

Synthesis of Strontium and Barium Bis{tris[(trimethylsilyl)methyl]zincates} via the Transmetalation of Bis[(trimethylsilyl)methyl]zinc

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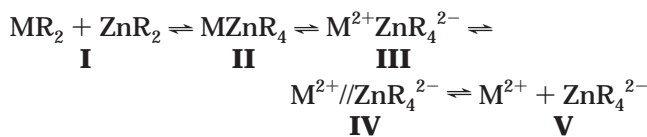
The transmetalation of bis[(trimethylsilyl)methyl]zinc in THF with distilled strontium and barium yielded bis(tetrahydrofuran)strontium and tetrakis(tetrahydrofuran)barium bis{tris[(trimethylsilyl)methyl]zincates} (**1** and **2**, respectively). The reaction of barium with $\text{Zn}(\text{CH}_2\text{SiMe}_3)_2$ in toluene gave bis(η^6 -toluene)barium bis{tris[(trimethylsilyl)methyl]zincate} (**3**) with rather short Ba–C bond lengths of 3.028(5) and 3.055(5) Å. All of these trialkylzincate anions coordinate as bidentate ligands with M–C–Zn three-center two-electron bonds. When carried out in the nondonor solvent heptane, the transmetalation reaction yielded barium bis{tris[(trimethylsilyl)methyl]zincate} (**4**), which reacts with THF to give the complex **2** and a small amount of $[(\text{THF})_3\text{Ba}]_2(\mu_4\text{-O})_2[(\text{Me}_3\text{SiCH}_2\text{ZnCH}_2)_2\text{SiMe}_2]_2$ (**5**). The central moiety is a centrosymmetric Ba_2O_2 cycle with Ba–O distances of 2.514(2) and 2.570(3) Å. The oxygen dianion is surrounded, distorted tetrahedrally by two barium and two zinc atoms.

Introduction

Compounds with bonds between the heavier alkaline-earth metals and carbon are gaining interest due to their expected reactivity and applicability. In contrast to the alkaline-earth metallocenes, which are a well-known substance class¹ there are only a few representatives of molecules with metal–carbon σ -bonds. Delocalized anionic charge on the ligand such as on 2-pyridylbenzyl,² 2,4-di-*tert*-butylpentadienyl,³ or 1,3-bis(trialkylsilyl)allyl⁴ often leads to a multihapto coordination to the alkaline-earth-metal centers. Difficulties in obtaining pure dialkyl alkaline-earth-metal compounds are the low reactivity of the metals and the insolubility of the compounds on one hand and a high reactivity of dissolved metalloorganic species on the other which often leads to ether cleavage reactions, as shown, for example, for calcium bis(trimethylsilyl)amide tetrakis(trimethylsilyl)methylaluminum.⁵ To obtain soluble molecules, steric shielding of the metal center by bulky aliphatic groups as well as the coordination of Lewis bases are suitable strategies. The metal center of alkenylbarium phospholide **A** employs both of these methods by use of a THF ligand, η^5 coordination of the sterically demanding phospholide substituent, and side-on binding of the

alkynyl fragment (Chart 1).⁶ Monomeric barium bis(alkynide) **B** could be isolated by shielding of the metal center with a crown ether.⁷ Metal–carbon σ -bonds were also found for the carbene adducts of decamethyl alkaline-earth metallocenes (**C**).⁸

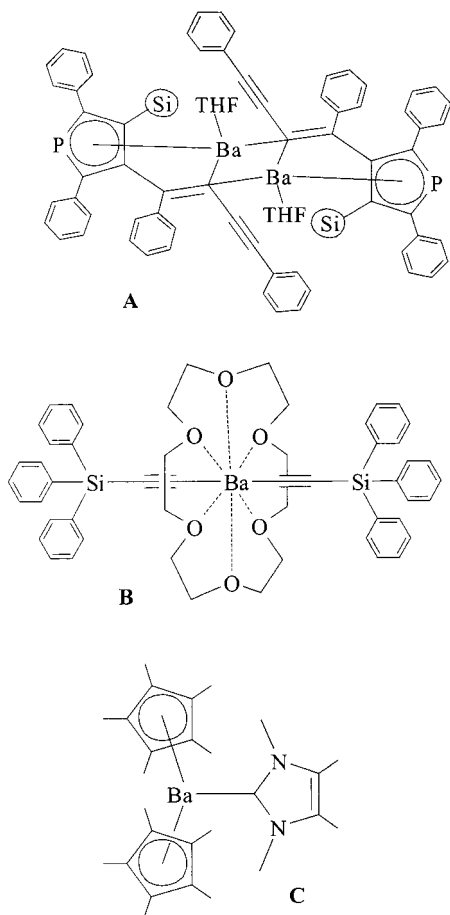
Zincates are a compound class of great interest for many years.⁹ The transmetalation of dialkylzinc compounds by barium has already been investigated by Gilman et al. 55 years ago. Barium metal was reacted with diethyl¹⁰ and dibutylzinc¹¹ to give compounds of the type $\text{BaR}_2 \cdot \text{ZnR}_2$. The NMR spectroscopic characterization was performed approximately 25 years later, and it was shown that the alkyl groups are chemically and magnetically equivalent on the NMR time scale.¹² Kaufmann et al.¹³ investigated the equilibria present in solution, considering the free alkyl compounds BaR_2 and ZnR_2 (**I**), the “ate” complex BaZnR_4 (**II**), the contact ion pair $\text{Ba}^{2+}\text{ZnR}_4^{2-}$ (**III**) (which can be solvated (**IV**)), and the free ions Ba^{2+} and ZnR_4^{2-} (**V**). The ionic species



dominate in donor solvents, whereas mainly **I** and **III**

- (1) Recent reviews: Jutzi, P. *J. Organomet. Chem.* **1990**, *400*, 1. Hanusa, T. P. *Polyhedron* **1990**, *9*, 1345. Hanusa, T. P. *Chem. Rev.* **1993**, *93*, 1023. Burkey, D. J.; Hanusa, T. P. *Comments Inorg. Chem.* **1995**, *17*, 41. Hays, M. L.; Hanusa, T. P. *Adv. Organomet. Chem.* **1996**, *40*, 117. Bridgeman, A. J. *J. Chem. Soc., Dalton Trans.* **1997**, 2887. Jutzi, P. *Chem. Unserer Zeit* **1999**, *33*, 342. Jutzi, P. *Chem. Rev.* **1999**, *99*, 969.
- (2) Gardiner, M. G.; Raston, C. L.; Viebrock, H. *Chem. Commun.* **1996**, 1795.
- (3) Overby, J. S.; Hanusa, T. P. *Angew. Chem.* **1994**, *106*, 2300; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2191.
- (4) Harvey, M. J.; Hanusa, T. P.; Young, V. G. *Angew. Chem.* **1999**, *111*, 241; *Angew. Chem., Int. Ed.* **1999**, *38*, 217.
- (5) Westerhausen, M.; Birg, C.; Nöth, H.; Knizek, J.; Seifert, T. *Eur. J. Inorg. Chem.* **1999**, 2209.

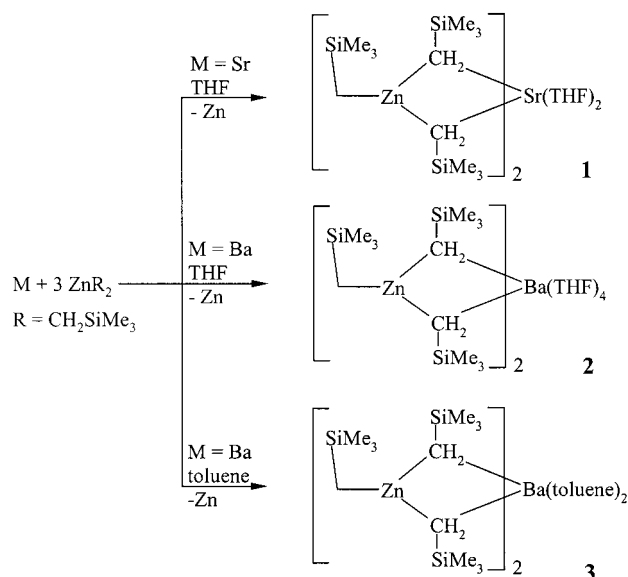
- (6) Westerhausen, M.; Digeser, M. H.; Nöth, H.; Seifert, T.; Pfitzner, A. *J. Am. Chem. Soc.* **1998**, *120*, 6722.
- (7) Green, D. C.; English, U.; Ruhlandt-Senge, K. *Angew. Chem.* **1999**, *111*, 365; *Angew. Chem., Int. Ed.* **1999**, *38*, 354.
- (8) Arduengo, A. J.; Davidson, F.; Krafczyk, R.; Marshall, W. J.; Tamm, M. *Organometallics* **1998**, *17*, 3375.
- (9) Tochtermann, W. *Angew. Chem.* **1966**, *78*, 355.
- (10) Gilman, H.; Woods, L. A. *J. Am. Chem. Soc.* **1945**, *67*, 520.
- (11) Gilman, H.; Haubein, A. H.; O'Donnell, G.; Woods, L. A. *J. Am. Chem. Soc.* **1945**, *67*, 922.
- (12) Kawakami, Y.; Yasuda, Y.; Tsuruta, T. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1164.

Chart 1. Schematic Representation of Selected Molecules with Alkaline-Earth-Metal–Carbon Bonds

are present in apolar solvents. The addition of pyridine to the zincate solution gave a red precipitate, and Kaufmann and co-workers¹³ suggested the formation of a mixture of $(py)_2ZnR_2$ and $(py)_2MR_2$. These authors were interested in these compounds due to their ability to polymerize isoprene.¹⁴

For calcium bis{tris[bis(trimethylsilyl)amino]zincate} the solvent dependency was elucidated from NMR spectroscopic experiments.¹⁵ Whereas in a nondonor solvent the equilibrium lies on the side of CaR_2 and ZnR_2 , stronger Lewis bases such as THF or 1,2-dimethoxyethane stabilize the zincate $Ca\{Zn[N(SiMe_3)_2]_3\}_2$ due to coordinative saturation of the electropositive metal by oxygen atoms. We were interested in barium bis-(trialkylzincates) because it had been mentioned that the reactions of alkaline-earth-metal zincate complexes may be considered as reactions of individual MR_2 and ZnR_2 species.¹⁶

Structurally characterized zincates of the alkaline-earth metals are well-known for magnesium. However, to our knowledge, there have been no reports for the heavier group 2 metals. The magnesium zincates crystallized as solvent-separated ion pairs with trigonal-

Scheme 1. Synthesis of the Alkaline-Earth-Metal Bis(trialkylzincates) 1–3

planar surroundings for the zinc atoms. Whereas in triphenyl- and tris(2,4,6-trimethylphenyl)zincate anions¹⁷ the C–Zn–C angles were nearly equal, strong distortions were observed for the tribenzylzincate anion with C–Zn–C angles of 112.8(1), 119.0(1), and 128.20(9)°.¹⁸ In all these cases, the hexacoordinate magnesium atoms are coordinatively saturated and, hence, they show no short contacts to the zincate counterions.

Results and Discussion

Synthesis. The transmetalation reaction has the enormous advantage that the incorporation of halides and pseudohalides such as alkoxides or amides into the organometallic product molecules can be avoided. For this purpose and to increase the reactivity, the strontium and barium metals were distilled prior to use.¹⁹ The transmetalation of bis[(trimethylsilyl)methyl]zinc with strontium and barium in THF at room temperature was complete after 24 h, as could be shown by NMR spectroscopy. The synthesis of colorless bis(tetrahydrofuran)strontium as well as colorless tetrakis(tetrahydrofuran)barium bis{tris[(trimethylsilyl)methyl]zincates} (**1** and **2**, respectively), is summarized in Scheme 1.

Carrying out the transmetalation reaction with barium in toluene yielded a yellow solution. After reduction of the volume and cooling of the solution colorless crystals of bis(η^6 -toluene)barium bis{tris[(trimethylsilyl)methyl]zincate} (**3**) precipitated (Scheme 2). To avoid use of a Lewis basic solvent, *n*-heptane was chosen. The transmetalation occurred in the same manner, but we were unable to crystallize the product. However, the NMR data confirmed the formation of a solvent-free barium bis{tris[(trimethylsilyl)methyl]zincate} (**4**). Therefore,

(17) Krieger, M.; Geiseler, G.; Harms, K.; Merle, J.; Massa, W.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1387.

(18) Rijnberg, E.; Jastrzebski, J. T. B. H.; Boersma, J.; Kooijman, H.; Spek, A. L.; van Koten, G. *J. Organomet. Chem.* **1997**, *541*, 181.

(19) Ehrlich, P.; Seifert, H. J. In *Handbuch der Präparativen Anorganischen Chemie*, 3rd ed.; Brauer, G., Ed.; F. Enke: Stuttgart, Germany, 1978; Vol. 2, p 917. Evers, J.; Weiss, A.; Kaldis, E.; Muheim, J. *J. Less-Common Met.* **1973**, *30*, 83. Kaldis, E.; Muheim, J.; Evers, J.; Weiss, A. *J. Less-Common Met.* **1973**, *31*, 169.

(13) Kaufmann, F.; Geraudelle, A.; Kaempf, B.; Schué, F.; Deluzarche, A.; Maillard, A. *J. Organomet. Chem.* **1970**, *24*, 13.

(14) Kaufmann, F.; Alev, S.; Collet, A.; Schué, F.; Kaempf, B.; Deluzarche, A. *Eur. Polym. J.* **1976**, *12*, 209.

(15) Westerhausen, M. *Z. Anorg. Allg. Chem.* **1992**, *618*, 131.

(16) Gowenlock, B. G.; Lindsell, W. E. *J. Organomet. Chem. Libr. 3, Organomet. Chem. Rev.* **1977**, *1*.

Scheme 2. Synthesis of 4 and Schematic Representation of Compound 5

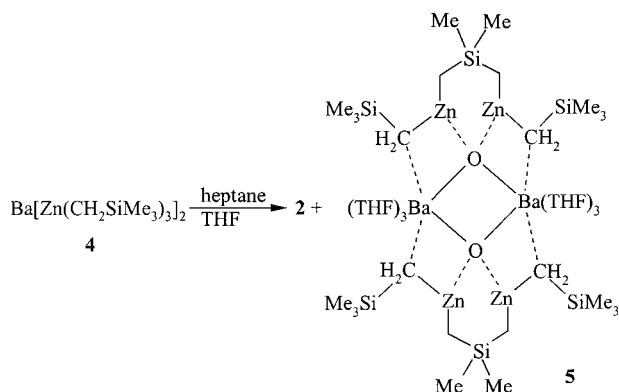


Table 1. NMR Parameters of 1–4 (R = CH₂SiMe₃)^a

	1	2	2 ^b	3	4
¹ H NMR					
δ(CH ₂)	-0.75	-0.70	-1.18	-0.70	-0.71
δ(SiMe ₃)	0.30	0.32	-0.16	0.16	0.19
¹³ C NMR					
δ(CH ₂)	8.32	10.98	0.96	4.76	6.07
δ(SiMe ₃)	3.79	3.84	3.71	3.03	3.09
²⁹ Si{ ¹ H} NMR					
δ(Si)	1.21	1.42		0.70	3.06

^a The solvent used was [D₆]benzene unless otherwise noted.

^b The solvent was [D₈]THF.

THF was added dropwise to allow the NMR spectroscopic comparison of this product with **2** (Scheme 2). Instead of quantitative formation of the THF complex **2**, a small amount of compound **5** had also been formed, together with tetramethylsilane, which was identified by NMR spectroscopy. Even though the interpretation of compound **5** as a metalation and THF cleavage product seems reasonable, a reaction of **4** with adventitious oxygen/water in the presence of THF also is a possible explanation. The central feature is a dimeric barium oxide with three THF ligands coordinated to each metal center. The coordinated (Me₃SiCH₂ZnCH₂)₂-SiMe₂ molecules are formed by intramolecular metalation reactions and bonded to each oxygen atom as chelating bidentate Lewis acids. A similar metalation reaction of a solvent molecule was observed previously for potassium tris(trimethylsilyl)methylzincate and benzene, which yields a heteroleptic phenylbis(trimethylsilyl)methylzincate.²⁰

The barium zincates formed quantitatively in THF, toluene, and *n*-heptane. A monomer–dimer equilibrium was not observed. A rapid exchange reaction leads to magnetically equivalent alkyl substituents on the NMR time scale. Therefore, we exclude the formation of dialkylbarium in an equilibrium reaction. Furthermore, in all these compounds the ratio of Ba to Zn was always 1:2. A further transmetalation was not observed with a huge excess of barium metal or by application of ultrasound to the reaction mixture, nor could an equimolar ratio of Ba to Zn and the formation of a zincate of the type BaZnR₄ be obtained.

NMR Spectroscopy. NMR data for **1–4** is summarized in Table 1. In comparison to bis(trimethylsilyl)methylzinc²¹ the formation of the zincates leads only

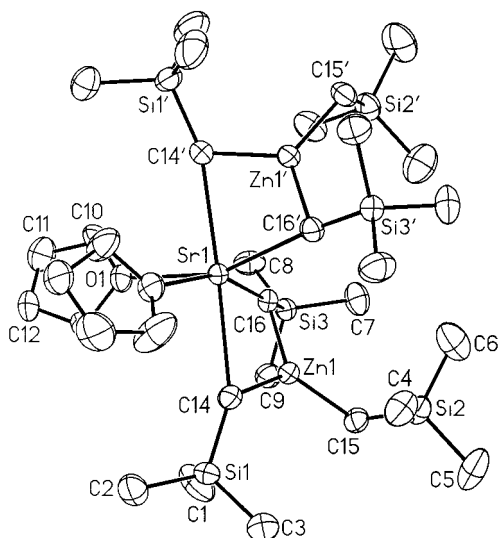


Figure 1. Molecular structure of **1**. Atoms marked with an prime are generated by crystallographic *C*₂ symmetry ($-x, y, -z + 0.5$). The ellipsoids represent a probability of 40%. The hydrogen atoms are omitted for clarity reasons. Selected bond lengths (Å): Sr1–O1 = 2.534(4), Sr1–C14 = 2.857(7), Sr1–C16 = 2.806(8), Zn1–C14 = 2.076(7), Zn1–C15 = 2.019(6), Zn1–C16 = 2.095(7), Si1–C14 = 1.860(8), Si2–C15 = 1.826(7), Si3–C16 = 1.855(9). Selected bond angles (deg): O1–Sr1–O1' = 79.9(2), C14–Sr1–C16 = 76.5(2), C14–Zn1–C15 = 120.1(3), C14–Zn1–C16 = 114.4(3), C15–Zn1–C16 = 125.4(3).

to small changes in the δ values in general. The δ_C values of the α -carbon atom show a low-field shift compared to Zn(CH₂SiMe₃)₂, which is extremely large for derivatives **1** and **2**. The proton resonance of the CH₂ moieties is shifted slightly toward higher field due to the anionic charge which is located on the ZnC₃ fragment. In contrast to the tris[bis(trimethylsilyl)amino]zincates¹⁵ the trimethylsilyl substituents of the tris-[(trimethylsilyl)methyl]zincates are nearly unaffected by the anionic charge. The solvent dependency is extremely strong, as shown by derivative **2**. Dissolving in [D₈]THF leads to an extremely low-field shift of the NMR parameters of the α -methylene group. This could account for a solvent-separated ion pair in THF solution, whereas in toluene or benzene a contact ion pair is formed. This explanation would also be in agreement with the values ($\delta(\alpha\text{-C})$ 4.41, $\delta(\alpha\text{-CH}_2)$ -1.15) reported by Purdy and George for potassium tris(trimethylsilyl)methylzincate.²⁰

Molecular Structures. Figure 1 shows the molecular structure as well as the numbering scheme of bis-(tetrahydrofuran)strontium bis{tris[(trimethylsilyl)methyl]zincate} (**1**). The atoms generated by crystallographic *C*₂ symmetry are marked with primes. The hexacoordinate strontium atom shows an octahedral surrounding with the THF molecules in cis positions. Distortions result from the small bite of the chelating zincate anion. The Sr–O bond length of 2.534(4) Å lies in the expected region, as described for numerous THF adducts of strontium-containing compounds.²²

(21) Moorhouse, S.; Wilkinson, G. *J. Organomet. Chem.* **1973**, *52*, C5. Moorhouse, S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1974**, 2187. Heinekey, D. M.; Stobart, S. R. *Inorg. Chem.* **1978**, *17*, 1463. Westerhausen, M.; Rademacher, B.; Poll, W. *J. Organomet. Chem.* **1991**, *421*, 175.

(22) Westerhausen, M. *Coord. Chem. Rev.* **1998**, *176*, 157.

(20) Purdy, A. P.; George, C. F. *Organometallics* **1992**, *11*, 1955.

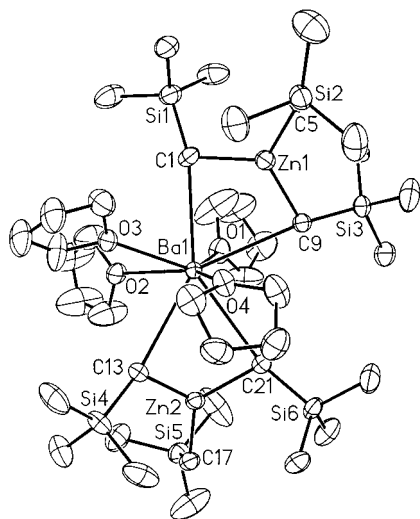


Figure 2. Molecular structure of **2**. The ellipsoids represent a probability of 40%. The hydrogen atoms are omitted for clarity reasons. Selected bond lengths (Å): Ba1–O1 = 2.873(6), Ba1–O2 = 2.782(5), Ba1–O3 = 2.861(5), Ba1–O4 = 2.779(5), Ba1–C1 = 3.085(7), Ba1–C9 = 3.229(7), Ba1–C13 = 3.179(7), Ba1–C21 = 3.171(7), Zn1–C1 = 2.125(7), Zn1–C5 = 2.013(8), Zn1–C9 = 2.066(7), Zn2–C13 = 2.064(7), Zn2–C17 = 2.017(7), Zn2–C21 = 2.082(7), Si1–C1 = 1.846(7), Si2–C5 = 1.840(8), Si3–C9 = 1.850(7), Si4–C13 = 1.834(7), Si5–C17 = 1.836(8), Si6–C21 = 1.848(7). Selected bond angles (deg): C1–Ba1–C9 = 68.5(2), C13–Ba1–C21 = 66.2(2), C1–Zn1–C5 = 120.5(3), C1–Zn1–C9 = 116.1(3), C5–Zn1–C9 = 123.3(3), C13–Zn2–C17 = 124.0(3), C13–Zn2–C21 = 113.5(3), C17–Zn2–C21 = 122.0(3), Zn1–C1–Ba1 = 84.4(2), Zn1–C9–Ba1 = 81.6(2), Zn2–C13–Ba1 = 83.8(2), Zn2–C21–Ba1 = 83.7(2).

The Sr–C distances with values of 2.806(8) and 2.857(7) Å are greater than those observed for bis[(triphenylsilyl)ethynyl]strontium (Sr–C = 2.692(4) and 2.723(4) Å).⁷ This observation can be attributed to the higher coordination number of the carbon atoms and to the fact that the bonding situation of **1** is best described as a Sr–C–Zn three-center–two-electron bond. This situation leads also to a lengthening of the Zn1–C14 and Zn1–C16 bonds of the bridging alkyl substituents, whereas the terminal Zn1–C15 value is markedly shorter. The four-membered SrC₂Zn cycle is folded, and the normals of the planes Sr1/C14/C16 and Zn1/C14/C16 include an angle of 38.6°.

The anionic charge on the α -methylene groups leads to a shortening of the Si–C bonds compared to those between silicon and the methyl C atoms. This effect is most striking for the terminal substituent and can be understood in terms of an electrostatic attraction between the negatively charged methylene groups and the partly positive silicon atoms.

Figure 2 represents the molecular structure as well as the numbering scheme of tetrakis(tetrahydrofuran)-barium bis{tris[(trimethylsilyl)methyl]zincate} (**2**). The larger alkaline-earth-metal atom displays a coordination number of 8. The Ba–O distances vary between 2.779(5) and 2.873(6) Å and lie in the characteristic range.²² Due to the rather irregular polyhedron the Ba–C bond lengths differ from 3.085(7) and 3.228(7) Å and are longer than those observed for alkenylbarium phospholide⁶ (**A**) and bis[(triphenylsilyl)ethynyl]barium (**B**).⁷

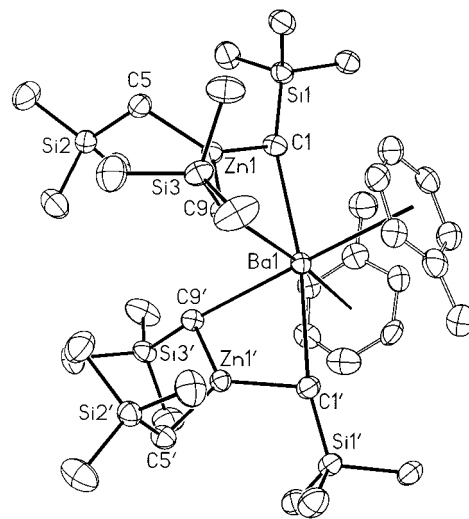


Figure 3. Molecular structure of **3**. Atoms marked with an prime are generated by the symmetry operation $-x, y, -z + 0.5$. The ellipsoids represent a probability of 40%. The hydrogen atoms are omitted for clarity reasons. The two-site disorder of the toluene ligands is not shown. Selected bond lengths (Å): Ba1–C1 = 3.028(5), Ba1–C9 = 3.055(5), Zn1–C1 = 2.080(5), Zn1–C5 = 2.012(5), Zn1–C9 = 2.072(4), Si1–C1 = 1.851(5), Si2–C5 = 1.834(5), Si3–C9 = 1.854(5). Selected bond angles (deg): C1–Ba1–C9 = 72.4(1), C1–Zn1–C5 = 119.6(2), C1–Zn1–C9 = 119.8(2), C5–Zn1–C9 = 120.6(2), Zn1–C1–Ba1 = 80.7(2), Zn1–C9–Ba1 = 80.1(1).

Even the dative bonds between a carbene and decamethylbarocene (**C**) with a value of 2.951(3) Å⁸ are shorter than the Ba–C bonds of these three-center–two-electron Ba–C–Zn bonds. Similar to **1**, the bridging methylene groups have shorter Zn–C bonds than the terminally bonded (trimethylsilyl)methyl substituents. The four-membered BaC₂Zn rings are folded; the normals of the planes Ba1/C1/C9 and Zn1/C1/C9 include an angle of 35.5°. The other BaC₂Zn ring shows a corresponding value of 40.9°.

Figure 3 displays the molecular structure and the numbering scheme of **3**. Atoms generated by crystallographic C₂ symmetry are marked with primes. The barium atom is coordinated to two toluene molecules and two zincate anions. Because of the rather low coordination number the Ba–C distances of 3.028(5) and 3.055(5) Å are shorter than those observed for **2**. The side-on coordination of toluene molecules to soft metal cations was observed earlier; an example of a toluene–barium interaction is mentioned for a barium tritin(II) tetrakis[μ_3 -(tri-*tert*-butylsilyl)phosphandiide].²³ The characteristic lengthening of the Zn–C bonds of the bridging alkyl groups is also observed in this anion. In this less crowded molecule the angle between the normals of the planes Ba1/C1/C9 and Zn1/C1/C9 adopts a smaller value of 31.8°.

Figure 4 represents the molecular structure and the numbering scheme of **5**. The atoms generated by crystallographic inversion symmetry are marked with primes. The central moiety is a Ba₂O₂ ring with Ba–O bond lengths of 2.514(2) and 2.570(3) Å, which are approximately 0.25 Å shorter than the Ba–O distances

(23) Westerhausen, M.; Krofta, M.; Wiberg, N.; Knizek, J.; Nöth, H.; Pfitzner, A. *Z. Naturforsch.* **1998**, *53B*, 1489.

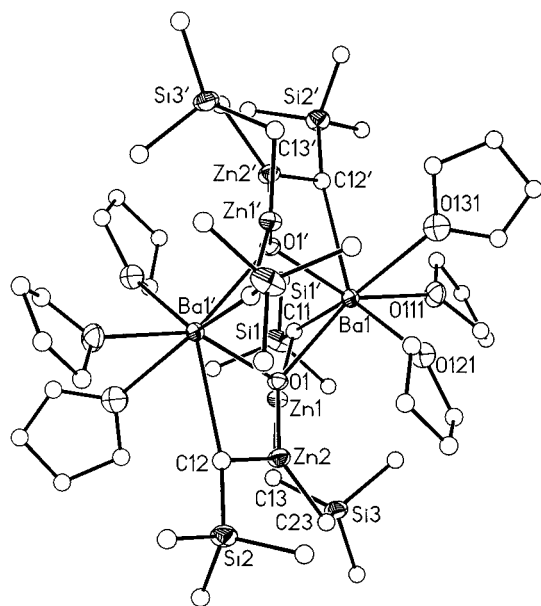


Figure 4. Molecular structure of **5**. The atoms marked with an prime are generated by inversion symmetry ($-x$, $-y$, $-z$). The ellipsoids represent a probability of 40%. The hydrogen atoms are omitted for clarity reasons. The two-site disorder of the THF ligands is not shown.

to the THF ligands. This fact is a consequence of strong electrostatic attractions between the dications and dianions. Because of short Ba–O bonds the nonbonding Ba \cdots Ba contact is only 3.8914(5) Å. The centrosymmetric Ba₂O₂ ring with an O1–Ba1–O1' angle of 80.13(8)° is a slightly distorted square, due to the electrostatic repulsion of the large dications.

This molecule can be understood as a dimeric barium oxide with coordinating THF ligands and a chelating bidentate Lewis acid. The Zn–O bonds show values of 1.964(3) and 1.972(3) Å, which are very short compared to other dative Zn–O bonds.²⁴ This finding can be attributed to the low coordination number of 3 at the zinc atoms. The Ba1–C11 and Ba1–C12' distances with values of 3.249(4) and 3.185(4) Å are longer than those in **3**, because here dialkylzinc compounds are coordinated to the oxygen atoms and no negative charge is located on these methylene fragments. Therefore, the Zn–C distances are shorter as well, because there is nearly no intramolecular electrostatic repulsion of three anionic alkyl groups, as observed for the zincates. The inner fragment of this molecule is shown in Figure 5. Whereas the two zinc atoms of (Me₃SiCH₂ZnCH₂)₂SiMe₂ bind to the same oxygen atom O1, the methylene groups C11 and C12 coordinate to different barium centers. Because of this fact, the Ba₂O₂ moiety is sterically shielded and a degree of aggregation higher than that of a dimer is not found.

Conclusion

The transmetalation of bis[tris(trimethylsilyl)methyl]zinc with distilled strontium and barium yielded the corresponding alkaline-earth-metal bis[tris(trimethylsilyl)methyl]zincates. The solid-state structures show that these trialkylzincate anions bind in a bidentate manner.

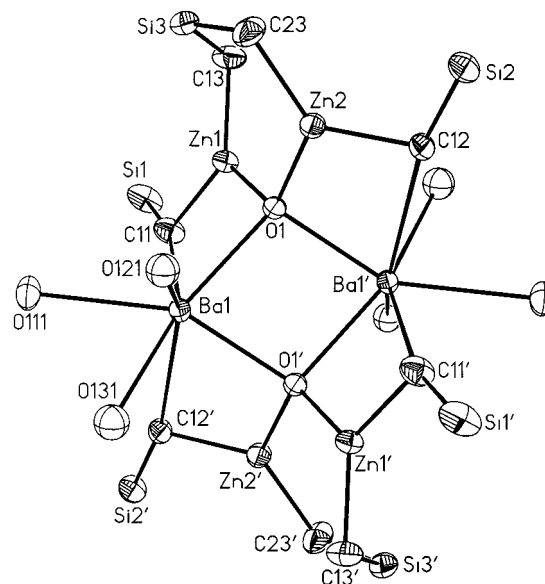


Figure 5. Structure of the inner core of **5**. The methyl groups, the methylene moieties of the THF ligands, and the hydrogen atoms are omitted for clarity reasons. The ellipsoids represent a probability of 40%. Selected bond lengths (Å): Ba1–O1 = 2.570(3), Ba1–O1' = 2.514(2), Ba1–O111 = 2.863(3), Ba1–O121 = 2.797(9), Ba1–O131 = 2.824(7), Ba1–C11 = 3.249(4), Ba1–C12' = 3.185(4), O1–Zn1 = 1.964(3), O1–Zn2 = 1.972(3), Si11–C11 = 1.829(5), C11–Zn1 = 2.025(4), Zn1–C13 = 1.995(4), C13–Si3 = 1.846(5), Si3–C23 = 1.821(5), C23–Zn2 = 2.006(4), Zn2–C12 = 2.043(4), C12–Si2 = 1.838(4). Selected bond angles (deg): O1–Ba1–O1' = 80.13(8), O1–Zn1–C11 = 110.0(2), O1–Zn1–C13 = 116.5(2), C11–Zn1–C13 = 132.6(2), O1–Zn2–C12 = 110.9(1), O1–Zn2–C23 = 120.1(2), C12–Zn2–C23 = 129.0(2), Si1–C11–Zn1 = 112.5(2), Zn1–C13–Si3 = 103.9(2), C13–Si3–C23 = 109.1(3), Si3–C23–Zn2 = 112.3(2), Zn2–C12–Si2 = 111.9(2).

However, in solution the exchange process between the bridging and the terminal alkyl substituents is fast on the NMR time scale. The formation of homoleptic compounds MR₂ (M = Sr, Ba, Zn) was not observed. The three-coordinate zinc atoms of the zincate anions are surrounded in a trigonal-planar arrangement. The four-membered MC₂Zn rings are not planar but folded with rather long M–C–Zn three-center–two-electron bonds.

Experimental Section

General Procedures. All experiments and manipulations were carried out under an atmosphere of argon. Reactions were performed using standard Schlenk techniques and dried, thoroughly deoxygenated solvents. NMR spectra were recorded on JEOL spectrometers GSX270 and EX400, and the NMR parameters are listed in Table 1. A Nicolet 520 FT-IR spectrophotometer was used to record the IR spectra; solid substances were measured in Nujol between KBr plates. The low carbon values at the elemental analysis result from carbide and carbonate formation as well as loss of neutral coligands during handling and combustion of the compounds.

Bis(tetrahydrofuran)strontium Bis[tris(trimethylsilyl)methyl]zincate (**1**). To a solution of 0.94 g of bis[tris(trimethylsilyl)methyl]zinc (3.92 mmol) in 20 mL of THF was added 0.52 g of distilled strontium (5.93 mmol). The solution was stirred at room temperature for 24 h. After removal of excess Sr and precipitated zinc metal the solvents were distilled and the residue redissolved in 5 mL of toluene. Cooling to –20 °C gave 3.08 g of colorless crystals of **1** (3.48 mmol, 79%). Mp:

(24) Melnik, M.; Skoršepa, J.; Györyová, K.; Holloway, C. E. *J. Organomet. Chem.* **1995**, *503*, 1.

Table 2. Summary of Crystallographic Data of 1–3 and 5 as well as Details of the Structure Solution and Refinement Procedures

	1	2	3	5
empirical formula	C ₃₂ H ₈₂ O ₂ Si ₆ SrZn ₂	C ₄₀ H ₉₈ BaO ₄ Si ₆ Zn ₂	C ₃₈ H ₈₂ BaSi ₆ Zn ₂	C ₄₈ H ₁₁₂ O ₈ Si ₆ Zn ₄ Ba ₂
fw	885.88	1079.80	975.66	1522.04
temp <i>T</i> (K)	188(2)	193(2)	173(3)	200(3)
space group ²⁶	<i>C2/c</i>	<i>P2₁/n</i>	<i>C2/c</i>	<i>P2₁/n</i>
unit cell dimens				
<i>a</i> (Å)	21.146(6)	18.596(3)	22.060(4)	15.142(1)
<i>b</i> (Å)	12.042(3)	17.488(2)	11.838(2)	15.2230(9)
<i>c</i> (Å)	20.385(5)	18.650(3)	22.577(4)	15.812(1)
β (deg)	91.556(4)	100.461(2)	116.458(3)	100.21(1)
<i>V</i> (Å ³)	5189(2)	5964(2)	5278(2)	3587.0(5)
<i>Z</i>	4	4	4	2
ρ _{calcd} (g cm ⁻³)	1.134	1.203	1.228	1.409
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
μ (cm ⁻¹)	2.102	1.602	1.797	2.536
abs cor	SADABS	SADABS	SADABS	numerical
<i>T</i> _{min} / <i>T</i> _{max}	0.571/0.979	0.513/0.647	0.312/0.564	0.577/0.687
no. of measd data	14 276	25 808	14 968	24 871
no. of indep data	4489	8399	5041	6925
wR2 ^a (all data, on <i>F</i> ²)	0.1759	0.1275	0.1253	0.0911
R1 ^a (all data)	0.1279	0.1044	0.0579	0.0482
no. of data with <i>I</i> > 2σ(<i>I</i>)	2762	5331	4118	5372
R1 ^a (<i>I</i> > 2σ(<i>I</i>))	0.0658	0.0526	0.0449	0.0323
goodness of fit <i>s</i> ^b on <i>F</i> ²	0.972	1.010	1.114	0.979
residual density (e Å ⁻³)	0.674/−0.622	1.575/−0.765	1.076/−1.527	1.015/−0.699

^a Definition of the *R* indices: $R1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$; $wR2 = \{\sum [w(F_o^2 - F_c^2)] / \sum [w(F_o^2)]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$.²⁶ ^b $s = \{\sum [w(F_o^2 - F_c^2)^2] / (N_o - N_p)\}^{1/2}$.

135 °C (dec). IR (cm⁻¹): 1608 s, 1586 s, 1507 sh, 1473 m, 1436 s, 1400 m, 1383 sh, 1349 m, 1307 m, 1287 m, 1247 vs, 1204 m, 1072 w, 1031 m, 976 m, 938 s, 857 vs, 826 vs, 747 s, 720 s, 694 sh, 681 m, 620 vw, 604 vw, 566 w, 5345 w, 507 sh, 491 w, 456 sh, 434 w, 396 sh, 372 w, 353 w, 323 w. Anal. Calcd for C₃₂H₈₂O₂SrSi₆Zn₂ (885.88): C, 38.86; H, 8.96. Found: C, 38.09; H, 8.33.

Tetrakis(tetrahydrofuran)barium Bis{tris[(trimethylsilyl)methyl]zincate} (2). Distilled barium (0.94 g, 6.85 mmol) was added to a solution of 1.34 g of Zn(CH₂SiMe₃)₂ (5.58 mmol) in 20 mL of THF. The solution was stirred at room temperature for 24 h. Then the metals (excess of barium and precipitated zinc) were removed. The volume of the solution was reduced to one-third of the original amount. Cooling to −20 °C led to the precipitation of 5.30 g of colorless crystals of **2** (4.91 mmol, 88%). Mp: 73 °C dec. IR (cm⁻¹): 1581 m, 1557 w, 1549 w, 1412 m, 1367 w, 1346 sh, 1279 s, 1243 vs, 1199 vs, 1149 vs, 1126 vs, 1099 s, 1075 s, 1041 vs, 1023 vs, 967 vs, 901 vs, 855 vs, 827 vs, 747 vs, 721 sh, 693 s, 673 s, 650 m, 602 m, 544 m, 522 m, 510 m, 501 m, 437 w, 348 m, 323 m, 297 m. Anal. Calcd for C₄₀H₉₈O₄BaSi₆Zn₂ (1079.80): C, 44.49; H, 9.15. Found: C, 43.59; H, 9.13.

Bis(η⁶-toluene)bariumBis{tris[(trimethylsilyl)methyl]zincate} (3). A solution of 0.97 g of bis[(trimethylsilyl)methyl]zinc (4.10 mmol) in 25 mL of toluene which contained 0.85 g of distilled barium (6.1 mmol) was stirred at room temperature for 36 h. Then the excess of barium and the formed zinc were removed and the yellow solution was concentrated to half of the original volume. Cooling to −20 °C resulted in precipitation of 1.42 g of colorless crystalline **3** (3.83 mmol or 93%). Mp: 113 °C dec. IR (cm⁻¹): 1581 m, 1492 w, 1478 sh, 1471 w, 1436 s, 1371 w, 1284 w, 1243 vs, 1025 vw, 921 sw, 858 vs, 823 vs, 743 s, 720 sh, 697 w, 678 w, 604 vw, 548 sh, 462 m, 454 m, 443 m, 439 m, 382 m, 379 m, 360 m, 347 m. Anal. Calcd for C₃₈H₈₂BaSi₆Zn₂ (975.66): C, 46.77; H, 8.47. Found: C, 46.70; H, 7.86.

Barium Bis{tris[(trimethylsilyl)methyl]zincate} (4) and Bis{tris(tetrahydrofuran)barium μ₄-oxide} Bis{bis-[3-(trimethylsilyl)-2-zincapropyl]dimethylsilane} (5). To a solution of 0.94 g of bis[(trimethylsilyl)methyl]zinc (3.92 mmol) in 20 mL of heptane was added 0.72 g of distilled barium. The solution was stirred for 72 h at room temperature.

The metals (barium and zinc) were removed, and the brown solution was reduced to half of the original volume. Cooling to 4 °C resulted in precipitation of a colorless powder of **4**, which was characterized by NMR spectroscopy (Table 1). The addition of THF yielded a red oil which contained mainly **2** (for physical data, see above) and **5**. Cooling of this oil to −20 °C resulted in precipitation of 131 mg of colorless crystals of **5** (172 μmol, 4.4%) within 12 h.

Physical data for **4** are as follows. Decomposition at 145 °C without melting. IR: 1577 w, 1465 s, 1454 sh, 1377 m, 1242 s, 1174 w, 1153 sh, 1015 sh, 919 s, 852 s, 822 s, 772 s, 741 s, 720 s, 678 sh, 514 m, 476 m, 473 m, 417 m, 341 m, 308 m, 278 m. Anal. Calcd for BaZn₂Si₆C₂₄H₆₆ (791.408): C, 36.42; H, 8.41. Found: C, 35.89; H, 8.27.

Physical data for **5** are as follows. Decomposition above 240 °C without melting. ¹H NMR (C₆D₆): δ −0.65 (ZnCH₂SiMe₃), −0.51 (ZnCH₂SiMe₂), 0.12 (CH₂SiMe₃), 0.30 (SiMe₂), 1.41 (THF), 3.58 (THF). ¹³C NMR (C₆D₆): δ 2.12 (SiMe₂), 3.84 (SiMe₃, ¹J_{CSi} = 48.4 Hz), 7.34 (broad, CH₂), 10.98 (broad, CH₂), 25.22 (THF), 68.36 (THF). ²⁹Si NMR (C₆D₆): δ 0.43 (CH₂SiMe₃), 1.67 (CH₂SiMe₂). IR: 1582 m, 1559 m, 1472 m, 1439 sh, 1422 m, 1370 m, 1370 w, 1286 w, 1247 s, 1042 s, 949 s, 941 s, 925 s, 860 vs, 832 s, 744 s, 716 m, 695 s, 676 s, 604 m, 465 s, 4554 s, 331 m, 298 m. Anal. Calcd for C₂₄H₅₆O₄BaSi₃Zn₂ (761.02): C, 37.41; H, 7.41. Found: C, 38.04; H, 7.49.

Crystallographic Analysis of 1–3 and 5. Data were collected on a Siemens P4 diffractometer with a Siemens SMART-CCD area detector (**1–3**) and on a Stoe-IPDS diffractometer (**5**) with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) using oil-coated rapidly cooled single crystals.²⁵ Absorption corrections were applied as given in Table 2. Crystallographic parameters, details of the data collection, and refinement procedures are also summarized in Table 2.

The structures were solved by direct methods and refined with the software packages SHELXL-93 and SHELXL-97.²⁷

(25) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615. Stalke, D. *Chem. Soc. Rev.* **1998**, *27*, 171.

(26) Hahn, T., Ed. *International Tables for Crystallography*, 2nd ed.; D. Reidel: Dordrecht, The Netherlands, 1984; Vol. A (Space Group Symmetry).

(27) Sheldrick, G. M. SHELXL-93; Universität Göttingen, Göttingen, Germany, 1993. Sheldrick, G. M. SHELXL-97; Universität Göttingen, Göttingen, Germany, 1997.

Neutral scattering factors were taken from Cromer and Mann²⁸ and for the hydrogen atoms from Stewart et al.²⁹ The non-hydrogen atoms were refined anisotropically. The H atoms were considered with a riding model under restriction of ideal symmetry at the corresponding carbon atoms. The toluene molecules of **3** are disordered on two positions, which are not shown in Figure 3. Furthermore, two of the three THF ligands of **5** show a two-site disordering which is not represented in Figure 4.

(28) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *24*, 321.

(29) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

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Supporting Information Available: Listings of crystal data, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters of non-hydrogen atoms for **1–3** and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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