

Syntheses and Structures of the First Heavy Alkaline Earth Metal Germanides $M(\text{THF})_n(\text{Ge}(\text{SiMe}_3)_3)_2$ ($M = \text{Ca}$, $n = 3$; $M = \text{Sr}$, $n = 3$; and $M = \text{Ba}$, $n = 4$)

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Calcium, strontium, and barium compounds involving heavy group 14 ligands have been recognized as useful initiators in the polymerization of acrylonitrile. Since little is known on the exact nature of the target compounds, including information on synthetic access and spectroscopic and structural details, we have prepared and characterized the first calcium, strontium, and barium germanides of the general formula $M(\text{THF})_n(\text{Ge}(\text{SiMe}_3)_3)_2$ ($M = \text{Ca}$, $n = 3$, **1**; Sr , $n = 3$, **2**; and Ba , $n = 4$, **3**). The title compounds are available by a convenient one-pot metathesis reaction.

Introduction

During the past few years, the chemistry of σ -bonded organometallic calcium, strontium, and barium compounds has received significant attention, owing in part to the importance of the target compounds in a variety of applications, paired with the desire to understand in detail the nature of the metal carbon bond.^{1–3} However, the high reactivity and frequent low solubility of the target compounds prevents the more rapid development of this field of organometallic chemistry. The investigation of the closely related heavy group 14 congeners will provide helpful information in regards to synthetic challenges and opportunities.

An additional incentive to explore the chemistry of alkaline earth metal silanides, germanides, and stannides is their successful employment in the polymerization of acrylonitrile, as described in the patent literature.⁴ However, no details are available in regards to synthetic access; neither is information on spectroscopic or structural data, preventing the ready access to the title compounds, which would allow the optimization of the polymerization process.

Well-characterized alkaline earth metal derivatives bearing heavy group 14 ligands are mainly limited to magnesium with $\text{Mg}(\text{donor})(\text{SiMe}_3)_2$, donor = DME,⁵ $\text{NMe}_2(\text{CH}_2)_3\text{NMe}_2$,^{6a} TMEDA^{6b} (DME = 1,2-dimethoxyethane, TMEDA = *N,N,N,N*-tetramethylethylenediamine), $[\text{Mg}(\text{TMEDA})\text{Br}(\text{SiMe}_3)_2]$,⁷ $\text{Mg}(\text{THF})_2\text{Br}(\text{Si}(\text{SiMe}_3)_3)$,⁸ $\text{Mg}(\text{THF})_2(\text{Si}(\text{SiMe}_3)_3)_2$,⁸ and $\text{Mg}(\text{DME})_2$ -

$(\text{GeMe}_3)_2$.⁹ For the heavier metals, examples are limited to silanides and stannides, including the THF adducts $M(\text{THF})_n(\text{Si}(\text{SiMe}_3)_3)_2$ ($M = \text{Ca}$, $n = 3$; $M = \text{Sr}$, $n = 3$; $M = \text{Ba}$, $n = 4$),¹⁰ the mixed THF/TMEDA derivative $\text{Sr}(\text{TMEDA})\text{THF}(\text{Si}(\text{SiMe}_3)_3)_2$,¹⁰ the separated ion $[\text{Ba}(\text{HMPA})_6][\text{Si}(\text{SiMe}_3)_3]_2$, and a species containing both contact and separated ions in the crystal, $[\text{Ba}(18\text{-crown-6})(\text{Si}(\text{SiMe}_3)_3)_2][\text{Ba}(\text{HMPA})_6][\text{Si}(\text{SiMe}_3)_3]_2$.¹¹ Well-characterized stannides are limited to $\text{Ca}(\text{THF})_4(\text{SnMe}_3)_2$ ¹² and $\text{Ba}(\text{Sn}(\text{O}^i\text{Bu}_3))_2(\text{Cr}(\text{CO})_5)_2$,¹³ as the only examples displaying alkaline earth metal–tin bonds. $[\text{Ba}(\text{HMPA})_2(18\text{-crown-6})][\text{SnPh}_3]_2$ and $[\text{M}(\text{HMPA})_2(18\text{-crown-6})][\text{Sn}(\text{SnPh}_3)_3]_2$ ($M = \text{Ca}$, Sr ; HMPA = hexamethylphosphoramide) consist of separate ions in both solution and the solid state.¹⁴

It is not only the chemistry of the heavy alkaline earth metals in conjunction with germanium that has received little attention, germanide chemistry overall is not well developed. In contrast, to the well-explored alkali metal silanides,^{15,16} germanide chemistry is mainly limited to the $\text{Ge}(\text{SiMe}_3)_3^-$ (hypergermanide) ligand with structurally characterized $\text{Li}(\text{THF})_3(\text{Ge}(\text{SiMe}_3)_3)$,¹⁷ $\text{Li}(\text{PMDTA})(\text{Ge}(\text{SiMe}_3)_3)$ (PMDTA = *N,N,N,N,N'*-pentamethyldiethylenetriamine),¹⁷ $[\text{Li}(12\text{-crown-4})][\text{Ge}(\text{SiMe}_3)_3]$,¹⁸ and $[\text{CsGe}(\text{SiMe}_3)_3]_2$,¹⁹ in addition to a small number of

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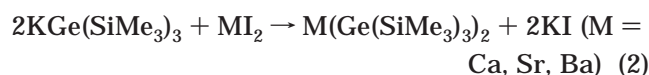
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transition metal hypergermanides²⁰ and main group analogues.²¹ The sterically demanding $\text{Ge}(\text{SiMe}_3)_3^-$ ligand is ideally suited for the preparation of alkaline earth metal germanides because of its ease of preparation, good solubility in hydrocarbon solvents, and large steric demand, providing the critical kinetic stabilization needed to obtain the target molecules.

We here report the first well-characterized heavy alkaline earth metal germanides, a family of calcium, strontium, and barium derivatives of the general formula $\text{M}(\text{THF})_n(\text{Ge}(\text{SiMe}_3)_3)_2$ ($\text{M} = \text{Ca}$, $n = 3$, **1**; Sr , $n = 3$, **2**; and Ba , $n = 4$, **3**), prepared by a convenient, one-pot metathesis route. The analysis of their reactivity and structural data will aid the further investigation of the organometallic chemistry of the heavy alkaline earth metals, while providing a reliable source of calcium, strontium, and barium germanide to advance applications in polymer chemistry.

Results and Discussion

Synthetic Aspects. The only well-characterized alkaline earth metal germanide, $\text{Mg}(\text{DME})_2(\text{GeMe}_3)_2$, was prepared by reacting $\text{Hg}(\text{GeMe}_3)_2$ with elemental magnesium.⁹ In an attempt to limit use of mercury and its compounds, we synthesized the target compounds by facile, straightforward metathesis chemistry. Compounds **1–3** were obtained in high yields and purity by a salt elimination reaction involving the treatment of alkaline earth metal iodides with 2 equiv of potassium germanide. Potassium germanide, $\text{KGe}(\text{SiMe}_3)_3$, is prepared in situ in good yield and purity by treating $\text{Ge}(\text{SiMe}_3)_4$ with potassium *tert*-butoxide in THF (eq 1), analogous to the preparation of $\text{KSi}(\text{SiMe}_3)_3$, as reported previously by Marschner.²²



In analogy with the previous observation for potassium silanide,¹⁶ extended exposure of potassium germanide to THF results in redox chemistry under SiMe_3 group migration and formation of elemental germanium and $\text{Ge}(\text{SiMe}_3)_4$. The redox chemistry occurs reproducibly, and tetrakis(trimethylsilyl)germane is detected frequently as a yield-reducing byproduct. In fact, if the reaction mixture is left in THF overnight, only $\text{Ge}(\text{SiMe}_3)_4$ can be identified by NMR spectroscopy. Attempts to suppress the SiMe_3^- migration by lowering the temperature of the reaction mixture were not

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Table 1. ²⁹Si NMR Shifts for Heavy Alkaline Earth Metal Germanides and Silanides

compound	δ (²⁹ Si) $\text{Ge}(\text{SiMe}_3)_3/\text{Si}(\text{SiMe}_3)_3$ (ppm)	ref
$\text{Ca}(\text{THF})_3(\text{Ge}(\text{SiMe}_3)_3)_2$, 1	-4.2	<i>a</i>
$\text{Sr}(\text{THF})_3(\text{Ge}(\text{SiMe}_3)_3)_2$, 2	-3.9	<i>a</i>
$\text{Ba}(\text{THF})_4(\text{Ge}(\text{SiMe}_3)_3)_2$, 3	-3.2	<i>a</i>
$\text{Ca}(\text{THF})_3(\text{Si}(\text{SiMe}_3)_3)_2$	-6.8	11
$\text{Sr}(\text{THF})_3(\text{Si}(\text{SiMe}_3)_3)_2$	-6.1	11
$\text{Ba}(\text{THF})_4(\text{Si}(\text{SiMe}_3)_3)_2$	-5.8	10

^a This work.

successful. However, it was found that the limited exposure to THF reduced the occurrence of $\text{Ge}(\text{SiMe}_3)_4$. Accordingly, $\text{KGe}(\text{SiMe}_3)_3$ was prepared in situ and combined immediately with the alkaline earth metal iodides dissolved in THF (eq 2). A systematic series of experiments indicated that a reaction time shorter than 30 min would result in reduced yields, whereas THF exposure of more than 30 min would promote the formation of $\text{Ge}(\text{SiMe}_3)_4$. Accordingly, a reaction time of 30 min was chosen.

Decomposition of alkali and alkaline earth metal group 14 derivatives has been observed previously, and the tendency increases, as descending group 14, accordingly, SiMe_3 migration is more pronounced in the germanides than the corresponding silanides. Typically, reduction and migration coincide as observed for the decomposition of $\text{M}(\text{SnPh}_3)_2$ ($\text{M} = \text{Ca, Sr}$), resulting in $\text{M}(\text{Sn}(\text{SnPh}_3)_2)_2$, $\text{Sn}(\text{SnPh}_3)_4$, SnPh_4 , and elemental Sn.¹⁴ Other examples include the decomposition of $\text{Li}(\text{PMDTA})\text{PbPh}_3$, where phenyl migration under formation of a black powder, presumably elemental Pb, was observed.²³ However, no further details are given about other products formed in this process. The increased tendency toward redox chemistry upon descending group 14 coincides with the decreasing bond strengths and increase in ionic bond character.

Compounds **1–3** are highly sensitive toward moisture and oxygen; accordingly, most careful handling techniques are required to synthesize and characterize the compounds. The sensitivity increases upon descending the group of alkaline earth metals, making the barium compound **3** significantly more reactive than the calcium analogue **1**.

Spectroscopic Studies. Compounds **1–3** were studied by ¹H, ¹³C, and ²⁹Si NMR techniques. ²⁹Si NMR values are included together with a few reference data in Table 1. Due to the sensitivity of the compounds toward THF and resulting redox chemistry, all NMR spectra were obtained in [D₆] benzene. The ²⁹Si NMR shifts for the group of germanides **1–3** show a clear trend, with the chemical shift increasing from -4.2 (1) to -3.2 ppm (3). An analogous increase was also observed for a series of silanides with values of -6.8 ppm for $\text{Ca}(\text{THF})_3(\text{Si}(\text{SiMe}_3)_3)_2$ and -5.8 ppm for $\text{Ba}(\text{THF})_4(\text{Si}(\text{SiMe}_3)_3)_2$.¹⁰ Similar trends have been observed for a group of alkali metal silanides [$\text{MSi}(\text{SiMe}_3)_3$]₂ ($\text{M} = \text{Na, K, Rb, Cs}$), with the chemical shift increasing from -6.0 to -5.3 ppm,¹⁵ as for a group of separated alkali metal silanides with -4.2 ppm for $[\text{K}(12\text{-crown-4})_2][\text{Si}(\text{SiMe}_3)_3]$ and -3.8 ppm for $[\text{Cs}(18\text{-crown-6})_2][\text{Si}(\text{SiMe}_3)_3]$.¹⁶ Klinkhammer suggests that the

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Table 2. Selected Bond Distances (Å) and Angles (deg) for Heavy Alkaline Earth Metal Germanides and Silanides

compound	M–Ge/M–Si (Å)	M–donor (Å)	Ge–Si/Si–Si (Å) (av)	Si–Ge–Si/Si–Si–Si (deg) (av)	Ge–M–Ge/Si–M–Si (deg)
Ca(THF) ₃ (Ge(SiMe ₃) ₃) ₂ , 1	3.022(2), 3.067(2)	2.364(7)–2.385(7)	2.388	101.16	125.43(6)
Sr(THF) ₃ (Ge(SiMe ₃) ₃) ₂ , 2	3.147(5), 3.198(5)	2.501(3)–2.536(3)	2.381	101.80	122.11(2)
Ba(THF) ₄ (Ge(SiMe ₃) ₃) ₂ , 3	3.398(9), 3.431(9)	2.711(6)–2.758(5)	2.383	100.55	140.52(2)
Ca(THF) ₃ (Si(SiMe ₃) ₃) ₂	3.042(9), 3.086(9)	2.348(2)–2.389(2)	2.344	101.75	125.53(3)
Sr(THF) ₃ (Si(SiMe ₃) ₃) ₂	3.167(1), 3.224(1)	2.507(3)–2.541(4)	2.317	102.59	122.23(4)
Ba(THF) ₄ (Si(SiMe ₃) ₃) ₂	3.419(1), 3.462(1)	2.717(3)–2.746(3)	2.339	101.47	140.62(3)

Table 3. Crystallographic Data for Compounds 1–3^a

	1	2	3
formula	C ₃₀ H ₇₈ CaGe ₂ O ₃ Si ₆	C ₃₀ H ₇₈ Ge ₂ O ₃ Si ₆ Sr	C ₃₄ H ₈₆ BaGe ₂ O ₄ Si ₆
fw	840.72	888.26	1010.09
a (Å)	18.8291(13)	18.7487(10)	19.2127(18)
b (Å)	14.9840(10)	15.1658(8)	17.2562(17)
c (Å)	17.0540(12)	17.1323(9)	31.651(3)
cryst syst	orthorhombic	orthorhombic	orthorhombic
V (Å ³)	4811.56(6)	4871.4(4)	10493.6(17)
Z	4	4	8
space group	<i>Pna2</i> /(1)	<i>Pna2</i> /(1)	<i>Pbca</i>
d _{calc} (g/cm ³)	1.161	1.211	1.279
linear abs coeff (mm ⁻¹)	1.530	2.489	2.047
T (K)	94	91	81
2θ range, deg	3.62–50.48	3.58–66.16	3.42–50.00
no. of indep reflns	8665	17349	9243
no. of params	383	374	424
R1, wR2 (all data)	0.0656, 0.1244	0.0530, 0.0907	0.0565, 0.1276
R1, wR2 (>2σ)	0.1269, 0.1497	0.0969, 0.1041	0.0941, 0.1468

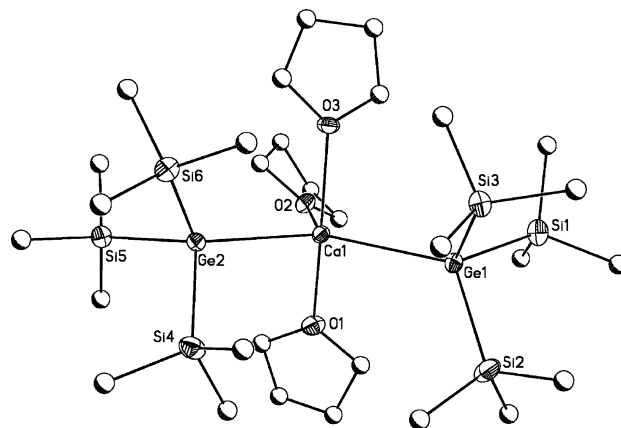
^a Radiation: Mo Kα (λ = 0.71073 Å). R1 = Σ||F_o – |F_c||/Σ|F_o|; wR2 = [Σw(F_o² – F_c²)²/Σw(F_o²)²]^{1/2}.

increased ligand–metal charge transfer and consequent changes in bond polarity are responsible for this trend,¹⁵ a conclusion that is also valid for compounds **1–3**. Increased bond polarity also coincides with increased pyramidity in the anion. Indeed, narrow Si–Ge–Si angles are observed for **1–3** (see Table 2). These angles agree well with those for the charge-separated [Li(12-crown-4)₂][Ge(SiMe₃)₃] (101.6° (av))¹⁸ and the related alkali and alkaline earth metal silanides, outlining the highly polar nature of the alkaline earth metal–germanium bond.

The highly polar nature of the metal–ligand bond should facilitate the formation of separated ions. This view is confirmed by the close similarity of ²⁹Si NMR shifts in compounds **1–3** and the separated [Li(12-crown-4)][Ge(SiMe₃)₃].¹⁸ The formation of separated ions upon dissolution in benzene is facilitated by the efficient coordination of the heavy alkaline earth metals to aromatic solvents.²⁴

Structural Aspects. Structure Descriptions. Crystallographic information and data collection parameters for compounds **1–3** are summarized in Table 3 and the Experimental Section. A compilation of selected geometrical parameters for all compounds is given in Table 2, while compounds **1** and **3** are represented in Figures 1 and 2. A graphical representation of compound **2** can be found on the Table of Contents page.

Compounds **1–3** display alkaline earth metal centers connected to two germanide ligands in addition to either three (Ca or Sr) or four (Ba) THF donors, as rationalized by the increasing alkaline earth metal radius. The influence of metal radius is also reflected by the increasing metal–germanium and metal–oxygen dis-

**Figure 1.** Graphical representation of compound **1**. Ellipsoids show 30% occupancy; hydrogen atoms have been removed for clarity.

tances with 3.045(2) and 2.372(7) Å (av) for **1**, 3.173(5) and 2.516(3) Å (av) for **2**, and 3.414(9) and 2.742(5) Å (av) for **3**.

The coordination environment in the five-coordinated **1** and **2** may be described as distorted trigonal bipyramidal, with two germanide ligands and one THF donor in the equatorial plane and two THF donors in axial positions. The trans angles for the THF donors in axial positions reflect the degree of distortion with 155.1(2)° in **1** and 150.13(10)° in **2**. The Ge–M–Ge angles of 125.43(6)° for **1** and 122.11(15)° for **2** agree well with their position in the equatorial plane. The slightly wider Ge–Ca–Ge angle may be explained by the larger steric demand of the ligand due to the shorter Ca–Ge bond length, as compared to the strontium analogue **2**. The Si–Ge–Si angle sum is 303.47° (av) for **1** and 305.41° (av) for **2**, indicating pronounced pyramidal geometry in the anions.

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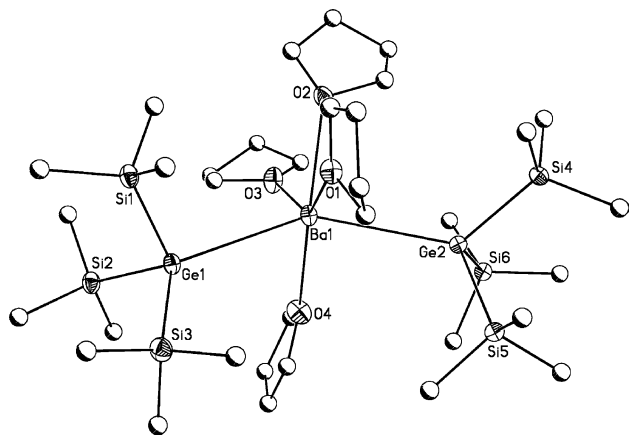


Figure 2. Graphical representation of compound **3**. Ellipsoids show 30% occupancy; hydrogen atoms have been removed for clarity.

The six-coordinated **3** exhibits a significant deviation from octahedral geometry with a trans Ge–Ba–Ge angle of $140.52(2)^\circ$. In accord with this distortion, O–Ba–O angles deviate from regular octahedral geometry with angles ranging from $71.87(18)^\circ$ to $143.90(18)^\circ$. The angle sum of the central germanium is 301.65° (av), indicating significant pyramidal geometry.

The series of alkaline earth metal silanides^{10,11} and germanides $M(\text{THF})_n(\text{E}(\text{SiMe}_3)_3)_2$ ($M = \text{Ca}$, $\text{E} = \text{Si}$, Ge , $n = 3$; $M = \text{Sr}$, $\text{E} = \text{Si}$, Ge , $n = 3$; $M = \text{Ba}$, $\text{E} = \text{Si}$, Ge , $n = 4$) display very similar structural features. Especially striking are the almost identical metal–silicon and –germanium distances (see Table 2). The initially surprising fact that the metal–germanium distances are slightly shorter than the metal–silicon bond lengths is in contrast to the larger germanium radius (ionic radius Si^{4+} (CN = 4) = 0.40 \AA , Ge^{4+} (CN = 4) = 0.53 \AA).²⁵ The large size of germanium is also evident in the trimeric $(\text{E}(\text{SiMe}_3)_2)_3$ ($\text{E} = \text{Ge}$, Si), where Si–Si distances of 2.351 \AA and significantly longer Ge–Ge distances (2.456 \AA) are observed.¹⁹ The shorter metal–germanium contact in compounds **1–3** can be explained by the increased polar character in the alkaline earth metal germanium bond, as reflected by electronegativity numbers (Allred Rochow electronegativity $\text{Si} = 1.74$, $\text{Ge} = 2.02$).²⁶

Due to the almost identical metal–silicon and –germanium bond lengths and resulting steric requirements, it is not surprising that the overall structural features in the silanides and germanides are very similar, as evidenced by the E–M–E ($\text{E} = \text{Si}$, Ge) angles of $125.43(6)^\circ$ for **1** and $125.53(3)^\circ$ for the corresponding silanide. This trend continues for the strontium and barium derivative with Ge–M–Ge angles of $122.11(15)^\circ$ for **2** and $140.52(2)^\circ$ for **3**. The silanides display a similar geometry with $122.23(4)^\circ$ and $140.62(3)^\circ$. This argument is also supported in earlier work by Mallela and Geanangel, who compared cone angles in a series of $\text{Sn–E}(\text{SiMe}_3)_3$ ($\text{E} = \text{Si}$, Ge) compounds. They concluded that despite the larger germanium radius the cone angles of the silanides and germanides are similar and thus the steric influence of both ligands is not significantly different.^{21c} This argument is further supported by comparing the structural features of a series of lithium

silanides and germanides, $\text{Li}(\text{THF})_3\text{E}(\text{SiMe}_3)_3$ ($\text{E} = \text{Si}$,²⁷ $\text{E} = \text{Ge}$ ¹⁷), where similar Li–Si ($2.669(13) \text{ \AA}$ ^{27a} and $2.644(12) \text{ \AA}$ ^{27b}) and Li–Ge distances ($2.666(6) \text{ \AA}$) are observed.

Compounds **1–3** exhibit a significant deviation from the linear trans angle, as expected in ideal trigonal bipyramidal and octahedral geometry. Interestingly, the angle decreases on descending group 2, with $155.1(2)^\circ$ and $150.13(10)^\circ$ in the trigonal bipyramidal **1** and **2** and $140.52(2)^\circ$ for the six-coordinate **3**. These values are in good agreement with those for the isomorphous silanides with $154.59(8)^\circ$ for $\text{Ca}(\text{THF})_3(\text{Si}(\text{SiMe}_3)_3)_2$, $149.52(13)^\circ$ for $\text{Sr}(\text{THF})_3(\text{Si}(\text{SiMe}_3)_3)_2$, and $140.62(3)^\circ$ for $\text{Ba}(\text{THF})_4(\text{Si}(\text{SiMe}_3)_3)_2$.^{10,11} Structural trends in regards to trans angle compression have been observed previously in alkaline earth metal chemistry, and routinely, angles as low as 132° are observed.²⁸ In general, the angles are narrower for the heavier alkaline earth metal derivatives, possibly a consequence of increased ionic bond character and weaker metal–ligand bond, allowing the facile distortion from ideal geometry. In addition, the increased bond length in the heavier analogues allows for a larger degree of structural flexibility, with a reduced amount of repulsion upon angle compression.

Conclusions

The first heavy alkaline earth metal hypergermanides were obtained utilizing a facile one-pot metathesis reaction. In the presence of THF, the compounds show a pronounced tendency toward redox chemistry through SiMe_3^- migration, resulting in the formation of the parent $\text{Ge}(\text{SiMe}_3)_4$ and elemental germanium. The compounds exhibit very close structural similarities to the isomorphous silanides.

Experimental Section

General Procedures. All reactions were performed using standard procedures using a purified nitrogen atmosphere by utilizing either modified Schlenk techniques and/or a Braun Labmaster drybox. $\text{Ge}(\text{SiMe}_3)_4$ was prepared following literature procedures;²⁹ alkaline earth metal iodides, potassium *tert*-butoxide, ClSiMe_3 , and GeCl_4 were obtained commercially. THF and hexanes were distilled prior to use from CaH_2 or a Na/K alloy. ^1H NMR and ^{13}C NMR were recorded on a Bruker DPX-300 spectrometer. ^{29}Si NMR spectra were obtained on a Bruker DPX 500 spectrometer with a wide bore probe (10 mm) using DEPT techniques.³⁰ The NMR spectra were recorded in C_6D_6 at room temperature and referenced to residual solvent resonances. Reliable elemental analyses could not be obtained, even when glovebox handling was attempted, due to the high reactivity of the compounds reported here. In fact, the reactivity of compounds **1–3** is so high that all spectral analysis had to be carried out within a few hours of isolating the compounds and transferring them into the freshly regenerated glovebox, precluding the shipment of intact samples for elemental analysis.³

General Procedure for Compounds 1–3. $\text{Ge}(\text{SiMe}_3)_4$ (2 mmol, 0.72 g) was dissolved in 15 mL of THF and added to a solution of 2 mmol (0.22 g) of KO^tBu in 20 mL of THF. After

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stirring for 15 min at room temperature, the resulting mixture was slowly added to a solution of 1 mmol of alkaline earth metal iodide (0.29 g of CaI_2 , 0.34 g of SrI_2 , and 0.39 g of BaI_2 , respectively) dissolved in 25 mL of THF. The mixture was then stirred for 30 min at room temperature, upon which the solvent was removed under reduced pressure. The residue was extracted with 80 mL of hexane and filtered through a Celite-layered filter frit, resulting in clear, pale yellow solutions that were reduced in volume to about 30 mL and stored at -20°C . Colorless crystals suitable for diffraction experiments were typically obtained in 4 days.

1: Yield: 0.59 g, 70.2%; mp 135°C (dec). ^1H NMR: δ (ppm) 3.67 (m, br, 28H, THF), 1.36 (m, br, 28H, THF), 0.51 (s, 54H, SiMe_3). ^{13}C NMR: δ (ppm) 7.0 (SiMe_3), 25.3 (THF), 68.9 (THF). ^{29}Si NMR: δ (ppm) -4.2 Ge(SiMe_3). IR (cm^{-1}) (KBr plates, Nujol mull): 2923 (s), 2853 (s), 1458 (m), 1377 (m), 1245 (w), 1074 (w), 960 (w), 838 (m), 747 (w), 721 (w), 688 (w), 667 (w).

2: Yield: 0.65 g, 73.0%; mp 125°C (dec). ^1H NMR: δ (ppm) 3.64 (m, br, 12H, THF), 1.36 (m, br, 12H, THF), 0.53 (s, 54H, SiMe_3). ^{13}C NMR: δ (ppm) 7.3 (SiMe_3), 25.1 (THF), 68.7 (THF). ^{29}Si NMR: δ (ppm) -3.9 Ge(SiMe_3). IR (cm^{-1}) (KBr plates, Nujol mull): 2921 (s), 2726 (m), 1454 (s), 1377 (s), 1304 (w), 1256 (m), 1244 (s), 1197 (m), 1076 (w), 962 (m), 836 (s), 722 (m), 687 (m), 666 (w), 619 (m).

3: Yield: 0.73 g, 72.3%; mp $162\text{--}166^\circ\text{C}$. ^1H NMR: δ (ppm) 3.62 (m, br, 16H, THF), 1.41 (m, br, 16H, THF), 0.55 (s, 54H, SiMe_3). ^{13}C NMR: δ (ppm) 7.4 (SiMe_3), 25.4 (THF), 68.3 (THF). ^{29}Si NMR: δ (ppm) -3.2 Ge(SiMe_3). IR (cm^{-1}) (KBr plates, Nujol mull): 2925 (s), 2855 (s), 1459 (m), 1377 (m), 1245 (m), 1231 (m), 1034 (m), 916 (w), 825 (s), 728 (w), 670 (m), 614 (m).

X-ray Diffraction Details. The crystals were mounted on the diffractometer as described previously.³¹ Due to the extreme moisture and oxygen sensitivity of the compounds, the microscope was placed inside the diffractometer enclosure, and the crystals were removed under inert gas from the mother liquor in immediate proximity to the microscope. The data were collected using a Bruker SMART system, complete with 3-circle goniometer and CCD detector, as described earlier.³²

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The data sets were collected using a custom-built low-temperature device from Professor H. Hope (UC Davis). Compound **1** was collected at 94 K, **2** at 91 K, and **3** at 81 K. Monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) was employed in all cases. The data collections nominally covered a hemisphere of reciprocal space utilizing a combination of three sets of exposures, each with a different ϕ angle and each exposure covering 0.3° in ω . Repeating the initial frames at the end of the data collection and analyzing the duplicate reflections monitored crystal decay. In all cases, no decay was observed. An absorption correction was applied utilizing the program SADABS.³³ The crystal structures were solved using direct or Patterson methods and were refined by full-matrix least-squares refinement on F^2 .³⁴ All non-hydrogen atoms were refined anisotropically. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. 218791–218793. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: This material is available free of charge via the Internet at <http://pubs.acs.org>.

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