

Barium Hypersilanides

Syntheses and Structures of Barium Silanides: Contact and Separated Ions**

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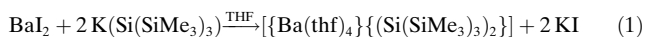
The chemistry of σ -bonded organometallic calcium, strontium, and barium derivatives is slowly emerging from obscurity, with a small but growing number of well-characterized target compounds published during the past decade.^[1] This surge in attention may be explained by the increasing prominence of the compounds in polymer and synthetic chemistry, as well as solid-state applications. Despite the increased attention many unanswered questions remain, a prominent one being the nature of the metal–carbon bond.

Research in our group focuses on heavy-alkaline-earth-metal organometallic complexes, where the identification of viable ligand and solvent systems and the exploration of facile synthetic access routes remain critical since the high reactivity of the target compounds imposes synthetic and analytical limitations. This is specifically important for the emerging group of σ -bonded organometallic complexes, where chemistry developed for the more robust cyclopentadienide, indenyl, or fluorenyl derivatives is not applicable.^[1] As such, investigation of the closely related silanides provides essential information towards the further development of the σ -bonded organometallic congeners.

To date, information on well-characterized alkaline-earth-metal silanides is limited to magnesium derivatives.^[2] A small group of heavy-metal derivatives was mentioned in a patent as polymerization initiators of acrylonitrile,^[3] but no synthetic, spectroscopic, or structural details are available.

Here we report a series of barium hypersilanides $[\text{Ba}(\text{SiMe}_3)_3]^-$ where the addition of various donors affects the formation of contact or separated ions in the solid state. $[\text{Ba}(\text{thf})_4(\text{Si}(\text{SiMe}_3)_3)_2]$ (**1**) exhibits Ba–Si bonds, while $[\{\text{Ba}(\text{hmpa})_6\}(\{\text{Si}(\text{SiMe}_3)_3\}_2)]$ (**2**) possesses separated ions (hmpa = hexamethylphosphoramide). In contrast, $[\{\text{Ba}([\text{18}]\text{crown-6})(\text{Si}(\text{SiMe}_3)_3)_2\}[\{\text{Ba}(\text{hmpa})_6\}(\{\text{Si}(\text{SiMe}_3)_3\}_2)]]$ (**3**) is a rare species containing both contact and separated ions, thus providing important information towards metal–ligand bond character and strength, and of the coordination chemistry of barium.

Compounds **1–3** have been prepared in high yield by metathesis involving the treatment of BaI_2 with two equivalents of potassium silanide in THF [Eq. (1)]. The addition of



appropriate donors dictates the formation of either contact or separated ions in the solid state.

It is critical to limit the exposure of the reaction products to THF, since extended contact results in the migration of SiMe_3 groups and subsequent redox chemistry through the formation of $\text{Si}(\text{SiMe}_3)_4$ and elemental silicon. In fact, if the reaction mixture is exposed to THF overnight, only $\text{Si}(\text{SiMe}_3)_4$ can be identified by NMR spectroscopy. Similarly, silyl-group migration has been identified as the major side reaction when treating R_3SiSiR_3 ($\text{R} = \text{Me}, \text{Ph}$) with elemental alkaline-earth metals in a THF/ NH_3 mixture.^[4] This chemistry is not limited to silyl derivatives, and $-\text{SnPh}_3$ migration was responsible for the concurrent formation of $[\{\text{M}([\text{18}]\text{crown-6})(\text{hmpa})_2\}(\{\text{Sn}(\text{SnPh}_3)_3\}_2)]$ and $\text{Sn}(\text{SnPh}_3)_4$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) from the reaction of $\text{Ph}_3\text{SnSnPh}_3$ with heavy alkaline-earth metals in a THF/ NH_3 mixture.^[5]

The title compounds are highly sensitive to moisture and oxygen, and most careful handling conditions are required. While compound **1** is extremely sensitive towards oxygen and moisture, compound **2** is even more reactive, decomposing violently upon exposure.

Compound **1**^[6] (Figure 1) exhibits a distorted octahedral environment for the barium center, which is comprised of two silanide ligands in addition to four THF donors. The average barium–silicon and barium–oxygen separations are 3.440(9) and 2.74(1) Å, respectively. The Ba–Si bond length compares well with $[\text{Mg}(\text{thf})_2(\text{Si}(\text{SiMe}_3)_3)_2]$ (2.682(2) Å)^[2a] considering the increased ionic radius of barium^[7] and higher metal coordination number. The Ba–O bond lengths are in accord with the structurally closely related $[\text{Ba}(\text{thf})_4\{\text{E}(2,4,6\text{-tBu}_3\text{C}_6\text{H}_2)_2\}]$ ($\text{E} = \text{S}, \text{Se}$).^[8] The distortion of **1** from octahedral geometry is significant, with a *trans* Si–Ba–Si angle of 140.62(3)°. In accord with this distortion, O–Ba–O angles are

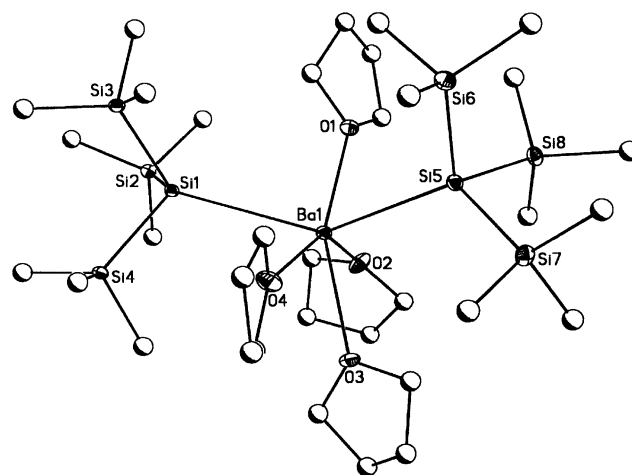


Figure 1. The crystal structure of **1**, with hydrogen atoms omitted for clarity.

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compressed, ranging between 71.69(9) and 144.25(9)°. The Si-Si-Si angle sums of the central silicon atoms (302.63 and 306.18°) indicate significant pyramidal geometry, which is in good agreement with related alkali-metal hypersilanides.^[9,10]

Compound **2** (Figure 2) exhibits separated ions in the solid state, with cation and anion separated by 10.553 Å.^[11] The barium cation is coordinated in a distorted octahedral

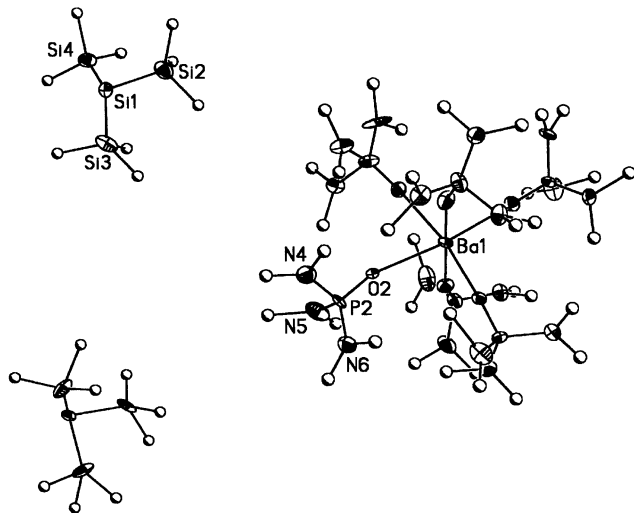


Figure 2. The crystal structure of **2**, with hydrogen atoms and disordered positions omitted for clarity.

fashion by six HMPA donors with average Ba–O separations of 2.641(6) Å. The O–Ba–O angles range from 82.4(4) to 98.2(3)°, with *trans* angles from 169.1(3) to 176.82(15)°. The two separated silanide anions display a pronounced pyramidal geometry with average angle sums at the central silicon atoms of 297.02°. These are in good agreement with the average value for the cesium hypersilanide $[\text{Cs}(\text{[18]crown-6})_2][\text{Si}(\text{SiMe}_3)_3]$ (298.55°).^[10]

The facile formation of the $[\text{Ba}(\text{[18]crown-6})(\text{hmpa})_2]$ cation was shown on several occasions.^[8,12] It was therefore expected that the combined addition of [18]crown-6 and HMPA would result in the quantitative formation of separated ions. Remarkably, compound **3**,^[13] which contains a contact molecule, $[\text{Ba}(\text{[18]crown-6})][\text{Si}(\text{SiMe}_3)_3]_2$ and a separated HMPA adduct $[\text{Ba}(\text{hmpa})_6][\text{Si}(\text{SiMe}_3)_3]_2$ was obtained. The separated ion in **3** shows essentially the same structural features as **2**. The cation–anion separation is 11.917 Å, and six HMPA donors coordinate to the metal center. As in **2**, the pyramidity of the anions is pronounced with a Si–Si–Si angle sum of 301.59°. In the contact molecule, the equatorial plane on barium is occupied by the [18]crown-6 macrocycle, while two silanide ligands are located in *trans* positions. A center of symmetry at barium requires a *trans* angle of 180°. The average Ba–O(crown) bond lengths are 2.779(4) Å, while the average Ba–Si separations are 3.645(4) Å. The sum of the Si–Si–Si angles is 310.17°.

Interestingly, the Ba–Si, and to a lesser extent, Ba–O bond lengths in the contact molecule in **3** are significantly elongated as compared to **1**. Previous evidence from barium thiolates and selenolates bearing either one [18]crown-6

macrocycle or four THF donors^[8] indicated only a negligible Ba–S or Ba–Se bond elongation upon replacing four THF donors by [18]crown-6. This initially surprising result was rationalized by the location of the crown in the equatorial plane and very comparable spatial requirements. In fact, the coordination sphere in the crown-ether-ligated derivatives was described as “pseudo-octahedral”, an arrangement made possible by the narrow O–Ba–O(crown) angles (60.047° (av)). However, in conjunction with an extremely bulky ligand such as hypersilanide, this argument no longer holds true, and the steric repulsion between the donor and ligand results in significant bond elongation.

A comparison of Si–Ba–Si angles in **1** and the contact molecule in **3** shows a significant variation, with 140.62(3)° for **1** and linear geometry in **3**. These two vastly different values suggest the facile distortion from ideal linear geometry, enabled by the highly polar nature of the Ba–Si bond, and consequent reduction of orbital control. In fact, the variation of *trans* angles in octahedral alkaline-earth-metal derivatives is significant; with values ranging from 132° to the ideal linear geometry.^[14] Theoretical studies to further investigate this phenomenon are currently in progress.

The significantly pyramidal Si–Si–Si angles in compounds **1–3** are in good agreement with previously published alkali-metal hypersilanides.^[9,10] For his series of alkali-metal hypersilanides, Klinkhammer observed an angle compression upon descending the alkali-metal group, which was interpreted through increased metal–ligand charge transfer.^[9] The extreme case of this trend, the separation of cation and anion, should result in the largest degree of angle compression. Indeed, slightly smaller angles are observed for the separated species in both the alkali-metal^[10] and the alkaline-earth-metal analogues **1–3**, consistent with the complete transfer of electron density from the metal to the ligand. However, the small reduction in angle upon separation of ions indicates a very polar Ba–Si bond that should allow for the facile formation of separated ions in solution.

NMR experiments were conducted to obtain information about the ion association in solution. ²⁹Si NMR experiments for compounds **1–3** yielded a close range of chemical shifts for the SiMe₃ groups ($\delta = -5.80$ (**1**), -4.70 (**2**), and -4.86 ppm (**3**)). However, the signals for the quaternary silicon atoms, which would provide the most direct information on solvation and ligation, could not be obtained even after extended run times (24 hrs) on a 500 MHz spectrometer using a wide bore probe with DEPT and/or ZG techniques. This might be due to the low sensitivity of the quaternary silicon atom coupled with the low solubility of the target compounds in C₆D₆ or CD₃C₆D₅.

While the SiMe₃ signals are less susceptible towards solvation effects, the close range of values, especially when compared with alkali-metal hypersilanides suggests the formation of identical ions upon dissolution. Due to the favorable formation of the $[\text{Ba}(\text{hmpa})_6]^{2+}$ ion and the polar nature of the Ba–Si bond, the formation of separated ions, as proposed for the related alkali-metal hypersilanides^[10] is likely. This view is further supported by the effective coordination of barium to the aromatic (C₆D₆) NMR solvent.^[15]

The puzzling coexistence of contact species and separated ions in the solid phase of **3** supports the assumption that Ba–Si bonds are weak and possess a large degree of ionic character. Selected examples of compounds containing both contact and separated ions in one crystal include a tetraphenyl butadiene disodium derivative,^[16] in addition to the rubidium silanide $[(\text{Rb}[\text{18crown-6}]_2)(\text{Si}(\text{SiMe}_3)_3)_2][\text{Rb}[\text{18crown-6}](\text{Si}(\text{SiMe}_3)_3)]_2$.^[10] In both cases, weak, predominantly ionic metal–ligand bonds are observed, which enable the facile formation of separated ions.

In summary, the first examples of barium hypersilanides have been synthesized and characterized. Depending on the donors, either contact or separated ions were obtained, in addition to a compound where both contact and separated ions coexist in the solid state. Upon dissolution in C_6D_6 the compounds dissociate into separated ions. The facile formation of separated ions classifies the barium–silicon bond as weak and largely ionic.

Experimental Section

All reactions were performed under a purified nitrogen atmosphere using strict anaerobic conditions. $[\text{K}(\text{thf})_n][\text{Si}(\text{SiMe}_3)_3]$ was prepared following literature procedures;^[17] alkaline-earth-metal iodides (>99% purity) were obtained commercially. All reagents and solvents were purified using standard procedures.

Compounds **1–3** were prepared by a similar route, differing only in the addition of donor molecules: A solution containing $[\text{K}(\text{thf})_n][\text{Si}(\text{SiMe}_3)_3]$ (2 mmol, 0.72 g) in THF (15 mL) was added to a solution of barium iodide (1 mmol, 0.39 g) in THF (25 mL) at room temperature. The mixture was stirred for about 45 min at room temperature, after which the solvent was removed under reduced pressure. The residue was extracted with hexane (80 mL) and filtered through a celite-layered filter frit, resulting in a clear, yellow solution that was reduced in volume to 40 mL. Crystals of **1** suitable for diffraction experiments were obtained after storing the solution for four days at -20°C . To obtain compound **2**, HMPA (6 mmol, 1.04 mL) was added dropwise, upon which yellow crystals formed rapidly. Compound **3** was obtained after dropwise addition of a solution containing [18]crown-6 (0.5 mmol, 0.13 g) and HMPA (3 mmol, 0.52 mL) in hexane (25 mL). Upon addition, a yellow turbid solution formed immediately, that became clear after the addition of THF (10 mL). The combined solvents were removed under reduced pressure, and the resulting oily residue taken up in hexane (40 mL). After storage at -20°C , crystals of compound **3** were obtained within 24 h.

1: Yield = 0.71 g (77%); mp $167\text{--}170^\circ\text{C}$; ^1H NMR (300 MHz, 25°C , C_6D_6): $\delta = 3.60$ (m, 16H, THF), 1.37 (m, 16H, THF), 0.49 ppm (s, 54H, SiMe_3); ^{13}C NMR (75 MHz, 25°C , C_6D_6): $\delta = 6.94$ (SiMe_3), 25.34, 68.29 ppm; ^{29}Si NMR (99 MHz, 25°C , C_6D_6): $\delta = -5.80$ ppm ($\text{Si}(\text{SiMe}_3)_3$) (see above for missing quaternary silicon resonance); IR (Nujol): $\tilde{\nu} = 2923$ (s), 2853 (s), 1462 (m), 1377 (w), 1232 (w), 1108 (w), 1034 (w), 828 (m), 728 (w), 670 (w), 618 cm^{-1} (m).

2: Yield = 1.17 g (68.7%); mp $160\text{--}164^\circ\text{C}$; ^1H NMR (300 MHz, 25°C , C_6D_6): $\delta = 2.43$ (d, 108H, CH_3 ; $J = 9.43$ Hz), 0.71 ppm (s, 54H, SiMe_3); ^{13}C NMR (75 MHz, 25°C , C_6D_6): $\delta = 8.58$ (SiMe_3), 36.93 ppm (CH_3); ^{29}Si NMR (99 MHz, 25°C , C_6D_6): $\delta = -4.70$ ppm ($\text{Si}(\text{SiMe}_3)_3$); IR (Nujol): $\tilde{\nu} = 2922$ (s), 2852 (s), 2806 (w), 1462 (m), 1377 (w), 1297 (w), 1223 (w), 1193 (w), 1163 (w), 1068 (w), 985 (w), 902 (w), 828 (w), 744 (w), 664 (w), 614 cm^{-1} (w).

3: Yield = 0.83 g (63.4%); mp $152\text{--}156^\circ\text{C}$; ^1H NMR (300 MHz, 25°C , C_6D_6): $\delta = 3.31$ (s, 24H, CH_2), 2.41 (d, 108H, CH_3 ; $J = 9.43$ Hz), 0.62 (s, 54H, SiMe_3), 0.51 ppm (s, 54H, SiMe_3); ^{13}C NMR (75 MHz, 25°C , C_6D_6): $\delta = 7.48$ (SiMe_3), 8.53 (SiMe_3), 36.92, 70.12 ppm; ^{29}Si

NMR (99 MHz, 25°C , C_6D_6): $\delta = -4.86$ ppm ($\text{Si}(\text{SiMe}_3)_3$); IR (Nujol): $\tilde{\nu} = 2918$ (s), 2034 (w), 1462 (s), 1377 (s), 1350 (w), 1300 (s), 1226 (m), 1194 (s), 1165 (s), 1068 (m), 989 (s), 962 (s), 900 (w), 825 (s), 745 (s), 660 (m), 615 cm^{-1} (m).

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