging benzyl groups, intramolecular coordination of the $Me_2N$ groups on different $Ca^{2+}$ ions, and terminal $Me_4EtCp^-$ ligands. Complex **8** is situated over a crystallographic $C_2$-axis, consequently showing perfect $C_2$-symmetry. The terminal $Me_4EtCp^-$ ligands show Ca−C bond distances varying from 2.640(2) to 2.690(2) Å (average 2.668(2) Å) and are therefore slightly more

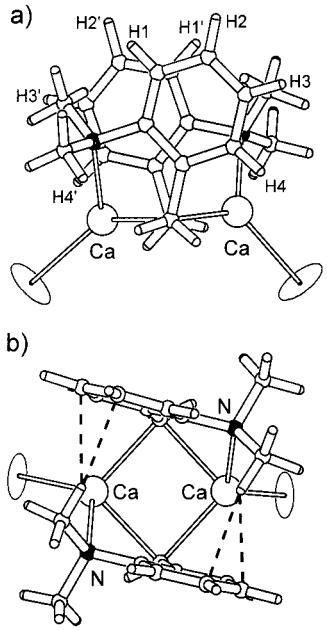



**Figure 3.** Core of dimer **6** viewed along the axis through the benzylic carbons (a) or perpendicular on this axis (b). The striped lines indicate nonclassical C−H···C hydrogen bridges.

strongly coordinated to the Ca than the $Me_3Si$-fluorenyl anions in **6** (average Ca−C distances: 2.742(3) and 2.759(3) Å). The strong bonding of the $Me_4EtCp^-$ ligands in **8** affects the bond distances in the central part of the dimer: Ca−C 2.607(2) and 2.621(2) Å; Ca−N 2.600(1) Å. These bonds in **8** are longer than the comparable bonds in **6**. Also, the Ca···Ca distance in **8** (3.585(3) Å) is longer than that in **6** (3.479(3) Å). The bridging benzyl groups in **8** display a hybridization close to $sp^3$ (the sum of the valence angles at the benzylic carbon is 337(2)°).

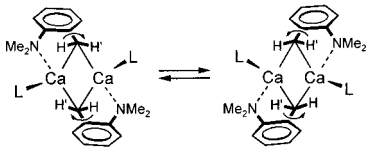
**Solution Behavior.** The dimeric benzylcalcium complexes **6** and **8** were studied in solution by NMR spectroscopy. The dimer **6** is only slightly soluble in apolar solvents such as benzene. NMR studies show evidence for the presence of dimers in solution. The most direct proof for the dimeric nature of **6** in solution comes from unusual but distinctive NOE signals between the $Me_2N$ group and some of its non-neighboring ring protons (H2 and H3 in Figure 3a). This observation agrees well with a solution structure very similar to the solid-state structure. The crystal structure shows short distances between one of the $Me_2N$ protons and the *meta* and *para* protons of the other benzyl moiety (2.98 and 3.07 Å, respectively). The distances between the $Me_2N$ proton and the corresponding aromatic carbons are even smaller (2.61 and 2.69 Å) and are in the range for a nonclassical C−H···C hydrogen bridge (Figure 3b).

Other proof for a dimeric structure comes from unusual chemical shifts observed for the aromatic ring protons. The $^1$H NMR spectra of anionic benzyl species generally show a high-field triplet, characteristic for the aromatic ring proton in *para*-position of the benzylic carbon (H2 in Figure 3a).[6] This phenomenon is due to charge-delocalization and therefore directly related to the nature of the benzyl−metal bond.[1,8] The more ionic species show the larger high-field shifts. Benzylcalcium

(8) Feil, F.; Harder, S. *Organometallics* **2001**, *20*, 4616.

complexes display chemical shifts for this *para*-H in the range 6.0−6.4 ppm. The $^1$H NMR spectrum of **6** shows a triplet in the expected range (H2: 6.01 ppm). However, the aromatic signal with the highest field (5.73 ppm) is a doublet and can be assigned to H1, a proton in *meta*-position with respect to the benzylic carbon. This anomaly can be explained by the anisotropy effect caused by ring currents[9] in a nearby aryl ring: H1 is positioned in the shielding cone of the neighboring ring, while H2, H3, and H4 remain unaffected (see Figure 3a).

Variable-temperature spectra of **6** show several interesting features. It should be noted that the $Ca^{2+}$ centers in the dimer are chiral. As a consequence of the $C_2$-symmetry of the core of the dimer, both $Ca^{2+}$ ions within a dimer have the same absolute configuration. These chiral Ca centers make all prochiral groups diastereotopic. Therefore, at lower temperatures two doublets arise for the benzylic $CH_2$ and two singlets for the $NMe_2$ group. Also, both sides of the $C_s$-symmetric $Me_3Si$-fluorenyl ligand are diastereotopic, and this results in four doublets and four triplets. At higher temperatures, the absolute configuration at the $Ca^{2+}$ centers inverts fast on the NMR time scale, giving rise to coalescence of signals for the diastereotopic groups. The different diastereotopic groups ($CH_2$, $NMe_2$, and $Me_3Si$-fluorenyl) coalesce at different temperatures, but the calculated activation energy ($\Delta G^{\ddagger}$ = 14.7(1) kcal/mol) is the same for all signals coalescing. This indicates that all coalescence is due to a single process: we propose a process that involves simultaneous cleavage of the Ca−N bonds followed by a 180° rotation around the $C_\alpha$−$C_{ipso}$ bonds and formation of new Ca−N bonds (eq 5). This process changes the absolute configuration

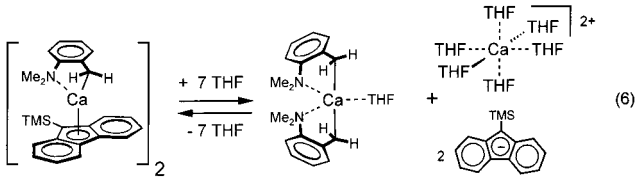



(5)

at both Ca centers simultaneously and will be the lowest energy pathway. Cleavage of a $Ca^{2+}$−$C^-$ needs more energy than that of a $Ca^{2+}\cdots NR_2$ bond.[2] The energy barrier for Ca−N cleavage in **6** is significantly lower than that in **3**.[5]

Dissolving **6** in THF-$d_8$ results in the immediate formation of an orange crystalline precipitate. NMR and X-ray-diffraction studies show that this newly formed compound is the solvent-separated ion-pair $[Ca^{2+}\cdot(THF)_6][Me_3Si\text{-fluorenyl}^-]_2$ (**9**).[10] The presence of large quantities of THF apparently results in rupture of the fluorenyl−Ca bond. Crystallization of homoleptic **9** results in a shift of the Schlenk equilibrium to the homoleptic side (eq 6). Complex **3** shows exactly the same behavior in THF.

Addition of 2 equiv of THF to **6** dissolved in benzene (Ca/THF ratio = 1:1) does not affect the $^1$H NMR spectrum. However, increasing the THF concentration to a Ca/THF ratio of 1:4 results in the appearance of a new species. A 0.12 M solution of **6** in a $C_6D_6$/THF-$d_8$

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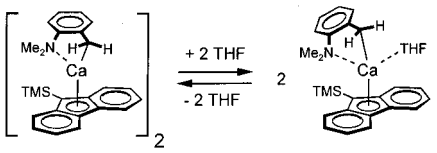
(6)

mixture (ratio 90:10) shows this species exclusively, and no precipitate of $[Ca^{2+}\cdot(THF)_6][Me_3Si\text{-fluorenyl}^-]_2$ is observed. The $^1$H NMR spectrum shows evidence for a monomer in solution. The aromatic ring protons show no unusual chemical shifts as observed for the dimer. The aromatic signal at the highest field (6.07 ppm) can be assigned to the hydrogen in *para*-position of the benzylic $CH_2$ group and is in the normal range expected for a benzylcalcium compound. Also, only NOE signals between the $Me_2N$ group and its neighboring ring proton can be observed. We propose that the excess THF results in cleavage of the dimer and in formation of a monomeric species: ($Me_3Si$-fluorenyl)(*o*-$Me_2N$-benzyl)Ca·$(THF)_n$ (**10**; see eq 7). The Ca metal in monomeric **10** is




6 10

(7)

also chiral; however, only one set of signals is observed for all diastereotopic groups ($Me_2N$, $CH_2$, and the $Me_3Si$-fluorenyl protons). Cooling the sample (**6** in toluene-$d_8$/THF-$d_8$ in ratio 90:10) results in broadening of the signals for the diastereotopic groups. Precipitation of $[Ca^{2+}\cdot(THF)_6][Me_3Si\text{-fluorenyl}^-]_2$ starts at −20 °C, and signals of the homoleptic dibenzylcalcium complex **5** appear. At this stage the slow exchange limit for inversion of the absolute configuration at Ca is not reached.

The dimeric complex **8** shows a solution behavior very similar to that of **6**. In benzene solution, a dimeric structure is proposed on the basis of NOE effects and unusual chemical shifts for the aromatic ring signals. The chirality at the Ca centers makes all prochiral sites unique. Inversion of chirality is slow at 10 °C, and four signals for the cyclopentadienyl-methyls arise. These signals merge into two singlets at higher temperature ($\Delta G^{\ddagger}$(15 °C, toluene) = 14.9 kcal/mol). Also coalescence for the signals arising from the prochiral $CH_2$ and $NMe_2$ groups is observed at higher temperature.

**Polymerization Results.** The dimeric benzylcalcium complex **6** is an initiator for the anionic polymerization of styrene. The polymerization is living and shows the same characteristics as polymerization with monomeric benzylcalcium complexes reported earlier.[1b,2] The obtained polymers, however, do not show an improved degree of syndiotacticity when compared with polymers obtained with the monomeric heteroleptic initiator **3** (Figure 4a and 4b). The presence of minor amounts of THF (THF/Ca ratios of 1:1) during the polymerization reaction does not influence the tacticity control. However, addition of 4 equiv of THF per Ca center already shows significant impairment of the syndiotacticity

(9) Haigh, C. W.; Mallion, R. B. *Prog. Nucl. Magn. Reson. Spectrosc.* **1980**, *13*, 303.
(10) Harder, S.; Feil, F.; Repo, T. *Chem. Eur. J.* **2002**, in press.

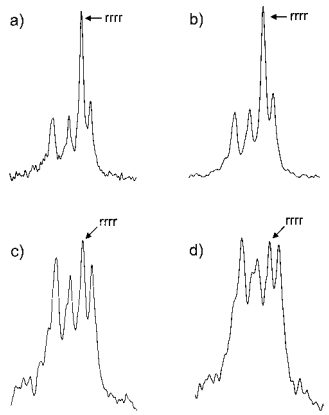



**Figure 4.** $^{13}C$ NMR signal for the $C_{ipso}$ phenyl ring of polystyrene obtained with the initiators (a) **3**, (b) **6**, (c) **6** + 8 THF (Ca/THF ratio = 1:4), and (d) **8**. Polymerizations were performed in pure styrene at 20 °C.

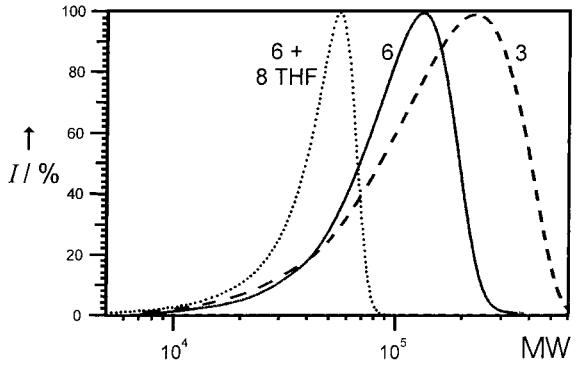



**Figure 5.** GPC curves of polystyrene obtained with the initiator **3** (striped line, PDI = 2.26, $M_n = 1.00 \times 10^5$), **6** (solid line, PDI = 2.04, $M_n = 1.09 \times 10^5$) and **6** + 8 THF (dotted line, PDI = 1.37, $M_n = 3.37 \times 10^4$).

(Figure 4c). Larger THF concentrations show similar effects and also slow the polymerization rate (comparable polymerization times result in shorter chains) probably by blocking open coordination sites at the metal.

The GPC spectra of selected polymers are presented in Figure 5. Polymer obtained with **3** typically shows a large polydispersion index and tailing in the low molecular weight range. This is due to slow initiation of the polymerization reaction and not to chain termination (the polymerization is living).[2] Polymer obtained with dimeric **6** shows a slightly smaller polydispersion index. Also less tailing is observed in the low molecular weight range. Apparently, dimeric **6** is a slightly faster initiator. This is in agreement with the stronger nucleophilicity of the $ArCH_2^-$ anion in **6** when compared with the $Me_3Si$-stabilized $ArCH(Me_3Si)^-$ anion in **3**. However, the polydispersion index is still quite broad, indicating a still sluggish initiation. Breaking of the dimer is most likely the first step in the polymerization reaction. Addition of only 4 equiv of THF per Ca center (**6** + 8 THF) shows a remarkable reduction of the polydispersion index (Figure 5) and therefore an increase in the initiation rate. This is likely due to THF-assisted cleavage of the dimer into the more reactive monomeric initiator **10**.

The dimeric complex **8** also is an initiator for the anionic living polymerization of styrene. NMR analysis of the polymer obtained shows poorer syndiotactity than that of polymer obtained with **6** (Figure 4d). This shows that the spectator ligand ($Me_3Si$-fluorenyl or $Me_4EtCp$) influences the stereochemistry in the insertion step and/or the rate of inversion of the chiral chain-ends.

## Conclusions

We here describe a synthetic method for heteroleptic THF-free benzylcalcium complexes (**6** and **8**). The complexes crystallize as dimers with bridging benzyl units, and this structure is preserved in solution when apolar solvents are used. The Schlenk equilibrium is completely at the heteroleptic side. Addition of polar solvents can break the aggregates into THF-solvated heteroleptic benzylcalcium monomers (**10**).

The THF-free dimeric benzylcalcium complex **6** initiates the living polymerization of styrene. The polymer obtained does not show increased syndiotacticity compared with polymer obtained in the presence of 1 equiv of THF (initiator **3**). Apparently, small amounts of THF do not disturb the stereocontrol in the polymerization reaction. A Ca/THF ratio of 1:4, however, significantly impairs the stereocontrol. We propose an insertion step that proceeds with a high degree of syndiotactic selectivity and an inversion mechanism that racemizes the chiral chain-ends. Excess THF increases the rates of inversion of the chiral carbanionic chain-ends, thus destroying the stereoregularity in the polymer chain.

The spectator ligand in the heteroleptic initiator ($Me_3Si$-fluorenyl or $Me_4EtCp$) influences the stereoregularity in the polymer chain significantly. The mode of interaction between the spectator ligand and the polymerization site is either steric or electronic (or a combination of these). We will report in greater detail on the influence of the ligands in the near future.

## Experimental Section

**General Comments** All experiments were carried out under argon using predried solvents and Schlenk techniques. Crystal structures were solved with DIRDIF[11] and refined with SHELXL-97.[12] Geometry calculations and graphics were done with PLATON.[13]

**Synthesis of *o*-(Dimethylamino)benzylpotassium (4).** *n*-Butyllithium (1.6 M, 10.6 mL, 17.0 mmol) was added dropwise to a solution of *o*-(dimethylamino)toluene (2.57 g; 19.0 mmol) in THF (15 mL) and potassium 2-methyl-2-pentanolate (2.53 g, 18.1 mmol) precooled at −70 °C (the BuLi was added such that drops float along the cooled walls of the Schlenk tube). The solution was stirred at this temperature for ca. 1−2 h and slowly turned orange-red. Subsequently, the solution was slowly warmed to 0 °C, and the solvents were removed under vacuum, allowing the temperature to rise to 20 °C in the later stages. The sticky orange-red product solidified overnight at −30 °C and was washed four times with 20 mL portions of hexane. Drying the product under vacuum (25 °C, 1 Torr, 30 min) resulted in an orange powder (yield: 2.89 g, 16.7 mmol, 98%). $^1H$ NMR (THF-$d_8$, 250 MHz, 20 °C): 1.85 (d, 2.8 Hz, 1H, $CH_2$); 2.39 (d, 2.8 Hz, 1H, $CH_2$); 2.48 (s, 6H,

(11) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R. *The DIRDIF Program System;* Crystallography Laboratory, University of Nijmegen: The Netherlands, 1994.
(12) Sheldrick, G. M *SHELXL-97, Programs for the Determination of Crystal Structures*; Universität Göttingen: Germany, 1997.
(13) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2000.

$NMe_2$); 4.94 (t, 6.9 Hz, 1H, aromatic); 5.85 (d, 8.0 Hz, 1H, aromatic); 5.99 (t, 7.5 Hz, 1H, aromatic); 6.09 (d, 6.8 Hz, 1H, aromatic). $^{13}$C NMR (THF-$d_8$, 250 MHz, 20 °C): 42.1 ($NMe_2$); 48.6 ($CH_2$); 96.0; 113.3; 117.4; 125.2; 133.5; 146.2 (aromatics).

**Synthesis of Bis[*o*-(dimethylamino)benzyl]calcium (5).** Addition of $CaI_2$ (1.18 g, 4.01 mmol) to a solution of *o*-(dimethylamino)benzyl potassium (1.40 g, 8.08 mmol) in 15 mL of THF resulted in a gradual color change of orange-red to dark yellow. The suspension was stirred for 24 h, and the mother liquor was isolated by centrifugation. The precipitate was extracted once more with 10 mL of THF. The solvent of the combined THF layers was removed under vacuum. The resulting foamy substance was suspended in hexane, and the solvent was removed under vacuum. Repeating this procedure finally resulted in a yellow powder, which was dried under vacuum (50 °C, 1 Torr, 30 min). Yield: 1.45 g, 3.81 mmol, 95%. Repeated syntheses showed that the Ca/THF ratio in the product can vary from 1 to 2 (depending on the drying times). $^1$H NMR (benzene-$d_6$/THF-$d_8$, 250 MHz, 20 °C): 1.78 (s, br, 2H, $CH_2$); 2.51 (s, br, 6H, $NMe_2$); 6.23 (t, 6.9 Hz, 1H, aromatic); 6.73 (d, 8.0 Hz, 1H, aromatic); 6.79 (t, 7.5 Hz, 1H, aromatic); 6.88 (d, 6.8 Hz, 1H, aromatic). $^{13}$C NMR (THF-$d_8$, 250 MHz, 20 °C): 39.4 (br, $CH_2$); 43.8 ($NMe_2$); 109.6; 118.6; 122.3; 125.9; 136.9; 149.2 (aromatics).

**Synthesis of {(Me$_3$Si-fluorenyl)[*o*-(dimethylamino)benzyl]Ca}$_2$ (6).** A solution of bis[*o*-(dimethylamino)benzyl]-calcium·THF (3.45 g, 9.06 mmol) and $Me_3Si$-fluorene (2.15 g, 9.02 mol) in 20 mL of benzene was heated to 60 °C for 30 min. Slow cooling of the bright orange solution to +5 °C afforded yellow-orange crystals of the dimer **6** (1.85 g, 2.25 mmol, 50%). $^1$H NMR (toluene-$d_8$, 250 MHz, +5 °C): −0.49 (d, 11.6 Hz, 1H, $CH_2$); −0.22 (d, 11.8 Hz, 1H, $CH_2$); 0.65 (s, 9H, $Me_3Si$); 0.85 (s, 3H, $NMe_2$); 1.80 (s, 3H, $NMe_2$); 5.73 (d, 7.6 Hz, 1H, $Me_2N$-benzyl); 6.01 (t, 7.6 Hz, 1H, $Me_2N$-benzyl); 6.06 (d, 7.4 Hz, 1H, $Me_2N$-benzyl); 6.50 (t, 7.3 Hz, 1H, $Me_2N$-benzyl); 7.15 (t, 7.8 Hz, 1H, $Me_3Si$-fluorenyl); 7.21 (t, 7.6 Hz, 1H, $Me_3Si$-fluorenyl); 7.36 (t, 7.8 Hz, 1H, $Me_3Si$-fluorenyl); 7.45 (t, 7.1 Hz, 1H, $Me_3Si$-fluorenyl); 8.03 (d, 8.2 Hz, 1H, $Me_3Si$-fluorenyl); 8.13 (d, 7.7 Hz, 1H, $Me_3Si$-fluorenyl); 8.16 (d, 7.9 Hz, 2H, $Me_3Si$-fluorenyl). $^{13}$C NMR (benzene-$d_6$, 250 MHz, 40 °C): 2.8 ($Me_3Si$); 37.6 ($CH_2$); 43.5 (v br, $NMe_2$); 116.1; 117.3; 118.1; 119.0; 121.7; 122.3; 124.2; 124.9; 128.5; 129.9; 141.5; 144.1; 146.6 (aromatics). $^1$H NMR (benzene-$d_6$/THF-$d_8$ in ratio 90:10, 250 MHz, +20 °C): 0.71 (s, 9H, $Me_3Si$); 1.78 (s, br, 2H, $CH_2$); 2.07 (s, br, 6H, $NMe_2$); 6.07 (m, 1H, $Me_2N$-benzyl); 6.38 (d, 7.8 Hz, 1H, $Me_2N$-benzyl); 6.69 (d, 4.1 Hz, 1H, $Me_2N$-benzyl); 6.69 (d, 4.1 Hz, 1H, $Me_2N$-benzyl); 6.99 (t, 7.2 Hz, 2H, $Me_3Si$-fluorenyl); 7.25 (t, 7.4 Hz, 2H, $Me_3Si$-fluorenyl); 8.04 (d, 7.4 Hz, 2H, $Me_3Si$-fluorenyl); 8.04 (d, 7.4 Hz, 2H, $Me_3Si$-fluorenyl). $^{13}$C NMR (benzene-$d_6$/THF-$d_8$ in ratio 90:10, 250 MHz, +20 °C): 2.50 ($Me_3Si$); 42.2 ($CH_2$); 43.3 (br, $NMe_2$); 110.3; 114.9; 118.3; 121.1; 121.3; 122.8; 123.1 124.2; 125.9; 128.5; 136.2; 142.1; 147.6 (aromatics).

**Synthesis of (EtMe$_4$Cp)$_2$Ca (7).** A mixture of anhydrous $CaI_2$ (1.63 g, 5.55 mmol), ($EtMe_4Cp$)K (2.10 g, 11.15 mmol), and 25 mL of $Et_2O$ was stirred for 24 h. The solvent was removed under vacuum, and the product was extracted from the residue with two 15 mL portions of hexane. Removal of the hexane from the extract resulted in honey-like light yellowish product that solidified overnight. The crude product contains 1 equiv of diethyl ether, which can be removed by dissolving the compound in toluene, removing the solvent under vacuum, and heating the product under vacuum (1 Torr, 85 °C, 1 h). Yield: 1.84 g (5.43 mmol, 98%). $^1$H NMR (benzene-$d_6$, 250 MHz, 20 °C): 0.88 (t, Hz, 6H, ethyl-$CH_3$); 1.90 (s, 12H, Cp-Me); 1.99 (s, 12H, Cp-Me); 2.35 (q, 8.0 Hz, 4H, ethyl-$CH_2$). $^{13}$C NMR (benzene-$d_6$, 250 MHz, 20 °C): 9.9; 10.3; 17.1; 18.7; 112.5; 114.6; 120.9.

**Synthesis of {(EtMe$_4$Cp)[*o*-(dimethylamino)benzyl]-Ca}$_2$ (8).** A mixture of ($EtMe_4Cp$)$_2$Ca (0.50 g, 1.48 mmol) and bis[*o*-(dimethylamino)benzyl]calcium·THF (0.56 g, 1.47 mmol) was dissolved in 8 mL of benzene and shortly heated to 60 °C. The yellow-orange solution was concentrated to 4 mL by partial removal of the benzene. Slow cooling of the benzene solution yielded large light yellow platelike crystals of the dimer **8** (yield: 0.38 g, 0.58 mmol, 39%). $^1$H NMR (toluene-$d_8$, 250 MHz, 20 °C): 0.83 (d, 10.5 Hz, 1H, benzyl-$CH_2$); 1.20 (t, 7.4 Hz, 3H, ethyl-Me); 1.46 (d, 10.5 Hz, 1H, benzyl-$CH_2$); 1.52 (s, 3H, N−$CH_3$); 2.19 (s, 3H, N-$CH_3$); 2.25 (s, 6H, Cp-Me); 2.30 (s, 6H, Cp-Me); 2.72 (q, 7.3 Hz, 2H, ethyl-$CH_2$); 6.09 (d, 7.5 Hz, 1H, aromatic); 6.20 (t, 7.4 Hz, 1H, aromatic); 6.50 (d, 7.5 Hz, 1H, aromatic); 6.61 (t, 7.4 Hz, 1H, aromatic). $^{13}$C NMR (toluene-$d_8$, 250 MHz, 20 °C): 11.7 ($CH_3$); 12.0 ($CH_3$); 16.8 ($CH_3$); 20.9 ($CH_2$); 36.9 ($CH_2$); 41.7 (NMe); 48.0 (NMe); 113.0; 113.9; 115.9; 117.3; 119.3; 120.8; 129.5; 143.9; 148.5 (aromatics). $^1$H NMR (benzene-$d_6$/THF-$d_8$ in ratio 90:10, 250 MHz, +20 °C): 1.19 (t, 7.4 Hz, 3H, ethyl-Me); 1.42 (d, 10.5 Hz, 1H, benzyl-$CH_2$); 2.16 (s, 6H, Cp-Me); 2.21 (s, 6H, Cp-Me); 2.44 (s, 6H, $NMe_2$); 2.61 (q, 7.3 Hz, 2H, ethyl-$CH_2$); 6.06 (m, 1H, aromatic); 6.52 (d, 7.3 Hz, 1H, aromatic); 6.50 (m, 2H, aromatic).

**Crystal Structure Data for {(Me$_3$Si-fluorenyl)[*o*-(dimethylamino)benzyl]Ca}$_2$·[C$_6$H$_6$] (6).** Yellow-orange blocks, monoclinic, $a = 10.958(3)$ Å, $b = 38.755(6)$ Å, $c = 11.620(4)$ Å, $\beta = 95.42(1)°$, $V = 4913(2)$ Å$^3$, space group $P2_1/n$; formula ($C_{50}H_{58}Ca_2N_2Si_2$)·($C_6H_6$), $M = 901.43$, $Z = 4$, $\rho_{calcd} = 1.219$ g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 0.319 mm$^{-1}$; 9590 reflections were measured (Mo K$\alpha$ graphite monochromator, $T = -90$ °C), 9104 independent reflections ($R_{int} = 0.018$), 6407 observed reflections with $I > 2.0\sigma(I)$. Full matrix least-squares refinement on $F^2$ to $R_1 = 0.043$, $wR_2 = 0.109$ and $S = 1.07$ (814 parameters). Non-hydrogens were refined anisotropically. All hydrogens have been taken from the difference Fourier map and were refined isotropically.

**Crystal Structure Data for {(EtMe$_4$Cp)[*o*-(dimethylamino)benzyl]Ca}$_2$ (8).** Light yellow plates, monoclinic, $a = 21.159(2)$ Å, $b = 10.674(7)$ Å, $c = 16.790(2)$ Å, $\beta = 105.340(5)°$, $V = 3656.9(6)$ Å$^3$, space group $C2/c$; formula ($C_{40}H_{58}Ca_2N_2$), $M = 647.04$, $Z = 4$, $\rho_{calcd} = 1.175$ g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 0.341 mm$^{-1}$; 4511 reflections were measured (Mo K$\alpha$ graphite monochromator, $T = -90$ °C), 4396 independent reflections ($R_{int} = 0.013$), 3684 observed reflections with $I > 2.0\sigma(I)$. Full matrix least-squares refinement on $F^2$ to $R_1 = 0.037$, $wR_2 = 0.109$ and $S = 1.04$ (315 parameters). Non-hydrogens were refined anisotropically. All hydrogens have been taken from the difference Fourier map and were refined isotropically.

**Crystal Structure Data for {(EtMe$_4$Cp)[*o*-dimethylamino)benzyl]Ca}$_2$ (8).** Light yellow plates, monoclinic, $a = 21.159(2)$ Å, $b = 10.674(7)$ Å, $c = 16.790(2)$ Å, $\beta = 105.340(5)°$, $V = 3656.9(6)$ Å$^3$, space group $C2/c$; formula ($C_{40}H_{58}Ca_2N_2$), $M = 647.04$, $Z = 4$, $\rho_{calcd} = 1.175$ g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 0.341 mm$^{-1}$; 4511 reflections were measured (Mo K$\alpha$ graphite monochromator, $T = -90$ °C), 4396 independent reflections ($R_{int} = 0.013$), 3684 observed reflections with $I > 2.0\sigma(I)$. Full matrix least-squares refinement on $F^2$ to $R_1 = 0.037$, $wR_2 = 0.109$ and $S = 1.04$ (315 parameters). Non-hydrogens were refined anisotropically. All hydrogens have been taken from the difference Fourier map and were refined isotropically.

**Polymerization Experiments.** Polymerizations of styrene were performed in a thermostated 100 mL stainless steel reactor at normal pressure and a temperature of 20 °C. In a typical polymerization experiment the reactor was loaded with 100 mL of freshly distilled (from alox-perls) styrene (no solvent was used!). A solution of the initiator (0.1 mmol) dissolved in 1.0 mL of benzene was added via a port. The usual appearance of an orange-red color indicated that the polymerization started immediately. After a polymerization time of 10 min the mixture was quenched with oxygen-free methanol and the polymer was obtained by evaporation of all liquids (the temperature should be kept low). The polymers cannot be separated by methyl ethyl ketone extraction.

Polymer analyses were carried out by GPC and high-temperature $^1$H and $^{13}$C NMR (solvent: tetrachloroethane-$d_2$, $T$ = 100 °C). The tacticity of the polymer was checked by analyzing the $^{13}$C NMR signal for the $C_{ipso}$ phenyl ring carbon (*rrrr* = 145.5 ppm).

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**Supporting Information Available:** Atomic fractional coordinates, bond distances and angles, hydrogen atom positions, anisotropic thermal parameters, and ORTEP plots with numbering schemes for complexes **6** and **8**, $^1$H NMR spectra of the new compounds, and variable-temperature spectra are available free of charge via the Internet at http://pubs.acs.org.

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