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Syntheses and Structures of the First Heavy-Alkali-Metal Tris(trimethylsilyl)germanides

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Dedicated to Professor Ulrich Müller on the occasion of his 65th birthday

Abstract: The first heavy-alkali-metal tris(trimethylsilyl)germanides were obtained in high yield and purity by a simple one-pot reaction involving the treatment of tetrakis(trimethylsilyl)germane, $Ge(SiMe_3)_4$, with various alkali metal *tert*-butoxides. The addition of different sizes of crown ethers or the bidentate TMEDA (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine) provided either contact or separated species in the solid state, whereas in aromatic solvents the germanides dissociate into separated ions, as shown by ^{29}Si NMR spectroscopic studies. Here we report on two series of germanides, one displaying M−Ge bonds in the solid state with the general formula $[M(donor)_nGe(SiMe_3)_3]$ (M = K, donor = [18]crown-6, $n = 1$, **1**; Rb, donor = [18]crown-6, $n = 1$, **4**; and M = K, donor = TMEDA, $n = 2$, **6**). The silicon analogue of **6**, $[K(tmeda)_2Si(SiMe_3)_3]$ (**7**) is also included to provide a point of reference. The second group of compounds consists of separated ions with the general formula $[M(donor)_2][Ge(SiMe_3)_3]$ (M = K, donor = [15]crown-5, **2**; M = K, donor = [12]crown-4, **3**; and M = Cs, donor = [18]crown-6, **5**). While all target compounds are highly sensitive towards hydrolysis, use of the tridentate nitrogen donor PMDTA (PMDTA = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine) afforded even more reactive species of the composition $[K(pmdta)_2Ge(SiMe_3)_3]$ (**8**). We also include the silanide analogue $[K(pmdta)_2Si(SiMe_3)_3]$ (**9**) for sake of comparison. The compounds were typically characterized by X-ray crystallography, and ^1H, ^{13}C, and ^{29}Si NMR and IR spectroscopy, unless extremely high reactivity, as observed for the PMDTA adducts **8** and **9**, prevented a more detailed characterization.

Keywords: alkali metals · germanium · ion association · metathesis · structure elucidation

Introduction

The chemistry of alkaline-earth-metal derivatives bearing heavy Group 14 ligands has attracted attention[1–13] due to applications in synthetic and polymer chemistry.[9,14] While alkali- and alkaline-earth-metal silanides have been studied in some detail,[1,2,4,7,9,15–25] little is known for the closely related, but more reactive germanides.[8,12,26–28] Specifically, difficulties in the preparation of the alkali-metal germanides needed to access the alkaline-earth-metal analogues by metathesis are responsible for this slow development. As such, a convenient access route to stable alkali-metal germanides is warranted.

Alkali-metal derivatives involving heavy Group 14 ligands are mainly limited to silanides. Amongst those, $[Si(SiMe_3)_3]^-$ (hypersilanide) has been widely used to prepare a host of transition-metal and main-group silanides.[29] The advantages of this ligand system are its ease of preparation, high solubility in a variety of solvent systems, and large steric demand allowing effective kinetic stabilization. Examples include the lithium silanides $[LiSi(SiMe_3)_3]$,[15] $[Li(thf)_3Si(SiMe_3)_3]$,[16,17] $[Li(thf)_3Si(SiMe_3)_3][Si(SiMe_3)_4]$,[16] and $[Li(dme)_{1.5}Si(SiMe_3)_3]$ (DME = 1,2-dimethyloxyethane).[18] Other silanides include an etherate of $KSiPh_3$, initially prepared by Gilman and Wu in 1951 by cleaving the silicon–silicon bond in hexaphenyldisilane with an Na–K alloy, followed by analogous chemistry for rubidium and cesium.[19] Later work by Wiberg et al. focused on the treatment of alkali-metal halides dissolved in ammonia with hexaphenyldisilanes.[20] Other examples include the $[MSi(tBu)_3]$ series (M = Na, K, Rb, Cs),[21] prepared by treating silylhalides with the appropriate alkali metals. A family of dimeric hypersilanides

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$[\{MSi(SiMe_3)_3\}_2]$, (M = Li, Na, K, Rb, Cs) was obtained by treatment of zinc, cadmium, or mercury silanides with the respective alkali metals.[22] An alternative synthetic route towards $[KSi(SiMe_3)_3]$ relies on the treatment of $Si(SiMe_3)_4$ with KO*t*Bu in either THF or DME.[23] While this route generally proceeds well, it critically depends on a supply of good quality potassium *tert*-butoxide. Experiments in our laboratory relying on commercial potassium *tert*-butoxide frequently yielded incomplete reactions under precipitation of the cluster species, $[\{K(thf)Si(SiMe_3)_3\}\{KOtBu\}_3]$, prompting us to develop an alternative synthetic route based on the treatment of lithium tris(trimethylsilyl)silanide with heavy-alkali-metal *tert*-butoxides.[25]

Replacement of the central silicon atom in $[Si(SiMe_3)_3]^-$ with germanium affords the closely related $[Ge(SiMe_3)_3]^-$ ligand. While the parent compound $Ge(SiMe_3)_4$ was reported decades ago,[30] metal derivatives are scarce and examples are mainly limited to a few lithium derivatives, including $[Li(thf)_3Ge(SiMe_3)_3]$,[26] $[Li(pmdta)Ge(SiMe_3)_3]$[26] (PMDTA = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine) and $[Li([12]crown\text{-}4)_2][Ge(SiMe_3)_3]$.[27] Amongst these, $[Li(thf)_3Ge(SiMe_3)_3]$ has been used in the preparation of a small group of main-group[31] and transition-metal germanides.[32] Germanides involving the heavier alkali metals are limited to $[\{CsGe(SiMe_3)_3\}_2]$.[28] The scarcity of heavy-alkali-metal germanide derivatives may be due to the high reactivity of the compounds caused by the increased weakness of the alkali-metal–germanium and the germanium–silicon bonds.

Since we were interested in using heavy-alkali-metal hypergermanides in metathesis chemistry, a facile synthetic route towards the target compounds, preferably without the use of toxic reagents, such as mercury and its derivatives, was needed. Relying on chemistry developed for the silanides, we here report on the first family of heavy-alkali-metal hypergermanides. Depending on the donor utilized, two groups of compounds displaying different ion association modes in the solid state were obtained, including the contact molecules $[K([18]crown\text{-}6)Ge(SiMe_3)_3]$ (**1**), $[Rb([18]crown\text{-}6)Ge(SiMe_3)_3]$ (**4**), and $[K(tmeda)_2Ge(SiMe_3)_3]$ (**6**; TMEDA = *N,N,N′,N′*-tetramethylethylenediamine). To add a point of reference, the silanide analogue of **6** $[K(tmeda)_2Si(SiMe_3)_3]$ (**7**), has also been incorporated. The second group of compounds consists of separated ions including $[K([15]crown\text{-}5)_2][Ge(SiMe_3)_3]$ (**2**), $[K([12]crown\text{-}4)_2][Ge(SiMe_3)_3]$ (**3**), and $[Cs([18]crown\text{-}6)_2][Ge(SiMe_3)_3]$ (**5**). Difficulties mounting the highly reactive **3** on the diffractometer and problems with disorder prevented a satisfactory structure refinement, but pertinent structure parameters are clearly visible. However, the identity of compound **3** has also been confirmed by ^1H, ^{13}C, and ^{29}Si NMR and IR spectroscopic data.

Use of the tridentate nitrogen donor PMDTA afforded $[K(pmdta)_2Ge(SiMe_3)_3]$ (**8**) and its silicon analogue $[K(pmdta)_2Si(SiMe_3)_3]$ (**9**), whose high reactivity prevented extensive characterization, since rapid decomposition under brown coloration was observed.

The purity of all germanides with the exception of **8** was confirmed by ^1H and ^{13}C NMR, and IR spectroscopy, while compounds **1**, **2**, and **4**–**7** were also characterized by single-crystal X-ray crystallography. Extensive ^{29}Si NMR studies were conducted on compounds **1**–**5** to investigate the ion association of the target compounds in solution.

Results and Discussion

The formation of alkali-metal derivatives by reaction of trimethylsilyl-substituted silanes ($Si(SiMe_3)_4$ [Eq. (1)]) or phosphanes ($P(SiMe_3)_3$) with alkali-metal *tert*-butoxides under formation of silylether has been well established.[23,24]

$$Si(SiMe_3)_4 + KOtBu \rightarrow KSi(SiMe_3)_3 + Me_3SiOtBu \qquad (1)$$

Made attractive by its simplicity and the easy availability of starting materials, the method appeared a desirable choice for the preparation of potassium germanides $[KGe(SiMe_3)_3]$ by treatment of $Ge(SiMe_3)_4$ with KO*t*Bu.[12] Indeed, the reaction proceeds well, affording colorless crystals of the parent compound $[K(thf)_nGe(SiMe_3)_3]$. However, the germanide is considerably more reactive than the corresponding silanide, and rapid desolvation upon removal of mother liquor and decomposition under production of flames is observed upon contact to trace amounts of air. As such, spectroscopic data are very challenging to obtain, and it is impossible to collect crystallographic data even under most careful handling conditions. It was not until the introduction of crown ethers and the nitrogen-based bidentate donor TMEDA that germanides were obtained that could be characterized in detail. Still, the target compounds remain extremely reactive making their characterization nontrivial.

As such, heavy-alkali-metal germanides may be obtained in a similar fashion to the silanides in a facile one-pot procedure by silylether elimination if differently sized crown ethers or the nitrogen-based donor TMEDA are utilized [Eq. (2)].

$$E(SiMe_3)_4 + MOtBu + n\text{Donor} \xrightarrow{\text{THF}} [M(\text{donor})_nE(SiMe_3)_3] + Me_3SiOtBu \qquad (2)$$

When considering the reactivity of the target molecules it is important to differentiate between reactivity in solution and the solid state. As discussed in detail in the next section, the germanides exist as separated ions in solution, and as such the cation environment has little influence on the reactivity of the anion, resulting in comparable trends towards hydrolysis for all germanides reported here. In contrast, in the solid state contact molecules and separated ions are observed depending on the steric saturation of the metal environment by donor molecules and ligands (see below). Generally, compounds displaying sterically well-saturated metal environments, as observed for the contact molecule [K([18]crown-6)Ge($SiMe_3$)$_3$] (**1**) or the separated cesium derivative [Cs([18]crown-6)$_2$][Ge($SiMe_3$)$_3$] (**5**) are less reactive than sterically less-saturated compounds, such as the contact molecules [Rb([18]crown-6)Ge($SiMe_3$)$_3$] (**4**), [K(tmeda)$_2$-Ge($SiMe_3$)$_3$] (**6**) or the separated ion [K([12]crown-4)$_2$] [Ge($SiMe_3$)$_3$] (**3**). These data indicate that it is not the ion association that is the determining factor in regards to reactivity, but rather the steric saturation of the metal center, regardless of ligand or donor coordination. Based on these trends, the high reactivity of the nitrogen-donated germanides **6** and **8** can be rationalized: bi- and tridentate donors are less effective than crown ether macrocycles to sterically saturate the metal centers. While the TMEDA adduct **6** displays the low metal coordination number of five, and the bulky nature of the donor does not allow for the coordination of a third TMEDA ligand, the bis-PMDTA adduct **8** is expected to display a coordination number of seven; however, the six coordination sites provided by the two bulky PMDTA donors require significantly more space than those of one [18]crown-6 macrocycle, leading to significant steric repulsion between the donors and the ligand and thus destabilization of the compound. On the other hand, two PMDTA molecules are not capable of sterically saturating a separated potassium cation, while potassium is too small to accommodate three PMDTA donors.

Using similar arguments the variation of reactivity in the crown ether derivatives may be rationalized: the high reactivity of compound **4** relative to **1** is due to the less effective steric saturation of the large rubidium center by one [18]crown-6 donor and a germanide ligand. On the other hand, rubidium is not large enough to accommodate two [18]crown-6 macrocycles under formation of a sandwich complex, as observed for the larger cesium ion under formation of compound **5**. Analogous trends can be seen for compound **3**, whose extremely high reactivity may be explained by the insufficient steric shielding of the metal provided by the two small crown ethers, making **3** the most reactive among the alkali-metal germanide series.

The germanides are highly sensitive towards hydrolysis, and trace amounts of water afforded a series of alkali-metal germanium hydrides,[33] a group of compounds previously only reported in the form of solid-state materials consisting of alkali-metal cations and GeH_3^- ions.[34] Interestingly, the germanides are significantly more sensitive towards hydrolysis than the silanides, for which the presence of an acid stronger than water appears to be necessary to affect the protonation of the silanides. This is indicated by Gilman et al. and Marschner who reported on the treatment of [LiSi($SiMe_3$)$_3$] and [K(thf)$_n$Si($SiMe_3$)$_3$] with acid to afford HSi($SiMe_3$)$_3$.[15b,23] An explanation for this significant difference in reactivity may be the increased polarity in the Ge–Si bond relative to the less polar Si–Si bond in the hypersilanide.

Spectroscopic studies: Compounds **1**–**7** were studied by ^1H and ^{13}C NMR spectroscopy, and the respective data are listed in the experimental section. A comparison of the ^{29}Si NMR chemical shifts for the $SiMe_3$ groups in **1**–**5** indicates that the clear distinction between contact and separated molecules, as observed in the solid state, is not maintained in solution. In fact, all $SiMe_3$ chemical shifts are observed in a small range, suggesting the formation of separated ions upon dissolution in [D$_6$]benzene. An analogous observation was made for the closely related hypersilanides, for which the formation of separated ions in an aromatic solvent was suggested.[25] The similarity of chemical shifts for the germanides and silanides suggests a close chemical relationship, an assumption also supported by the closely related values for atomic size and electronegativity.[35,36]

The high reactivity of compound **8** did not allow its characterization by ^{13}C and ^{29}Si NMR spectroscopy, since the sample decomposed rapidly even when handled in the freshly regenerated glove box. However, ^1H NMR data indicate a 2:1 ratio of donor and ligands, suggesting the molecular composition of [K(pmdta)$_2$Ge($SiMe_3$)$_3$]. ^1H NMR studies also suggest an analogous composition for the silanide analogue **9**.

Structural aspects: Crystallographic information and data collection parameters for compounds **1**, **2**, **4**–**7** are summarized in Table 1, while a summary of structural parameters is given in Table 2. The high reactivity of compounds **8** and **9** prevented their crystallographic characterization. Among the hypergermanides, compounds **1**, **4**, and **6** display an alkali metal germanium bond in the solid state, while **2**, **3**, and **5** display separated ions. Compounds **6** and **7** display very similar metal coordination environments, and will be described together.

[K([18]crown-6)Ge($SiMe_3$)$_3$] (**1**) is shown in Figure 1. No crystallographically imposed symmetry is observed. The compound displays contact molecules with the central metal connected to an [18]crown-6 macrocycle and a hypergermanide anion, resulting in a metal coordination number of seven. Potassium–oxygen distances are between 2.768(2) and 2.910(2) Å. The potassium–germanium distance is 3.399(8) Å and Ge–Si distances range from 2.381(1) to 2.388(9) Å. The Si-Ge-Si angle sum is 302.64°.

[K([15]crown-5)$_2$][Ge($SiMe_3$)$_3$] (**2**), illustrated in Figure 2, displays separated cations and anions. The central potassium atom is coordinated to two [15]crown-5 macrocycles resulting in a metal coordination number of ten and potassium–oxygen distances between 2.88(2) and 2.90(1) Å. The germanide anion is formally separated from the cation by more than 9.50 Å. The Ge–Si distances in the anion range from 2.380(2) to 2.386(2) Å, with an angle sum at the central germanium atom of 302.88°.

[Rb([18]crown-6)Ge($SiMe_3$)$_3$] (**4**), illustrated in Figure 3, displays two independent molecules in each asymmetric unit. The compound exhibits contact molecules with the central metal connected to an [18]crown-6 macrocycle and a hypergermanide anion. The coordination environment about the Rb2 center is completed by an agostic interaction (3.097 Å) from the hydrogen atom of one of the $SiMe_3$

Table 1. Crystallographic data for heavy alkali metal hypergermanides and potassium TMEDA hypersilanide.

	1	**2**	**4**	**5**	**6**	**7**
formula	$C_{21}H_{51}GeKO_6Si_3$	$C_{29}H_{67}GeKO_{10}Si_3$	$C_{21}H_{51}GeRbO_6Si_3$	$C_{33}H_{75}CsGeO_{12}Si_3$	$C_{21}H_{59}GeKN_4Si_3$	$C_{21}H_{59}KN_4Si_4$
M_r	595.58	771.79	641.95	953.70	563.68	519.18
a [Å]	9.6694(2)	15.4387(2)	10.141(2)	57.0263(2)	12.2695(7)	12.2604(7)
b [Å]	19.8644(3)	28.4014(3)	17.165(3)	12.9491(10)	14.7767(8)	14.7058(9)
c [Å]	17.4298(4)	9.461	19.032(4)	27.6038(4)	19.4081(11)	19.4619(11)
α [°]			85.69(3)			
β [°]	90.91		82.99(3)	107.2450(10)	93.4330(10)	93.3720(10)°
γ [°]			89.58(3)			
V [Å^3]	3347.43(12)	4148.60(7)	3278.9(11)	19467.4(3)	3512.4(3)	3502.9(4)
Z	4	4	4	16	4	4
space group	$P2_1/n$	$Ama2$	$P\bar{1}$	$C2/c$	$P2_1/n$	$P2_1/n$
ρ_{calcd} [g cm^{-3}]	1.182	1.236	1.300	1.302	1.066	0.984
μ [mm^{-1}]	1.174	0.970	2.547	1.488	1.107	0.302
T [K]	93	91	96	95	91	87
2θ range [°]	4.68–50.00	3.90–50.00	4.04–50.00	3.48–50.00	3.46–56.00	3.48–50.00
independent reflns	5852	3706	13725	17016	8482	6154
parameters	289	212	578	898	271	290
$R1/wR2$ (all data)	0.0736/0.0861	0.0579/0.1374	0.0987/0.0752	0.0594/0.1248	0.0597/0.1058	0.0822/0.1295
$R1/wR2$ [$I>2\sigma(I)$]	0.0456/0.0786	0.0553/0.1353	0.0455/0.0661	0.0506/0.1191	0.0397/0.0950	0.0499/0.1142

Radiation: $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å). $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond lengths [Å] and angles [°] for heavy-alkali-metal hypergermanides and -silanides (NA = not applicable).

Compound	M−Ge/M−Si	M−donor	Ge−Si/Si−Si	Si-Ge-Si/Si-Si-Si	Ref.
[K([18]crown-6)Ge($SiMe_3$)$_3$] (**1**)	3.399(8)	2.768–2.910	2.383[a]	100.9[a]	this work
[K([18]crown-6)Si($SiMe_3$)$_3$]	3.447(8)	2.787–2.926	2.348[a]	102.0[a]	[10]
[K([15]crown-5)$_2$][Ge($SiMe_3$)$_3$] (**2**)	NA	2.88–2.902	2.384[a]	101.0[a]	this work
[Rb([18]crown-6)Ge($SiMe_3$)$_3$] (**4**)	3.480(2), 3.539(2)	2.842–3.025	2.365[a]	102.2[a]	this work
[Rb([18]crown-6)Si($SiMe_3$)$_3$]$_2$·	3.436(8)[c], 3.452(7)[c]	2.826–2.984[c]	2.326[a,c]	102.8[a,c]	[10]
[Rb([18]crown-6)$_2$][Si($SiMe_3$)$_3$][b]	NA[d]	3.119–3.431[d]	2.327[a,d]	99.4[a,d]	
[Cs([18]crown-6)$_2$][Ge($SiMe_3$)$_3$][e] (**5**)	NA	3.153–3.574	2.396[a]	98.2[a]	this work
[Cs([18]crown-6)$_2$][Si($SiMe_3$)$_3$][e]	NA	3.141–3.560	2.336[a]	99.5[a]	[10]
[K(tmeda)$_2$Ge($SiMe_3$)$_3$] (**6**)	3.373(5)	2.807–2.933	2.373	100.81	this work
[K(tmeda)$_2$Si($SiMe_3$)$_3$] (**7**)	3.390(1)	2.808–2.935	2.329	101.92	this work

[a] Average. [b] Contact and separated ion-pair in one crystal. [c] Contact ion-pair. [d] Separated ion-pair. [e] Two independent molecules.

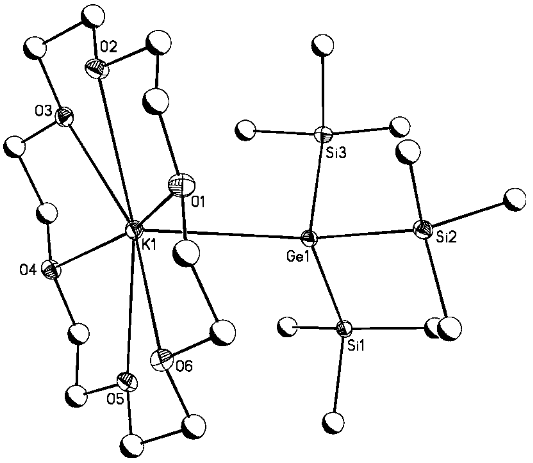

Figure 1. Graphical representation of compound **1**. Ellipsoids show 30% occupancy, hydrogen atoms have been removed for clarity.

groups. The second rubidium center (Rb1) also displays a weak agostic interaction, but here a hydrogen atom from the ligand of the second independent molecule binds to the rubidium in a *trans* position to the ligand (3.005 Å). These

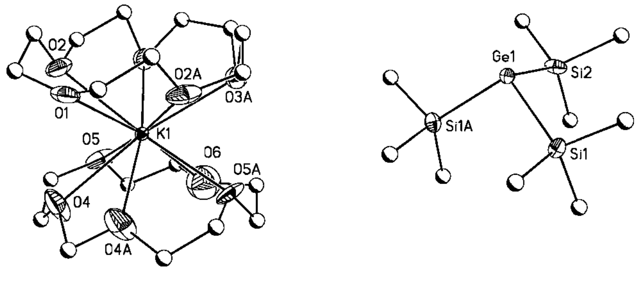

Figure 2. Graphical representation of compound **2**. Ellipsoids show 30% occupancy, hydrogen atoms have been removed for clarity.

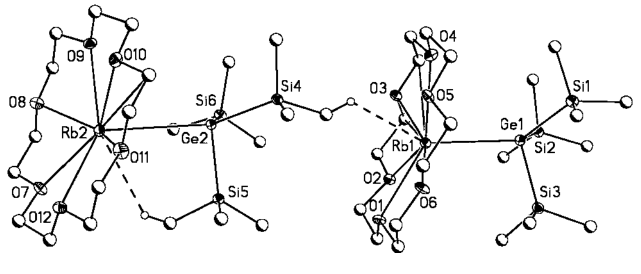

Figure 3. Graphical representation of compound **4**. Ellipsoids show 30% occupancy, hydrogen atoms have been removed for clarity.

interactions increase the metal coordination numbers in both molecules to eight. Rubidium–oxygen distances are between 2.842(4) and 3.025(4) Å, while rubidium–germanium distances are between 3.480(2) and 3.539(2) Å. The Ge−Si bonds range from 2.346(2) to 2.375(2) Å, with a Si-Ge-Si angle sum of 306.46° (av).

$[Cs([18]crown\text{-}6)_2][Ge(SiMe_3)_3]$ (**5**), shown on the Table of Contents page, displays two independent molecules in each asymmetric unit, of which only one is shown. The compound consists of cations and anions separated by more than 10.16 and 10.27 Å. The cesium cation is surrounded by two [18]crown-6 macrocycles, resulting in a metal coordination number of twelve. Cesium–oxygen distances are observed between 3.156(3) and 3.571(4) Å. The germanide anion displays average Ge−Si distances of 2.397(8). The angle sums at the central germanium atoms for the two independent anions are rather narrow with 293.11° and 296.38°.

$[K(tmeda)_2Ge(SiMe_3)_3]$ (**6**) (Figure 4) and $[K(tmeda)_2Si(SiMe_3)_3]$ (**7**) are isostructural and will be described together. Both molecules crystallize with one independent molecule per asymmetric unit with no crystallographically imposed symmetry. The compounds exhibit contact molecules with the central metal connected to two TMEDA donors and a hypergermanide/-silanide anion, resulting in a metal coordination number of five, which can be described as a significantly distorted trigonal bipyramid. The potassium–germanium distance is 3.373(5) Å, while the potassium–silicon distance is slightly longer with 3.390(1). Potassium–nitrogen distances are between 2.807(2) and 2.933(2) Å for **6** and 2.808(3) to 2.935(3) Å for **7**, respectively. Ge−Si distances in **6** range from 2.368(7) to 2.379(7) Å, while the Si−Si distances in **7** are between 2.324(1) and 2.335(1) Å. The Si-Ge-Si angle sum in **6** is 302.44°, while the Si-Si-Si angle sum in **7** is 305.76°.

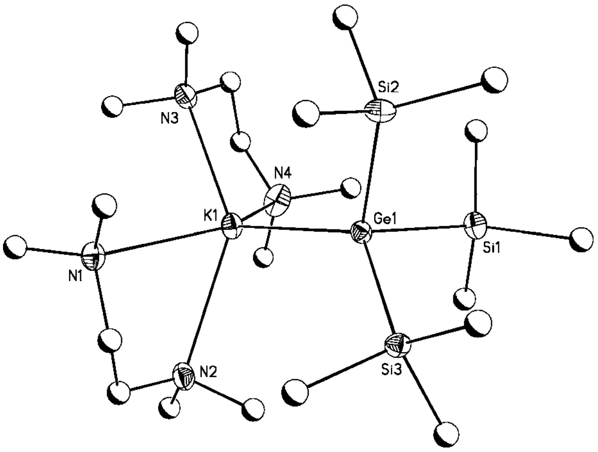

Figure 4. Graphical representation of compound **6**. Ellipsoids show 30% occupancy, hydrogen atoms have been removed for clarity.

The two main structural motifs in the target compounds, the presence of contact molecules and separated ions can be rationalized by the nature of the donor molecules. The ion association in the solid state strongly depends on the cation size and crown ether diameter, the denticity of the donor, and the strength of the metal–ligand bond.

Only two crown ether-containing contact molecules, $[K([18]crown\text{-}6)Ge(SiMe_3)_3]$ (**1**) and $[Rb([18]crown\text{-}6)Ge(SiMe_3)_3]$ (**4**), are observed due to the good size match between the cation and the macrocycle. If, however, a crown ether with cavity size that is too small to fully encapsulate the metal center is used, the metal coordination sphere will be typically saturated by the coordination of a second macrocycle under formation of sandwich complexes. The drive towards coordinative saturation is so strong that the formation of sandwich complexes is also observed if only one equivalent of crown ether is present. The separated ions resulting from this arrangement are observed for a potassium cation coordinated to two [15]crown-5 macrocycles, as shown in compounds **2** and **3** with two [12]crown-4 macrocycles, and for the larger cesium ion with the coordination of two [18]crown-6 macrocycles, as observed in compound **5**.

Earlier work in our laboratory had shown the simultaneous presence of contact molecules and separated ions in the closely related rubidium hypersilanide $[Rb([18]crown\text{-}6)Si(SiMe_3)_3]_2[Rb([18]crown\text{-}6)_2][Si(SiMe_3)_3]$,[25] indicating energetic similarities between solvation and ligation processes. Since the size of rubidium lies between potassium and cesium, 1.5 equivalents of [18]crown-6 were added to the rubidium hypergermanide reaction mixture to explore if an analogous germanide would form. Interestingly, only the contact molecule **4** was isolated. Repetition of the reaction under addition of either one or two equivalents of [18]crown-6 afforded the same result, indicating reproducibility.

In the presence of multidentate nitrogen donors essentially analogous trends are observed, and the ability of a donor to sterically saturate a metal center is the dominating factor. Here, use of the bidentate TMEDA allowed the preparation and characterization of the five-coordinate bis-TMEDA adducts $[K(tmeda)_2E(SiMe_3)_3]$ (E = Ge, **6**; E = Si, **7**). In contrast, use of the tridentate PMDTA affords compounds too reactive to be characterized extensively. The presence of only one PMDTA donor would likely support contact molecules with the unsustainable coordination number of four, whereas in the presence of two PMDTA donors destabilization due to significant ligand–donor repulsion or insufficient stabilization of a separated cation is likely. The coordination of a third PMDTA is not supported by the small potassium ion.

The overall coordination environment in compounds **6** and **7** is distinctly different from the other compounds reported here, since these compounds display the lowest coordination numbers of any of the donor-containing silanides and germanides. Accordingly, metal–germanium/silicon bond lengths are significantly shorter (see Table 2), and the metal environment can be described as distorted trigonal bipyramidal, with the sterically demanding germanide and silanide ligands located in the equatorial plane. The bidentate TMEDA donors each span to occupy one equatorial and one axial position with N-M-N angles of 65.57(6) and 64.04(7)° for **6** and 65.61(7) and 64.05(8)° for **7**, inducing significant deviation from ideal geometry, as evidenced by the narrow *trans* angles of 143.28(7)° for **6** and 142.87(8)° for **7**. In accord with this distortion, the angles in the equatorial plane are as wide as 136.30(6)° (**6**) and 134.41(8)° (**7**), and as narrow as 99.52(5)° (**6**) and 99.87(6)° (**7**).

The comparison of metal–silicon and metal–germanium distances in the potassium silanides and germanides indicates shorter bond lengths for germanide [K([18]crown-6)Ge($SiMe_3$)$_3$] (3.399(8) Å) relative to the silanide, with a K–Si distance of 3.447(8) Å.[25] This initially curious result, considering the larger germanium radius (ionic radius Ge^{4+} (CN = 4) = 0.53 Å) relative to silicon (Si^{4+} (CN = 4) = 0.40 Å,),[35] may be explained by the increased polarity in the metal–germanium bond[35] due to the larger differences in electronegativity (Allred Rochow electronegativity Si = 1.74, Ge = 2.02).[36] Similar trends are observed for other members of the series, such as the potassium germanide **6** (K–Ge 3.373(5) Å) and the corresponding silanide **7** (K–Si 3.390(1) Å). This observation is complemented by trends within series of lithium silanides and germanides, in which consistently shorter Li–Ge bonds with respect to Li–Si were observed.[26] Similarly, heavy-alkaline-earth-metal silanides and germanides display the same trend, slightly shorter M–Ge bonds than M–Si bonds.[11–13]

On first sight, the argument of bond polarity as the deciding factor for metal–ligand bond length seems to contradict itself when comparing rubidium silanides and germanides, since slightly longer rubidium–germanium bonds than rubidium–silicon contacts are observed. However, the presence of agostic interactions in the germanide derivative (3.0 and 3.1 Å) provides a straightforward rationale for this deviation. A small selection of rubidium compounds with agostic interactions in the range of about 3 Å involving sterically demanding ligands afford metal centers with low coordination numbers.[37]

Ge–Si distances in the Ge($SiMe_3$)$_3$ anions range from 2.381(1) to 2.388(9) for **1**, 2.346(2) to 2.375(2) Å for **4**, and 2.391(1) to 2.402(1) Å for **5**, essentially identical to the Si–Si distance in the corresponding silanides (see Table 2). Again, the closeness of these values indicates the ionic bond contribution in the Ge–Si bond, resulting in almost identical element–element bonds despite the smaller silicon radius.

All hypergermanides display significant pyramidal geometry at the central germanium atom, with the Si-Ge-Si angles of about 100°, and angle sums at the central germanium of 302.64° (**1**), 302.88° (**2**), 306.46° (av) (**4**), 294.75° (av) (**5**), and 302.44° (**6**). These values are very similar to those of the silanides (see Table 2),[25] underscoring their close chemical relationship. In analogy to the silanides no discernable trend differentiating between contact molecules or separated ions could be identified. The pyramidicity of the silanides has been discussed in detail, and the angle compression was interpreted as increased metal–ligand charge transfer. With very similar values for contact molecules and separated ions, the charge transfer between cation and anion must be substantial in all cases, supporting the view that the metal–ligand bond is highly polar. The separation of cation and anion, the extreme form of charge transfer, results in only minor further angle compression. This interpretation is also supported by the formation of separated ions upon dissolution in aromatic solvents, facilitated by the favorable coordination of the alkali metals to aromatic solvents.[38] The significant pyramidal nature of the anions has been observed in a range of heavy Group 14 derivatives, in which significant bond polarization resulted in increased s-character at the lone pair, and consequently higher p-character in the element–element bond. This trend becomes more significant upon descending Group 14, with a C-Pb-C angle of 94.3° (av) in [Li(pmdta)$PbPh_3$],[39] while the lighter analogues such as [Li(pmdta)$SnPh_3$] and [Li(thf)$_3$$SiPh_3$] display C-M-C angles of 96.1 and 101.3° (av).[40,17] The comparison of silanides and germanides shows an analogous trend, and in all cases slightly increased pyramidicity is observed for the germanides relative to the silanides (see Table 2). For example, [K([18]crown-6)E($SiMe_3$)$_3$] (E = Si, Ge) shows Si-E-Si angles of 102.0° (av) for the silanide, and 100.9° (av) for the germanide, the separated cesium derivatives [Cs([18]crown-6)$_2$][E($SiMe_3$)$_3$] display Si-E-Si angles of 99.5° (av) for the silanides and 98.2° (av) for the germanides. Analogous values are also observed for the TMEDA adducts **6** and **7**. While the trend confirms previous results, the similarity of values underscores the close chemical relationship between the silanides and germanides.

As expected, metal–oxygen distances in the germanides and silanides are quite similar, and generally follow the ionic radii trend. Potassium–oxygen distances in **1** are between 2.768(2) and 2.910(2) Å, with very similar values for the silicon analogue (2.787(2) to 2.926(2) Å). Analogously, rubidium–oxygen distances in **4** range from 2.842(4) to 3.025(4) Å, while Rb–O distances in the contact silanide species range from 2.826(19) to 2.984(2) Å. This trend is continued in the cesium derivatives with Cs–O distances from 3.153(3) to 3.574(3) Å in **5** and from 3.141(2) to 3.560(2) Å in the corresponding silanide [Cs([18]crown-6)$_2$][Si($SiMe_3$)$_3$]. The potassium–nitrogen distances in compounds **6** and **7** are essentially identical, ranging from 2.807(2) to 2.933(2) Å for **6** and 2.808(3) to 2.935(3) Å for **7**. These values agree well with previously reported potassium–nitrogen (TMEDA) distances in compounds [K(tmeda){N(*i*Pr)$_2$}]$_2$] (*i*Pr = isopropyl) (2.878 and 2.894 Å)[41] and [K(tmeda)$_2$(η^5-fluorenide)] (2.824 and 3.057 Å).[42]

Conclusion

In summary, a series of the first heavy-alkali-metal hypergermanides has been prepared by a simple one-pot procedure. By utilizing differently sized crown ethers or the nitrogen donors TMEDA or PMDTA, contact molecules and separated ions were obtained in the solid state, whose formation can be rationalized by principles of steric saturation of the metal centers. In aromatic solution, the compounds dissociate into separated ions, as evidenced by extensive NMR studies. The comparison of this series of germanides with the closely related silanides indicates that the germanides are significantly more reactive and sensitive towards hydrolysis.

Experimental Section

General procedures: All reactions were performed by using standard procedures under a purified nitrogen atmosphere by utilizing either modified Schlenk techniques and/or a Braun Labmaster dry-box. THF, *n*-hexane, and pentane were distilled prior to use from CaH_2 or a Na/K alloy, followed by two freeze-pump-thaw cycles. Commercially available KO*t*Bu was of 99 % purity. $Si(SiMe_3)_4$,[15] $Ge(SiMe_3)_4$,[30] RbO*t*Bu,[43] and CsO*t*Bu[43] were prepared according to literature procedures. [18]crown-6, [15]crown-5, [12]crown-4, TMEDA, and PMDTA were obtained commercially. [18]crown-6 was purified by solvation in freshly distilled diethylether and stirred with finely cut sodium metal for one day. After filtration from excess metal, the crown was recrystallized at −20 °C from hexanes. [15]crown-5 and [12]crown-4 were stored over molecular sieves (4 Å) in the dry-box. TMEDA and PMDTA were stirred over CaH_2 and distilled prior to use. All ^{1}H NMR and ^{13}C NMR were recorded on a Bruker DPX-300 spectrometer. ^{29}Si NMR data were recorded on a Bruker DPX-500 instrument using a wide-bore probe. All NMR spectra were recorded in C_6D_6. Infrared spectra were recorded as Nujol mulls between KBr plates on a Perkin–Elmer PE 1600 FT-IR spectrometer. Reliable elemental analyses could not be obtained for all compounds, even when glove-box handling was attempted, due to the high reactivity of the compounds reported here. This is a well-known problem in alkali-metal chemistry.[44]

General procedure for the synthesis of 1–5: In a typical experiment alkali-metal *tert*-butoxide, $Ge(SiMe_3)_4$ and crown ether ([18]crown-6, [15]crown-5 or [12]crown-4) were combined and dissolved in THF (15 mL). The resulting yellow solutions were stirred for 15 minutes, followed by filtration over a Celite padded filter frit. Pentane was added drop-wise to the clear solution. Crystals either deposited immediately or formed at −20 °C within in a day.

[K([18]crown-6)Ge(SiMe$_3$)$_3$] (1): KO*t*Bu (0.12 g, 1.1 mmol), $Ge(SiMe_3)_4$ (0.36 g, 1 mmol) and [18]crown-6 (0.26 g, 1 mmol). Colorless plates were obtained (0.52 g, 0.87 mmol, 87.4 % yield); m.p. 216–217 °C; ^{1}H NMR (300 MHz, C_6D_6, 25 °C, TMS): $\delta=0.77$ (s, 27H; $SiMe_3$), 3.14 ppm (s, 24H; CH_2); ^{13}C NMR (75 MHz, C_6D_6, 25 °C, TMS): $\delta=8.14$ ($SiMe_3$), 69.98 ppm (CH_2); ^{29}Si NMR (99 MHz, C_6D_6, 25 °C, TMS) $\delta=-3.25$ ppm ($(SiMe_3)_3$); IR (Nujol): $\tilde{\nu}=2925$, 2743, 2712, 2688, 1469, 1455, 1434, 1377, 1351, 1284, 1249, 1239, 1223, 1112, 1058, 963, 824, 729, 666, 612 cm^{-1}.

[K([15]crown-5)$_2$][Ge(SiMe$_3$)$_3$] (2): KO*t*Bu (0.12 g, 1.1 mmol), $Ge(SiMe_3)_4$ (0.36 g, 1 mmol) and [15]crown-5 (0.44 g, 2 mmol). Colorless plates were obtained (0.59 g, 0.77 mmol, 76.5 % yield); m.p. 212–214 °C; ^{1}H NMR (300 MHz, C_6D_6, 25 °C, TMS): $\delta=0.83$ (s, 27H; $SiMe_3$), 3.42 ppm (s, 40H; CH_2); ^{13}C NMR (75 MHz, C_6D_6, 25 °C, TMS): $\delta=8.50$ ($SiMe_3$), 70.52 ppm (CH_2); ^{29}Si NMR (99 MHz, C_6D_6, 25 °C, TMS): $\delta=-2.96$ ppm ($(SiMe_3)_3$); IR (Nujol): $\tilde{\nu}=2888$, 1459, 1377, 1361, 1303, 1247, 1224, 1122, 1093, 1028, 941, 856, 817, 724, 661, 609 cm^{-1}.

[K([12]crown-4)$_2$][Ge(SiMe$_3$)$_3$] (3): KO*t*Bu (0.12 g, 1.1 mmol), $Ge(SiMe_3)_4$ (0.36 g, 1 mmol) and [12]crown-4 (0.35 g, 2 mmol). Colorless plates were obtained (0.49 g, 0.72 mmol, 71.7 % yield); m.p. 220–222 °C; ^{1}H NMR (300 MHz, C_6D_6, 25 °C, TMS): $\delta=0.82$ (s, 27H; $SiMe_3$), 3.40 ppm (s, 32H; CH_2); ^{13}C NMR (75 MHz, C_6D_6, 25 °C, TMS): $\delta=8.33$ ($SiMe_3$), 69.72 ppm (CH_2); ^{29}Si NMR (99 MHz, C_6D_6, 25 °C, TMS): $\delta=-3.72$ ppm ($(SiMe_3)_3$); IR (Nujol): $\tilde{\nu}=2924$, 2854, 1459, 1377, 1364, 1304, 1290, 1250, 1225, 1135, 1096, 1022, 913, 825, 722, 665, 611 cm^{-1}.

[Rb([18]crown-6)Ge(SiMe$_3$)$_3$] (4): RbO*t*Bu (0.17 g, 1 mmol), $Ge(SiMe_3)_4$ (0.36 g, 1 mmol) and [18]crown-6 (0.26 g, 1 mmol). Colorless blocks were obtained (0.44 g, 0.69 mmol, 68.6 % yield); m.p. 158 °C (decomp); ^{1}H NMR (300 MHz, C_6D_6, 25 °C, TMS): $\delta=0.78$ (s, 27H; $SiMe_3$), 3.14 ppm (s, 24H; CH_2); ^{13}C NMR (75 MHz, C_6D_6, 25 °C, TMS): $\delta=8.28$ ($SiMe_3$), 70.20 ppm (CH_2); ^{29}Si NMR (99 MHz, C_6D_6, 25 °C, TMS): $\delta=-3.38$ ppm ($SiMe_3$); IR (Nujol): $\tilde{\nu}=2924$, 2854, 1459, 1377, 1351, 1283, 1249, 1224, 1109, 960, 823, 724, 663, 610 cm^{-1}.

[Cs([18]crown-6)$_2$][Ge(SiMe$_3$)$_3$] (5): CsO*t*Bu (0.22 g, 1 mmol), $Ge(SiMe_3)_4$ (0.36 g, 1 mmol) and [18]crown-6 (0.53 g, 2 mmol). Colorless blocks suitable for X-ray analysis were obtained in two days from the yellow solution in the −20 °C freezer (0.81 g, 0.85 mmol, 84.6 % yield). M.p. 151–153 °C; ^{1}H NMR (300 MHz, C_6D_6, 25 °C, TMS): $\delta=0.82$ (s, 27H; $SiMe_3$), 3.28 ppm (s, 48H; CH_2); ^{13}C NMR (75 MHz, C_6D_6, 25 °C, TMS): $\delta=8.50$ ($SiMe_3$), 70.52 ppm (CH_2); ^{29}Si NMR (99 MHz, C_6D_6, 25 °C, TMS): $\delta=-3.18$ ppm ($SiMe_3$); IR (Nujol): $\tilde{\nu}=2921$, 1457, 1377, 1353, 1300, 1252, 1236, 1222, 1113, 1044, 951, 861, 822, 724, 661, 609 cm^{-1}.

General procedure for the synthesis of 6–9: In a typical experiment potassium *tert*-butoxide was dissolved in THF (20 mL). In another Schlenk tube, an equimolar amount of $E(SiMe_3)_4$ (E = Ge, Si) was dissolved in THF (15 mL), followed by addition of the solution of the *tert*-butoxide through a cannula. The resulting yellow solutions were stirred for 15 minutes, upon which an excess of TMEDA and PMDTA was added. The mixture was stirred for another 30 minutes and filtered over a Celite padded filter frit. The reaction was pumped to dryness under vacuum. The residue was extracted with hexane (15 mL). Single crystals suitable for X-ray measurements were obtained at −20 °C within a week.

[K(tmeda)$_2$Ge(SiMe$_3$)$_3$] (6): KO*t*Bu (0.22 g, 2 mmol), $Ge(SiMe_3)_4$ (0.73 g, 2 mmol), and TMEDA (0.40 mL, 2.65 mmol). Colorless plates (0.71 g, 1.26 mmol, 63.1 % yield); m.p. 186 °C (decomp); ^{1}H NMR (300 MHz, C_6D_6, 25 °C, TMS): $\delta=0.68$ (s, 27H; $SiMe_3$), 1.96 (s, 24H; Me-TMEDA), 2.10 ppm (s, 8H; CH_2-TMEDA); ^{13}C NMR (75 MHz, C_6D_6, 25 °C, TMS): $\delta=7.92$ ($SiMe_3$), 45.71 (Me-TMEDA), 57.43 ppm (CH_2-TMEDA); IR (Nujol): $\tilde{\nu}=2921$, 1462, 1377, 1296, 1243, 1226, 1173, 1152, 1135, 1096, 1079, 1024, 945, 836, 778, 724, 666, 612 cm^{-1}.

[K(tmeda)$_2$Si(SiMe$_3$)] (7): KO*t*Bu (0.22 g, 2 mmol), $Si(SiMe_3)_4$ (0.64 g, 2 mmol), and TMEDA (0.40 mL, 2.65 mmol). Yellow blocks were obtained (0.65 g, 1.25 mmol, 62.7 % yield); m.p. 203–205 °C; ^{1}H NMR (300 MHz, C_6D_6, 25 °C, TMS): $\delta=0.65$ (s, 27H; $SiMe_3$), 1.87 (s, 24H; Me-TMEDA), 1.92 ppm (s, 8H; CH_2-TMEDA); ^{13}C NMR (75 MHz, C_6D_6, 25 °C, TMS): $\delta=7.51$ ($SiMe_3$), 45.64 (Me-TMEDA), 57.29 ppm (CH_2-TMEDA); IR (Nujol): $\tilde{\nu}=2922$, 2780, 2709, 1462, 1377, 1362, 1295, 1226, 1174, 1153, 1135, 1096, 1079, 1038, 1024, 946, 826, 780, 741, 728, 666, 616 cm^{-1}.

[K(pmdta)$_2$Ge(SiMe$_3$)$_3$] (8): KO*t*Bu (0.22 g, 2 mmol), $Ge(SiMe_3)_4$ (0.73 g, 2 mmol), and PMDTA (0.52 mL, 2.5 mmol). Yellow blocks were obtained (1.06 g, 1.57 mmol, 78.3 % yield); ^{1}H NMR (300 MHz, C_6D_6, 25 °C, TMS): $\delta=0.72$ (s, 27H; $SiMe_3$), 2.02 (s, 6H; Me-PMDTA), 2.04 (s, 24H; Me-PMDTA), 2.19, 2.17, 2.22, 2.23 ppm (q, 16H; CH_2-PMDTA).

[K(pmdta)$_2$Si(SiMe$_3$)$_3$] (9): KO*t*Bu (0.22 g, 2 mmol), $Si(SiMe_3)_4$ (0.64 g, 2 mmol), and PMDTA (0.52 mL, 2.5 mmol). Yellow plates were obtained (1.02 g, 1.61 mmol, 80.7 % yield); m.p. 129–132 °C; ^{1}H NMR (300 MHz, C_6D_6, 25 °C, TMS): $\delta=0.69$ (s, 27H; $SiMe_3$), 1.75 (s, 6H; Me-PMDTA), 1.90 (s, 24H; Me-PMDTA), 1.93, 1.94 ppm (d, 16H; CH_2-PMDTA); ^{13}C NMR (75 MHz, C_6D_6, 25 °C, TMS): $\delta=7.61$ ($SiMe_3$), 40.63 (Me-PMDTA), 45.03 (Me-PMDTA), 55.52 ppm (CH_2-PMDTA); IR (Nujol): $\tilde{\nu}=2925$, 1459, 1377, 1309, 1290, 1226, 1163, 1115, 1096, 1022, 931, 827, 668, 616 cm^{-1}.

X-ray crystallographic studies: X-ray quality crystals for all compounds were grown as described above. The crystals were removed from the Schlenk tube under a stream of N_2 and immediately covered with a layer of viscous hydrocarbon oil (Infineum). A suitable crystal was selected under the microscope, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream of the diffractometer.[45] Due to the extreme moisture and oxygen sensitivity of the compounds, the microscope was placed inside the diffractometer enclosure, and the crystals removed under inert gas from the mother liquor in immediate proximity to the microscope. All data sets were collected using a Siemens SMART system, complete with three-circle goniometer and CCD detector operating at low temperature. The data sets were collected using a custom-built low-temperature device from Professor H. Hope (UC Davis). Compound **1** was collected at 93 K, **2** at 91 K, **4** at 96 K, **5** at 95 K, **6** at 91 K, and **7** at

87 K. Monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) 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.[46] The crystal structures of all compounds were solved by either direct or Patterson methods, as included in the SHELX program package.[47] Missing atoms were located in subsequent difference Fourier maps and included in the refinement. The structures were refined by full-matrix least-squares refinement on F^2.[47] Compound **4** was identified as a non-merohedral twin from the initial diffraction pattern by using the Cell-Now program, which indicated that the compound was composed of two crystal domains with the second domain rotated by 180° in respect to the first.[48] The structure was solved by creating and importing a twin law into the SAINT-Plus software package,[49] with which the data were corrected for Lorentz and polarization effects and absorption by using the program TWINABS.[50] Hydrogen atoms for all compounds were placed geometrically and refined using a riding model, including free rotation about C−C bonds for methyl groups. Thermal parameters for hydrogen atoms were refined with U_{iso} constrained at 1.2 (for non-methyl groups), and 1.5 (for methyl groups) times U_{eq} of the carrier C atom. The crystallographic programs used for structure refinement and solutions were installed on a PC clone and a Silicon Graphics Indigo^2 R10000 Solid Impact. Scattering factors were those provided with the SHELX program system.[47] All non-hydrogen atoms, with the exception of some disordered or restrained positions were refined anisotropically. Disorder in compounds **2** and **7** was handled by including split positions for the affected groups, and included the refinement of the respective occupancies. A set of restraints was applied to aid in modeling the disorder. Further details about the refinements and how disorder was handled are outlined in the supplementary crystallographic data.

CCDC-245379–245384 (compounds **1**, **2** and **4**–**7**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound **3** was highly reactive, making mounting the crystals on the diffractometer very challenging. In addition, severe disorder problems did not allow for a satisfactory refinement of the structure, but pertinent structural details are clearly visible. As such, detailed crystallographic data for compound **3** are not presented.

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