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$\{Ge_9[Si(SiMe_3)_2(SiPh_3)]_3\}^-$: Ligand Modification in Metalloid Germanium Cluster Chemistry

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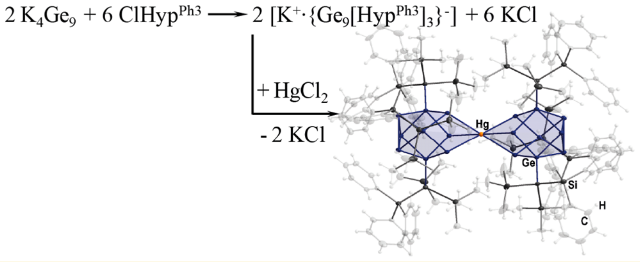
Supporting Information

ABSTRACT: The influence of the stabilizing ligand on the physical and chemical properties of a metalloid cluster compound is important for nanotechnology as metalloid clusters are ideal model compounds for metal nanoparticles. Here we present the synthesis of a differently substituted metalloid $\{Ge_9R_3\}^-$ cluster: $\{Ge_9[Si(SiMe_3)_2(SiPh_3)]_3\}^-$ **1**, which is obtained in good yield by the reaction of K_4Ge_9 with $ClSi(SiMe_3)_2(SiPh_3)$. **1** is characterized via NMR and mass spectrometry, but crystallization is hindered. However, the reaction with $HgCl_2$ gives the neutral compound $HgGe_{18}[Si(SiMe_3)_2(SiPh_3)]_6$ **2**, which can be crystallized and structurally characterized. The presented results are a first step for the investigation of the ligand's influence on the properties of a metalloid germanium cluster compound.



INTRODUCTION

Metalloid clusters of the general formula M_nR_m ($n > m$; M = metal like Al, Au, etc.; R = ligand like $S-C_6H_4-COOH$, $N(SiMe_3)_2$, etc.) are ideal model species for the nanoscaled area between molecules and the solid state. Hence, reactions with these compounds open our eyes for chemical and physical properties of nanoscaled materials.[1] In this respect it was recently shown by Power et al. that the metalloid tin cluster $Sn_8[Ar]_4$ [Ar = 2,6-Mes_2-C_6H_3, Mes = 2,4,6-Me_3-C_6H_2] can be used for the activation of small molecules like ethylene or hydrogen.[2] These reactions were possible as the tin atoms of the cluster core are available for subsequent reactions. Another metalloid group 14 cluster with an open ligand shell is $\{Ge_9[Hyp]_3\}^-$ **3** [Hyp = $Si(SiMe_3)_3$],[3] where the nine germanium atoms are incompletely shielded by the three bulky Hyp ligands. As a consequence of this, for example, transition metal bound "dimeric" cluster compounds could be synthesized, exhibiting 19 atom cluster cores $\{MGe_{18}[Hyp]_6\}^X$ ($X = -1$: M = Cu, Ag, Au; $X = 0$: M = Zn, Cd, Hg).[4] The synthesis of **3** was first performed via a quite complex disproportionation reaction, starting from metastable Ge(I) halide[5] solutions. Another possibility to obtain germanium clusters starts from the Zintl anion $\{Ge_9\}^{4-}$, where clusters with up to 18 or 45 germanium atoms[6,7] can be obtained.[8] Comparable tin and lead clusters are similarly available from the corresponding Zintl anions $\{Sn_9\}^{4-}$ and $\{Pb_9\}^{4-}$, respectively.[9] Very recently Sevov et al. showed that $\{Ge_9[Hyp]_3\}^-$ **3** can be obtained by the reaction of the Zintl anion $\{Ge_9\}^{4-}$ with Cl[Hyp] in quite high yield.[10] Additionally he showed that neutral compounds like $\{Ge_9[Hyp]_3Et\}$ can be obtained from **3** by the reaction with EtBr.[11]

Consequently, a fruitful synthetic route was established to further investigate the chemistry of the metalloid germanium cluster **3**. We wondered if this synthetic route is only possible for Cl[Hyp] as the ligand source or if also other ligand systems can be used to obtain differently substituted $\{Ge_9R_3\}^-$ clusters. If yes, this will open the door to establish an experimental basis for the investigation of the ligand's influence on the chemical and physical properties of a metalloid cluster compound. Consequently, such investigations are important to establish an atomistic basis for the question, how the ligand has an influence on physical and/or chemical properties of nanoparticles.[12] A first example in this regard is the change of the structure and bonding within the Ge_8 cluster core in two metalloid Ge_8L_6 cluster compounds [L = $N(SiMe_3)_2$[13] or 2,6-$(OtBu)_2$-C_6H_3[14]].[15] However, in the case of the metalloid Ge_8L_6 clusters, only a small amount is available. Thus, further investigations were not possible until now. As the synthesis of **3** starting from $\{Ge_9\}^{4-}$ gives access to large amounts of the metalloid cluster, such investigations might be possible if differently substituted clusters are available. In the following we present first results of a metalloid $Ge_9R_3^-$ cluster exhibiting a modified ligand.

RESULT AND DISCUSSION

To investigate if another ligand can be introduced in the synthesis of the metalloid cluster $\{Ge_9[Hyp]_3\}^-$ **3** by the reaction of $\{Ge_9\}^{4-}$ with Cl[Hyp] the right starting material must be identified first. There are many other examples of disubstituted Ge_9-Zintl ions ($\{Ge_9L_2\}^{2-}$),[6] which are thus not useful for a comparison. Additionally, first mass spectrometric and NMR spectroscopic indications of other trisubstituted $Ge_9R_3^-$ clusters have been described.[10,16] However, these

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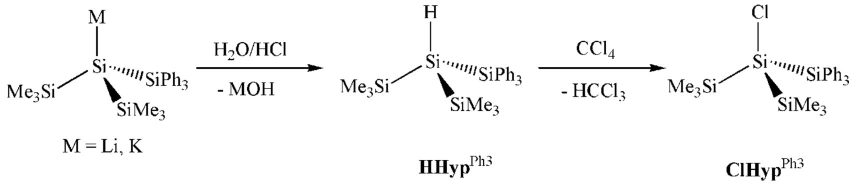
Scheme 1. Reaction Sequence for the Synthesis of Cl[Hyp]^{Ph3}



compounds could not be isolated so far. Therefore, we thought that another bulky silyl ligand would be most appropriate. Referring to our recent investigation of the ligand system $Si(SiMe_3)_2(SiPh_3)$ (Hyp^{Ph3}) for tin chemistry[17] we asked ourselves if this ligand can also be used for the stabilization of a metalloid Ge_9 cluster. However, as only the anionic compound M[Hyp^{Ph3}] (M = Li, K) is available, the halogenated compound Cl[Hyp^{Ph3}] must be synthesized first. Thereby the synthesis should be performed straightforwardly in a similar way as already described for the compound Cl[Hyp][18] (Scheme 1).

Thus, quenching M[Hyp^{Ph3}] with a diluted aqueous acid gives the silane H[Hyp^{Ph3}], which is transferred into the halide Cl[Hyp^{Ph3}] via the room-temperature reaction with CCl_4. The silane H[Hyp^{Ph3}] as well as the halide Cl[Hyp^{Ph3}] are obtained as crystalline solids, so both compounds could be structurally characterized, showing the expected molecular structure. Hence, the central silicon atom is surrounded tetrahedrally by four bonding partners (Figure 1). The Si−Cl bond of 214.0 pm is thereby in the range of a normal single bond[19] and comparable to the one found in the symmetric compound Cl[Hyp] (215.5 pm).[20] Hence, from a structural point of view both compounds are similar. However, the main difference between both compounds is their physical properties; for example, Cl[Hyp] has a melting point of 50 °C, whereby Cl[Hyp^{Ph3}] melts at 83 °C. Thus, the intermolecular forces are quite different, which may lead to a different reactivity.

Nevertheless, the differences between Cl[Hyp] and Cl[Hyp^{Ph3}] are small and thus we checked whether Cl[Hyp^{Ph3}] can be used for the synthesis of metalloid germanium clusters via Sevov's synthetic route.[10] We reacted a K_4Ge_9 suspension in acetonitrile with 3 equiv of Cl[Hyp^{Ph3}]. Thereby the color of the solution changed to red indicating that a reaction took place. The reaction mixture was stirred for 2 d, and after filtration we obtained a red solution. After workup procedures a dark red oily residue is obtained, which we tried to crystallize from different organic solvents (tetrahydrofuran (THF), toluene, CH_3CN). Regretfully, until now these attempts failed, and only oily phases and glasslike solid particles were obtained. Also the addition of a complexing reagent for potassium cations (2,2,2-crypt or 18-crown-6) did not give the desired results. However, proton-, ^{13}C-, and ^{29}Si NMR measurements indicate that after workup a quite pure compound (90% purity according to NMR) seems to be present as only one signal in the methyl region and one signal set in the phenyl region in the predicted ratio of 6:5 is present.[21] Mass spectrometric investigations (Figure 2) show that the compound is the targeted metalloid cluster $\{Ge_9[Hyp^{Ph3}]_3\}^-$ **1**, which is identified by its signal at $m/z = 1964.8$. Thereby, the calculated and measured isotopic pattern fit perfectly as shown by the inset in Figure 2.

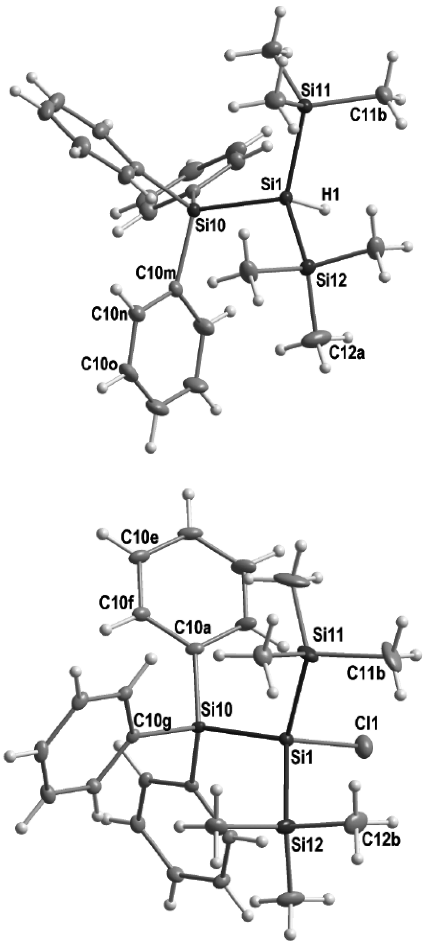


Figure 1. Molecular structure of H[Hyp^{Ph3}] (top) and Cl[Hyp^{Ph3}] (bottom). Displacement ellipsoids are drawn with 25% probability. Selected bond lengths [pm] and angles [deg]: **H[Hyp^{Ph3}]**: Si1−Si10, 235.49(12); Si1−Si11, 234.55(12); Si1−Si12, 235.25(13); Si1−H1, 148.2; Si11−C11b, 187.2(3); Si12−C12a, 185.8(4); Si10−C10m, 188.4(3); C10m−C10n, 139.6(4); C10n−C10o, 139.6(5); Si10−Si1−Si11, 114.35(5); Si11−Si1−Si12, 110.58(5); Si10−Si1−H1, 103.7. **Cl[Hyp^{Ph3}]**: Si1−Si10, 236.05(11); Si1−Si11, 236.53(11); Si1−Si12, 234.62(12); Si1−Cl1, 214.03(12); Si11−C11b, 188.0(4); Si12−C12b, 187.4(4); Si10−C10g, 187.6(3); Si10−C10a, 187.7(3); C10a−C10f, 139.9(4); C10f−C10e, 139.2(4); Si10−Si1−Si11, 113.74(4); Si11−Si1−Si12, 108.03(4); Si10−Si1−Cl1, 107.97(5).

To get further insight into the structure of $\{Ge_9[Hyp^{Ph3}]_3\}^-$ **1** we performed quantum chemical calculations.[22] Thereby two different isomers are taken into account.[23] In one isomer all three $SiPh_3$ groups point to one side ($\mathbf{1}_{3,0}$), and in the other isomer ($\mathbf{1}_{2,1}$) two $SiPh_3$ groups point to one side and one to the other side of the cluster (Figure 3). In both cases the Ge_9 core shows an arrangement that is between a D_{3d} and a C_{4v} symmetric structure as it is frequently observed in nine-atom deltahedral group 14 clusters.[24] The calculated bond distances for $\mathbf{1}_{3,0}$ and $\mathbf{1}_{2,1}$ are similar to the one found in $\{Ge_9[Hyp]_3\}^-$ **3**. Hence, the ligand-bound germanium atoms exhibit shorter average Ge−Ge bonds ($\mathbf{1}_{3,0}$: 260 pm; $\mathbf{1}_{2,1}$: 261 pm; **3**: 253 pm),

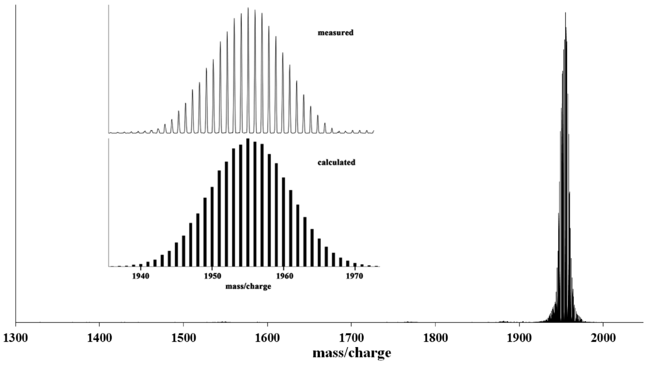


Figure 2. FT/ICR-mass spectrum of $\{Ge_9[Hyp^{Ph3}]_3\}^-$ **1** in THF after electrospray ionization. (inset) Comparison of the measured (upper) and simulated (lower) isotopic pattern of **1**.

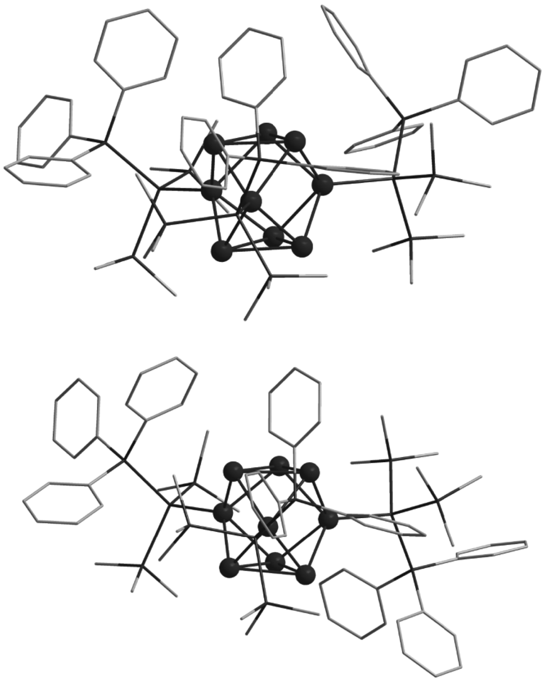


Figure 3. Calculated molecular structure of $\{Ge_9[Hyp^{Ph3}]_3\}^-$ **1** without hydrogen atoms. (Top) Isomer $\mathbf{1}_{3,0}$ where all $SiPh_3$ groups point in one direction. (Bottom) Isomer $\mathbf{1}_{2,1}$ where only two $SiPh_3$ groups point in one direction.

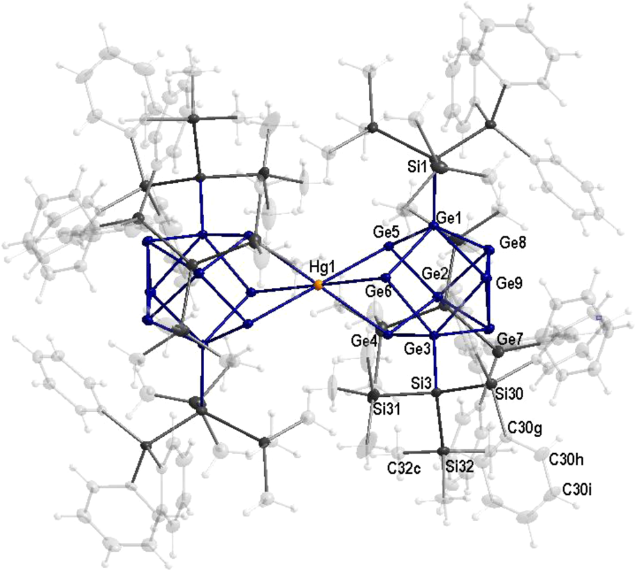


Figure 4. Molecular structure of $HgGe_{18}[Hyp^{Ph3}]_6$ **2**. Displacement ellipsoids are drawn with 25% probability, and the Me as well as the Ph groups are drawn with 70% transparency. Selected bond lengths [pm] and angles [deg]: Hg1−Ge4, 286.61(6); Hg1−Ge5, 284.11(6); Hg1−Ge6, 282.94(6); Ge4−Ge5, 295.4(2); Ge5−Ge6, 296.5(3); Ge6−Ge4, 295.0(4); Ge6−Ge1, 249.07(8); Ge6−Ge3, 249.71(8); Ge4−Ge3, 250.44(9); Ge5−Ge2, 249.79(8); Ge1−Ge8, 257.00(8); Ge1−Ge9, 257.44(9); Ge2−Ge7, 256.86(9); Ge2−Ge8, 257.87(9); Ge7−Ge8, 264.11(8); Ge7−Ge9, 265.19(9); Ge8−Ge9, 265.04(9); Ge1−Si1, 238.8(2); Ge3−Si3, 238.5(2); Si3−Si30, 236.3(2); Si3−Si31, 236.1(2); Si3−Si32, 236.1(2); Si32−C32c, 187.2(7); Si30−C30g, 188.5(6); C30g−C30h, 139.4(10); C30h−C30i, 139.3(10); Hg1−Ge5−Ge1, 106.26(2); Ge6−Ge1−Ge5, 72.94(2); Ge5−Ge1−Ge8, 81.68(3); Ge7−Ge8−Ge9, 60.10(2); Ge3−Si3−Si30, 108.99(7); Ge3−Si3−Si31, 107.49(8).

while the naked germanium atoms show longer average Ge−Ge bonds ($\mathbf{1}_{3,0}$: 272 pm; $\mathbf{1}_{2,1}$: 272 pm; **3**: 268 pm).[25]

Surprisingly, $\mathbf{1}_{3,0}$ is energetically more favorable than $\mathbf{1}_{2,1}$ by 9 kJ/mol although all three bulky $SiPh_3$ groups point in one direction. However, the energy difference is small, so an equilibrium between both isomers is expected in solution.

As we were not able to obtain **1** in a single crystalline form we wondered if a subsequent product might be crystallized to get also structural information about the metalloid cluster **1**. Consequently we reacted an NMR pure THF solution of $\{Ge_9[Hyp^{Ph3}]_3\}^-$ **1** with $HgCl_2$, leading to an instant color change. After workup of the reaction mixture we were able to obtain dark red crystals of a reaction product. X-ray crystal structure analysis reveals that indeed the linked compound $HgGe_{18}[Hyp^{Ph3}]_6$ **2** has formed.

2 crystallizes together with 19 THF molecules per cluster molecule. Hence, the crystals must be transferred as cold and as fast as possible, so that THF remains within the crystal. Heating or drying leads to an instantaneous amorphization of the crystals. The molecular structure of **2** is shown in Figure 4 and is best described as a central mercury atom to which two Ge_9 units are bound, whereby quite long Ge−Hg distances of ~284 pm [282.9−286.6 pm] are realized. The distances are thereby similar to the ones found in $HgGe_{18}[Hyp]_6$ **4** (average Ge−Hg-distance: 286 pm [282.7−289.7 pm]). In **2** all three $[Hyp^{Ph3}]$ ligands are oriented in one direction, so that the $SiPh_3$ groups all point away from the central Hg atom. This leads to another significant difference of **2** and **4**, which is obvious by an inspection of the space-filling model along the threefold axis of the clusters (Figure 5). In case of **2**, the cluster core is completely shielded by the ligand shell, while in the case of **4** the three-membered ring of naked germanium atoms is still available for further reactions. Another difference comparing **2** and **4** are their solubility properties; while **4** is easily dissolved in pentane, **2** is only sparsely soluble in THF. However, a fresh THF solution of **2** obtained after filtration and concentration of the reaction mixture appears to be quite concentrated, but dark red crystals of **2** are redissolved again in THF only in very limited amount. This peculiarity of **2** creates certain difficulties for NMR investigation. Therefore, only proton NMR spectra of **2** are recorded, where the signal intensity of **2** is comparable to the residue peaks of solvent (0.5% H in THF-d_8). Because of the low concentration of **2** in THF-d_8 we were not able to obtain reliable ^{13}C and ^{29}Si spectra. However, comparison of proton NMR spectra of $K\{Ge_9[Hyp^{Ph3}]_3\}$ **1** and $HgGe_{18}[Hyp^{Ph3}]_6$ **2** showed some unexpected results. With

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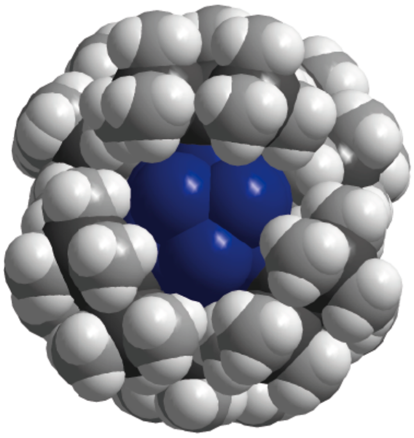

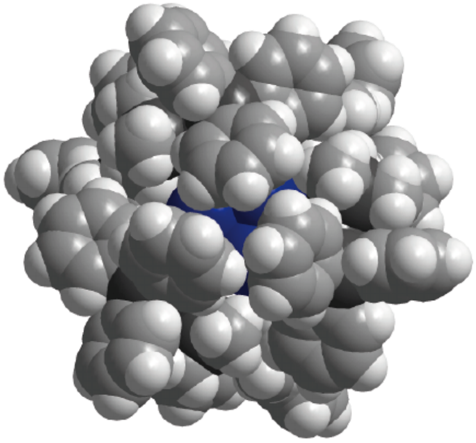

Figure 5. Space-filling models of $HgGe_{18}[Hyp]_6$ **4** (top) and $HgGe_{18}[Hyp^{Ph3}]_6$ **2** (bottom). View along the threefold axis of the clusters.

changing from the free $\{Ge_9[Hyp^{Ph3}]_3\}^-$ anion **1** in solution to bound $\{Ge_9[Hyp^{Ph3}]_3\}$ units in **2**, quite notable shifts of all proton signals are observed. That means, going from **1** to **2** the proton signals for the $SiMe_3$ groups shift from 0.07 to 0.20 ppm. Additionally the signals of the protons of the phenyl rings shift around 0.1 ppm (see Figure S7 in Supporting Information for details).

■ SUMMARY AND OUTLOOK

The reaction of $\{Ge_9\}^{4-}$ with $Cl[Hyp^{Ph3}]$ gives the metalloid cluster $\{Ge_9[Hyp^{Ph3}]_3\}^-$ **1** in good yield of ~60%, showing that $\{Ge_9R_3\}^-$ clusters with different silyl substituents can be obtained via this route. **1** cannot be obtained in the crystalline state. However, **1** is identified by NMR spectroscopy and mass spectrometry. Further reaction of **1** with $HgCl_2$ gives the neutral compound $HgGe_{18}[Hyp^{Ph3}]_6$ **2**, which can be obtained in crystalline form from a THF solution. As **1** is obtained in good yield, further research concerning the influence of the stabilizing ligand on the properties of a metalloid cluster is possible. This can establish a basis for understanding the ligand influence of metal nanoparticles on an atomic scale. Thereby gas phase measurements would be an important first step as such investigations are well-established for $\{Ge_9[Hyp]_3\}^-$ **3**[26] and seem possible for $\{Ge_9[Hyp^{Ph3}]_3\}^-$ **1**, as **1** is easily transferred intact into the gas phase (Figure 2).

■ EXPERIMENTAL SECTION

General Considerations. All reactions were performed under nitrogen atmosphere using Schlenk techniques. THF was dried over sodium, CCl_4 over molecular sieves (3 Å), and acetonitrile over P_2O_5. All organic solvents were freshly distilled under nitrogen atmosphere. Bruker DRX-250 and AV-400 spectrometers were used to obtain ^1H, ^{13}C, and ^{29}Si spectra. ^1H, ^{13}C, and ^{29}Si chemical shifts δ are given in parts per million and were referenced to Me_4Si. NMR spectra were recorded at room temperature. Elemental analyses were performed on a varioMICROcube in the CHNS mode.

K_4Ge_9 was prepared from a mixture of elements (Ge, ABCR, 99.999%), whereby potassium is used in 20% excess with respect to stoichiometric amounts. The mixture was heated for 3 d at 650 °C in an evacuated flame-sealed quartz ampule. According to XRPD the product consists of a mixture of K_4Ge_9 and elemental Ge (elemental Ge is absolutely inert during further reactions). Though the content of K_4Ge_9 in the mixture cannot be calculated precisely due to the low quality of obtained XRPD pattern, it was estimated as 80% on the base of its consumption during our experiments.

Caution! *At elevated temperature potassium is highly aggressive to quartz. Experiments should be performed with precautions against explosion and burning in case of depressurization of the ampule. Also opening of the ampule requires more accuracy, as due to reaction with potassium quartz glass becomes breakable.*

Synthesis of $HSi(SiMe_3)_2(SiPh_3)$ ($H[Hyp^{Ph3}]$). To a solution of freshly prepared $K[Hyp^{Ph3}]$ (4.7 g, 10 mmol)[17] in THF a cold solution of 200 mL of diluted aqueous hydrochloric acid was added, whereby the yellow color instantly vanishes and a white precipitate is observed. Afterward, the aqueous reaction mixture was extracted three times by 100 mL of diethyl ether, leading to a pale yellow organic solution. All organic solutions were combined and dried over Na_2SO_4. All volatile compounds were removed in vacuum, and the waxy residue was recrystallized from hot ethanol, leading to colorless plates of $H[Hyp^{Ph3}]$. Yield: 3.56 g (8.2 mmol, 82%)

^{1}H NMR (250 MHz, C_6D_6): δ 0.13 (s, 18H, Si*Me*$_3$), 3.18 (s, 1H, *H*Si(SiMe$_3$)$_2$(SiPh$_3$)), 7.13−7.16 (m, 9H, Si*Ph*$_3$), 7.69−7.72 (m, 6H, Si*Ph*$_3$); **^{13}C{^{1}H} NMR** (62.5 MHz, C_6D_6): δ 2.0 (s, Si*Me*$_3$), 128.2 (s, Si*Ph*$_3$), 129.4 (s, Si*Ph*$_3$), 136.4 (s, Si*Ph*$_3$), 136.8 (s, Si*Ph*$_3$); **^{29}Si NMR** (50 MHz, C_6D_6): δ −11.3 (decet, *Si*Me$_3$), −12.7 (m, *Si*Ph$_3$), −116.2 (d, H*Si*(SiMe$_3$)$_2$(SiPh$_3$)). Anal. measured (calculated): C 66.8% (66.3%), H 7.6% (7.8%). mp 56 °C.

Synthesis of $ClSi(SiMe_3)_2(SiPh_3)$ ($Cl[Hyp^{Ph3}]$). $H[Hyp^{Ph3}]$ (3.56 g, 8.2 mmol) was dissolved in 200 mL of CCl_4 and stirred at room temperature for one week. Afterward, all volatile compounds were removed in vacuum, and the remaining colorless residue was recrystallized from ethanol leading to colorless plates of $Cl[Hyp^{Ph3}]$. Yield: 3.5 g (7.5 mmol, 92%)

^{1}H NMR (250 MHz, C_6D_6): δ 0.14 (s, 18H, Si*Me*$_3$), 7.14−7.16 (m, 9H, Si*Ph*$_3$), 7.74−7.77 (m, 6H, Si*Ph*$_3$); **^{13}C{^{1}H} NMR** (62.5 MHz, C_6D_6): δ 0.3 (s, Si*Me*$_3$), 129.8 (s, Si*Ph*$_3$), 135.1 (s, Si*Ph*$_3$), 136.7 (s, Si*Ph*$_3$); **^{29}Si NMR** (50 MHz, C_6D_6): δ −10.4 (decet, *Si*Me$_3$), −13.5 (m, *Si*Ph$_3$). Anal. measured (calculated): C 62.4% (61.4%), H 7.1% (7.2%). mp 83 °C.

Synthesis of $K\{Ge_9[Hyp^{Ph3}]_3\}$. 400 mg of the above-mentioned K_4Ge_9 (assumed 0.40 mmol of pure K_4Ge_9) and $Cl[Hyp^{Ph3}]$ (576 mg, 1.23 mmol) were weighed and transferred to a Schlenk vessel in an argon-filled glovebox. CH_3CN (5 mL) was added as a reaction medium, and the mixture was stirred for 2 d. However, NMR measurements of the samples taken from the reaction solution showed that the reaction proceeds completely after 1 d. Afterward, the reaction mixture was dried in vacuum and washed by pentane to remove byproducts and the nonreacted $Cl[Hyp^{Ph3}]$. After this **1** was extracted by a large amount of THF and filtered from the solid precipitate, which consists of KCl and elemental germanium, which was the contamination of K_4Ge_9. The brightly orange THF solution of **1** was analyzed by proton NMR, which reveals ~90% purity of reagent. Mass spectrometry of an additionally purified solution showed the presence of only $\{Ge_9[Hyp^{Ph3}]_3\}^-$ anions **1**. Total amount of $K\{Ge_9[Hyp^{Ph3}]_3\}$

Table 1. Crystal Data and Details of Structural Determinations

	$H[Si(SiMe_3)_2SiPh_3]$ $H[Hyp^{Ph3}]$	$Cl[Si(SiMe_3)_2SiPh_3]$ $Cl[Hyp^{Ph3}]$	$HgGe_{18}[Hyp^{Ph3}]_6$ **2**·19THF
formula wt	434.87	469.31	5480.37
T [K]	150	100	150
crystal system	orthorhombic	monoclinic	triclinic
space group	$Pna2_1$	$C2/c$	$P\bar{1}$
a [Å]	16.7748(19)	21.9446(10)	19.1052(19)
b [Å]	9.3516(11)	16.8185(10)	20.270(2)
c [Å]	16.7511(18)	17.7551(11)	20.835(2)
α [deg]	90	90	112.591(2)
β [deg]	90	124.799(3)	108.382(2)
γ [deg]	90	90	103.660(2)
V [Å^3]	2627.8(5)	5381.0(5)	6454.6(11)
Z	4	8	1
μ [mm^{-1}]	0.234	0.329	2.817
ρ [g cm^{-3}]	1.099	1.159	1.410
Θ range [deg]	1.72–28.29	1.66–26.21	1.68–26.39
index range	$-21 \leq h \leq 22$	$-27 \leq h \leq 27$	$-20 \leq h \leq 23$
	$-12 \leq k \leq 12$	$-20 \leq k \leq 20$	$-25 \leq k \leq 23$
	$-22 \leq l \leq 22$	$-22 \leq l \leq 22$	$-25 \leq l \leq 25$
reflections measured	27 989	36 757	54 773
independent reflections	6318	5399	25 981
R(int)	0.0870	0.0313	0.0399
GOF	1.051	1.090	1.030
parameters/restraints	258/1	262/0	1108/180
min/max e-density [e Å^{-3}]	−0.275/0.258	−0.915/1.265	−1.044/1.396
final R indices $I > 2\sigma$	R_1 = 0.0504	R_1 = 0.0567	R_1 = 0.0493
	wR_2 = 0.0912	wR_2 = 0.1364	wR_2 = 0.1170
final R indices (all data)	R_1 = 0.0905	R_1 = 0.0663	R_1 = 0.0965
	wR_2 = 0.1061	wR_2 = 0.1422	wR_2 = 0.1394
CCDC no.	1063363	1063361	1063362

isolated from a THF extract is 480 mg, which is 59% calculated with respect to the used reagent $Cl[Hyp^{Ph3}]$.

^{1}H NMR (400 MHz, THF-d_8): δ 0.07 (s, 6H, SiMe_3), 7.19–7.22 (m, 3H, SiPh_3), 7.66–7.68 (m, 2H, SiPh_3); **^{13}C{^{1}H} NMR** (62.5 MHz, THF-d_8): δ 4.1 (s, SiMe_3), 128.3 (s, SiPh_3), 129.1 (s, SiPh_3), 138.2 (s, SiPh_3), 138.6 (s, SiPh_3); **^{29}Si NMR** (50 MHz, THF-d_8): δ −9.3 (decet, *Si*Me_3), −12.2 (m, *Si*Ph_3), −105.9 (s, *Si*$(SiMe_3)_2(SiPh_3)$).

Synthesis of $HgGe_{18}[Hyp^{Ph3}]_6$·19THF. $K\{Ge_9[Hyp^{Ph3}]_3\}$ (160 mg, 0.08 mmol) was dissolved in 5 mL of THF and mixed with a solution of $HgCl_2$ (10 mg, 0.04 mmol) in 3 mL of THF. The mixture was stirred for 1 d, though visually the reaction proceeds much faster as the solution become dark brown to black immediately after mixing of reagents. After filtration, the reaction mixture was concentrated to half the volume and stored at 6 °C, whereby dark red crystals of $HgGe_{18}[Hyp^{Ph3}]_6$·19THF were isolated. Proton NMR investigations of the reaction mixture after 1 d reveal the yield of **2** to be ∼60% with respect to $K\{Ge_9[Hyp^{Ph3}]_3\}$ used.[21] However, this value is somewhat ambiguous as crystals of **2** cannot be completely redissolved in THF after drying, and therefore the amount of **2** in THF-d_8 solution suitable for NMR measurement appears to be understated.

^{1}H NMR (400 MHz, THF-d_8): δ 0.20 (s, 6H, SiMe_3), 7.26–7.37 (m, 3H, SiPh_3), 7.51–7.53 (m, 2H, SiPh_3).

Mass Spectrometry. The anionic cluster compounds were brought into the gas phase by electrospraying[27] a THF solution of $K\{Ge_9[Hyp^{Ph3}]_3\}$. The end-plate of the electrospray source was typically held at a potential of +3.2 kV relative to the electrospray needle, which was grounded. A potential of +3.3 kV was applied to the entrance of the metal-coated quartz capillary.

X-ray Structural Characterization. Table 1 contains the crystal data and details of the X-ray structural determination for $H[Si(SiMe_3)_2(SiPh_3)]$ ($H[Hyp^{Ph3}]$), $Cl[Si(SiMe_3)_2(SiPh_3)]$ ($Cl[Hyp^{Ph3}]$), and $HgGe_{18}[Hyp^{Ph3}]_6$ (**2**·19THF). The data were collected on a Bruker APEXII diffractometer employing monochromated Mo Kα (λ = 0.710 73 Å) radiation from a sealed tube and equipped with an Oxford Cryosystems cryostat. A numeric absorption correction was applied using the optically determined shape of the crystals. The structure was solved by direct methods and refined by full-matrix least-squares techniques (programs used: SHELXS and SHELXL[28]). The non-hydrogen atoms that are not on a splitting position were refined anisotropically, and the hydrogen atoms were calculated using a riding model. In case of **2**·19THF, one $SiMe_3$ group as well as four THF molecules were refined using a split model. Additional crystallographic information is available in the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

Pictures of crystals of metalloid clusters, NMR spectra, XRPD diffractogram, and crystallographic information in CIF files. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01130. CCDC-1063361 ($Cl[Hyp^{Ph3}]$), CCDC-1063362 (**2**·19THF), and CCDC-1063363 ($H[Hyp^{Ph3}]$) contain the supplementary crystallographic data for this paper. These data can be obtained online free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+44) 1223-336-033; or e-mail deposit@ccdc.cam.ac.uk.

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Notes

The authors declare no competing financial interest.

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