Hypersilyl-Substituted Complexes of Group 1 and 2 Metals: Syntheses, Structures and Use in Styrene Polymerisation

Florian Feil[a] and Sjoerd Harder*[a]

In memory of Professor Ron Snaith

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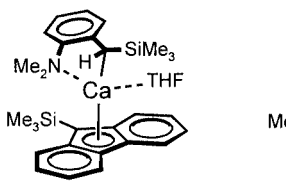
Alkali and alkaline-earth metal complexes with sterically demanding hypersilyl-substituted cyclopentadienyl or fluorenyl ligands [hSi-Cp or hSi-Flu; hSi = $(Me_3Si)_3Si$] were prepared. The crystal structures of $[Li(hSi\text{-}Flu)(THF)_2]$, [K(hSi-Flu)(THF)], $[Ca(hSi\text{-}Flu)_2(THF)_2]$, $[Sr(hSi\text{-}Flu)_2(THF)_2]$ and $[Ca(hSi\text{-}Cp)_2(THF)]$ were determined. All structures show the enormous steric bulk of the hypersilyl substituent, which either results in a reduction in the number of solvent molecules in the coordination sphere of the metal or in a distortion of the ligand-metal interaction. Heteroleptic calcium and strontium complexes with a benzyl ligand (2-Me_2N-α-Me_3Si-benzyl) and a sterically demanding hSi-Flu ligand were prepared and used as initiators in the polymerization of styrene. The polymers produced with the heteroleptic benzylcalcium initiator are enriched in syndiotactic sequences, although they show the same tacticities as polymers obtained with benzylcalcium initiators containing the less bulky Me_3Si-Flu ligand. Introduction of the bulky hypersilyl group in heteroleptic benzylstrontium initiators resulted in a slight increase of the syndiotacticity of the polymers.

Introduction

We recently introduced novel heteroleptic benzylcalcium complexes (e.g. **1**)[1] as initiators for the living anionic polymerization of styrene. The polymers obtained show a high degree of syndiotacticity.[2] Syndioselective chain growth arises from a chain-end controlled insertion mechanism (**2**) in which communication between the chiral chain-end and the chiral carbon of a coordinated styrene monomer is responsible for stereocontrol. The 9-Me_3Si-fluorenyl group in **1** is a spectator ligand, i.e. it fills one side of the coordination sphere around calcium and is passive during the polymerization. We are currently studying the influence of the spectator ligand on the syndioselectivity in styrene polymerization.

A highly sterically demanding spectator ligand, like 9-hypersilyl-fluorenyl [9-$(Me_3Si)_3Si$-fluorenyl), would confine the remaining coordination sphere around calcium and decrease the distance between the chiral centers in the polymerization active species **3**. This might lead to a more efficient communication between chain-end and monomer, thus improving stereocontrol.



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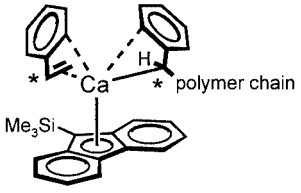

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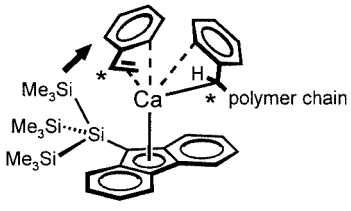

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Here we describe the syntheses and structures of hypersilyl-substituted fluorenyl and cyclopentadienyl complexes of alkali and alkaline-earth metals. Also, the syntheses and applications in styrene polymerization of heteroleptic benzylcalcium and -strontium complexes containing the hypersilyl-substituted ligands are described.

[a] University of Konstanz
Postfach 5560 (M738), 78457 Konstanz, Germany
Fax: (internat.) +49-7531/883-137
E-mail: harder@chemie.uni-konstanz.de
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Results and Discussion

Direct lithiation of 9-hypersilyl-fluorene (hSi-FluH) with *n*BuLi in THF gave the lithium complex 9-hypersilyl-fluorenyllithium Li(hSi-Flu) in quantitative yield. Recrystallization of the crude product yielded bright-red, plate-like crystals with the composition [Li(hSi-Flu)(THF)$_2$]. The monomeric lithium complex (Figure 1) contains a Li^+ ion with a nearly planar trigonal coordination sphere: the sum of the valence angles between O1, O2 and ring$_{center}$ is 357.2°. The Li^+ ion is bonded over the five-membered ring of the hSi-Flu ligand and, despite the steric bulk of the hypersilyl group, is situated slightly closer to the carbon attached to Si. This situation has also been observed in Me_3Si-fluorenyl complexes of the alkaline-earth metals[1,3] and is likely attributed to the higher charge-density at the silyl-substituted carbon. A space-filling model of Li(hSi-Flu) (Figure 1b) shows the extraordinary steric bulk of the hypersilyl substituent. This substituent is efficiently shielding a large part of the metal's coordination sphere, although no indication of agostic $SiCH_3\cdots Li^+$ interactions is found (the shortest C···Li distance observed is 3.975 Å).

The number of THF ligands attached to Li^+ is another measure of the steric bulk of the hSi-Flu anion. The *ansa*-lithocene anion $[Me_2Si(Flu)_2Li]^-$ also crystallizes with two THF ligands bonded to Li^+.[4] Likewise, a fluorenyllithium complex with a pendant chelating $CH_2CH_2NMe_2$ arm in the 9-position crystallizes with two THF ligands at the Li^+ ion.[5] Therefore, the steric demand of the hSi-Flu$^-$ ligand is similar to that of 9-$(Me_2NCH_2CH_2)$Flu$^-$ or to that of the dianionic *ansa*-ligand $Me_2Si(Flu)_2{}^{2-}$.

Reaction of 9-hypersilyl-fluorene with the superbase mixture *n*BuLi/KOCMe(Et)$_2$ yielded 9-hypersilyl-fluorenylpotassium K(hSi-Flu) in 85% isolated yield. Recrystallization of the raw product from a benzene/THF mixture gave orange needle-like crystals with the composition [K(hSi-Flu)(THF)(C_6H_6)]. The K(hSi-Flu) units form a polymer chain (Figure 2) in which the K^+ ions are sandwiched between the six-membered rings of neighbouring hSi-Flu anions. The large hypersilyl substituents of neighbouring hSi-Flu anions point in opposite directions. The THF ligands complete the planar trigonal coordination of the K^+ ions (the sum of the valence angles between O and the aryl ring centers is 359.4°). Vacant sites in the coordination sphere of K^+ are shielded by the bulk of the hypersilyl groups. Short $Si-CH_3\cdots K^+$ contacts (Figure 2) point to weak agostic interactions. The benzene solvent fills channels between the chains; there is no interaction between benzene and K^+. A similar chain structure was observed

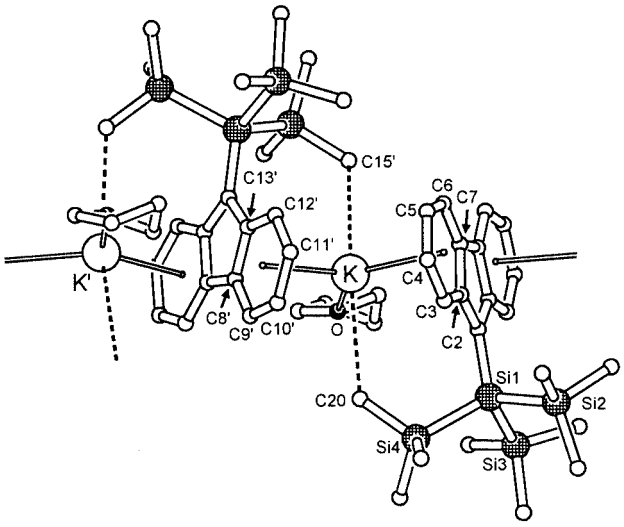


Figure 2. The crystal structure of {K(hSi-Flu)(THF)}$_\infty$ (hydrogens omitted for clarity); C−K bond lengths (Å) for atoms in the ring C2, C3, C4, C5, C6, C7 are respectively 3.053(4), 3.258(6), 3.391(8), 3.385(7), 3.210(6) and 3.015(4), ring$_{center}$−K = 2.903(3) Å; C−K bond lengths (Å) in the ring C8′, C9′, C10′, C11′, C12′, C13′ are respectively 3.114(4), 3.209(6), 3.240(7), 3.187(7), 3.117(6) and 3.072(4), ring$_{center}$−K 2.829(3) Å; O−K 1.919(4) Å; weak agostic $Si-CH_3\cdots K^+$ interactions: C15′···K 3.80(1) Å and C20···K 3.40(1) Å

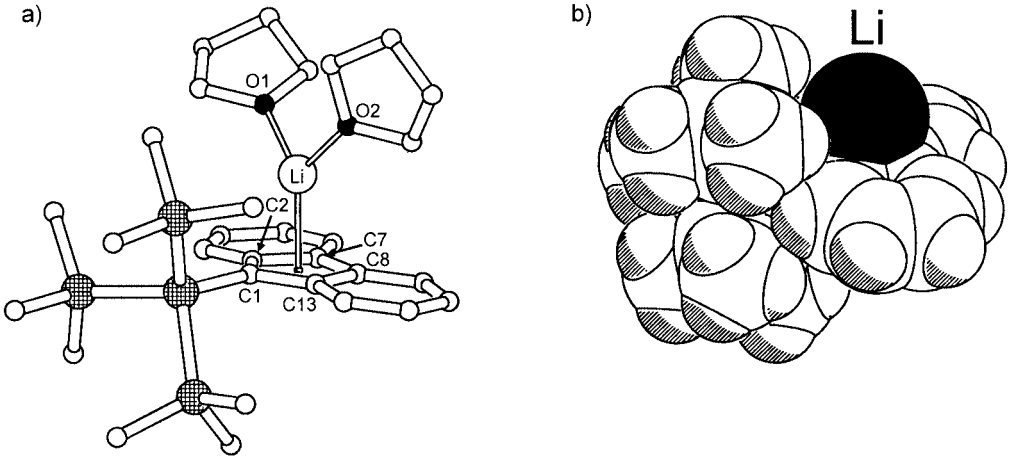


Figure 1. a) The crystal structure of [Li(hSi-Flu)(THF)$_2$] (hydrogens omitted for clarity); C−Li bond lengths (Å) for atoms in the ring C1, C2, C7, C8, C13 are respectively 2.321(5), 2.400(4), 2.486(4), 2.503(4) and 2.389(4), ring$_{center}$−Li 2.088(4) Å, O1−Li 1.919(4) Å and O2−Li 1.919(4) Å; b) space-filling model of the hSi-FluLi unit

for K(9-*t*Bu-Flu),[6] which crystallizes with two, instead of one, THF ligands coordinated to K^+, again showing the steric bulk of the hypersilyl substituent.

Reaction of two equivalents of K(hSi-Flu) with CaI_2 in THF gave bis[9-hypersilyl-fluorenyl]calcium, Ca(hSi-Flu)$_2$. Recrystallization of the crude product from hot benzene yielded red, needle-like crystals with the composition [Ca(hSi-Flu)$_2$(THF)$_2$(C_6H_6)]. The crystal structure of this monomeric calcium complex is shown in Figure 3. One of the hSi-Flu$^-$ ligands binds the Ca^{2+} ion in an η^5 fashion with Ca−C bond lengths in the narrow range of 2.722(4)−2.785(4) Å. The second hSi-Flu$^-$ ligand binds to Ca^{2+} only with the outer edge of the fluorenyl ring. This is a rather unusual and hitherto unseen bonding mode for a fluorenyl ligand in a non-polymeric coordination complex. The enormous bulk of the hypersilyl group apparently blocks η^5 coordination of a second hSi-Flu ligand. Also, the shallow potential energy surface of the fluorenyl anion allows easy migration of the metal cations.[7] The structure of [Ca(hSi-Flu)$_2$(THF)$_2$] can be interpreted as an intermediate on the pathway for formation of the solvent-separated ion-pair (ssip) [hSi-FluCa$^+$·(THF)$_3$] [hSi-Flu$^-$]. Structures of the first ssip's with calcium have been reported only recently: the structure of [Cp*Ca$^+$·(O=PPh$_3$)$_3$][I$^-$][8] and the structure of a complete ssip [Me_3Si-Flu$^-$]$_2$ [C_6H_6]$_2$ [Ca^{2+}·(THF)$_6$], which was described with the "metal-in-a-box" model.[9]

The analogous Sr complex, Sr(hSi-Flu)$_2$, was obtained by reacting two equivalents of hSi-FluK with SrI_2 in THF. Recrystallization from hot hexane yielded dark-red crystals with the composition [Sr(hSi-Flu)$_2$(THF)$_2$]. The crystal structure of [Sr(hSi-Flu)$_2$(THF)$_2$] (Figure 4) is similar to that of its Ca analogue. One of the hSi-Flu$^-$ ligands is coordinated through the five-membered ring, whereas the other ligand coordinates through the aryl part of the fluorenyl ring. Despite the larger radius of Sr^{2+} (Ca: 0.99 Å, Sr 1.12 Å), a second coordination through the five-membered ring is still not possible on the basis of steric congestion. However, the larger Sr^{2+} ion allows a more extended aryl-metal interaction than in the Ca complex.

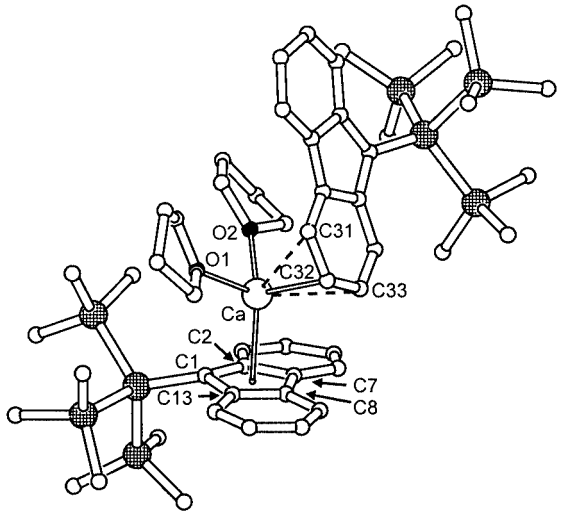


Figure 3. The crystal structure of [Ca(hSi-Flu)$_2$(THF)$_2$] (hydrogens omitted for clarity); C−Ca bond lengths (Å) for atoms in the ring C1, C2, C7, C8, C13 are respectively 2.748(4), 2.785(4), 2.766(4), 2.735(4) and 2.722(4), ring$_{center}$−Ca = 2.462(2) Å; Ca−O1 2.296(3), Ca−O2 2.376(4), Ca−C31 2.993(4), Ca−C32 2.662(4), Ca−C33 2.833(4)

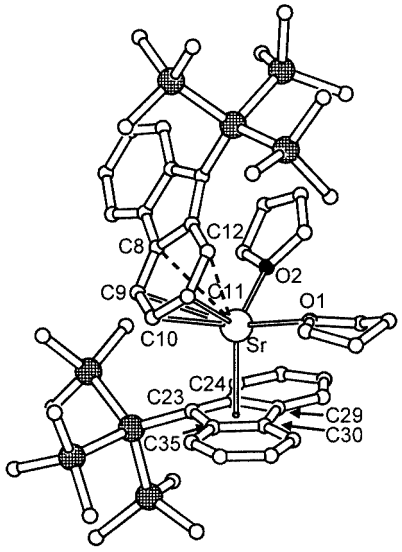


Figure 4. The crystal structure of [Sr(hSi-Flu)$_2$(THF)$_2$] (hydrogens omitted for clarity); C−Sr bond lengths (Å) for atoms in the ring C23, C24, C29, C30, C35 are respectively 2.913(3), 2.891(3), 2.852(3), 2.863(3) and 2.876(3), ring$_{center}$−Sr = 2.606(2) Å; Sr−C8 3.095(3), Sr−C9 2.927(4), Sr−C10 2.853(4), Sr−C11 2.929(4), Sr−C12 3.099(3), Sr−O1 2.466(3), Sr−O2 2.551(2)

The various crystal structures of alkali and alkaline-earth metal complexes with the hSi-Flu ligand show the enormous steric bulk of the hypersilyl substituent. The $(Me_3Si)_3Si$ substituents all display normal Si−Si and Si−C bond lengths, as well as expected tetrahedral Si−Si−Si, Si−Si−C and C−Si−C angles. This means that steric stress is relieved rather by deformation of the metal coordination sphere than by deformation of the hypersilyl substituent. It should be mentioned, however, that whereas the $(Me_3Si)_3Si$ geometry itself is practically undisturbed, the (Flu)C−Si bond is slightly elongated: bond lengths in the complexes reported here vary from 1.864(4) to 1.885(3) Å. In comparison, a typical (sp^2)C−Si bond length is tabulated as 1.84(1) Å[10] and the (Flu)C−Si bond length in **1** is 1.851(2) Å.[1] A similar situation was observed in the sterically congested $(Me_3Si)_3Si$-fluorene itself: the (Flu)C−Si bond of 1.947(4) Å[11] is significantly longer than an average (sp^3)C−Si bond [1.865(8) Å].[10] All structures reported here also show a similar rotation of the $(Me_3Si)_3Si$ substituent with respect to the fluorenyl plane: typically, one of the Me_3Si groups eclipses the plane of the fluorenyl ring, whereas the other two are in gauche positions. Especially noteworthy are the geometries of the (η^5)hSi-Flu ligands in the complexes [Ca(hSi-Flu)$_2$(THF)$_2$] and [Sr(hSi-Flu)$_2$(THF)$_2$]. The fluorenyl rings show deviations from planarity, with the aryl

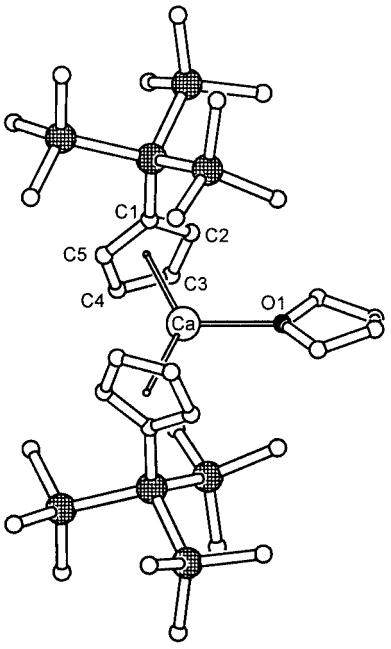


Figure 5. The crystal structure of [Ca(hSi-Cp)$_2$(THF)] (hydrogens omitted for clarity; crystallographic C_2 axis through Ca−O); C−Ca bond lengths (Å) for atoms in the ring C1, C2, C3, C4, C5 are respectively 2.667(3), 2.655(3), 2.657(3), 2.649(3) and 2.649(3), ring$_{center}$−Ca = 2.371(2) Å; Ca−O1 2.381(3)

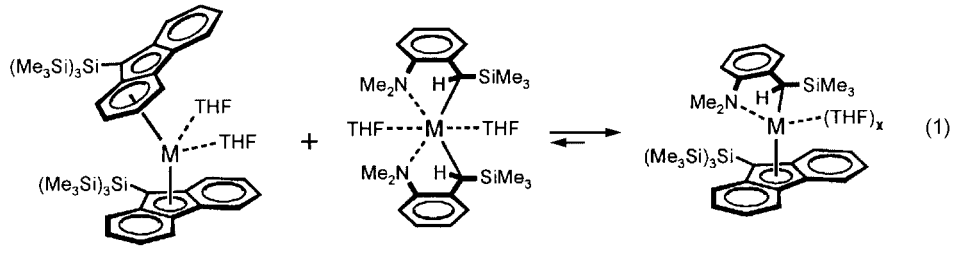
parts being slightly bent away from the metal. More importantly, the $(Me_3Si)_3Si$ substituents are bent out of the C_5 plane away from the metal [Ca: 16.1(2)° and 13.9(2)°; Sr: 20.2(2) and 10.3(2)°]. Out-of-plane bending of silyl substituents costs only half the energy of that of alkyl substituents[4] and maximizes the Coulomb attraction between Flu^- and M^{2+}.[12] We attribute these deviations also partly to steric stress between the hypersilyl substituent and the rest of the structure.

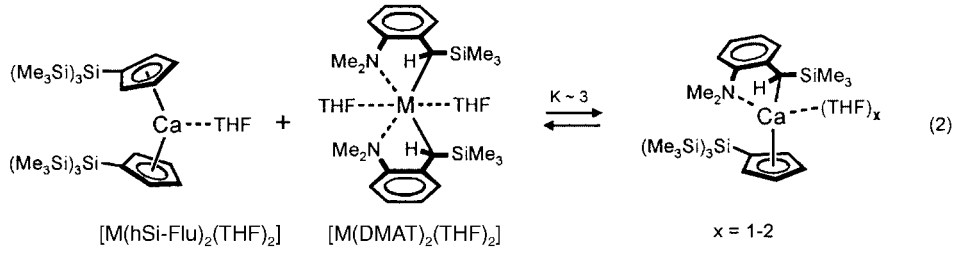
In order to evaluate the effect of a large hypersilyl substituent in a Cp ring, we also prepared Ca(hSi-Cp)$_2$ from K(hSi-Cp) and CaI_2. The compound crystallized from a hexane/THF mixture in the form of colourless plates with the composition [Ca(hSi-Cp)$_2$(THF)]. The crystal structure (Figure 5) shows a C_2-symmetric sandwich complex with a perfectly trigonal planar coordination at Ca.

The hSi-Cp ligands coordinate to the Ca^{2+} ion in an η^5 fashion with Ca−C bond lengths in the narrow range of 2.649(3) to 2.667(3) Å. Steric stress is avoided by the orientation of the two hypersilyl substituents in different directions rather than by a distortion of the Cp-Ca coordination. The two sterically demanding hSi-Cp ligands leave room for coordination of only one THF ligand [all other monosubstituted calcocenes, Ca(RCp)$_2$, possess two THF ligands]. The steric bulk of the hSi-Cp ligand can be compared to that of 1,3-$(Me_3Si)_2$Cp or *i*Pr$(Me)_4$Cp, which both form calcocenes with only one THF ligand.[13,14]

The heteroleptic alkaline-earth metal complexes containing the hypersilyl-substituted ligands are of particular interest as initiators in stereoselective styrene polymerization.[1] These initiators were prepared by mixing the homoleptic bis-fluorenyl and bis-cyclopentadienyl complexes of Ca (or Sr) with a polymerization-active homoleptic dibenzylcalcium (or strontium) complex.

Reaction of [Ca(hSi-Flu)$_2$(THF)$_2$] with [Ca(DMAT)$_2$(THF)$_2$] in C_6D_6 [Equation (1)] resulted in the quantitative formation of the heteroleptic calcium complex [Ca(DMAT)(hSi-Flu)(THF)$_x$] with x = 1 or 2. The heteroleptic nature of the newly formed complex is clear from NOE's observed between protons of the hSi-Flu ligand and protons of the DMAT ligand. Low temperature NMR spectra (0 °C) of the heteroleptic complex show unique signals for all fluorenyl protons, which are diastereotopic due to the chirality of the benzylic carbon [$\Delta G^{\ddagger}$(20 °C) = 15.3 kcal





mol^{-1}]. Fast exchange proceeds either by inversion of the chiral benzyl carbon or by a dissociation/association process of the hSi-Flu$^-$ ligand. It is unclear how many THF molecules coordinate at the Ca^{2+} ion. Evaporation of the solvent and drying of the complex under vacuum (0.01 Torr) at 60 °C yielded the complex [Ca(DMAT)(hSi-Flu)(THF)]. The NMR spectra of [Ca(DMAT)(hSi-Flu)(THF)] redissolved in C_6D_6 also display signals originating from small amounts of the homoleptic precursors ($K \approx 20$). This means that the Schlenk equilibrium is dependent on the Ca/THF ratio.

Reaction of the homoleptic complexes [Ca(hSi-Cp)$_2$(THF)] and [Ca(DMAT)$_2$(THF)$_2$] in C_6D_6 [Equation (2)] resulted in a mixture of both a homoleptic and a heteroleptic calcium complex ($K \approx 3$). In this case no strong preference for the formation of the heteroleptic complex was found. The use of fluorenyl ligands seems therefore to be essential in directing the Schlenk equilibrium to the heteroleptic side. This might originate from the steric stress observed in the crystal structure of homoleptic [Ca(hSi-Flu)$_2$(THF)$_2$], making this particular homoleptic species energetically unfavourable. Steric stress is less severe in homoleptic [Ca(hSi-Cp)$_2$(THF)]: the Cp-Ca coordination observed for both hSi-Cp ligands is not distorted from an ideal η^5 geometry.

Reaction of the homoleptic complexes [Sr(hSi-Flu)$_2$(THF)$_2$] and [Sr(DMAT)$_2$(THF)$_2$] in C_6D_6 [Equation (1)] resulted in the formation of the heteroleptic strontium complex as the major product. Only traces of the homoleptic compounds were detected ($K \approx 800$). Evaporation of the solvent and drying of the complex under vacuum (0.01 Torr) at 60 °C yielded the complex [Sr(hSi-Flu)(DMAT)(THF)]. The Schlenk equilibrium for this compound dissolved in C_6D_6 is similar as above ($K \approx 800$). The heteroleptic complex shows NOE's between the two different ligands. Also, at lower temperatures diastereotopic fluorenyl signals were observed [$\Delta G^{\ddagger}$(5 °C) = 14.2 kcal mol^{-1}].

Styrene polymerizations with a mixture of [Ca(hSi-Flu)$_2$(THF)$_2$] and [Ca(DMAT)$_2$(THF)$_2$], i.e. with the pure heteroleptic compound, were carried out. ^{13}C NMR analyses of the polymers obtained show that there is no significant improvement in the syndiotacticity when compared with polymers obtained by polymerization with **1** (r = 92%, rr = 85%).[2] However, it was found that, under the same reaction conditions, the chain lengths of the polymers obtained with the more bulky hypersilyl-substituted initiator are only 10% of those of polymers obtained with initiator **1**. Apparently, the chain-growth step for the hypersilyl-substituted species **3** is significantly slower than that for the less bulky active species **2**. It should be mentioned that a discussion on the relation of polymer tacticity and spectator ligand is hampered by the possible existence of small quantities of homoleptic polymerylcalcium species which might influence the overall stereoselectivity of monomer insertion.

Styrene polymerization with a mixture of [Sr(hSi-Flu)$_2$(THF)$_2$] and [Sr(DMAT)$_2$(THF)$_2$], i.e. with a predominantly heteroleptic compound, were carried out. ^{13}C NMR analyses of the polymers obtained show that there is a slight improvement in syndiotacticity when compared with polymers obtained by polymerization with a mixture of [Sr(Me$_3$Si-Flu)$_2$(THF)] and [Sr(DMAT)$_2$(THF)$_2$].[15] The syndiotacticity of the polymers is, however, lower than that of polymers obtained with analogous Ca initiators and no estimation of r and rr J-ades could be made. The use of the bulky hSi-Flu ligand in Sr initiators also resulted in short chain lengths, indicative of a sluggish chain growth.

Conclusion

Homoleptic hypersilyl-substituted cyclopentadienyl and fluorenyl complexes of alkali and alkaline-earth metals are readily accessible in crystalline purity. All crystal structures of these compounds show the enormous bulk of the hypersilyl substituent, which either limits the number of THF ligands coordinated at the metal center or distorts the metal-anion coordination geometry. The homoleptic [M(hSi-Flu)$_2$(THF)$_2$] complexes of Ca and Sr, both show structures in which one of the hSi-Flu$^-$ ligands is only weakly bound through the edge of the aryl ring. These compounds are intermediates on the reaction path to the solvent-separated ion-pair [hSi-FluM$^+$(THF)$_3$] [hSi-Flu$^-$].

Heteroleptic benzylcalcium and -strontium complexes with hSi-Flu spectator ligands were generated by ligand exchange between the homoleptic compounds. The Schlenk equilibrium for the fluorenyl complexes lies largely towards the heteroleptic side. Exchange of the fluorenyl group for a cyclopentadienyl group resulted in mixtures of homo- and heteroleptic complexes.

Styrene polymerization with benzylcalcium initiators containing the sterically demanding hSi-Flu spectator ligand gave predominantly syndiotactic polymers (r = 92%, rr = 85%). However, no improvement was observed in comparison with polymers obtained with **1**, i.e. with Me$_3$Si-Flu as a spectator ligand. Only in the case of benzylstrontium initiators containing the hSi-Flu spectator ligand was a slight improvement in the syndiotacticity of the obtained polymer observed. In all cases the large hypersilyl substituent retarded the chain growth step.

Experimental Section

General Remarks: All experiments were carried out under argon using dry solvents and Schlenk techniques. The following compounds were prepared according to literature procedures: 9-tris(trimethylsilyl)silylfluorene,[11] bis(2-dimethylamino-α-Me$_3$Si-benzyl)-bis(tetrahydrofuran)calcium[16] and bis(2-dimethylamino-α-Me$_3$Si-benzyl)bis(tetrahydrofuran)strontium.[17] NMR spectra were recorded on Bruker AC250 (250 MHz) and Bruker DRX600 (600 MHz) machines.

Polymerizations of styrene were performed in a thermostatted 100 mL stainless-steel reactor at normal pressure. Polymerizations were either carried out in a 1 M styrene solution (90 mL cyclohexane and 11.5 mL styrene at 50 °C) or in pure styrene (at 20 °C).

Styrene was freshly distilled from CaH_2 and kept over dry aloxperls. A solution of the initiator (0.1 mmol of active benzyl anion) in 1.0 mL of benzene/cyclohexane was added via a port. After a polymerization time of 30 minutes the mixture was quenched with oxygen-free methanol. The tacticity of the polymer was checked by analyzing the ^{13}C NMR signal (solvent: [D_2]tetrachloroethane) for the C_{ipso} phenyl ring carbon.[2]

[Li(hSi-Flu)(THF)$_2$]: *n*-Butyllithium (1.6 M in hexane, 1.06 mL, 1.70 mmol) was added dropwise to a solution of 9-tris(trimethylsilyl)silylfluorene (0.70 g, 1.70 mmol) in 10 mL of THF at −68 °C. The solution was stirred at this temperature for 1 h and slowly turned orange. Thereafter the solution was warmed slowly to room temperature, and the solvents were removed. The sticky orange product was washed with 10 mL of hexane and dissolved in a mixture of warm benzene (10 mL) and THF (2 mL). Cooling to room temperature overnight afforded bright-red, plate-like crystals of the title compound (98%, 0.94 g). ^1H NMR (250 MHz, [D_6]benzene): δ = 0.48 [s, 27 H, $(Me_3Si)_3Si$], 1.03 (m, 8 H, THF), 2.67 (m, 8 H, THF), 7.07 (dd, *J* = 7.2 Hz, 2 H, fluorenyl), 7.39 (dd, *J* = 7.5 Hz, 2 H, fluorenyl), 8.12 (d, *J* = 8.3 Hz, 2 H, fluorenyl), 8.28 (d, *J* = 7.8 Hz, 2 H, fluorenyl) ppm. $^{13}C\{^1H\}$ NMR ([D_8]THF): δ = 4.0 [$(Me_3Si)_3Si$], 25.2 (THF), 67.4 (THF), 87.2 (fluorenyl), 114.4 (fluorenyl), 119.9 (fluorenyl), 121.2 (fluorenyl), 122.2 (fluorenyl), 124.4 (fluorenyl), 141.7 (fluorenyl) ppm.

[K(hSi-Flu)(THF)]: *n*-Butyllithium (1.6 M in hexane, 2.27 mL, 3.63 mmol) was added dropwise to a mixture of 9-tris(trimethylsilyl)silylfluorene (1.50 g, 3.63 mmol) and potassium 3-methyl-3-pentanolate in 30 mL of THF at −68 °C. The solution was stirred at this temperature for about one hour and slowly turned red. Thereafter the solution was warmed slowly to room temperature and the solvents were removed. The orange residue was washed five times with 10 mL portions of hexane and was dissolved in a mixture of warm benzene (10 mL) and THF (2 mL). Cooling to 20 °C overnight yielded orange-red needles of a benzene solvate of the title compound (85%, 1.85 g) which can be freed from THF and benzene under vacuum. ^1H NMR (250 MHz, [D_6]benzene/[D_8]THF 10:1): δ = 0.44 [s, 27 H, $(Me_3Si)_3Si$], 1.43 (m, 4 H, THF), 3.56 (m, 4 H, THF), 6.90 (dd, *J* = 7.6 Hz, 2 H, fluorenyl), 7.28 (dd, *J* = 7.1 Hz, 2 H, fluorenyl), 7.64 (d, *J* = 8.3 Hz, 2 H, fluorenyl), 8.19 (d, *J* = 7.7 Hz, 2 H, fluorenyl) ppm. $^{13}C\{^1H\}$ NMR ([D_8]THF): δ = 3.6 [$(Me_3Si)_3Si$], 25.8 (THF), 67.8 (THF), 83.0 (fluorenyl), 111.1 (fluorenyl), 119.0 (fluorenyl), 120.2 (fluorenyl), 120.3 (fluorenyl), 125.9 (fluorenyl), 144.0 (fluorenyl) ppm.

[Ca(hSi-Flu)$_2$(THF)$_2$]: A mixture of THF-free K(hSi-Flu)$_2$ (0.80 g, 1.77 mmol) and CaI_2 (0.27 g, 0.92 mmol) in 20 mL of THF was stirred for two days at room temperature. The THF solvent was then evaporated and the remaining residue was extracted with two 10 mL portions of dry benzene. Evaporation of the solvent from these combined extracts resulted in a red solid, which was crystallized from 12 mL of warm hexane. Cooling to 4 °C yielded red needles of a benzene solvate of the title compound in 49% yield (0.47 g). ^1H NMR (250 MHz, [D_6]benzene): δ = 0.37 [s, 54 H, $(Me_3Si)_3Si$], 1.01 (m, 8 H, THF), 2.77 (m, 8 H, THF), 6.80 (dd, *J* = 7.2 Hz, 4 H, fluorenyl), 7.10 (dd, *J* = 7.6 Hz, 4 H, fluorenyl), 7.86 (dd, *J* = 7.1 Hz, 8 H, fluorenyl) ppm. $^{13}C\{^1H\}$ NMR ([D_8]THF): δ = 3.3 [$(Me_3Si)_3Si$], 26.1 (THF), 70.4 (THF), 83.1 (fluorenyl), 113.5 (fluorenyl), 120.7 (fluorenyl), 121.9 (fluorenyl), 122.6 (fluorenyl), 124.6 (fluorenyl), 142.8 (fluorenyl) ppm.

[Sr(hSi-Flu)$_2$(THF)$_2$]: A mixture of THF-free K(hSi-Flu)$_2$ (1.50 g, 3.33 mmol) and SrI_2 (0.58 g, 1.70 mmol) in 20 mL of THF was stirred for three days at room temperature. The THF solvent was evaporated and the remaining residue was extracted with two 10 mL portions of dry benzene. Evaporation of the solvent from these combined extracts resulted in a red solid, which was crystallized from 30 mL of warm hexane. Cooling to 20 °C yielded dark-red blocks of the title compound in 72% yield (1.27 g). ^1H NMR (250 MHz, [D_6]benzene): δ = 0.40 [s, 54 H, $(Me_3Si)_3Si$], 1.05 (m, 8 H, THF), 2.62 (m, 8 H, THF), 6.82 (dd, *J* = 7.2 Hz, 4 H, fluorenyl), 7.18 (dd, *J* = 7.5 Hz, 4 H, fluorenyl), 7.83 (d, *J* = 7.6 Hz, 4 H, fluorenyl), 7.91 (d, *J* = 8.3 Hz, 4 H, fluorenyl) ppm. $^{13}C\{^1H\}$ NMR ([D_8]THF): δ = 3.6 [$(Me_3Si)_3Si$], 25.1 (THF), 68.4 (THF), 80.5 (fluorenyl), 112.9 (fluorenyl), 120.5 (fluorenyl), 121.6 (fluorenyl), 122.1 (fluorenyl), 126.0 (fluorenyl), 143.2 (fluorenyl) ppm.

[K(hSi-Cp)(THF)]: A solution of tris(trimethylsilyl)silyl chloride (1.00 g, 3.55 mmol) and cyclopentadienylsodium (0.30 g, 3.40 mmol) in 15 mL of THF was stirred for 16 hours at room temperature. The THF solvent was evaporated and the remaining residue was extracted with two 10 mL portions of dry diethyl ether. Potassium bis(trimethylsilyl)amide (0.60 g, 3.00 mmol) dissolved in 15 mL of THF was added to the combined ether extracts of [tris(trimethylsilyl)silyl]cyclopentadiene and the resulting solution was stirred for 15 hours at room temperature. The solvent was evaporated and the remaining white residue was crystallized from 30 mL of hot THF. Cooling to −30 °C yielded crystalline [K(hSi-Cp)(THF)] in the form of white needles (98%, 1.25 g, 2.95 mmol) which can be freed from THF under vacuum. ^1H NMR (250 MHz, [D_8]THF): δ = 0.17 [s, 27 H, $(Me_3Si)_3Si$], 1.78 (m, 4 H, THF), 3.63 (m, 4 H, THF), 5.88 (dd, *J* = 1.9 Hz, 2 H, Cp), 5.89 (dd, *J* = 1.9 Hz, 2 H, Cp) ppm. $^{13}C\{^1H\}$ NMR ([D_8]THF): δ = 2.0 [$(Me_3Si)_3Si$], 25.3 (THF), 67.4 (THF), 98.8 (Cp), 109.0 (Cp), 116.6 (Cp) ppm.

[Ca(hSi-Cp)$_2$(THF)]: A mixture of THF-free K(hSi-Cp) (0.70 g, 2.00 mmol) and CaI_2 (0.30 g, 1.02 mmol) in 50 mL of THF was stirred for two days at room temperature. The THF solvent was evaporated and the remaining residue was extracted with two 20 mL portions of dry benzene. Evaporation of the solvent from these combined extracts resulted in a white solid, which was crystallized from a mixture of warm toluene (10 mL) and THF (1 mL). Cooling to −80 °C yielded colourless crystals of [Ca(hSi-Cp)$_2$(THF)] in 60% yield (0.44 g). ^1H NMR (250 MHz, [D_6]benzene/[D_8]THF 10:1): δ = 0.36 [s, 54 H, $(Me_3Si)_3Si$, 1.43 (m, 4 H, THF), 3.56 (m, 4 H, THF), 6.20 (dd, *J* = 2.3 Hz, 4 H, Cp), 6.39 (dd, *J* = 2.3 Hz, 4 H, Cp) ppm. $^{13}C\{^1H\}$ NMR ([D_8]THF): δ = 1.9 [$(Me_3Si)_3Si$], 25.8 (THF), 67.8 (THF), 104.8 (Cp), 111.0 (Cp), 120.1 (Cp) ppm.

[Ca(DMAT)(hSi-Flu)(THF)$_x$]: [Ca(DMAT)$_2$(THF)$_2$] (7.1 mg, 12 μmol) and [Ca(hSi-Flu)$_2$(THF)$_2$] (12 mg, 12 μmol) were mixed in an NMR tube and dissolved in [D_6]benzene (0.5 mL). Heating to 60 °C immediately resulted in the quantitative formation of [Ca(DMAT)(hSi-Flu)(THF)$_x$] (*x* = 1 or 2). Evaporation of the solvent and drying under vacuum yielded the complex [Ca(DMAT)(hSi-Flu)(THF)]. Upon redissolving this complex in [D_6]benzene the constant of the Schlenk equilibrium is approximately 20. NMR spectra before and after removal of one equivalent of THF are similar and show maximum chemical shift differences of 0.02 ppm. ^1H NMR (600 MHz, [D_6]benzene): δ = 0.34 [s, 27 H, $(Me_3Si)_3Si$], 0.42 (s, 9 H, Me_3Si-benzyl), 0.74 [s, 1 H, $CH(SiMe_3)$], 1.06 (m, 4 H, THF), 1.93 (s, 3 H, Me_2N), 2.04 (s, 3 H, Me_2N), 2.71 (m, 4 H, THF), 6.14 (dd, *J* = 7.0 Hz, 1 H, benzyl), 6.31 (d, *J* = 7.8 Hz, 1 H, benzyl), 6.63 (dd, *J* = 7.3 Hz, 1 H, benzyl), 6.85 (d, *J* = 7.9 Hz, 1 H, benzyl), 6.99 (dd, *J* = 8.3 Hz, 1 H, fluorenyl), 7.02 (dd, *J* = 8.3 Hz, 1 H, fluorenyl), 7.27 (dd, *J* = 7.1 Hz, 1 H, fluorenyl), 7.30

Table 1. Crystal data

Compound	[Li(hSi-Flu)(THF)$_2$]	[K(hSi-Flu)(THF)]	[Ca(hSi-Flu)$_2$(THF)$_2$]	[Sr(hSi-Flu)$_2$(THF)$_2$]	[Ca(hSi-Cp)$_2$(THF)]
Formula	$C_{30}H_{51}LiO_2Si_4$	$C_{32}H_{49}KOSi_4$	$C_{58}H_{92}CaOSi_8$	$C_{52}H_{86}SrO_2Si_8$	$C_{32}H_{70}CaOSi_8$
Weight	563.01	601.17	1086.12	1055.55	735.68
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$C2/c$
a (Å)	11.4724(15)	14.407(2)	9.860(6)	9.7034(15)	14.648(3)
b (Å)	16.5382(14)	13.1977(10)	17.554(6)	31.200(4)	10.2742(16)
c (Å)	19.716(2)	22.810(5)	20.475(12)	20.391(3)	30.436(5)
α (°)	90	90	67.02(5)	90	90
β (°)	113.277(7)	124.26(1)	84.59(4)	108.42(1)	93.11(2)
γ (°)	90	90	83.90(4)	90	90
V (Å^3)	3437.6(7)	3584(1)	3239(3)	5857(1)	4574(1)
Z	4	4	2	4	4
μ(MoKa) (mm^{-1})	0.196	0.304	0.282	1.120	0.369
Crystal size	0.5 × 0.4 × 0.4	0.6 × 0.2 × 0.2	0.5 × 0.4 × 0.3	0.5 × 0.5 × 0.5	0.5 × 0.4 × 0.2
T (°C)	−90	−90	−90	−90	−90
θ max (°)	26.0	25.0	25.0	26.0	25.0
Data(total)	7077	6617	12048	11871	4208
Data(unique), R_{int}	6728, 0.016	6347, 0.041	11324, 0.039	11534, 0.029	4036, 0.039
Data[$I > 2\sigma(I)$]	4695	3825	6560	9404	3121
R1	0.039	0.077	0.054	0.037	0.043
$wR2$	0.103	0.234	0.137	0.136	0.132
GOF	1.02	1.03	1.00	1.05	1.04
ρ−/ρ+ (e.A^{-3})	−0.35/+0.36	−0.50/+0.65	−0.32/+0.46	−0.57/+0.79	−0.32/+0.40
Abs. corr.	−	−	−	psi scan	−
$T_{min.}/T_{max.}$	−	−	−	0.90/0.97	−

(dd, J = 7.6 Hz, 1 H, fluorenyl), 8.00 (d, J = 8.0 Hz, 1 H, fluorenyl), 8.04 (d, J = 7.7 Hz, 1 H, fluorenyl), 8.21 (d, J = 7.5 Hz, 1 H, fluorenyl), 8.21 (d, J = 7.5 Hz, 1 H, fluorenyl) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]benzene): δ = 2.6 (Me$_3$Si-benzyl), 3.5 [(Me$_3$Si)$_3$Si-fluorenyl], 24.9 (THF), 41.9 (Me$_2$N), 45.0 (Me$_2$N), 47.6 [CH(Me$_3$Si)], 68.9 (THF), aromatics: 81.6, 113.3, 115.0, 115.7, 119.4, 121.6, 121.9, 122.2, 122.3, 123.4, 123.9, 124.9, 125.5, 126.5, 128.2, 135.2, 142.3, 143.4 147.4 ppm.

[Sr(DMAT)(hSi-Flu)(THF)$_x$]: [Sr(DMAT)$_2$(THF)$_2$] (10.5 mg, 16 μmol) and [Sr(hSi-Flu)$_2$(THF)$_2$] (16 mg, 16 μmol) were mixed in an NMR tube and dissolved in [D$_6$]benzene (0.5 mL). Heating to 60 °C immediately resulted in the formation of the heteroleptic strontium complex as the major product. Only traces of the homoleptic starting materials were detected (Schlenk equilibrium $K \approx$ 800). Evaporation of the solvent and drying under vacuum yielded the complex [Sr(DMAT)(hSi-Flu)(THF)]. NMR spectra and the constant of the Schlenk equilibrium of this compound are similar as with two equivalents of THF. ^1H NMR (600 MHz, [D$_6$]benzene): δ = 0.39 [s, 27 H, (Me$_3$Si)$_3$Si], 0.44 (s, 9 H, Me$_3$Si-benzyl), 0.76 [s, 1 H, CH(SiMe$_3$)], 1.18 (m, 4 H, THF), 2.05 (s, 3 H, Me$_2$N), 2.15 (s, 3 H, Me$_2$N), 3.00 (m, 4 H, THF), 6.10 (dd, J = 7.2 Hz, 1 H, benzyl), 6.36 (d, J = 7.8 Hz, 1 H, benzyl), 6.67 (dd, J = 7.3 Hz, 1 H, benzyl), 6.91 (d, J = 8.0 Hz, 1 H, benzyl), 7.02 (t, broad, 2 H, fluorenyl), 7.34 (t, broad, 2 H, fluorenyl), 8.04 (d, J = 6.9 Hz, 2 H, fluorenyl), 8.15 (d, broad, 2 H, fluorenyl) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]benzene): δ = 2.8 (Me$_3$Si-benzyl), 3.6 [(Me$_3$Si)$_3$Si-fluorenyl], 25.2 (THF), 41.8 (Me$_2$N), 43.7 (Me$_2$N), 50.2 [CH(Me$_3$Si)], 68.2 (THF), aromatics: 85.2, 111.2, 113.8, 120.0, 120.8, 121.6, 122.4, 123.5, 126.3 128.3, 134.3, 143.4, 147.3 ppm.

X-ray Crystallographic Studies: Crystals protected with a layer of dry paraffin oil were mounted in the cold nitrogen stream (−90 °C) on an Enraf−Nonius CAD4 diffractometer. Structures were solved with SHELXL-97[18] and the PLATON program package[19] (the latter was also used for geometrical calculations and illustrations). All crystal data are summarized in Table 1. CCDC entries 205469−205473 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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