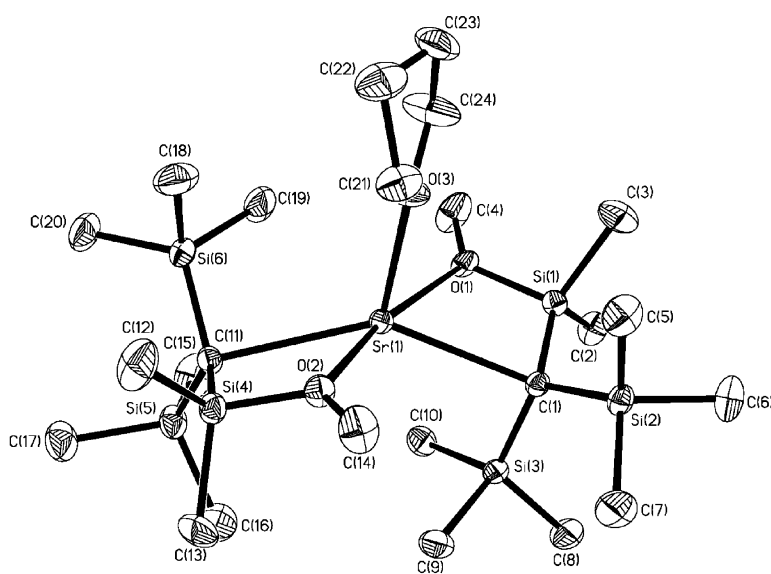


Alkyl Complexes of Strontium and Barium: Synthesis and Structural Characterization of $\{(MeSi)(MeOMeSi)C\}Sr(THF)$ and $\{(MeSi)(MeOMeSi)C\}Ba(MeOCHCHOMe)$

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Alkyl Complexes of Strontium and Barium: Synthesis and Structural Characterization of $\{(\text{Me}_3\text{Si})_2(\text{MeOMe}_2\text{Si})\text{C}\}_2\text{Sr}(\text{THF})$ and $\{(\text{Me}_3\text{Si})_2(\text{MeOMe}_2\text{Si})\text{C}\}_2\text{Ba}(\text{MeOCH}_2\text{CH}_2\text{OMe})$

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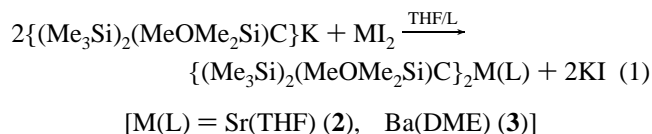
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Since the pioneering work of Barbier and Grignard at the turn of the 20th century organomagnesium compounds have become established as indispensable reagents in organic and organometallic synthesis.¹ In contrast, with the notable exception of the well-established cyclopentadienyl derivatives,² the organometallic chemistry of the heavier alkaline earth metals Ca, Sr, and Ba has remained largely undeveloped, and σ -bonded organometallic complexes of these metals are extremely rare.^{1a,3} This is principally due to the high reactivity of such species and to their limited solubility in common organic solvents, associated with the highly ionic nature of the alkaline earth metal–carbon bond and the large ionic radii of the heavier elements of the group.

Recent observations that alkaline earth metal organometallics are efficient initiators for the anionic living polymerization of styrene and butadiene⁴ have led to several reports of calcium, strontium, and barium complexes, including benzylic,^{4c–g,5} acetylenic,⁶ and heterometallic “ate” derivatives,⁷ as well as carbene adducts of the decamethylmetallocenes.⁸ However, examples of simple alkyl complexes are limited to two calcium compounds, $\{(\text{Me}_3\text{Si})_2\text{CH}\}_2\text{Ca}$ (1,4-dioxane)^{9a} and $\{(\text{Me}_3\text{Si})_3\text{C}\}_2\text{Ca}$.^{9b}

We recently found that by incorporating additional donor functionality within the periphery of a silicon-stabilized carbanion we were able to isolate and structurally characterize the first example of a samarium(II) σ -bonded organometallic complex, $\{(\text{Me}_3\text{Si})_2(\text{MeOMe}_2\text{Si})\text{C}\}_2\text{Sm}(\text{THF})$ (**1**).¹⁰ Given the close analogy between the chemistry of Sm(II) and Sr(II), this appeared to be a potentially useful strategy for the synthesis of Sr and Ba alkyl complexes [according to Shannon the ionic radii of Sm(II) and Sr(II) differ by just 0.01 Å].¹¹ We now report the synthesis of two such compounds and their structural characterization.

A straightforward metathesis reaction between either SrI_2 or BaI_2 and 2 equiv of $\{(\text{Me}_3\text{Si})_2(\text{MeOMe}_2\text{Si})\text{C}\}_2\text{K}$ in THF gives the corresponding alkaline earth dialkyls $\{(\text{Me}_3\text{Si})_2(\text{MeOMe}_2\text{Si})\text{C}\}_2\text{M}(\text{THF})_n$ [M = Sr, Ba] as slightly sticky solids. Recrystallization of these solids from methylcyclohexane [M = Sr] or hexamethyl-disiloxane/DME [M = Ba] yields the complexes $\{(\text{Me}_3\text{Si})_2(\text{MeOMe}_2\text{Si})\text{C}\}_2\text{M}(\text{L})$ [M(L) = Sr(THF) (**2**), Ba(DME) (**3**) (DME = 1,2-dimethoxyethane)] as colorless X-ray quality crystals in good yield (eq 1).¹²



The ¹H and ¹³C NMR spectra and elemental analyses of **2** and **3** are consistent with these formulations; the identities of **2** and **3** were confirmed by X-ray crystallography.¹³ Interestingly, while the calcium dialkyl $\{(\text{Me}_3\text{Si})_3\text{C}\}_2\text{Ca}$ reacts rapidly with ethers,^{9b} compounds **2** and **3** are indefinitely stable in THF or DME solutions

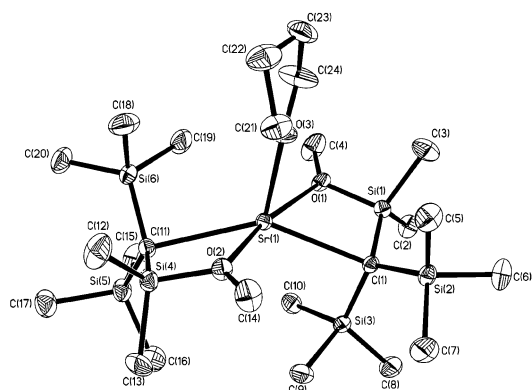
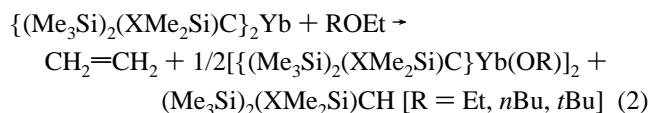


Figure 1. Molecular structure of **2** with 50% probability ellipsoids and with H atoms and minor THF disorder component omitted for clarity. Selected bond lengths (Å) and angles (deg): Sr–C(1) 2.786(3), Sr–C(11) 2.849(3), Sr–O(1) 2.5425(18), Sr–O(2) 2.4928(19), Sr–O(3) 2.5235(19), C(1)–Sr–O(1) 62.39(7), C(11)–Sr–O(2) 62.02(7), C(1)–Sr–C(11) 144.92(8).

and are isolated as the corresponding ether adducts. This parallels the reactivity exhibited by the analogous lanthanide(II) complexes; whereas the compounds $\{(\text{Me}_3\text{Si})_2(\text{XMe}_2\text{Si})\text{C}\}_2\text{Yb}$ [X = Me, OMe, CH=CH₂], containing the relatively small Yb(II) cation,¹⁴ react with ethers according to eq 2,¹⁵ complex **1**, containing the larger, less Lewis acidic Sm(II) center, is indefinitely stable toward ethers and is isolated as a THF adduct.¹⁰



Compound **2** crystallizes as a discrete molecular species; the Sr atom is coordinated by the C and O atoms of two chelating σ -alkyl ligands, generating two four-membered chelate rings, and by the O atom of a molecule of THF (Figure 1). The Sr atom is thus five-coordinate and adopts a distorted square pyramidal geometry, with THF in the apical position. The bite angles of the ligands are 62.39(7) and 62.02(7)°; these compare with bite angles of 62.19(2) and 62.11(12)° in **1**, which is essentially isostructural with **2**.¹⁰

The Sr–C distances of 2.786(3) and 2.849(3) Å compare with Sr–C distances of 2.692(4) and 2.723(4) Å in the acetylide complex $(\text{Ph}_3\text{SiCC})_2\text{Sr}$ (18-crown-6),⁶ 2.798(2) and 2.770(2) Å in the benzylic complex $\{(\text{Me}_3\text{Si})\text{CH}(\text{C}_6\text{H}_4-2\text{-NMe}_2)\}_2\text{Sr}(\text{THF})_2$,^{5a} and 2.857(7) and 2.806(8) Å in the heterometallic “ate” complex $\{\text{Me}_2\text{Si}(\text{CH}_2\text{ZnCH}_2\text{-SiMe}_3)_2\}_2\text{Sr}(\text{THF})_2$.^{7c} The low formal coordination number of the Sr atom is supplemented by weak Sr···Me–Si interactions [Sr···C(10) 3.394, Sr···C(19) 3.302 Å]. Similar short Sr···C distances have been observed between the Sr atom and the methylene carbons of two of the ethyl groups in the heterometallic “ate” complex $\text{Sr}\{\text{N}(\text{SiMe}_3)_2(\text{GaEt}_3)\}_2$ [Sr···CH₂ 3.363(4) and 3.398(3) Å].¹⁶

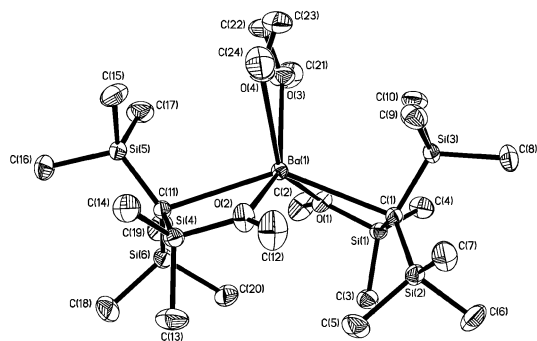


Figure 2. Molecular structure of **3** with 50% probability ellipsoids and with H atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Ba–C(1) 3.049(2), Ba–C(11) 3.0363(18), Ba–O(1) 2.7086(15), Ba–O(2) 2.6765(15), Ba–O(3) 2.7805(17), Ba–O(4) 2.7709(19), C(1)–Ba–O(1) 57.66(5), C(11)–Ba–O(2) 58.29(5), C(1)–Ba–C(11) 139.89(6) O(3)–Ba–O(4) 58.30(6).

The Ba atom in **3** is six-coordinate, bound by the C and O atoms of two chelating alkyl ligands and the two O atoms of a molecule of DME, in a distorted trigonal antiprismatic geometry (Figure 2). The C–Ba–O ligand bite angles of 57.66(5) and 58.29(5)° are smaller than the equivalent angles in **2**, consistent with the smaller ionic radius of Sr(II) compared to Ba(II) [1.32 and 1.49 Å, respectively, for a six-coordinate cation].¹¹

The Ba–C distances of 3.049(2) and 3.0363(18) Å compare with Ba–C distances of 2.981(6)–3.454(6) Å in the phosphonium dibenzylidene complex {Ph₂P(ChC₆H₄-4-Me)₂}₂Ba,¹⁷ 2.852(3) and 2.853(3) Å in the acetylidene complex (Ph₃SiCC)₂Ba(18-crown-6),⁶ and 3.071(5) and 2.881(5) Å in an unusual vinyl phospholide complex obtained from the reaction of Ba{P(SiMe₃)₂}₂ with diphenylbutadiyne.¹⁸ In contrast to **2** there are no short Ba···Me distances in **3**. The isolation of **3** allows the measurement of a nonbridging Ba–C(sp³) distance for the first time.

The chemistry of **2** and **3** is currently under investigation.

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Supporting Information Available: For **2** and **3** details of structure determination, atomic coordinates, bond lengths and angles, and displacement parameters in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (12) **2** was prepared by the addition of a solution of {(Me₃Si)₂(MeOMe₂Si)C}K (1.85 g, 6.45 mmol) in THF (30 mL) to a suspension of SrI₂ (1.10 g, 3.22 mmol) in THF (15 mL). This mixture was stirred at room temperature for 12 h, and then solvent was removed in vacuo. The residue was extracted into light petroleum (30 mL) and filtered, and solvent was removed in vacuo from the filtrate to give a sticky, colorless solid. Crystals of **2** were obtained from cold (–30 °C) methylcyclohexane. Yield 1.51 g, 72%. Anal. Calcd for C₂₄H₆₂O₃Si₆Sr: C, 44.02; H, 9.54%. Found: C, 43.61; H, 9.57%. ¹H NMR (C₆D₆): 0.41 (s, 12H, SiMe₂), 0.43 (s, 36H, SiMe₃), 1.41 (m, 4H, THF), 3.29 (s, 6H, OMe), 3.58 (m, 4H, THF). ¹³C{¹H} NMR (C₆D₆): 3.42 (SiMe₂), 7.92 (SiMe₃), 16.75 (CSi₃), 25.13 (THF), 50.73 (OMe), 69.23 (THF). Compound **3** was synthesized in an analogous manner from {(Me₃Si)₂(MeOMe₂Si)C}K (0.84 g, 2.93 mmol) and BaI₂ (0.55 g, 1.41 mmol). Crystals of **3** were obtained from cold (–30 °C) hexamethyldisiloxane containing a few drops of DME. Yield 0.72 g, 68%. Anal. Calcd for C₂₄H₆₄BaO₄Si₆: C, 39.89; H, 8.93%. Found: C, 39.72; H, 8.81%. ¹H NMR (C₆D₆): 0.35 (s, 36H, SiMe₃), 0.38 (s, 12H, SiMe₂), 2.83 (s, 4H, DME), 2.91 (s, 6H, DME), 3.19 (s, 6H, OMe). ¹³C{¹H} NMR (C₆D₆): 3.92 (SiMe₂), 7.59 (SiMe₃), 20.71 (CSi₃), 50.47 (DME), 59.46 (DME), 70.97 (OMe).
- (13) Crystallographic data for **2**: C₂₄H₆₂O₃Si₆Sr, monoclinic P2₁, colorless blocks, *a* = 9.4865(5) Å, *b* = 16.5147(8) Å, *c* = 12.2829(6) Å, β = 106.567(2)°, *T* = 150 K, *Z* = 2, *R* = 0.0253 (*F*² > 2σ), *wR*₂ = 0.0581 (all data), GOF = 0.817. One of the THF carbons C(23) is disordered over two positions with almost equal occupancy. **3**: C₂₄H₆₄BaO₄Si₆, orthorhombic, *Pca*2₁, colorless blocks, *a* = 17.7600(7) Å, *b* = 13.1490(5) Å, *c* = 16.8334(6) Å, *T* = 150 K, *Z* = 4, *R* = 0.0196 (*F*² > 2σ), *wR*₂ = 0.0434 (all data), GOF = 1.035.
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