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Structure of a Benzylcalcium Diastereomer: An Initiator for the Anionic Polymerization of Styrene

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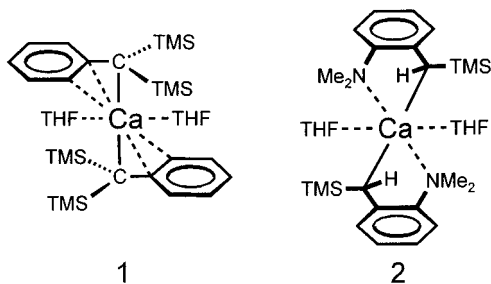
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Summary: A new dibenzylcalcium compound with chiral anionic centers has been prepared and was structurally characterized. The compound, which shows slow inversion of the chiral carbanions, is an active initiator for the living polymerization of styrene.

Introduction

Very recently we published the first crystal structure of a dibenzylcalcium compound (**1**).¹ This compound is kinetically as well as thermodynamically stabilized with two trimethylsilyl (TMS) groups attached directly to the carbanionic carbon. Although this approach greatly facilitates the synthesis and handling of the compound, it likewise diminishes its reactivity in the initiation of styrene polymerization, and no polymer could be obtained.

To obtain dibenzylcalcium compounds that are nucleophilic enough for the initiation of styrene polymerization, we replaced one of the TMS substituents with a hydrogen and compensated for the loss in stabilization by introducing intramolecular coordination via a dimethylamino group (**2**). The latter form of stabilization does not affect the nucleophilicity of the carbanionic center.



Results and Discussion

The compound bis(2-NMe₂- α -Me₃Si-benzyl)calcium·(THF)₂ (**2** or (DMAT)₂Ca·(THF)₂) was prepared in good yield via an efficient ligand metathesis reaction between (2-NMe₂- α -Me₃Si-benzyl)potassium (DMAT-K) and CaI₂ in THF. The product was crystallized easily from THF/hexane, and this warrants its purity for use in anionic polymerization reactions.

The new benzylcalcium compound, (DMAT)₂Ca·(THF)₂, crystallizes as the diastereomer with *R* and *S* configuration at the benzylic carbons (Figure 1). The anionic ligand binds Ca in a bidentate mode, and in contrast to the structure of **1**, no significant aryl ring···Ca coordination is observed. The C _{α} –Ca bonds

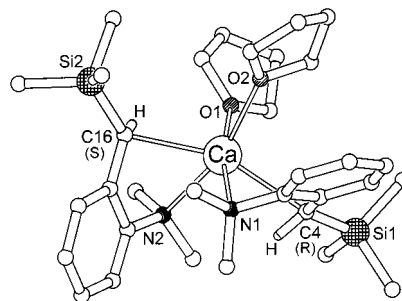
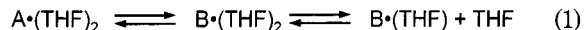


Figure 1. Crystal structure of (DMAT)₂Ca·(THF)₂ (**2**) (for clarity only the benzylic protons are shown). Selected bond distances (Å): Ca–N1 2.567(2), Ca–N2 2.632(2), Ca–O1 2.441(2), Ca–O2 2.373(2), Ca–C4 2.638(3), Ca–C16 2.618(3). Selected bond angles (deg): O1–Ca–O2 80.85(6), N1–Ca–N2 102.19(7), C4–Ca–C16 157.54(8).

in (DMAT)₂Ca·(THF)₂ of 2.638(3) and 2.618(3) Å are slightly shorter than that in **1** (2.649(2) Å). The coordination sphere around calcium is a distorted octahedron with the carbanions in trans position and the four neutral coordinating groups in one plane. The benzylic carbon shows a hybridization between sp³ and sp²: the sum of the angles at C _{α} is 342(1)° and 346(1)°. The C_{ipso}–C _{α} bond distances in (DMAT)₂Ca·(THF)₂ (1.453(3) and 1.445(3) Å) are shorter than that in **1** (1.484(3) Å). The diminished charge delocalization in the latter is due to the electron-localizing effect by two Si substituents.

¹H NMR measurement on a room-temperature sample of (DMAT)₂Ca·(THF)₂ dissolved in benzene shows two separate sets of signals, i.e., two diastereomers in slow exchange. However, only one set of THF signals is observed, indicating fast exchange for the THF ligands. The diastereomer ratio is not only temperature dependent (*T* = 30 °C, A/B = 40/60; *T* = –50 °C, A/B = 79/21)² but also concentration dependent (0.33 M, A/B = 53/47; 0.06 M, A/B = 31/69). This indicates at least partial loss of THF in going from diastereomer A to a more sterically congested diastereomer B (eq 1). This is in



agreement with the fact that the chemical shifts for THF vary with concentration and temperature and with the observation that diastereomer A is predominant in pure THF solution (A/B = 92/8 at –10 °C).

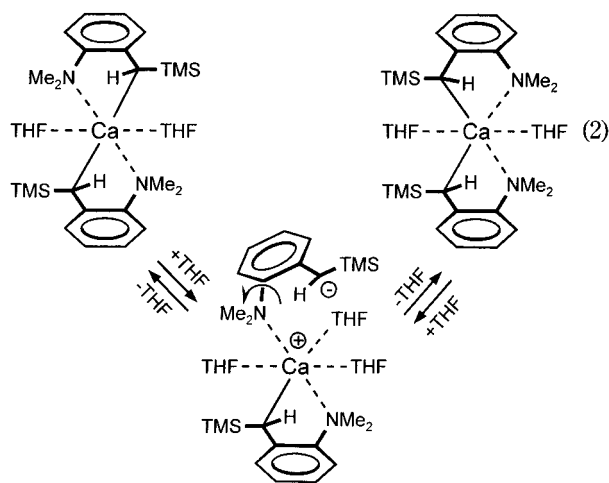
At higher temperatures coalescence and fast exchange between both diastereomers is observed. The coalescence temperature is lower at higher concentration (0.06

(2) An Eyring plot of *K*-values determined in the temperature region –50/+30 °C shows $\Delta H^\ddagger = 1.74(4)$ kcal mol^{–1} and $\Delta S^\ddagger = -6.1(1)$ cal mol^{–1} K^{–1} (data for a toluene solution).

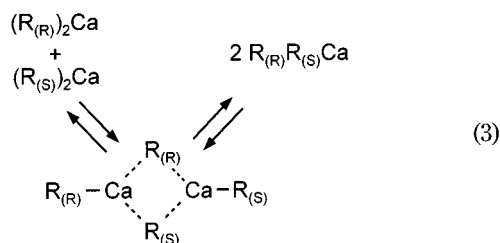
(1) Feil, F.; Harder, S. *Organometallics* 2000, 19, 5010.

M, $\Delta G^\ddagger(60^\circ\text{C}) = 16.8 \text{ kcal mol}^{-1}$; 0.33 M, $\Delta G^\ddagger(40^\circ\text{C}) = 15.8 \text{ kcal mol}^{-1}$). Likewise, addition of excess THF enormously accelerates exchange between the diastereomers (in pure THF, 0.07 M, $\Delta G^\ddagger(-5^\circ\text{C}) = 13.7 \text{ kcal mol}^{-1}$). Barriers for enantiomerization in chiral benzyl-lithium compounds usually vary from 9 to 12 kcal mol⁻¹.³ The higher stability of chiral carbanions attached to Ca²⁺ might be useful in stereoselective syntheses using chiral carbanions.⁴

The mechanism for exchange between the diastereomers is still unclear, and even different mechanisms might be operative. In the case where considerable amounts of free uncoordinated THF have been added, the diastereomer exchange likely proceeds via a dissociative mechanism in which free THF adds to an open coordination site of the intermediate (eq 2). The case in



which crystals of **2** have been dissolved in pure benzene (or toluene) is more complicated. The experimentally observed correlation between the exchange rate and the absolute concentration usually indicates an associative mechanism with bridging benzyl anions in the intermediate (eq 3). However, it should be noticed that the



solvated complex **2** partly lost coordinated THF (eq 1). Therefore, the influence of the absolute concentration on the exchange rate can also be explained as follows: a higher absolute concentration results in a higher concentration of free THF, which accelerates exchange of diastereomers. Presently, there is no indication for

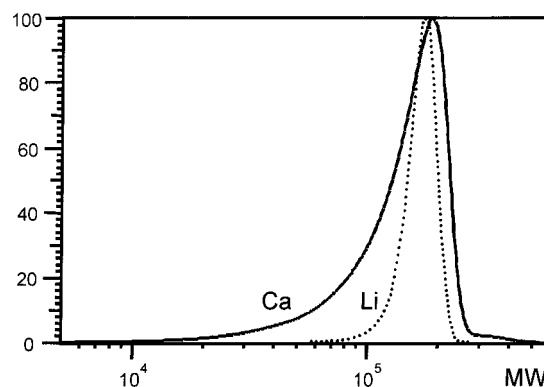


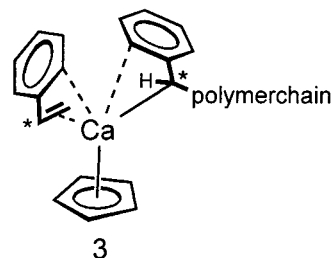
Figure 2. GPC's of polystyrene obtained with a *sec*-BuLi initiator (dotted line, $M_n = 1.091 \times 10^5$, $D = 1.039$) and the $(\text{DMAT})_2\text{Ca} \cdot (\text{THF})_2$ initiator (solid line, $M_n = 1.093 \times 10^5$, $D = 1.369$). The initiator-anion/monomer ratio was 1/1000.

the existence of dimers in which benzyl anions bridge between two Ca centers.

Another possible mechanism might involve an intermediate calcate species R_3Ca^- , of which a first example in the form of $[\text{R}_3\text{Ca}^-][\text{Na}^+]$ has been established very recently.⁵ With no alkali metal present in our samples, the existence of an intermediate calcate species would also require a cation $[\text{RCa}^+(\text{THF})_x]$.

The new compound, $(\text{DMAT})_2\text{Ca} \cdot (\text{THF})_2$, turned out to be an active initiator for the anionic polymerization of styrene. The molecular weight distribution (Figure 2) shows a light tailing in the low molecular weight range which is presumably due to slow initiation compared to propagation.⁶ Stepwise addition of styrene at certain intervals shows no significant chain termination, which indicates that the polymerization reaction is living. This enables the synthesis of block polymers. ¹³C NMR analysis shows predominant atactic polymeric material.

The next goal is the synthesis of stable heteroleptic calcium compounds with a polymerization active benzyl ligand and a nonactive spectator ligand, e.g., cyclopentadienyl. It is anticipated that such single-site catalysts might produce stereoregular polystyrene via chain-end control (**3**).



Earlier experiments with similar heteroleptic barium compounds did not show any stereocontrol for the insertion reaction.⁷ This is presumably due to rapid

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

(4) (a) Hoffmann, R. W.; Nell, P. G. *Angew. Chem.* **1999**, 111, 354; *Angew. Chem., Int. Ed.* **1999**, 111, 354. (b) Clark Still, W.; Sreekumar, C. *J. Am. Chem. Soc.* **1980**, 102, 1201. (c) Strohmman, C.; Abele, B. C.; Schildbach, D.; Strohfeldt, K. *J. Chem. Soc., Chem. Commun.* **2000**, 865.

(5) Knapp, V.; Müller, G. *Angew. Chem.* **2001**, 113, 187; *Angew. Chem., Int. Ed.* **2001**, 40, 183.

(6) NMR experiments showed that a *sec*-BuLi initiator reacts instantaneously with styrene at room temperature (no free styrene could be detected within minutes), whereas $(\text{DMAT})_2\text{Ca} \cdot (\text{THF})_2$ showed no sign of reaction at room temperature and only initiated the polymerization after heating to 60 °C.

(7) Weeber, A.; Harder, S.; Brintzinger, H.-H.; Knoll, K. *Organometallics* **2000**, 19, 1325.

epimerization of the chiral anionic chain-ends, that is, the rate of inversion at the chiral carbon is approximately equal to or faster than the chain propagation. The stability of the benzylic stereocenter in $(\text{DMAT})_2\text{Ca}\cdot(\text{THF})_2$ suggests that a heteroleptic benzylcalcium compound might be a promising initiator for the stereoregular polymerization of styrene.

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Supporting Information Available: Experimental information and NMR data for DMAT-K and $(\text{DMAT})_2\text{Ca}\cdot(\text{THF})_2$, the polymerization procedure and crystal structure data, atomic fractional coordinates, bond distances and angles, hydrogen atom positions, anisotropic thermal parameters, and an ORTEP plot for $(\text{DMAT})_2\text{Ca}\cdot(\text{THF})_2$ are available free of charge via the Internet at <http://pubs.acs.org>.

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