α,α-Bis(trimethylsilyl)-Substituted Benzyl Complexes of Potassium and Calcium

Florian Feil and Sjoerd Harder*

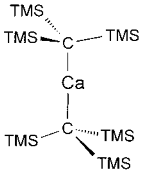
Universität Konstanz, Postfach 5560, M738, 78457 Konstanz, Germany

Received July 18, 2000

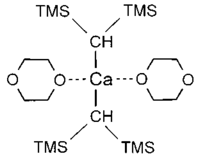
The first benzylcalcium complex, (α,α-bis(trimethylsilyl)benzyl)$_2$calcium·(THF)$_2$ (**7**), has been prepared by reacting CaI_2 with α,α-bis(trimethylsilyl)benzylpotassium (**6**) in THF. The solid state structure of the K precursor shows an interesting Lewis base-free coordination polymer in which the coordination sphere of K is additionally saturated by agostic Si−Me···K interactions. The crystal structure of the Ca product displays a THF-solvated monomeric compound, which shows considerably less delocalization of negative charge into the phenyl ring than the corresponding K compound. NMR investigations as well as ab initio calculations show that the TMS substituents at the benzylic carbon have a charge-localizing influence. Only the more ionic K precursor shows activity in initiating the polymerization of styrene.

Introduction

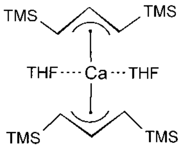
Although the organometallic chemistry of magnesium has been developed already in a very early stage, chemistry of the heavier alkaline-earth metals (Ca, Sr, and Ba) attracted increased attention only over the past decade.[1] Research, however, mainly focused on the more volatile and less reactive cyclopentadienides and alkoxides for use in CVD[2] or on the amides[3] which show potential in syntheses of Ca, Sr, and Ba compounds of intermediate basicity (e.g., fluorenyl[4] or acetylide[5] complexes). Only a few reports appeared on well-defined more basic and more reactive compounds, e.g., TMS-substituted alkylcalcium (**1**, **2**)[6,7] or allylcalcium (**3**)[8] compounds, a *t*Bu-substituted pentadienyl calcium compound (**4**),[9] and a mixed phospholide/alkenide barium compound **5**.[10]



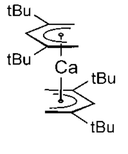
1



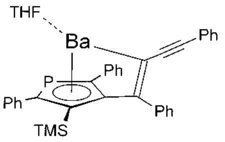
2



3



4



5

It is our aim to find an easy route for the preparation of reactive benzylcalcium compounds which could be used as initiators for the anionic polymerization of styrene. The only benzylcalcium compound described in the literature so far has been prepared via the highly undesired mercurial route:[11a] $(PhCH_2)_2Hg + Ca^0 \rightarrow (PhCH_2)_2Ca + Hg^0$. We recently developed an easy and efficient method for the synthesis of dibenzylbarium from benzyllithium and a barium amide (see eq 1).[11b] This metal exchange reaction is based on the HSAB principle[12] and similarly works with barium alkoxides and dibenzylmagnesium as the starting materials. Hitherto, any attempts to prepare benzylcalcium compounds in an analogous manner failed due to incomplete

---

(1) For reviews see: (a) Lindsell, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: Oxford, 1982; Vol. 1, Chapters 2−4. (b) Hanusa, T. P. *Polyhedron* **1990**, *9*, 1345. (c) Hanusa, T. P. *Chem. Rev.* **1993**, *93*, 1023. (d) Burkey, D. J.; Hanusa, T. P. *Comm. Inorg. Chem.* **1995**, *17*, 41.

(2) Hubert-Pfalzgraf, L. G. *New J. Chem.* **1987**, *11*, 663. (b) Bradley, D. C. *Chem. Rev.* **1989**, *89*, 1317. (c) Hubert-Pfalzgraf, L. G. *Appl. Organomet. Chem.* **1992**, *6*, 627. (d) Herrmann, W. A.; Huber, N. W.; Priermeier, T. *Angew. Chem.* **1994**, *106*, 102; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 105.

(3) Bradley, D. C.; Hursthouse, M. B.; Ibrahim, A. A.; Abdul Malik, K. M.; Motevalli, M.; Möseler, R.; Powell, H.; Runnacles, J. D.; Sullivan, A. C. *Polyhedron* **1990**, *9*, 2959. (b) Hitchcock, P. B.; Lappert, M. F.; Lawless, G. A.; Royo, B. *J. Chem. Soc., Chem. Commun.* **1990**, 1141. (c) Westerhausen, M. *Inorg. Chem.* **1991**, *30*, 96. (d) Vaartstra, B. A.; Huffman, J. C.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 121. (e) Westerhausen, M.; Schwarz, W. *Z. Anorg. Allg. Chem.* **1991**, *604*, 127.

(4) Harder, S.; Lutz, M.; Straub, A. W. G. *Organometallics* **1997**, *16*, 107.

(5) Green, D. C.; Englich, U.; Ruhlandt-Senge, K. *Angew. Chem.* **1999**, *111*, 365; *Angew. Chem., Int. Ed.* **1999**, *38*, 354. (b) Burkey, D. J.; Hanusa, T. P. *Organometallics* **1996**, *15*, 4971.

(6) Cloke, F. G. N.; Hitchcock, P. B.; Lappert, M. F.; Lawless, G. A.; Royo, B. *J. Chem. Soc., Chem. Commun.* **1991**, 724.

(7) Eaborn, C.; Hawkes, S. A.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Chem. Commun.* **1997**, 1961.

(8) Harvey, M. J.; Hanusa, T. P.; Young, V. G., Jr. *Angew. Chem.* **1999**, *111*, 241; *Angew. Chem., Int. Ed.* **1999**, *38*, 217.

(9) Overby, J. S.; Hanusa, T. P. *Angew. Chem.* **1994**, *106*, 2300; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2191.

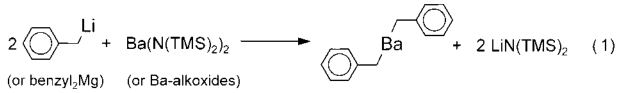
(10) Westerhausen, M.; Digeser, M. H.; Gückel, C.; Nöth, H.; Knizek, J.; Ponikwar, W. *Organometallics* **1999**, *18*, 2491.

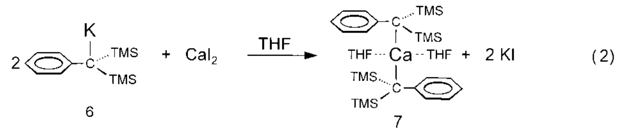
(11) Takahashi, K.; Kondo, Y.; Asami, R. *J. Chem. Soc., Perkin Trans 2* **1978**, 577. (b) Weeber, A.; Harder, S.; Brintzinger, H.-H.; Knoll, K. *Organometallics* **2000**, *19*, 1325;

(12) Grovenstein, E., Jr. In *Recent Advances in Anionic Polymerization*; Hogen-Esch, T. E., Smid, J., Eds.; Elsevier: Amsterdam, 1987; p 3. (b) Harder, S.; Streitwieser, A. *Angew. Chem.* **1993**, *105*, 1108; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1066. (c) Kremer, T.; Harder, S.; Junge, M.; Schleyer, P. v. R. *Organometallics* **1996**, *15*, 585.

10.1021/om0006209 CCC: $19.00
Publication on Web 10/27/2000

metal exchange. This results in mixtures of Ca and Li (or Mg) compounds that still contain amide (or alkoxide) anions.





We here present the synthesis of the first benzylic organocalcium compound (**7**) via the ligand metathesis reaction (eq 2), a synthetic route that also has been used for the preparation of **1**, **3**, **4**, and many cyclopentadienyl[13] or indenylcalcium[14] compounds. The TMS substituents are chosen for some thermodynamic stabilization of the carbanion by negative hyperconjugation and polarization effects,[15] but also for kinetic stabilization of the complex by steric saturation of the calcium coordination sphere. The concomitant advantage of the TMS substituents is an increase in the solubility of the Ca product which facilitates separation from the KI. The approach of using bulky stabilizing TMS substituents has been successfully applied to the chemistry of highly ionic alkylmetal compounds.[16]

The crystal structures of both the potassium precursor (**6**) and the calcium product (**7**) are described. In addition, the calcium complex as well as the potassium precursor have been tested as initiators for the anionic polymerization of styrene.

Results

α,α-Bis(trimethylsilyl)benzylpotassium (**6**) can be prepared by metalation of α,α-bis(trimethylsilyl)toluene with a BuLi/KOR superbase mixture in THF. All coordinated THF can be removed easily under vacuum, resulting in a Lewis base-free product. Because it is generally impossible to remove coordinated THF from Ca complexes, the subsequent preparation of a donor-free Ca complex was attempted by reaction of **6** with CaI_2 in benzene. The potassium compound is only very slightly soluble in benzene, whereas the calcium product is expected to show a pronounced solubility in this solvent. The benzene-soluble product extracted from the reaction mixture, however, turned out not to be pure **7**, but an undefined mixture of **6** and **7** is formed instead (a ^{1}H NMR spectrum shows broadened signals of which the chemical shifts are between that of **6** and **7**). This mixture could partly contain a calcate complex, [(α,α-bis(trimethylsilyl)benzyl)$_3$Ca$^-$]·K$^+$, in which the Ca center is surrounded with three benzyl anions. Even reaction times of up to 2 weeks and a slight excess of CaI_2 did not result in complete conversion: attempted crystallization from benzene gave considerable quantities of the pure donor-free potassium compound (**6**) in the form of large yellow single crystals which were used for a single-crystal structure determination. Powder diffraction methods have been successfully applied in the investigation of several simple donor-free organopotassium compounds, but this is one of the few single-crystal studies on this class of compounds.[17]

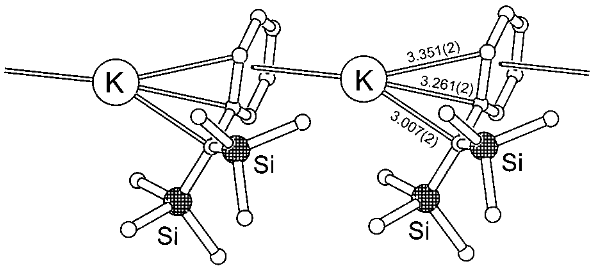


Figure 1. Crystal structure of α,α-bis(trimethylsilyl)benzylpotassium (**6**), forming a linear array of organopotassium units (protons omitted for clarity).

The crystal structure of donor-free α,α-bis(trimethylsilyl)benzylpotassium (**6**) shows a linear polymer of organopotassium units (Figure 1). The potassium cation binds mainly to the benzylic carbon (3.007(2) Å) and to a lesser extent to the aromatic ring (contacts to C_{ipso} and C_{ortho} are respectively 3.261(2) and 3.351(2) Å). It bridges to the phenyl group of a neighboring unit with K−C distances ranging from 3.093(2) to 3.522(2) Å, thus forming a coordination polymer. The benzylic carbon is nearly planar (the sum of the valence angles at C_α is 357.4(2)°), and the TMS_2C unit is rotated with respect to the phenyl ring (see Figure 2a).

The coordination sphere of potassium is saturated by several agostic interactions with Me_3Si groups. Agostic interactions can be recognized within the coordination polymer chain (Figure 2a) and might be responsible for the out-of-plane rotation of the TMS_2C unit. Apart from intrachain interactions, also agostic interactions between chains are observed. Thus, the solid state structure of **6** can be described as a two-dimensional sheetlike coordination polymer (Figure 2b). The γ-agostic interactions observed in the solid state structure of **6** are relatively rare,[18] but are probably strong on account of the $C^{\delta-}-Si^{\delta+}$ polarization. Recently, similarity in behavior of agostic interactions toward alkali metals and the heavier transition metals has been observed.[19]

Reaction of α,α-bis(trimethylsilyl)benzylpotassium (**6**) with CaI_2 in THF results in the corresponding Ca complex in good yield. One aim of this work is the testing of the obtained Ca product in initiating the anionic polymerization of styrene. For this reason the product purity is of major importance. It can, however, never be ruled out that some amount of the potassium precursor is included in the product. Deliberately introducing some potassium starting material in an NMR sample of the organocalcium product dissolved in benzene does not result in an additional set of signals but in broadening of all signals and a high-field shift of the

---

(13) Williams, R. A.; Tesh, K. F.; Hanusa, T. P. *J. Am. Chem. Soc.* **1991**, *113*, 4843.

(14) Overby, J. S.; Hanusa, T. P. *Organometallics* **1996**, *15*, 2205.

(15) Larson, J. S.; Epiotis, N. D. *J. Am. Chem. Soc.* **1981**, *103*, 410. (b) Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rohde, C.; Arad, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 6467. (c) Lehn, J.-M.; Wipff, G. *J. Am. Chem. Soc.* **1976**, *98*, 7498.

(16) For a recent review see: Eaborn, C.; Izod, K.; Smith, J. D. *J. Organomet. Chem.* **1995**, *500*, 89.

(17) Eaborn, C.; Hitchcock, P. B.; Izod, K.; Jaggar, A. J.; Smith, J. D. *Organometallics* **1994**, *13*, 753.

(18) Hitchcock, P. B.; Howard, J. A. K.; Lappert, M. F.; Leung, W.-P.; Mason, S. A. *J. Chem. Soc., Chem. Commun.* **1990**, 847.

(19) Braga, D.; Grepioni, F.; Biradha, K.; Desiraju; G. R. *J. Chem. Soc., Dalton Trans.* **1996**, 3925.

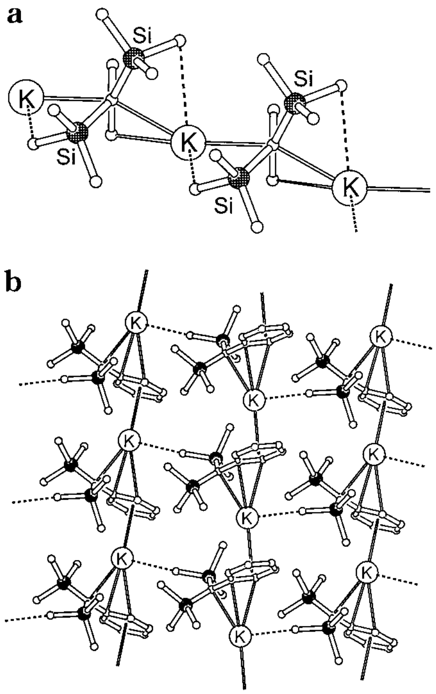


Figure 2. (a) Crystal structure of α,α-bis(trimethylsilyl)-benzylpotassium (**6**). View along the phenyl rings (protons omitted for clarity). Agostic Si−Me···K interactions are shown by dotted lines (shortest K···H and K···C distances are 3.00(3) and 3.550(3) Å, respectively). (b) The polymeric chains bind to each other via interchain agostic interactions (shortest K···H and K···C distances are 2.99(3) and 3.290(3) Å, respectively).

para-H (i.e., the NMR signals are a weighted average of the signals for the pure K and Ca compounds). Apparently, exchange of the anions between K and Ca centers exists.[20] To gain more certainty on the purity of our desired Ca compound, the raw reaction product was crystallized from a hexane/THF mixture and gave well-defined large single crystals of uniform habit and all with a similar orange color.

A single-crystal X-ray diffraction investigation on one of these large orange crystals shows the complex (α,α-bis(trimethylsilyl)benzyl)$_2$calcium·(THF)$_2$ with crystallographic C_2-symmetry (Figure 3). The Ca ion is bound mainly to the benzylic carbon (2.649(2) Å) and to a lesser extent to the aromatic ring (contacts to C_{ipso} and C_{ortho} are respectively 2.893(2) and 2.959(2) Å). The benzylic carbon is considerably more pyramidal (sum of valence angles at C_α is 342.6(2)°) than the benzylic carbon in the analogue potassium structure. One of the TMS substituents is situated nearly in the phenyl ring plane (C−C−C−Si is 10.4(3)°), whereas the other is rotated out of plane (C−C−C−Si 59.9(2)°). Due to the solvation of the metal center by two THF molecules, no intramolecular nor intermolecular agostic SiMe···Ca interactions are observed.

An interesting aspect of benzylanion structures in general is the significant deformation of the phenyl ring.[21] Charge delocalization from the negatively charged benzylic carbon atom into the phenyl ring is usually described by three resonance structures, of which the one with the negative charge on the *para*-C is most important. Due to these various resonance structures, extended bond shortening for the $C_\alpha-C_{ipso}$ and the $C_{ortho}-C_{meta}$ bonds is expected. Similar, significant bond lengthening for the $C_{ipso}-C_{ortho}$ bonds and slight bond lengthening for the $C_{meta}-C_{para}$ bonds are expected. Charge delocalization also results in deformation of the angles within the ring: the angle at C_{ipso} is considerably smaller than the standard 120° value and also the C_{para} angle is squeezed, but to a lesser extent. The angles at C_{ortho} and C_{meta} show widening and are larger than 120°. These deformations can be rationalized by applying VSEPR theory on the various resonance valence structures (repulsion between double and single bonds is larger than that between single bonds). The ring geometries for **6** and **7** are listed in Scheme 1. Both show the distortions expected due to charge delocalization; however, the Ca complex shows much less distortion than the K complex. Some factors are responsible for this observation.

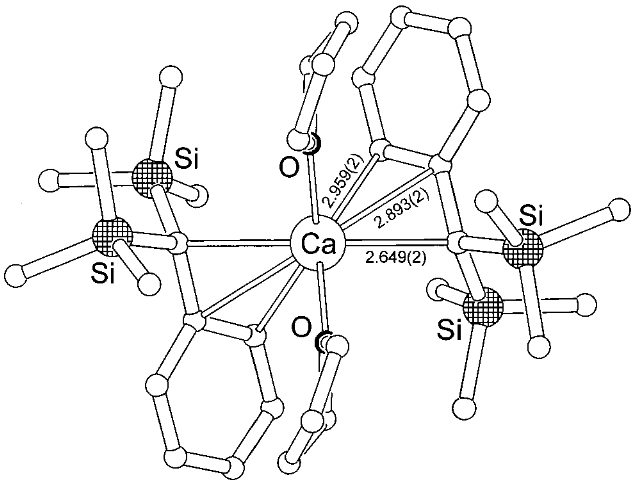


Figure 3. Crystal structure of (α,α-bis(trimethylsilyl)-benzyl)$_2$calcium·(THF)$_2$ (**7**) (protons omitted for clarity).

(i) The Ca−C bond is expected to be less ionic than the K−C bond on the basis of electronegativity considerations: the electronegativity of Ca is comparable to that of Li (Ca 1.0; Li 1.0; and K 0.9).

(ii) The positively charged cation acts as an electron localizer and counteracts delocalization of negative charge into the phenyl ring. The Ca^{2+} ion is higher charged than the K^+ ion and has a smaller ionic radius than the K^+ ion (Ca^{2+} 0.99 Å; K^+ 1.33 Å). The consequences of this larger charge/size ratio is a significantly more extended charge localization at C_α in **7** and a strong polarization of negative charge toward the Ca^{2+} ion (i.e., $sp^2 \rightarrow sp^3$ rehybridization).

(iii) In the solid-state structure of the potassium complex **6** the phenyl ring is bonded to a neighboring K^+ ion, thus attracting negative charge in the ring and improving charge delocalization.

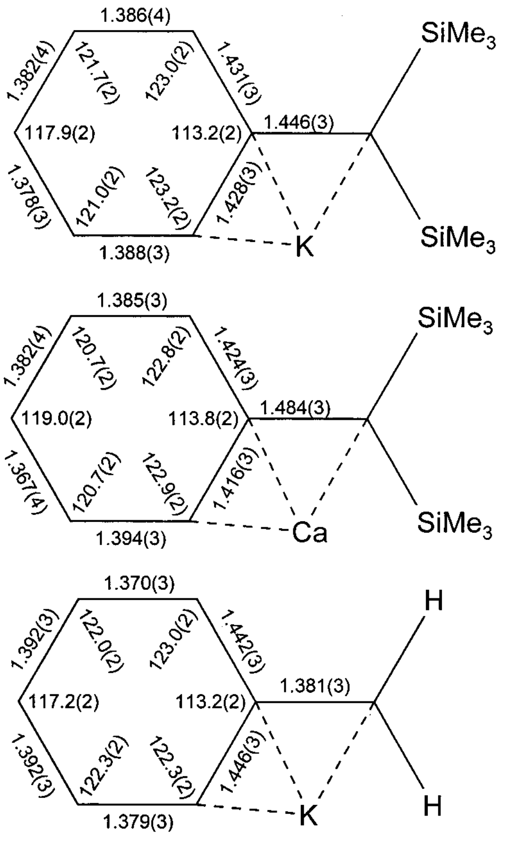
The TMS-substituted benzylpotassium compound **6** shows a much longer $C_\alpha-C_{ipso}$ bond and less distortion of the phenyl ring than the literature known benzylpotassium·(pmdta).[21] This is due to the localizing influence of the two positively charged Si atoms, which counteract delocalization of negative charge into the phenyl ring. Also, part of the negative charge at C_α is

---

[20] Low-temperature NMR studies failed due to solubility problems.

[21] Hofmann, D.; Bauer, W.; Hampel, F.; van Eikema Hommes, N. J. R.; Schleyer, P. v. R.; Otto, P.; Pieper, U.; Stalke, D.; Wright, D. S.; Snaith, R. *J. Am. Chem. Soc.* **1994**, *116*, 528.

Scheme 1



distributed over the silicon-bound methyl groups through negative hyperconjugation.

Charge delocalization considerably affects the NMR chemical shifts for benzyl anions. The ^{1}H NMR frequencies for the *para*-H (and to a lesser extent the *ortho*-H's) show a typical high-field shift with respect to benzene and are a measure of the extent of charge delocalization. The *para*-H resonance for **6** (6.07 ppm) is more high-field shifted than that for **7** (6.33 ppm), but less than that observed for benzylpotassium·(pmdta) (4.72 ppm).[21] A similar observation is made for the ^{13}C NMR frequencies: the shifts for the *para*-C's in **6**, **7**, and benzylpotassium·(pmdta) are 107.3, 114.3, and 95.2 ppm, respectively. Thus, the extent of charge delocalization in the solid state corresponds to that in solution.

The extent of pyramidalization at C_α in solution is usually evaluated through examination of the $C_\alpha{-}H$ one-bond coupling constant,[22] which is proportional to the percentage of s-character in this bond. The C−Si coupling constants have been measured for **6** (Me−Si 47.4 Hz and $C_\alpha{-}Si$ 69.9 Hz) and for **7** (Me−Si 48.6 Hz and $C_\alpha{-}Si$ 53.8 Hz). No quantitative relationship between C−Si coupling constants and the hybridization at C is known; however, qualitatively a correlation between C−Si coupling constants and hybridization at C seems to exist. The following $^1J_{C-Si}$ values have been reported: $(CH_3)_4Si$ 50.3, $(CH_3)_3Si{-}CH{=}CH_2$ 64.0, and $(CH_3)_3Si{-}CH{\equiv}CPh$ 83.6.[23] Thus, $^1J_{C-Si}$ values increase with the percentage of s-character on carbon. The C−Si coupling constants observed in **6** and **7** clearly indicate the larger pyramidalization at C_α in the Ca complex.

Ab initio calculations on the α,α-bis(silyl)-substituted benzyl anion are in agreement with the experimental observations. The geometry calculated for $C_6H_5C(SiH_3)_2^-$ (Figure 4) compares well with that of the anion in the structurally determined potassium compound **6**. The similar $C_\alpha{-}C_{ipso}$ bond distance and the similar degree of phenyl ring distortion indicate a comparable extent of charge delocalization. However, the calculated geometry for $PhC(SiH_3)_2^-$ compares less so with the anion in the corresponding Ca compound (**7**). The benzylic carbon in **7** is considerably more pyramidalized due to the charge-localizing influence of the Ca^{2+} ion, and therefore a significantly longer $C_\alpha{-}C_{ipso}$ bond results.

A comparison of the geometries calculated for $PhCH_2^-$ and $PhC(SiH_3)_2^-$ (Figure 4) clearly shows the charge-localizing influence of the SiH_3 group: the silicon substituents counteract delocalization of negative charge in the phenyl ring by electrostatic attraction. This is also confirmed by comparison of the NPA charges: 0.57 and 0.26 electron are delocalized in the phenyl rings of $PhCH_2^-$ and $PhC(SiH_3)_2^-$, respectively. The reduced delocalization of negative charge affects the double-bond character of the $C_\alpha{-}C_{ipso}$ bond enormously and is responsible for the much lower rotation barrier of the $C(SiH_3)_2^-$ group (6.8 kcal/mol) compared with that of the CH_2^- group (25.2 kcal/mol).[24] The partly out-of-plane rotated $C(SiH_3)_2$ group in the crystal structure of **6** is therefore not an anomaly. It is interesting to note that the phenyl ring distortion still partly exists in the perpendicular structures for which charge delocalization has been shut off completely. This is due to the considerably σ-donor character of the electron-rich benzylic carbon. Therefore, this type of distortion can be compared with that observed in aryl compounds bearing electropositive substituents such as Li or Mg.[25]

Both the Ca complex **7** and its K precursor **6** have been tested for their activity in the initiation of styrene polymerization. Whereas the Ca compound did not initiate the anionic polymerization of styrene at all, its K analogue turned out to be active. GPC analysis of the product showed a dispersion index M_w/M_n of 1.35 at a M_n of ca. 350 000. There is a light tailing at the low molecular weight side, which is most likely due to a slow initiation reaction in comparison with the propagation reaction. This is undoubtedly due to the TMS substituents at the benzylic carbon, which sterically hinder the initiation reaction but also thermodynamically stabilize the carbanion with respect to the living polystyrene chain end. Ab initio calculations, for example, show the stabilizing influence of a silicon substituent to be only slightly smaller than that of an aryl group (eqs 3, 4).

---

(22) Lett, R.; Chassaing, G.; Marquet, A. *J. Organomet. Chem.* **1976**, *111*, C17. (b) Zarges, W.; Marsch, M.; Harms, K.; Koch, W.; Frenking, G.; Boche, G. *Chem. Ber.* **1991**, *124*, 543. (c) Ahlbrecht, H.; Harbach, J.; Hauck, T.; Kalinowski, H.-O. *Chem. Ber.* **1992**, *125*, 1753.

(23) Kalinowski, H.-O.; Berger, S.; Braun, S. *^{13}C NMR Spektroskopie*; Thieme: New York, 1984.

(24) It should be noted that the C_{2v} structure for the rotational transition state of $PhCH_2^-$ is not a true transition state due to the presence of two imaginary frequencies: one for rotation around the $C_\alpha{-}C_{ipso}$ bond and one for pyramidalization at C_α. The C_{2v} geometry for $PhC(SiH_3)_2^-$ is a true transition state with one imaginary frequency corresponding to rotation around the $C_\alpha{-}C_{ipso}$ bond. The favored planarity of the $C(SiH_3)_2^-$ moiety is due to negative hyperconjugation of the p lone-pair into the SiH_3 substituents.

(25) Harder, S.; Ekhart, P. F.; Brandsma, L.; Kanters, J. A.; Duisenberg, A. J. M.; Schleyer, P. v. R. *Organometallics* **1992**, *11*, 2623. (b) Domenicano, A.; Vaciago, A.; Coulson, C. A. *Acta Crystallogr.* **1975**, *B31*, 1630.

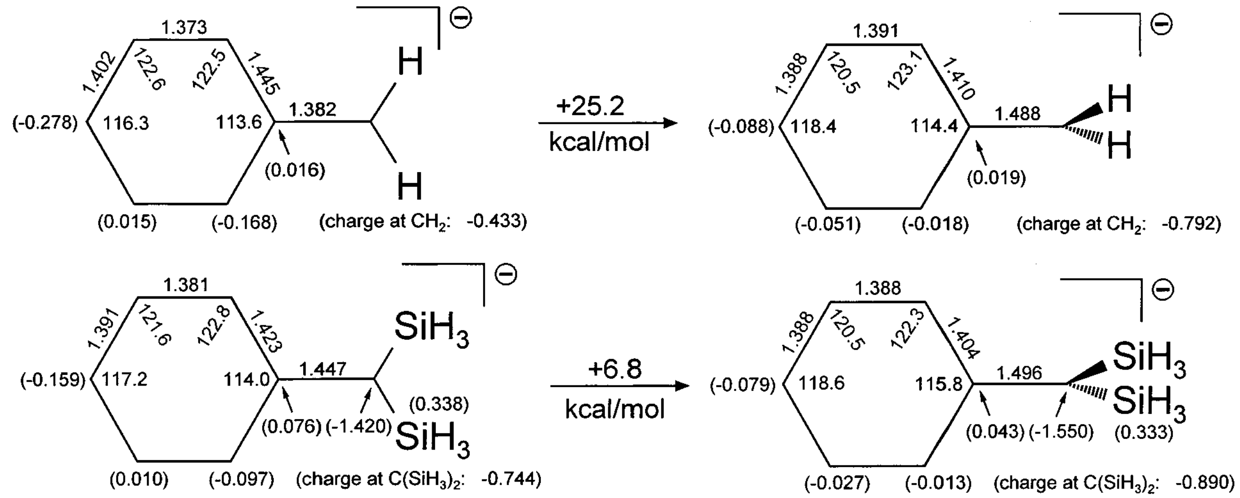
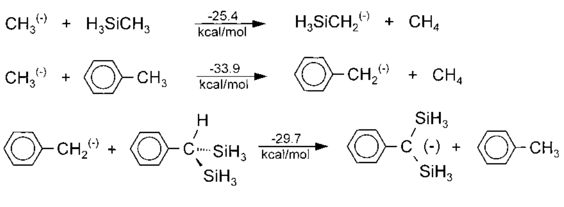


Figure 4. Ab initio calculations (MP2(full)/6-31+G*//RHF/6-31+G*). Distances and angles are given in angstroms and degrees, respectively. Group charges, i.e., the charge on carbon + attached hydrogen(s), are shown in parentheses.

The two silicon substituents in **6** stabilize the benzyl anion by nearly 30 kcal/mol (eq 5).



(3)

(4)

(5)

The failure of the Ca compound (**7**) in initiating anionic polymerization of styrene is probably due to the fact that the C−Ca bond is more covalent and much stronger[26] than a C−K bond. Also, the extended shielding of the metal cation by two benzyl anions in **7** compared with only one anion in **6** might explain the difference in their reactivities toward styrene (precoordination of styrene to the metal center is most likely an important step in the addition reaction mechanism). Future research will be directed to the syntheses of benzylcalcium complexes with less TMS-substituted and more reactive benzylic carbon centers.

Experimental Section

General Procedures. All experiments were carried out under argon using predried solvents and Schlenk techniques. α,α-Bis(trimethylsilyl)toluene was prepared according to a literature procedure.[27] 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) and quenched with oxygen-free methanol.

Computational Methods. All geometries were fully optimized within the designated symmetry constraints at the restricted Hartree−Fock level by using gradient optimization techniques and the standard basis set, 6-31+G*, incorporated in the GAUSSIAN 94 program system.[28] All stationary points were checked to be real minima by frequency analyses (no imaginary frequencies were found). Single-point energy calculations were performed at the MP2(full)/6-31+G* level. Charges have been calculated by use of the Natural Population Analysis.[29]

Crystal structures were solved by direct methods with the program DIRDIF[30] and refined with SHELXL93.[31] Plots and geometry calculations were made with the EUCLID package.[32]

Synthesis of α,α-Bis(trimethylsilyl)benzylpotassium (6). A 1.6 M solution of butyllithium in hexane (13.7 mL, 21.9 mmol) was added over a 3 min interval to a precooled (−80 °C) solution of α,α-bis(trimethylsilyl)toluene (5.80 g, 24.5 mmol) and potassium 3-methyl-3-pentanolate (3.09 g, 22.0 mmol) in 15 mL of THF. The reaction solution turned red immediately and was allowed to warm to room temperature within 2 h. All THF was removed under vacuum. Addition of 20 mL of pentane resulted in a yellow precipitate, which was isolated by centrifugation and washed three times with 20 mL portions of pentane. The remaining product was dried (0.01 mmHg, 50 °C, 30 min) and isolated as a yellow powder in nearly quantitative yield (5.96 g, 21.7 mmol). ^{1}H

---

(26) Although no experimental data on C−K and C−Ca bond strengths are known, the latter bond is much stronger for obvious reasons. The bond energy in such ionic species can be roughly estimated by Coulomb's law. Therefore, the smaller ionic radius and higher charge on the Ca^{2+} ion when compared with the K^+ ion result in much stronger bonding to anionic ligands. High-level ab initio calculations (MP2(fc)/6-31G* + ZPE) on several light group I and II benzylmetal compounds indeed confirm that anion−cation bond energies for the group II metals are much higher when compared with their group I neighbors. We calculated the following heterolytic disociation energies: first-row benzylmetal compounds ($PhCH_2Li \rightarrow PhCH_2^- + Li^+$ 149.3 kcal/mol and $PhCH_2BeCH_3 \rightarrow PhCH_2^- + CH_3Be^+$ 242.4 kcal/mol) and second-row benzylmetal compounds ($PhCH_2Na \rightarrow PhCH_2^- + Na^+$ 127.1 kcal/mol; $PhCH_2MgCH_3 \rightarrow PhCH_2^- + CH_3Mg^+$ 186.7 kcal/mol).

(27) Brandsma, L. *Preparative Polar Organometallic Chemistry, Vol. 2*; Springer-Verlag: Heidelberg, Germany, 1990; p 122.

(28) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 94*, Revision C.3; Gaussian Inc.: Pittsburgh, PA, 1995.

(29) Mulliken population analyses fail to give a useful and reliable characterization of the charge distribution in many cases, especially when highly ionic compounds are involved. Charges calculated according to the Natural Population Analysis (NPA) do not show these deficiencies and are relatively basis set independent. NPA analysis: (a) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (b) Reed, A. E.; Curtis, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(30) 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.

(31) Sheldrick, G. M. *SHELXL93, Program for Crystal Structure Refinement*; University of Göttingen: Germany, 1993.

(32) Spek, A. L. The EUCLID package. *Computational Crystallography*; Sayre, D., Ed.; Clarendon Press: Oxford, 1982.

NMR (C_6D_6/THF-d_8 in a 9/1 ratio, 20 °C): 0.41 (s, 9H, Me_3Si); 6.07 (t, 6.9 Hz, 1H, H_{para}); 6.71 (d, 7.8 Hz, 2H, H_{ortho}); 6.81 (t, 7.5 Hz, 2H, H_{meta}). ^{13}C NMR (C_6D_6/THF-d_8 in a 9/1 ratio, 20 °C): 4.8 (Me_3Si); 49.6 (C_α); 107.3 (C_{para}); 124.0 (C_{ortho}); 128.8 (C_{meta}); 159.2(C_{ipso}).

Synthesis of (α,α-Bis(trimethylsilyl)benzyl)$_2$calcium·(THF)$_2$ (7). A mixture of **6** (1.32 g, 4.81 mmol) and CaI_2 (0.75 g, 2.55 mmol) in 20 mL of THF was stirred in a glovebox for 2 days. Evaporation of the solvent under vacuum yielded an orange-brown solid, which was extracted with 20 mL of hexane. The yellow-brown mother liquor was concentrated to half its volume, and 0.5 mL of THF was added. Slowly cooling the solution to −30 °C yielded large yellow crystals of **7** (0.98 g, 1.50 mmol, 62.4%). ^1H NMR (C_6D_6/THF-d_8 in a 9/1 ratio, 20 °C): 0.39 (s, 18H, Me_3Si); 1.32 (m, 8H, THF); 3.41 (m, 8H, THF); 6.33 (t, 7.0 Hz, 2H, H_{para}); 6.87 (t, 8.2 Hz, 4H, H_{meta}); 6.96 (d, 8.3 Hz, 4H, H_{ortho}). ^{13}C NMR (C_6D_6/THF-d_8 in a 9/1 ratio, 20 °C): 4.7 (Me_3Si); 25.6 (THF); 53.2 (C_α); 68.2 (THF); 114.3 (C_{para}); 127.4 (C_{ortho}); 130.9 (C_{meta}); 158.0 (C_{ipso}).

Crystal Structure Data for α,α-Bis(trimethylsilyl)-benzylpotassium (6): orthorhombic, $a = 6.5946(6)$, $b = 13.388(1)$, $c = 17.544(2)$ Å, $V = 1548.9(3)$ Å^3, space group $P2_12_12_1$; formula ($C_{13}H_{23}Si_2K$), $M = 274.59$, $Z = 4$, $\rho_{calcd} = 1.178$ g cm^{-3}, μ(Mo Kα) = 0.474 mm^{-1}; 4306 reflections were measured (Mo Kα, graphite monochromator, $T = -90$ °C), 3731 independent reflections ($R_{int} = 0.0192$), 3129 observed reflections with $I > 2.0\sigma(I)$. Solution by direct methods, full matrix least-squares refinement on F^2 to $R_1 = 0.034$, $wR_2 = 0.070$ (237 parameters; check for absolute structure by refinement of the Flack parameter). Non-hydrogens were refined anisotropically. All hydrogens have been taken from the difference Fourier map and were refined isotropically with free displacement factors.

Crystal Structure Data for (α,α-Bis(trimethylsilyl)-benzyl)$_2$calcium·(THF)$_2$ (7): monoclinic, $a = 19.974(5)$, $b = 9.900(1)$, $c = 22.472(2)$ Å, $\beta = 122.375(9)$°, $V = 3753(1)$ Å^3, space group $C2/c$; formula ($C_{34}H_{62}Si_4O_2Ca$), $M = 655.28$, $Z = 4$, $\rho_{calcd} = 1.160$ g cm^{-3}, μ(Mo Kα) = 0.322 mm^{-1}; 4401 reflections were measured (Mo Kα, graphite monochromator, $T = -90$ °C), 4095 independent reflections ($R_{int} = 0.0214$), 2963 observed reflections with $I > 2.0\sigma(I)$. Solution by direct methods, full matrix least-squares refinement on F^2 to $R_1 = 0.042$, $wR_2 = 0.100$ (310 parameters). Non-hydrogens were refined anisotropically. All hydrogens have been taken from the difference Fourier map and were refined isotropically with free displacement factors.

Acknowledgment. We are grateful to the BASF AG (Ludwigshafen, Germany) for financing this project and GPC analyses of the polymers. Prof. Dr. H.-H. Brintzinger (Konstanz) and Dr. K. Knoll (Ludwigshafen) are kindly acknowledged for helpful discussions. Mrs. Anke Friemel is thanked for measuring 600 MHz spectra.

Supporting Information Available: Atomic fractional coordinates, bond distances and angles, hydrogen atom positions, and anisotropic thermal parameters for **6** and **7** are available free of charge via the Internet at http://pubs.acs.org.

OM0006209