Synthesis and Structure of a Dimeric Alkyldibariumtriszincate with a Tetraanionic Triszincate Ligand and a Unique Central $Ba_4Zn_2C_6$ Moiety[**]

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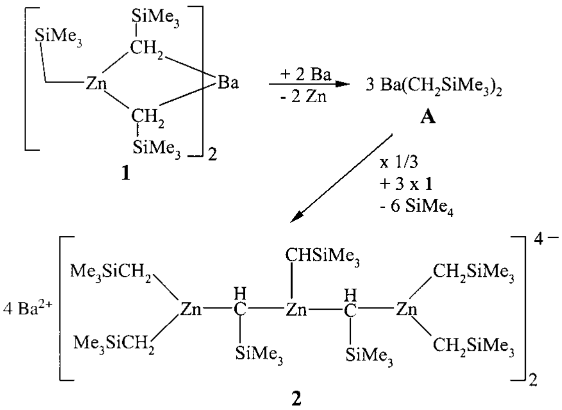
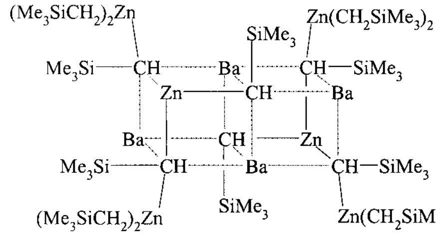
The interest in molecules with Ba–C σ bonds has risen over the years,[1] although the structural proof of a dialkylbarium compound is still lacking.[2] Already many years ago, it was expected[3] that the alkyl compounds of the heavy alkaline earth metals would represent a valuable expansion of the series of organometallic reagents. The application of dibenzylbarium as a polymerization initiator serves as an example,[4] however, here as in other benzyl compounds,[5] side-on-bonded benzyl anions should be present. Even though barocenes are a well-documented substance class,[6] there are only very few examples of σ-bonded organyl groups.[2] Bis(triphenylsilylethynyl)barium was structurally characterized after complexation of the metal atoms with crown ethers.[7] A dimeric alkenylbarium phospholide[8] contains a central planar Ba_2C_2 cycle. Furthermore, the coordination of carbenes at barocenes leads to molecules with Ba–C bonds,[9] on the other hand the carbene adducts of barium bis[bis(trimethylsilyl)amide] dissociate in solution.[10] Barium zincates were investigated many years ago[11] because they are useful polymerization catalysts for isoprene.[12] Through the activation of barium metal, we have recently transmetalated bis(trimethylsilylmethyl)zinc and thereby isolated barium bis[tris(trimethylsilylmethyl)zincate] (**1**).[13] In toluene or THF the corresponding solvate adducts of barium bis[tris(trimethylsilylmethyl)zincate] were isolated, whereas from aliphatic hydrocarbons the coligand-free derivative was obtained.[13] Even by using ultrasound no further transmetalation was observed. But if this zincate suspension in heptane reacts with additional distilled barium metal under application of ultrasound of high energy, the color of the solution turns red and the precipitation of elemental zinc is observed. Cooling of this solution yields colorless crystals of compound **2** and tetramethylsilane can be detected in the reaction solution by NMR spectroscopy (Scheme 1).

These drastic reaction conditions lead to a further transmetalation of the tris(trimethylsilylmethyl)zincate anions and to the formation of bis(trimethylsilylmethyl)barium **A**. This reactive compound, which is not detectable in solution, immediately metalates a methylene group of zincate anions still present in solution. The resulting dianion again metalates a methylene group of the zincate anion. Finally, the triszincate tetraanion forms, which precipitates from heptane in the form of the dimeric barium salt shown in Scheme 2. Tetramethylsilane was detected in the solution; however, there were no indications of the development of hydrogen gas.



Scheme 1. Synthesis of **2** by transmetalation of barium bis[tris(trimethylsilylmethyl)zincate] with barium.



Scheme 2. Constitution of compound **2**.

The molecular structure[14] of compound **2** is easily understood starting from the central $Ba_4Zn_2C_6$ cage, which can be regarded as a distorted double cube with a common Ba_2C_2 face. This structure is depicted in Figure 1; the central structural moiety is highlighted. On the one hand distortions

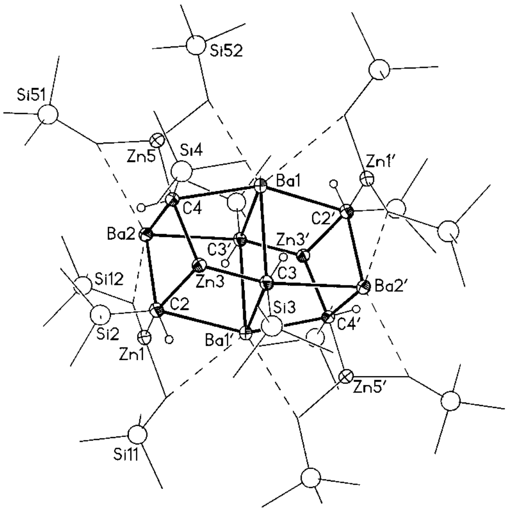


Figure 1. Molecular structure of **2**. The ellipsoids represent a probability of 60 %, the Si atoms were drawn with arbitrary radii. The atoms generated by inversion symmetry are marked with primes. Selected bond lengths [pm]: Ba1-C2′ 299.4(4), Ba1-C3 320.0(4), Ba1-C3′ 286.2(4), Ba1-C4 289.8(3), Ba2-C2 283.6(3), Ba2-C3′ 302.8(3), Ba2-C4 299.0(4), Zn3-C2 213.0(4), Zn3-C3 207.0(3), Zn3-C4 211.2(4).

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are induced by the nearly trigonal-planar environment of Zn3 (angle sum $\Sigma(CZnC) = 357.6°$), on the other hand the Ba–C bonds are clearly longer than the Zn–C bonds.

This dimeric alkyldibarium triszincate is also remarkable in that this compound represents only the second structurally characterized example of a geminal biszincated alkane.[15] In this molecule several carbon atoms show an unusual high coordination number; the coordination spheres of C2 (Ba1′, Ba2, Si2, Zn1, Zn3, and H2), C3 (Ba1, Ba1′, Ba2′, Si3, Zn3, and H3), and C4 (Ba1, Ba2, Si4, Zn3, Zn5, and H4) are distorted octahedra. The hydrogen atoms at these carbon centers were refined isotropically without restraints. These large coordination numbers as well as the anionic charges partly located on neighboring atoms lead to very large Zn–C bond lengths of up to 215 pm (Zn5–C4), an elongation of approximately 20 pm in comparison to the Zn–C bond in dialkylzinc.[16] Figure 2 shows the tetraanionic tris(zincate) ligand of **2**; to clarify the distorted octahedral coordination of the carbanionic centers, the bonds to the barium atoms are shown as thin lines. In contrast to the Zn–C bonds the Si–C distances show no dependency on the coordination number of the corresponding carbon atoms. An expected elongation of the Si–C bonds of the hypervalent C atoms is compensated by the electrostatic attraction between the carbanions and the silicon atoms.

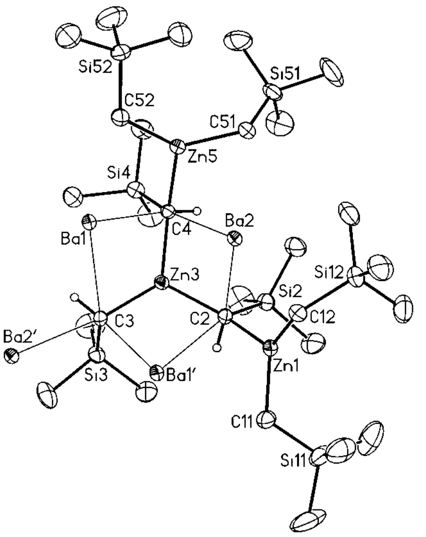

Figure 2. Structure and coordination behavior of the tetraanionic tris(zincate) ligand of **2**. The ellipsoids represent a probability of 50%, the H atoms at C2, C3, and C4 are shown with arbitrary radii and were refined isotropically. Selected bond lengths [pm] and angles [°]: Zn1-C11 202.6(4), Zn1-C12 206.3(4), Zn1-C2 214.0(4), C2-Si2 185.5(4), C2-H2 103(4), Zn3-C2 213.0(4), Zn3-C3 207.0(3), Zn3-C4 211.2(4), C3-Si3 184.3(3), C3-H3 100(5), C4-Si4 185.2(4), C4-H4 95(4), Zn5-C4 215.2(3), Zn5-C51 203.3(4), Zn5-C52 203.6(4); C11-Zn1-C12 122.1(2), C11-Zn1-C2 110.6(2), C12-Zn1-C2 124.2(2), C2-Zn3-C3 118.4(2), C2-Zn3-C4 113.2(1), C3-Zn3-C4 126.0(2), C4-Zn5-C51 112.2(2), C4-Zn5-C52 117.8(2), C51-Zn5-C52 127.9(2).

The Ba–C bond lengths within the $Ba_4Zn_2C_6$ cage vary between 283.6 (Ba2–C2) and 320.0 pm (Ba1–C3). The coordination spheres of the barium atoms are completed by agostic bonds to methylene groups (symbolized as broken lines in Figure 1). The shortest Ba–C bonds lie in the range of σ bonds, for example, in the crown ether complex of barium bis(triphenylsilylacetylide) (285 pm)[7] and in the dimeric alkenylbarium phospholide (288 and 307 pm).[8] Significantly longer Ba–C bonds are found in the barium bis[tris(trimethylsilylmethyl)zincates].[13]

The preparation of **2** proves that the transmetalation of zincates offers a strategy for the synthesis of alkylbarium compounds. Owing to the high reactivity of dialkylbarium, zincate anions that are still present in solution are metalated immediately, which leads finally to the above-mentioned tetraanion. The structure contains a centrosymmetric $Ba_4Zn_2C_6$ double cage as the central moiety, in which carbon atoms with unusual coordination numbers of 6 are present. Long Zn–C distances occur owing to the high negative charges.

Experimental Section

All experiments were carried out under an argon atmosphere. The solvents were dried according to common procedures and distilled under argon, deuterated solvents were degassed and saturated with argon. The distillation of barium was performed according to a literature procedure.[17] The NMR spectra were recorded on Jeol GSX-270 and EX-400 spectrometers, positive signs describe low field shifts. Melting points were determined from compounds which were sealed under argon in capillaries.

Barium bis[tris(trimethylsilylmethyl)]zincate (**1**) (1.04 g, 1.31 mmol), prepared from bis(trimethylsilylmethyl)zinc (0.94 g, 3.92 mmol) and distilled barium (0.28 g, 2.03 mmol), was dissolved in heptane (20 mL). Distilled barium (0.30 g, 2.18 mmol) was added to this solution under the argon atmosphere. The solution was stirred continually for seven days under simultanous treatment with ultrasound (Branson Sonifier W-450 with a titanium resonator), during which time the solution turned red. The excess barium and precipitated zinc metal were then removed. The solution was reduced to half of the original volume. Cooling to +4 °C yielded colorless crystals of **2** (0.64 g, 0.60 mmol; 76%) within a few days. M.p. 195 °C (decomp; carbonization). ^1H NMR (C_6D_6): $\delta = -0.65$ (brs; CH_2), 0.20–0.37 (m; $SiMe_3$), an unambiguous assignment of the CH groups was not possible; $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 3.50$ (brs; $SiMe_3$), 7.68 (brs; CH_2), further signals were neither detectable at high nor at low temperatures; IR: $\tilde{\nu} = 1582$ m, 1473 w, 1437 w, 1384 sh, 1373 w, 1353 sh, 1287 sh, 1245 vs, 1165 vw, 1132 vw, 1096 vw, 1051 w, 1023 w, 930 s, 856 vs, 838 sh, 829 sh, 745 s, 718 sh, 697 sh, 685 sh, 513 w, 480 w, 465 sh, 424 sh, 363 w, 347 w, 319 sh; elemental analysis (%) calcd ($C_{28}H_{74}Ba_2Si_7Zn_3$, 1078.32): C 31.18, H 6.92; found: C 30.87, H 6.91.

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[14] Crystal structure determination of **2**: $C_{56}H_{148}Ba_4Si_{14}Zn_6$, 2156.62 g mol^{-1}, triclinic, space group $P\bar{1}$, $a = 1397.7(1)$, $b = 1421.9(2)$, $c = 1445.6(1)$ pm, $\alpha = 98.85(1)$, $\beta = 110.37(1)$, $\gamma = 108.89(1)°$, $V = 2.4304(4)$ nm^3, $Z = 1$, $T = 200(2)$ K, $3.6 < 2\theta < 51.8°$, colorless platelet, $0.25 \times 0.15 \times 0.07$ mm, $\rho = 1.474$ g cm^{-3}, $\mu = 3.244$ mm^{-1}, numerical absorption correction ($T_{min}/T_{max} = 0.579/0.814$), 17137 reflections, 8753 independent reflections ($R_{int} = 0.0271$), 6775 observed reflections ($I > 2\sigma(I)$), 373 parameters, $wR_2 = 0.0589$ (all reflections, on F^2), $R_1 = 0.0355$ (all reflexes, on F^2), $R_1 = 0.0216$ (observed reflections), goodness-of-fit $s = 0.923$. Residual electron density: $597/-700$ e nm^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-157452. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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