

# α-Methyl-benzylcalcium complexes: syntheses, structures and reactivity

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## Abstract

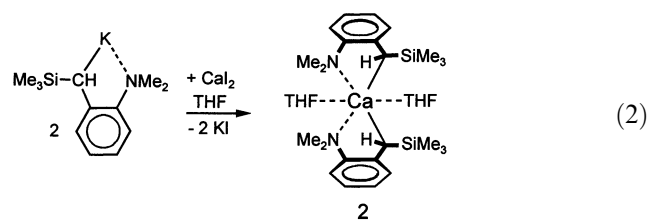
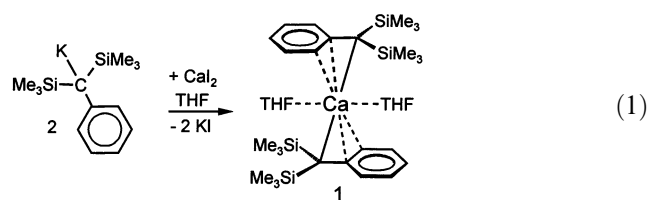
α-Methyl-benzylcalcium complexes were prepared analogue to α-Me<sub>3</sub>Si-benzylcalcium complexes for which procedures were reported earlier. The crystal structures of homoleptic bis(2-Me<sub>2</sub>N-α-Me-benzyl)calcium·(THF)<sub>2</sub> and heteroleptic (9-Me<sub>3</sub>Si-fluorenyl)(2-Me<sub>2</sub>N-α-Me-benzyl)calcium·(THF) were determined. For both compounds only one of the two diastereomers crystallized. Barriers for inversion of the chiral benzylic carbon were estimated by variable temperature NMR spectroscopy. The α-methyl-benzylcalcium compounds are less stable and show a higher reactivity and faster initiation of styrene polymerization than the analogue α-Me<sub>3</sub>Si-benzylcalcium complexes. Intramolecular C–H activation in a heteroleptic α-methyl-benzylcalcium complex was observed and the product, a calcium complex with a dianionic alkyl/fluorenyl *ansa*-ligand, was characterized by crystal structure determination.

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**Keywords:** Calcium; Carbanion; Polystyrene; C–H activation

## 1. Introduction

We recently introduced the first well-defined homoleptic dibenzylcalcium complexes **1** [1] and **2** [2]. These complexes were prepared by metal exchange between a benzylpotassium precursor and CaI<sub>2</sub> (Eqs. (1) and (2)). Both dibenzylcalcium complexes possess Me<sub>3</sub>Si-substituents in α-position. These α-Me<sub>3</sub>Si-substituents stabilize the carbanion by (i) negative hyperconjugation and (ii) steric shielding of the reactive center. Steric shielding has the concomitant effect of solubilizing the dibenzylcalcium complex, which enables its separation from the byproduct KI. Stabilization of carbanions by Me<sub>3</sub>Si-substituents is a well-known approach, which has been quite successful in the isolation of a wide range of previously inaccessible compounds [3].



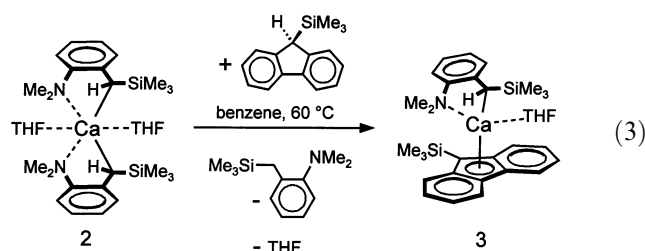
The advantage of stabilization by silyl-substitution is the easier handling of the complexes (the compounds are less air-sensitive). The disadvantage, however, is decreased reactivity and therefore limitation of their scope in reactions. The benzylcalcium complex **1** is extensively stabilized with two α-Me<sub>3</sub>Si-substituents and is not sufficiently nucleophilic and too sterically hindered for use as an initiator in styrene polymerization. On the other hand, complex **2** possesses only one α-Me<sub>3</sub>Si-

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substituent and has been successfully used in the living anionic polymerization of styrene [2]. It was observed, however, that the initiation of the polymerization reaction is slower than chain propagation: the polymers obtained display a typical tailing in the lower range of the molecular weight distribution [4].

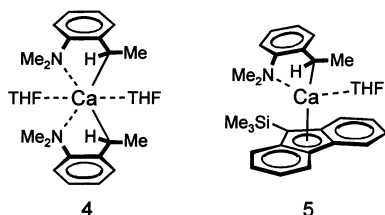
The dibenzylcalcium complex **2** is a precursor for a range of heteroleptic benzylcalcium initiators (e.g. Eq. (3)). Complex **3** is isolobal to  $\text{CpTiMe}^+$  (the proposed catalytical active species in the syndioselective styrene polymerization [5]) and was recently introduced as an initiator for a living and syndioselective styrene polymerization [6]. Stabilization of **3** by the benzylic  $\text{Me}_3\text{Si}$ -substituent likewise results in a sluggish initiation of styrene polymerization.



Although a slow initiation step does not disturb the living nature or the syndioselectivity of the polymerization reaction, it can be a nuisance in the syntheses of well-defined block-copolymers. It is therefore one of our goals to prepare more reactive unstabilized benzylcalcium initiators. We here describe the syntheses, structures and reactivities of  $\alpha$ -alkylated benzylcalcium complexes.

## 2. Results and discussion

The syntheses of bis(2-dimethylamino- $\alpha$ -methyl-benzyl)calcium (**4**) proceeds analogue to that of **2** (Eq. (2)). Whereas **2** can be isolated as a raw product in essentially quantitative yield, the poor solubility of **4** only enables the isolation of the raw product in a yield of 55%. Crystallization of the raw product yields **4** in the form of extremely air-sensitive yellow–orange crystals.



The crystal structure of **4** shows a monomeric complex comparable to that of **2**. The  $\text{Ca}^{2+}$  ion is bonded to two (C,N)-bidentate benzyl anions and two THF ligands (Fig. 1). Only the diastereomer with *R*, *S*-configuration at the benzylic carbons crystallizes. The

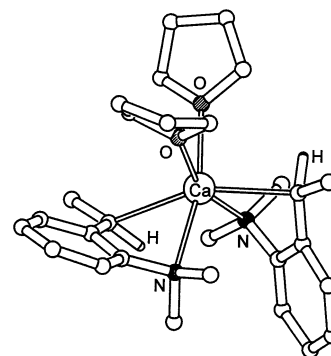


Fig. 1. Graphical abstract of the crystal structure of bis(2-dimethylamino- $\alpha$ -methyl-benzyl)calcium (**4**). All hydrogens have been omitted for clarity (except for the hydrogens at the benzylic carbons which were observed in the difference Fourier map).

coordination sphere around calcium is a distorted octahedron with the carbanions in *trans* position and the four neutral coordinating groups in one plane. Due to twinning problems the structure could not be refined satisfactory and therefore bond distances and angles are not discussed.

The  $^1\text{H-NMR}$  spectrum of the dibenzylcalcium complex **4** (toluene- $d_8$ ) at low temperature consists of two sets of signals for the two possible diastereomers. The ratio of circa 1/1 does not change with temperature or concentration. Fast exchange between the diastereomers is reached at higher temperature:  $\Delta G^\ddagger(30^\circ\text{C}) = 16.0(1) \text{ kcal mol}^{-1}$ .

The  $\alpha$ -methyl-benzylcalcium complex **4** is, as expected, much more reactive than its  $\alpha$ - $\text{Me}_3\text{Si}$ -analogue (**2**). Complex **2** reacts with  $\text{Me}_3\text{Si}$ -fluorene only at elevated temperatures (Eq. (3)). The heteroleptic product **3** does not react with excess  $\text{Me}_3\text{Si}$ -fluorene. On the other hand, **4** reacts with  $\text{Me}_3\text{Si}$ -fluorene to **5** already at

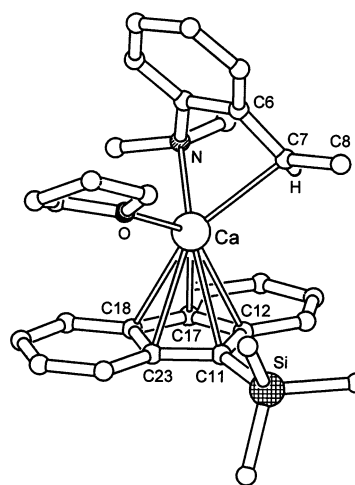


Fig. 2. Crystal structure of **5**. All hydrogens have been omitted for clarity (except for the hydrogen at the benzylic carbon which was observed in the difference Fourier map).

Table 1  
Selected bond distances (Å) and bond angles (°) for the crystal structures of **5** and **8**

Complex <b>5</b>			
Ca–C7	2.502(2)	O–Ca–C7	104.81(6)
Ca–N	2.451(2)	N–Ca–O	107.45(5)
Ca–O	2.319(2)	N–Ca–C7	71.71(6)
Ca–C11	2.647(2)	C6–C7–H	116.3(2)
Ca–C12	2.730(2)	C6–C7–C8	119.4(2)
Ca–C17	2.811(2)	C8–C7–H	115.7(1)
Ca–C18	2.776(2)		
Ca–C23	2.682(2)		
C6–C7	1.453(3)		
Complex <b>8</b>			
Ca1–C22	2.619(13)	Ca2–C22	2.499(11)
Ca1–C44	2.627(12)	Ca2–C44	2.496(13)
Ca1–C26	2.779(12)	Ca2–O1	2.311(9)
Ca1–C27	2.852(11)	Ca2–F12	2.616(12)–2.899(12)
Ca1–F11	2.646(11)–2.841(11)	(average)	2.741(12)
(average)	2.760(12)		
Ca3–C70	2.594(13)	Ca4–C70	2.557(11)
Ca3–C92	2.549(12)	Ca4–C92	2.597(12)
Ca3–O2	2.309(9)	Ca4–C81	2.821(11)
Ca3–F13	2.694(11)–2.797(12)	Ca4–C82	2.948(12)
(average)	2.752(12)	Ca4–F14	2.611(13)–2.824(12)
		(average)	2.716(12)

room temperature. Any excess of Me<sub>3</sub>Si-fluorene immediately reacts with **5** to bis(Me<sub>3</sub>Si-fluorenyl)calcium.

The crystal structure of **5** (Fig. 2) compares very well to that of **3**. It shows an η<sup>5</sup> fluorenyl–Ca coordination that is somewhat distorted to η<sup>3</sup>: the shortest distance is

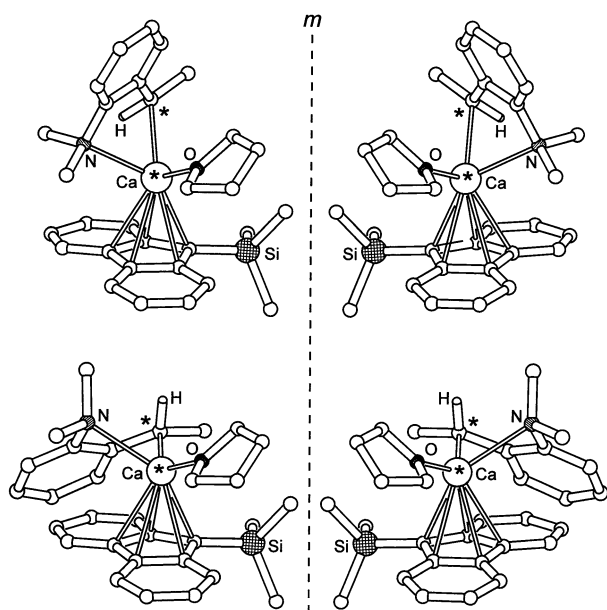


Fig. 3. Structures of the observed and hypothetical diastereomer pairs of **5** (the α-Me substituent is always directed away from the Me<sub>2</sub>N-substituent for steric reasons). The hypothetical diastereomer pair (the lower pair) displays severe steric repulsion between aryl and fluorenyl rings

measured between Ca and the carbon attached to Si (i.e. C11). The benzyl anions coordinate to Ca in a C,N-bidentate fashion and the coordination sphere is completed with one THF ligand. Selected bond distances and angles are summarized in Table 1. The structure contains two chiral centers, the benzylic carbon and the Ca<sup>2+</sup> ion, but only one diastereomer pair crystallized. The other (hypothetical) diastereomer pair displays severe steric interaction between fluorenyl and aryl ring (Fig. 3).

The <sup>1</sup>H-NMR spectrum of **5** (20 °C, toluene-*d*<sub>8</sub>) shows that also in solution only one of the diastereomers is present (a similar observation was made for complex **3**). The chiral center at the benzylic carbon causes two diastereotopic sides in the fluorenyl ligand and unique signals for all its protons are observed. Fast inversion of the benzylic carbon results in exchange of the two diastereotopic sides and can be achieved by raising the temperature ( $T_{\text{coal}} = 70$  °C;  $\Delta G^\ddagger = 17.2$  kcal mol<sup>-1</sup>). The energy barrier for inversion is concentration independent, indicating a dissociative mechanism that involves a Ca–C<sub>α</sub> bond rupture. The barrier for inversion is somewhat lower than that observed in **3** ( $T_{\text{coal}} = 90$  °C;  $\Delta G^\ddagger = 18.8$  kcal mol<sup>-1</sup>). The transition state for inversion is stabilized by the addition of a few equivalents of THF: fast inversion of the chiral center is observed already at room temperature. The mechanisms for inversion of the chiral benzylic carbon have been discussed earlier in detail [2,6]. The proposed mechanism inverts the chirality at C<sub>α</sub> as well as at the Ca<sup>2+</sup> ion.

Complex **5** is, like complex **3**, an initiator for the living polymerization of styrene. The GPC-spectra (Fig. 4) of the polymer obtained with the α-alkylated benzylcalcium initiator (**5**) show less tailing in the low molecular weight regions, a narrower distribution and a slightly lower dispersion index than polymer obtained with the α-Me<sub>3</sub>Si-benzylcalcium initiator (**3**). This is consistent with a faster initiation reaction for **5** and confirms the higher reactivity of the α-alkylated benzyl anion. The GPC-spectra show that the initiation of

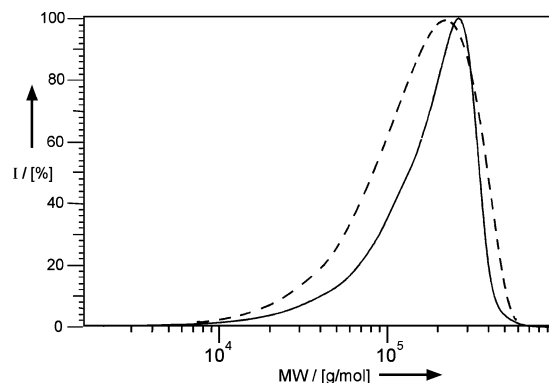
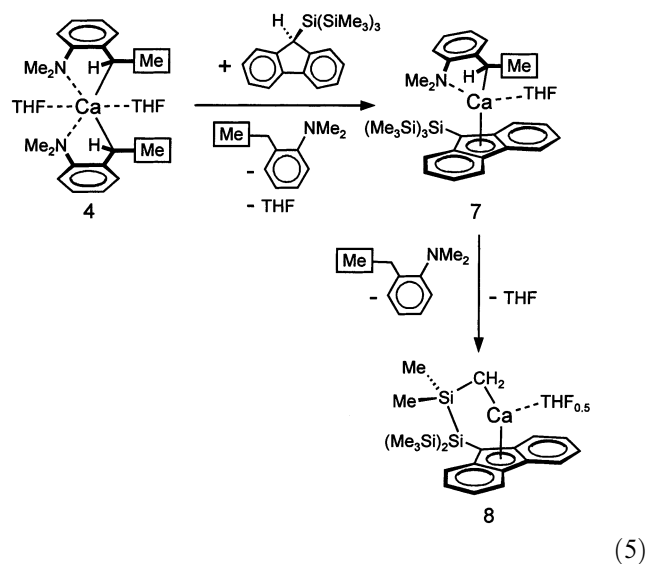
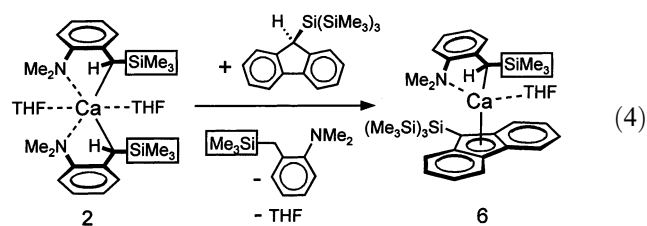


Fig. 4. GPC's of polystyrene obtained with initiator **5** (solid line,  $D = 2.062$ ) and initiator **3** (striped line,  $D = 2.272$ ).

styrene polymerization with **5** is still slow compared to chain-growth. This can be attributed to the chelating Me<sub>2</sub>N-substituent, which coordinates to Ca<sup>2+</sup> and blocks the metal for styrene coordination. This effect will be noticeable especially in the initiation step and after the first styrene insertions, but will become less important when the distance between the amino group and Ca increases, i.e. after substantial chain growth.

The tacticity of the polystyrene obtained with the initiators **3** and **5** is, as expected, comparable [7]. We are currently varying the nature of the spectator ligand and studying its influence on the stereoselectivity of the styrene insertion. A heteroleptic  $\alpha$ -Me<sub>3</sub>Si-benzylcalcium initiator with increased steric bulk at the metal center was prepared by reacting **2** with 9-hypersilyl-fluorene (Eq. (4)). The preparation of the similar  $\alpha$ -alkylated-benzylcalcium initiator, however, resulted in the isolation of a completely different species (Eq. (5)). The presumed heteroleptic intermediate **7** cannot be observed in NMR but immediately reacts to **8** which crystallizes from solution. Apparently the reactivity of the  $\alpha$ -alkylated-benzyl anion is much higher than that of the  $\alpha$ -Me<sub>3</sub>Si-benzyl anion. The deprotonation reaction can be classified as an intramolecular C–H activation (or cyclometallation), a reaction type that is common for early transition metal complexes [8]. It also clearly confirms the higher reactivity of the  $\alpha$ -alkylated-benzyl anion: complex **6** is stable even in refluxing benzene.



Complex **8** crystallizes in a monoclinic crystal system with two independent but similar dimers in the unit cell (Fig. 5; Table 1). In both dimers, the Ca<sup>2+</sup> ions are bridged by SiCH<sub>2</sub><sup>−</sup> groups (due to poor crystal quality the hydrogens could not be located). The Ca<sub>2</sub>C<sub>2</sub> cycles show butterfly conformations (with dihedral Ca–C–Ca' angles of 41.6 and 47.4°). In one of the dimers slight asymmetry in the bridging is observed; the Ca–CH<sub>2</sub> bonds vary from 2.496(13) to 2.627(12) Å and compare well with Ca–CH<sub>2</sub> bond distances in a benzylcalcium dimer (2.537(3)–2.571(3) Å [9]). All Ca<sup>2+</sup> ions are bonded over the central C<sub>5</sub>-ring of a fluorenyl moiety. The bond distance between Ca and the carbon attached to Si is in all cases the shorter one. Each dimer contains a THF ligand completing the coordination spheres of one of the Ca<sup>2+</sup> ions. The other Ca<sup>2+</sup> ion displays short interactions to the edge of a fluorenyl ligand.

The structures of both dimers are largely similar, except for the orientation of one of the Si(SiMe<sub>3</sub>)<sub>3</sub> groups (the ones attached to F11 and F14). The most favourable rotamer has one of the Me<sub>3</sub>Si-substituents in the plane of the fluorenyl ring. This leaves the two possible conformations both found in the crystal (Fig. 5). The different orientations of the Si(SiMe<sub>3</sub>)<sub>3</sub> substituents result in a difference in the puckering of the F1–Si–Si–CH<sub>2</sub>–Ca metallacycles. This also affects the orientation of the THF ligand by steric interactions.

<sup>1</sup>H-NMR spectra of **8** dissolved in benzene show broad signals over the whole temperature range. This is likely due to slow exchange of the inequivalent fluorenyl ligands. Addition of small amounts of THF results in sharpening of the <sup>1</sup>H-NMR spectra. This is either due to the formation of a monomeric species, as observed for another CH<sub>2</sub><sup>−</sup>-bridged benzylcalcium dimer [9], or to THF-assisted fast exchange between the different fluorenyl ligands within a dimer (i.e. a dynamic process that involves a shift of THF from one to the other Ca<sup>2+</sup>). The limited solubility of **8** in aromatic solvents does not allow a low temperature study.

The <sup>1</sup>H-NMR signal for the SiCH<sub>2</sub><sup>−</sup> group is shifted to the high-field region ( $\delta = -1.27$  ppm) indicating a considerable carbanionic character. Comparable chemical shifts have been observed for bridging SiCH<sub>2</sub><sup>−</sup> moieties in lithiumaluminates [10] or for the (Me<sub>3</sub>Si)<sub>2</sub>CH<sup>−</sup> ligand in a homoleptic calcium complex [11].

Complex **8** is not active in the polymerization of styrene. This could be due to the steric shielding of the polymerization active SiCH<sub>2</sub><sup>−</sup> group.

### 3. Conclusion

$\alpha$ -Methyl-benzylcalcium complexes can be prepared analogue to  $\alpha$ -Me<sub>3</sub>Si-benzylcalcium complexes. The crystal structures of the homoleptic and heteroleptic  $\alpha$ -

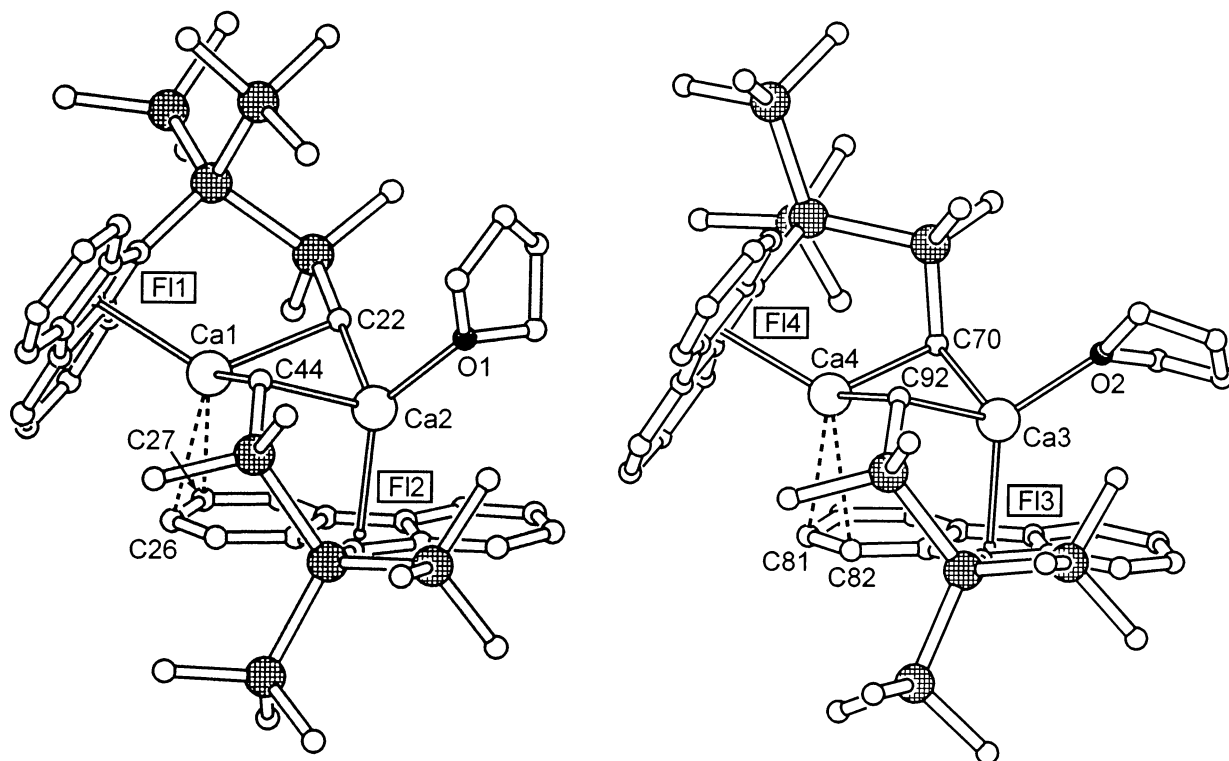


Fig. 5. Crystal structure of **8**. The two independent molecules differ in the orientation of one of the  $\text{Si}(\text{SiMe}_3)_3$  groups (the ones attached to F11 and F14). All hydrogens have been omitted for clarity.

methyl-benzylcalcium complexes are, despite a considerable reduction in steric bulk, comparable to those of the analogue  $\alpha\text{-Me}_3\text{Si}$ -benzylcalcium complexes.

$\alpha$ -Methyl-benzylcalcium complexes are less stable, show a higher reactivity and faster initiation of styrene polymerization than the analogue  $\alpha\text{-Me}_3\text{Si}$ -benzylcalcium complexes. The initiation step in styrene polymerization is, however, still slower than chain propagation. This is likely due to the chelating *ortho*-amino substituent, which blocks a potential coordination site at the metal. We are currently preparing benzylcalcium compounds without any stabilization via intramolecular coordinating groups.

The high reactivity of the  $\alpha\text{-Me}$ -benzyl anion can lead to intramolecular deprotonation of ligands. This reaction is comparable to the well-documented examples for intramolecular C–H activation (or cyclometallation) in organometallic compounds of the early d-block metals.

## 4. Experimental

### 4.1. General procedures

All experiments were carried out under argon using dry solvents and Schlenk techniques. The following compounds were prepared according to literature pro-

cedures: 2-ethyl-*N,N*-dimethylamino)aniline [12], 9- $(\text{Me}_3\text{Si})_3\text{Si}$ -fluorene [13], bis(2- $\text{Me}_2\text{N}$ - $\alpha\text{-Me}_3\text{Si}$ -benzyl)calcium $\cdot(\text{THF})_2$  (**2**) [2]. NMR spectra were recorded on Bruker AC250 (250 MHz) and Bruker DRX600 (600 MHz) machines.

Polymerizations of styrene were performed in a thermostated 100 ml stainless steel reactor at normal pressure (cyclohexane, 50 °C). In a typical polymerization experiment the reactor was loaded with 90 ml of dry cyclohexane and 11.5 ml (ca. 100 mmol) of freshly distilled (from alox-perls) styrene. A solution of the initiator (0.1 mmol of active benzyl anion) in 1.0 ml of benzene/cyclohexane was added via a port. The usual appearance of a red colour indicated that the polymerization started immediately. After a polymerization time of 30 min the mixture was quenched with oxygen-free methanol. Evaporation of all solvents yields the polymer in quantitative yields. Polymer analyses were carried out by GPC and high temperature  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR (solvent: tetrachloroethane- $d_2$ ). The tacticity of the polymer was checked by analyzing the  $^{13}\text{C}$ -NMR signal for the  $\text{C}_{\text{ipso}}$  phenyl ring carbon. Isotactic or syndiotactic arrangements would give singlets at 146.1 and 145.5 ppm, respectively. A new assignment based on hexads and heptads has been recently published by us [7].

Crystal structures were determined with the programs SHELXL-97 [14] and PLATON [15].

#### 4.2. Synthesis of 2-Me<sub>2</sub>N- $\alpha$ -Me-benzylpotassium

*n*-BuLi (30 ml, 1.6 M in hexane, 48 mmol) was added dropwise to a precooled (–70 °C) solution of 2-ethyl-(*N,N*-dimethylamino)aniline (8.94 g, 60.0 mmol) and potassium 3-methyl-3-pentanoate (7.40 g, 52.2 mmol) in 40 ml of THF. The temperature was slowly raised to 0 °C within 4 h. Evaporation of the solvent resulted in a sticky red residu to which 50 ml of hexane were added. Keeping the reaction mixture overnight at –80 °C gave an orange–red precipitate, which was washed three times with 50 ml portions of hexane. Drying the product under vacuum (1 Torr, 30 °C, 30 min) yielded the extremely air-sensitive 2-Me<sub>2</sub>N- $\alpha$ -Me-benzylpotassium in quantitative yield (8.95 g, 47.8 mmol). <sup>1</sup>H-NMR (benzene-*d*<sub>6</sub>/THF-*d*<sub>8</sub> mixture, 20 °C):  $\delta$  1.78 (d, 6.2 Hz, 3H, CHMe), 2.53 (s, 6H, NMe<sub>2</sub>), 2.83 (q, 6.2 Hz, 1H, CHMe), 5.02 (t, 7.5 Hz, 1H, aryl), 5.55 (d, 8.1 Hz, 1H, aryl), 6.14 (d, 7.2 Hz, 1H, aryl), 6.41 (t, 7.5 Hz, 1H, aryl). <sup>13</sup>C{<sup>1</sup>H}-NMR (benzene-*d*<sub>6</sub>/THF-*d*<sub>8</sub> mixture, 20 °C):  $\delta$  14.5 (CHMe), 41.9 (NMe<sub>2</sub>), 58.6 (CHMe), aryl: 92.0, 104.0, 115.7, 126.2, 133.9, 138.9.

#### 4.3. Synthesis of bis(2-Me<sub>2</sub>N- $\alpha$ -Me-benzyl)calcium·(THF)<sub>2</sub> (4)

A solution of 2-Me<sub>2</sub>N- $\alpha$ -Me-benzylpotassium (4.40 g, 23.5 mmol) was added to a suspension of CaI<sub>2</sub> (3.23 g, 11.0 mmol) in 60 ml of THF at room temperature. The red colour of the benzylpotassium compound disappeared immediately and the resulting yellow suspension was stirred for 2 h. The reaction mixture is centrifuged and the clear THF-solution was isolated. The yellow residu was extracted three times with 50 ml portions of hot benzene. Evaporation of the solvent of the combined THF and benzene extractions yielded a yellow-orange powder in a 55% yield (2.93 g, 6.1 mmol). The raw product contained traces of the potassium compound but could be crystallized from hot benzene/THF mixtures in yields varying between 10 and 50%. <sup>1</sup>H-NMR (benzene-*d*<sub>6</sub>/THF-*d*<sub>8</sub> mixture, 70 °C):  $\delta$  1.49 (m, 4H, THF), 1.62 (q broad, 8.0 Hz, 1H, CHCH<sub>3</sub>), 1.83 (d, 8.1 Hz, 3H, CHCH<sub>3</sub>), 2.48 (s broad, 6H, NMe<sub>2</sub>), 3.55 (m, 4H, THF), 6.21 (t, 7.3 Hz, 1H, aryl), 6.63 (d, 7.8 Hz, 1H, aryl), 6.75 (d, 7.3 Hz, 1H, aryl), 7.02 (t, 7.8 Hz, 1H, aryl). <sup>13</sup>C{<sup>1</sup>H}-NMR (benzene-*d*<sub>6</sub>/THF-*d*<sub>8</sub> mixture, 70 °C):  $\delta$  16.3 (CHMe), 44.1 (NMe<sub>2</sub>), 45.1 (CHMe), 25.8 (THF,  $\beta$ -CH<sub>2</sub>), 67.8 (THF,  $\alpha$ -CH<sub>2</sub>), aryl: 108.1, 115.8, 118.0, 127.1, 129.4, 148.4.

#### 4.4. Synthesis of (9-Me<sub>3</sub>Si-fluorenyl)(2-Me<sub>2</sub>N- $\alpha$ -Me-benzyl)calcium·(THF) (5)

A yellow solution of bis(2-Me<sub>2</sub>N- $\alpha$ -Me-benzyl)calcium·(THF)<sub>2</sub> (4, 1.92 g, 4.0 mmol) and 9-Me<sub>3</sub>Si-fluorene (0.95 g, 4.0 mmol) in 25 ml of benzene was

stirred for 3 h at room temperature. The colour of the solution changed to deep orange. Evaporation of the solvent resulted in an essentially quantitative yield of **5** in the form of an orange-red powder. Crystals for X-ray diffraction were obtained by cooling a highly concentrated benzene solution to 5 °C. <sup>1</sup>H-NMR (toluene-*d*<sub>8</sub>, 20 °C):  $\delta$  0.60 (s, 9H, Me<sub>3</sub>Si), 0.84 (q, 5.4 Hz, 1H, CHCH<sub>3</sub>), 1.73 (d, 5.4 Hz, 3H, CHCH<sub>3</sub>), 1.84 (s, 3H, NMe), 1.89 (s, 3H, NMe), 6.01 (t, 7.8 Hz, 1H, aryl), 6.23 (d, 7.6 Hz, 1H, aryl), 6.44 (d, 7.9 Hz, 1H, aryl), 6.78 (t, 7.8 Hz, 1H, aryl), 6.97 (t, 7.5 Hz, 1H, fluorenyl), 7.09 (t, 7.6 Hz, 1H, aryl), 7.18 (t, 7.6 Hz, 1H, aryl), 7.33 (t, 7.5 Hz, 1H, aryl), 7.88 (d, 7.5 Hz, 1H, aryl), 8.07 (d, 7.8 Hz, 1H, aryl), 8.04 (d, 7.6 Hz, 1H, aryl), 8.10 (d, 7.7 Hz, 1H, aryl). <sup>13</sup>C{<sup>1</sup>H}-NMR (toluene-*d*<sub>8</sub>, 20 °C):  $\delta$  2.4 (Me<sub>3</sub>Si), 15.2 (CHCH<sub>3</sub>), 41.4+43.9 (NMe<sub>2</sub>), 45.4 (CHCH<sub>3</sub>), aryl: 109.4, 117.3, 118.4, 127.4, 132.6, 146.6, fluorenyl: 87.3, 116.4, 116.9, 120.9, 121.4, 121.5, 121.5, 123.4, 123.5, 123.9, 124.4, 140.5, 140.7.

#### 4.5. Synthesis of 6

A solution of bis(2-Me<sub>2</sub>N- $\alpha$ -Me<sub>3</sub>Si-benzyl)calcium·(THF)<sub>2</sub> (2, 1.56 g, 2.60 mmol) and 9-(Me<sub>3</sub>Si)<sub>3</sub>Si-fluorene (1.08 g, 2.60 mmol) in 25 ml of THF was stirred for 3 h at 60 °C. The solvent was evaporated and the remaining orange–red solid was washed with 10 ml of hexane and dried under vacuum (0.01 Torr, 50 °C) yielding **6** in quantitative yield. <sup>1</sup>H-NMR (toluene-*d*<sub>8</sub>+5% THF-*d*<sub>8</sub>, 20 °C):  $\delta$  0.34 (s, 27H, (Me<sub>3</sub>Si)<sub>3</sub>Si-fluorenyl), 0.42 (s, 9H, Me<sub>3</sub>Si), 0.74 (s, 1H, CHSiMe<sub>3</sub>), 1.06 (m, 4H, THF), 1.93 and 2.04 (double s, 6H, NMe<sub>2</sub>), 2.71 (m, 4H, THF), 6.14 (t, 7.0 Hz, 1H, aryl), 6.31 (d, 7.8 Hz, 1H, aryl), 6.63 (t, 7.3 Hz, 1H, aryl), 6.85 (d, 7.9 Hz, 1H, aryl), 6.99 (t, 8.3 Hz, 1H, fluorenyl), 6.02 (t, 8.3 Hz, 1H, fluorenyl), 7.27 (t, 7.1 Hz, 1H, fluorenyl), 7.30 (t, 7.6 Hz, 1H, fluorenyl), 8.00 (d, 8.0 Hz, 1H, fluorenyl), 8.04 (d, 7.7 Hz, 1H, fluorenyl), 8.20 (d, 7.5 Hz, 1H, fluorenyl), 8.21 (d, 7.5 Hz, 1H, fluorenyl). <sup>1</sup>H-NMR (toluene-*d*<sub>8</sub>+5% THF-*d*<sub>8</sub>, 20 °C):  $\delta$  2.6 (Me<sub>3</sub>Si), 3.5 ((Me<sub>3</sub>Si)<sub>3</sub>Si), 24.9 (THF), 41.9 and 45.0 (NMe<sub>2</sub>), 47.6 (benzylic C), 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.

#### 4.6. Synthesis of 8

A solution of bis(2-Me<sub>2</sub>N- $\alpha$ -Me-benzyl)calcium·(THF)<sub>2</sub> (4, 0.43 g, 0.89 mmol) and 9-(Me<sub>3</sub>Si)<sub>3</sub>Si-fluorene (0.37 g, 0.89 mmol) in 10 ml of benzene and 2 ml of THF was stirred for 3 h at 70 °C. Cooling of the solution gave the extremely air-sensitive **8** in the form of yellow-orange clear crystalline blocks (yield: 0.36 g, 0.37 mmol, 83%). <sup>1</sup>H-NMR (benzene-*d*<sub>6</sub>/THF-*d*<sub>8</sub> in a ratio 20/1, 20 °C):  $\delta$  –1.27 (s, 4H, Ca–CH<sub>2</sub>Si), 0.66 (s, 36H, Si–Si(CH<sub>3</sub>)<sub>3</sub>), 0.78 (s, 12H, CaCH<sub>2</sub>Si(CH<sub>3</sub>)<sub>2</sub>), 1.49 (m, 4H,

THF), 3.55 (m, 4H, THF), 6.95 (t, 7.2 Hz, 4H, fluorenyl), 7.32 (t, 7.4 Hz, 4H, fluorenyl), 8.07 (d, 7.8 Hz, 4H, fluorenyl), 8.31 (d, 7.9 Hz, 4H, fluorenyl).  $^{13}\text{C}\{^1\text{H}\}$ -NMR (benzene- $d_6$ /THF- $d_8$  in a ratio 20/1, 20 °C):  $\delta$  4.2 (Si–Si(CH $_3$ ) $_3$ ), 9.3 (CaCH $_2$ Si(CH $_3$ ) $_2$ ), 10.1 (Ca–CH $_2$ Si), 25.8 (THF,  $\beta$ -CH $_2$ ), 67.8 (THF,  $\alpha$ -CH $_2$ ), fluorenyl: 82.9, 114.9, 120.6, 122.3, 122.9, 123.3, 140.3.

#### 4.7. Crystal structure determination for bis(2-Me $_2$ N- $\alpha$ -Me-benzyl)calcium·(THF) $_2$ (4)

Air-sensitive yellow–orange block (0.5 × 0.4 × 0.4 mm $^3$ ), tetragonal,  $a = b = 15.619(1)$ ,  $c = 22.347(4)$  Å,  $V = 5451(1)$  Å $^3$ , space group  $P4_32_12$ ; formula (C $_{28}$ H $_{44}$ CaN $_2$ O $_2$ ),  $M = 480.73$ ,  $Z = 8$ ,  $\rho_{\text{calc}} = 1.171$  g cm $^{-3}$ ,  $\mu(\text{Mo–K}\alpha) = 0.256$  mm $^{-1}$ ; 5190 reflections were measured (Mo–K $\alpha = 0.71073$  Å, graphite monochromator,  $T = -90$  °C) on an Enraf Nonius CAD4 diffractometer, 4800 independent reflections ( $R_{\text{int}} = 0.024$ ), 3274 observed reflections with  $I > 2.0\sigma(I)$ . The structure was solved by direct methods but could not be refined satisfactory due to twinning problems: full matrix least-squares refinement on  $F^2$  to  $R_1 = 0.090$ ,  $wR_2 = 0.245$  and  $S = 1.07$  (340 parameters). Only a graphical abstract is given (Fig. 1) and bond distances and angles are not discussed.

#### 4.8. Crystal structure determination for (9-Me $_3$ Si-fluorenyl)(2-Me $_2$ N- $\alpha$ -Me-benzyl)calcium·(THF) (5)

Air-sensitive orange block (0.5 × 0.4 × 0.3 mm $^3$ ), monoclinic,  $a = 16.775(2)$ ,  $b = 11.0599(7)$ ,  $c = 15.451(2)$  Å,  $\beta = 101.341(6)^\circ$ ,  $V = 2810.6(5)$  Å $^3$ , space group  $P2_1/c$ ; formula (C $_{30}$ H $_{39}$ CaNOSi),  $M = 497.79$ ,  $Z = 4$ ,  $\rho_{\text{calc}} = 1.176$  g cm $^{-3}$ ,  $\mu(\text{Mo–K}\alpha) = 0.288$  mm $^{-1}$ ; 6591 reflections were measured (Mo–K $\alpha = 0.71073$  Å, graphite monochromator,  $T = -90$  °C) on an Enraf Nonius CAD4 diffractometer, 6349 independent reflections ( $R_{\text{int}} = 0.015$ ), 4875 observed reflections with  $I > 2.0\sigma(I)$ . Solution by direct methods, full matrix least-squares refinement on  $F^2$  to  $R_1 = 0.039$ ,  $wR_2 = 0.108$  and  $S = 1.03$  (432 parameters). Absorption correction was not applied. Non-hydrogens were refined anisotropically. Part of the hydrogens have been taken from the difference Fourier map and part were calculated and refined with a riding model. The benzylic hydrogen was observed and refined isotropically.

#### 4.9. Crystal structure determination for (8)

Air-sensitive yellow block (0.5 × 0.5 × 0.5 mm $^3$ ), monoclinic,  $a = 17.470(2)$ ,  $b = 17.851(2)$ ,  $c = 18.050(1)$  Å,  $\beta = 90.358(7)^\circ$ ,  $V = 5629(1)$  Å $^3$ , space group  $Pc$ ; formula (C $_{48}$ H $_{72}$ Ca $_2$ OSi $_8$ ),  $M = 969.94$ ,  $Z = 4$ ,  $\rho_{\text{calc}} = 1.145$  g cm $^{-3}$ ,  $\mu(\text{Mo–K}\alpha) = 0.404$  mm $^{-1}$ ; 10 263 reflec-

tions were measured (Mo–K $\alpha = 0.71073$  Å, graphite monochromator,  $T = -120$  °C) on an Enraf Nonius CAD4 diffractometer, 10 263 independent reflections, 9081 observed reflections with  $I > 2.0\sigma(I)$ . Solution by direct methods, full matrix least-squares refinement on  $F^2$  to  $R_1 = 0.080$ ,  $wR_2 = 0.204$  and  $S = 1.13$  (1085 parameters). Absorption correction was not applied. Non-hydrogens were refined anisotropically. Part of the hydrogens have been taken from the difference Fourier map and part were calculated and refined with a riding model. Severe disorder in some of the Me $_3$ Si-groups and THF ligands has been treated with refinement of disorder models (Fig. 5 shows the structures with the highest occupation). Although the Ca–CH $_2$ Si parts of the structure were ordered, the positions of its hydrogens could not be located due to insufficient crystal quality (likely due to disorder).

The two independent dimers are structurally different and cannot be projected on each other by additional symmetry elements. Transformation in the higher symmetry space group  $P2_1/c$  is therefore excluded.

## 5. Supplementary material

Crystallographic data (excluding structure factors) for the structures of **5** and **8** reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-204122 and CCDC-204123, respectively. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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