Synthesis, Structure and Bonding in Triorganogermyl-alanes and Triphenylgermyl-aluminates

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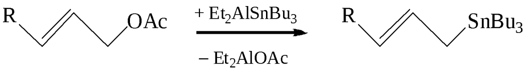
Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

Triphenylgermyl-lithium in diethyl ether/THF did not react with Al_2Me_6 to form $[(Ph_3Ge)AlMe_3]$-$Li(THF)_n$. Addition of TMEDA to this solution yielded crystalline $Ph_3GeLi(THF)TMEDA$. The reaction of Ph_3GeLi in diethyl ether/hexane solution with H_3Al-NMe_3 in diethyl ether/THF generated $[Ph_3GeAlH_3]Li(THF)_4$ while the reaction with Me_2AlCl led to $Ph_3GeAlMe_2(OEt_2)$ and the trigermyl-aluminate $[(Ph_3Ge)_3AlMe]Li$. The analogous aluminate $[(Ph_3Ge)_3AlH]Li(THF)_3$ was obtained by reacting $LiGePh_3$ with $AlH_2Cl(OEt_2)$ in the presence of THF. It was expected that the bulky bis(tetramethylpiperidino)chloroalane would react with Ph_3GeLi to give the germyl-alane $tmp_2AlGePh_3$ which was observed when only diethyl ether was used as a solvent, but in an Et_2O/toluene mixture only Ph_8Ge_3 could be isolated. Increasing the steric requirement of the germyllithium compound by using the bulky $(t\mathrm{Bu}_3\mathrm{Si})\mathrm{Me}_2\mathrm{Ge}$ group instead of the Ph_3Ge group led to a straightforward reaction generating the first structurally characterized germyl-alane $(t\mathrm{Bu}_3\mathrm{Si})\mathrm{Me}_2\mathrm{Ge}$-$Al(tmp)_2$ with a planar tri-coordinated Al center. The X-ray structure determinations showed that the germyl-aluminates have shorter Ge–Al bonds than the germyl-alane inspite of the lower coordination number.

Key words: Triphenylgermyl-aluminates, Triorganogermyl-alanes, X-Ray Strucrures

Introduction

Today, organyl compounds of group III and IV elements are important reagents in organic synthesis [1]. The growing interest and pretension regarding regio- and stereoselectivity in organic chemistry requires new and improved metalorganic systems. In this respect multinuclear homometallic compounds with *e. g.* B–B or Sn–Sn bonds find growing interest because they provide enhanced stereoselectivity in metallation reactions [2]. The use of heterometallic compounds instead of homometallic species often leads to a much higher stereoselectivity and also a more pronounced regioselectivity [3]. Compounds with Al–Ge or Al–Sn bonds find applications in organic synthesis. For instance, the *in situ*-prepared compound Et_2Al-$Sn(n\text{-}Bu)_3$, generated from lithium tri(n-butyl)stannide and $AlEt_2Cl$, was used for the stannylation of 1-acetoxyallyls to the corresponding 1-allylstannanes in the presence of a palladium catalyst [4], as shown in Eq. 1. Due to the nucleophilic character of these allylstannanes they are important intermediates for reactions with electrophiles, and they are used *e. g.* for the synthesis of (+/–)-11,*O*(3)-dihydropseudopterolide [5].



(1)

Apart from the practical application of Al-E(IV) systems (E = Ge, Sn) these compounds have so far neither be studied in detail nor isolated and structurally characterized. Although the structures of several silyl aluminum compounds have been determined, *e. g.* for $Al(SiMe_3)_3$ [6], tmp_2Al-$Si(SiMe_3)_3$ [7], or $[Li(THF)_4][Cl_3AlSi(SiMe_3)_3]$ [8], almost no structural information exists for germyl- or stannyl-aluminum compounds.

The first aluminum-germanium compounds were reported in 1978: $[Ph_3GeAlH_3]Li$ and $[Me_3GeAlH_3]Li$ [9] as well as $Al(GeMe_3)_3$ [10]. To prove the presence of the Al–Ge bond in these species at that time, hydrolysis of the compounds to R_3GeH and $Al(OH)_3$ was used. The first structurally characterized compound was $Ge(AlCl_2OEt_2)_4$ obtained from the re-

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action of $Ge(Cp^*)_2$ and AlCl in diethyl ether [11]. The second structurally characterized compound was $(Et_2O)_2Li[MeAl(GePh_3)_3]$ [12]. In order to learn more about the nature of the Ge–Al bond, more species with this kind of bonding involving not only tetra-coordinated Al but also tri-coordinated Al atoms are essential. We report here on some examples.

Studies on these compounds are necessary to understand the observation that B-E(IV) compounds show a *shortening* of the B–E bond length for tetra-coordinated species as compared to tri-coordinated ones. This is unusual because normally the E–X bond lengths increase as the coordination number increases [12, 13]. To contribute to the understanding of this effect it is necessary to determine the structures of more compounds with Al–Ge and Al–Sn bonds, and to see how these results fit with theoretical studies.

Results

New triphenylgermyl-lithium complexes

Compounds with a germanium-aluminum bond are best prepared by reacting triorgano-germyl lithium compounds with a tri-coordinated aluminum species (Eq. 2). In case of triorganyl-alanes germyl-alanates are expected to be formed, but in case of organylaluminiumhalides the products could be germyl-alanes (Eq. 3).

$$R_3GeLi + AlR'_3 \rightarrow [R_3Ge\text{-}AlR'_3]Li \qquad (2)$$

$$R_3GeLi + R'_2AlX \rightarrow R_3Ge\text{-}AlR'_2 + LiX \qquad (3)$$

$$\underset{\mathbf{1}}{Ph_3GeH + LiBu \rightarrow Ph_3GeLi + BuH} \qquad (4)$$

$$Me_2(tBu_3Si)GeCl + 2\ Li \rightarrow \underset{\mathbf{2}}{Me_2(tBu_3Si)GeLi} + LiCl \qquad (5)$$

$$Ph_3GeLi(THF) + Me_2NCH_2CH_2NMe_2 \rightarrow \underset{\mathbf{3}}{Ph_3GeLi(THF)(TMEDA)} \qquad (6)$$

For the present study we used triphenylgermyl lithium, **1**, as the starting material because it can be readily prepared quantitatively by reacting triphenylgermane with butyllithium according to Eq. 4 in diethyl ether or in a diethyl ether/THF mixture. This reaction can be readily controlled by ^{7}Li NMR (**1**: δ = 1.4 ppm).

In order to prepare monomeric germylalanes we used the tri(*tert*-butyl)silyl-dimethyl germanium substituent. This bulky group should prevent the association of the corresponding germylalanes, as has been demonstrated for many "supersilyl" derivatives [14]. In addition, the asymmetry of this group should be helpful in growing crystals of monomeric germyl alanes. The respective germyl lithium compound **2** can be easily prepared by reacting $(tBu_3Si)\ Me_2GeCl$ with Li powder at −78 °C in THF according to Eq. 5. This compound shows a ^{27}Si NMR signal at 1.4 ppm which is deshielded relative to the starting material. Its ^{7}Li NMR signal at 3.3 ppm is typical for germyl lithium compounds, while the ^{1}H signals are shifted by 0.3 ppm to higher field compared to $(tBu_3Si)Me_2GeCl$. Both, the chemical shifts for ^{7}Li as well as for ^{1}H are in accord with a decrease of the positive charge at the Ge atom compared to the chloride.

One may expect that the easiest way to new germyl-aluminum compounds is the addition of an AlX_3 unit to an R_3Ge anion resulting in a germylaluminate $[X_3Al\text{-}GeR_3]^-$. Therefore, we thought that $LiGePh_3$ might add to $(AlMe_3)_2$ to form the aluminate $[Ph_3Ge\text{-}AlMe_3]^-$ in analogy to the formation of $[Ph_3Ge\text{-}AlH_3]^-$ (see below). However, no such adduct was observed in diethyl ether/THF/hexane solution because the ^{27}Al NMR spectrum remains identical with that of $(AlMe_3)_2$ (δ^{27}Al = 157 ppm [15]). Also, the addition of tetramethylethylenediamine (TMEDA) does not improve the nucleophilicity of the germyl anion by making the Li center more electropositive in order to achieve the formation of an Al–Ge bond. The crystals that separated from the solution of the 2:1 mixture of Ph_3GeLi and $(AlMe_3)_2$ turned out to be $Ph_3GeLi(THF)(TMEDA)$, **3** (Eq. 6). Because dimeric $AlMe_3$ forms no adducts with Et_2O the germyllithium compound $LiGePh_3$ obviously cannot break the Al_2Me_2 bridge bonds of the dimeric trimethylalane.

Compound **3** crystallizes in the monoclinic space group *Pn* with *Z* = 2. Its molecular structure is depicted in Fig. 1. The Li–Ge bond length is 2.732(6) Å which is longer than in the germyl lithium compounds $(Me_3Si)_3GeLi(THF)_3$ [2.666(6) Å] and $(Me_3Si)_3GeLi(PMDTA)$ [2.653(9) Å] [16 – 18] but slightly shorter than the Li–Ge bond length in $Ph_3GeLi(OEt_2)_3$ [2.758(8) Å] [13]. An explanation for the longer Ge–Li bond lengths may be due to changes of the electron density at the Ge atom (*v. i.*). As expected, the Li–N bonds of **3** are longer with

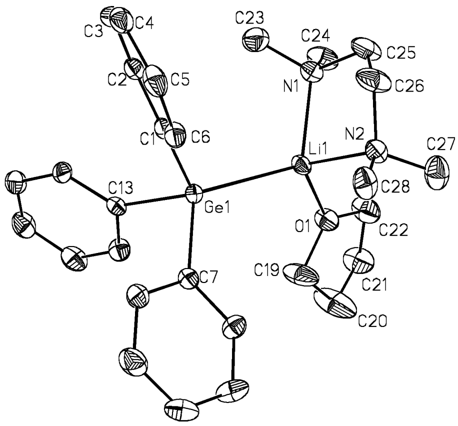

Fig. 1. Molecular structure of $Ph_3GeLi(THF)(TMEDA)$, **3**. Selected bond lengths (Å) and angles (deg): Li1–Ge1 2.732(6), Ge1–C1 2.010(3), Ge1–C7 2.017(3), Ge1–C13 2.017(4), Li1–O1 2.950(6), Li1–N1 2.129(7), Li1–N2 2.114(8); C1–Ge1–C7 100.2(1), C1–Ge1–C13 101.6(2), C7–Ge1–C13 96.8(2), C1–Ge1–Li1 115.6(2), C7–Ge1–Li1 118.8(2), C13–Ge1–L1 109.1(2), O1–Li1–Ge1 118.3(3), O1–Li1–N1 114.8(3), O1–Li1–N2 109.7(3), N1–Li1–N2 87.0(3), N1–Li1–Ge1 115.1(3), N2–Li1–Ge1 106.9(2).

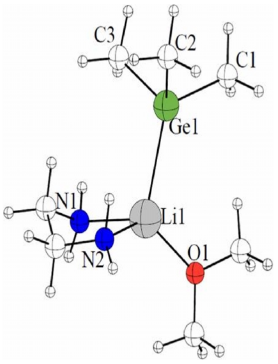

Fig. 2. The calculated structure of the model compound $Me_3GeLi(OMe_2)(H_2NCH_2CH_2NH_2)$ as obtained on the B3LYP basis set level of theory [21]. Calculated bond lengths (Å) and angles (deg): Li1–Ge1 2.690, Li1–N1 2.123, Li1–N2 2.125, Li1–O1 1.977, Ge1–C1 2.061, Ge1–C2 2.050, Ge1–C3 2.052; Li1–Ge1–C1 120.4, Li1–Ge1–C2 123.6, Li1–Ge1–C3 112.1, C1–Ge1–C2 98.8, C1–Ge1–C3 98.7, C2–Ge1–C3 98.7, N1–Li1–N2 85.0, N1–Li1–O1 118.5, O1–Li1–Ge1 117.9, N2–Li1–Ge1 103.3.

2.129(7) and 2.114(8) Å [19] than the Li–O bond length of 1.950(6) Å. They lie in the range as observed for $[Me_2AlCl_2]Li(TMEDA)_2$ [19] or $[(t\mathrm{BuO})_2(\mathrm{R}(+)\text{-binaphthoxo})\mathrm{Al}]\text{-}\mathrm{Li(PMDETA)}$ [20].

Due to the TMEDA ligand the bond angles at the Li atom result in a distorted tetrahedral geometry with values ranging from 87.0(3) to 118.3(3)° for N–Li–N and O–Li1–Ge1. The C–Ge1–C bond angles are close to those found in $Ph_3GeLi(OEt_2)_3$ [13]. Calculations for the compound $Me_3GeLi(OMe_2)(H_2NCH_2CH_2NH_2)$ led to C–Ge–C bond angles of 98.7° which are close to the average C–Ge–C bond angle determined for **3** [21]. The C–Ge–Li bond angles are rather large with an average value of 118.1(2)°, and this fits well with the calculated values of 112.1 to 123.7°. Fig. 2 shows the calculated molecular structure of $Me_3GeLi(OMe_2)(EDA)$. These latter refers of course to an undisturbed molecule, and the data should deviate from the structure of **3** as a result of the larger groups associated with the latter compound.

It should be mentioned that the Li–Ge bond lengths of the (trimethylsilyl)germyl lithium compounds are shorter than those of the triphenyl germyl derivatives. This may be due to the steric requirement of the phenyl group (shorter C–Ge bonds) as compared to the longer Ge–Si bond. Electronegativity may also play a role: the Ge–C bond should be less polar than a Si–C bond, and this change in polarity may influence the Ge–Li interaction. On the other hand, the Si–Li bond lengths of $(Me_3Si)_3SiLi(THF)_3$ and of $Ph_3SiLi(THF)_3$ are identical with 2.67(1) Å [17], *i. e.* the Si subsitutents do not influence the Si–Li bond.

Syntheses of germyl-alanes and -alanates

The reaction of $LiGePh_3$ with $AlCl_3$ in a Et_2O/THF/hexane solution led to an unexpected result. We assumed that the product would either be $[Ph_3GeAlCl_3]Li(THF)_n$ or $Ph_3Ge\text{-}AlCl_2$ as its Et_2O or THF adduct. However, the ^{27}Al NMR spectrum of the 1:1 reaction showed three strong signals at 60, 104,

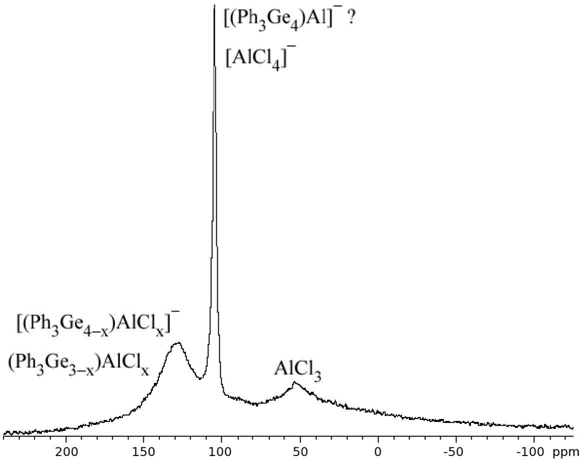

Fig. 3. The ^{27}Al NMR spectrum of the reaction solution of $LiGePh_3$ with $AlCl_3$ in THF.

and 130 ppm (Fig. 3). The signal at 104 ppm is very sharp, typical for the $AlCl_4^-$ anion. A signal at 60 ppm corresponds to $AlCl_3(THF)_2$, and the broad signal at 130 ppm may result from anions of the type $(Ph_3Ge)_{4-n}AlCl_n)^-$ (see Fig. 3). It was not possible to separate the compounds formed, but it is not unusual that several products form by reacting electrophilic Al species with nucleophiles. On the other hand, the 1:1 reaction of $LiGePh_3$ with Me_2AlCl in hexane/Et_2O in a 1:1 ratio produced $Ph_3GeAlMe_2(OEt_2)$, **4**, in 20 % yield, besides $[(Ph_3Ge)_3AlMe]Li(OEt_2)$, **5**. Compound **4** was characterized by X-ray structure analysis, while compound **5** was only detected in the ^{27}Al NMR spectrum of the reaction mixture.

$$\begin{aligned}&\mathrm{Ph_3GeLi + Me_2AlCl(OEt_2)}\\&\rightarrow \mathrm{Ph_3Ge\text{-}AlMe_2(OEt_2) + LiCl}\end{aligned}\tag{7}$$

4

$$\begin{aligned}&\mathrm{3\ Ph_3GeLi + 2\ Me_2AlCl(OEt_2)}\\&\rightarrow \mathrm{[(Ph_3Ge)_3AlMe]Li(OEt_2)_n}\end{aligned}\tag{8}$$

5

$$\begin{aligned}&\mathrm{3\ Ph_3GeLi + AlHCl_2(THF) + 2\ THF}\\&\rightarrow \mathrm{[(Ph_3Ge)_3AlH]Li(THF)_3) + 2\ LiCl}\end{aligned}\tag{9}$$

6

$$\begin{aligned}&\mathrm{Ph_3GeLi + AlH_3(NMe_3) + 4\ THF}\\&\rightarrow \mathrm{[Ph_3GeAlH_3]Li(THF)_4 + NMe_3}\end{aligned}\tag{10}$$

7

The reaction solution showed ^{27}Al NMR signals a 189 and 160 ppm for the aluminate **5** and the alane diethyl ether adduct **4**, (Eqs. 7 and 8). The formation of the aluminate species could not be supressed. However, if dichloroalane is used instead of Me_2AlCl for the reaction with Ph_3GeLi in diethyl ether/THF the aluminate $[(Ph_3Ge)_3AlH]Li(THF)_3$, **6**, resulted in good yield according to Eq. 9. Moreover, the triphenylgermylalanate **7** is generated from Ph_3GeLi and the alane-trimethylamine adduct (Eq. 10). Compound **6** shows a broad ^{27}Al NMR signal at $\delta = 71$ ppm with a half height of 5350 Hz, and the presence of Al–H bonds is recorded in its Raman spectrum at $\nu = 1586\ \mathrm{cm}^{-1}$, and at $\nu = 1600\ \mathrm{cm}^{-1}$ in its IR spectrum. On the other hand, we could neither find a significant peak in the ^{27}Al NMR spectrum of compound **7**, nor in its ^{1}H NMR spectrum, but there were two Al–H stretching bands in the IR spectrum at 1621 and 1595 cm^{-1}.

In order to prepare germyl alanes it is obviously necessary to start from an aluminum compound carrying bulky substituents to prevent the formation of germyl aluminates. For this reason we reacted tmp_2haloalanes [22] (tmp = 2,2,6,6-tetramethylpiperidinium) with R_3GeLi compounds. Thus the reaction between Ph_3GeLi and tmp_2AlBr provided compound **8** in 51 % yield (Eq. 11) as very thin platelets which were not suitable for a crystal structure determination. However, when tmp_2AlCl was used instead of the bromide in toluene/diethyl ether as solvent, the crystals that separated after several weeks proved to be octaphenyl-trigermane, which was characterized by its crystal structure [23, 24]. This compound might have formed by a decomposition of **8**, as shown in Eq. 12. On the other hand, suitable crystals of **9** were obtained from $LiGeMe_2Si(tBu)_3$ and tmp_2AlCl, as shown in Eq. 13.

$$\mathrm{Ph_3GeLi + tmp_2AlBr} \rightarrow \mathrm{tmp_2Al\text{-}GePh_3 + LiBr}\tag{11}$$

8

$$\begin{aligned}&\mathrm{3\ tmp_2Al\text{-}GePh_3} \rightarrow \mathrm{Ph_3Ge\text{-}GePh_2\text{-}GePh_3}\\&\mathrm{+\ tmp_2Al\text{-}Al(tmp)_2 + tmp_2AlPh}\end{aligned}\tag{12}$$

$$\begin{aligned}&\mathrm{LiGe(Me_2)Si(\mathit{t}Bu)_3 + tmp_2AlCl}\\&\rightarrow \mathrm{tmp_2Al\text{-}GeMe_2Si(\mathit{t}Bu)_3 + LiCl}\end{aligned}\tag{13}$$

9

The ^{27}Al NMR spectrum of **8** did not show a well defined ^{27}Al NMR signal. However, for **9** a broad signal at 60 ppm could be recorded. The ^{27}Al chemical shift of this signal seems to fit best with a penta-coordinated Al atom. However, a tri-coordinated Al atom has been observed in its crystal structure which seems do be contradictory. Monomeric tmp_2Al(halides) featuring tri-coordinated Al atoms show ^{27}Al resonances around 130 ppm [tmp_2AlCl: $\delta^{27}\mathrm{Al} = 134$, tmp_2AlBr: $\delta^{27}\mathrm{Al} = 130.9$, tmp_2AlI: $\delta^{27}\mathrm{Al} = 130$]. However, the introduction of a Ph_2As group leads to an upfield shift for $tmp_2AlAsPh_2$ to $\delta^{27}\mathrm{Al} = 74$ ppm [25]. Obviously the germyl group leads to a much better shielding of the ^{27}Al nucleus, in analogy to the arsenic compound.

The replacement of the Br atom of $(tBu_3Si)Me_2GeBr$ ($\delta^{27}\mathrm{Si} = 16.6$ ppm) by Li results in a low-field shift of the ^{29}Si NMR signal which is now found at 23.3 ppm. The methyl protons of the tmp group in the germylalane **9** are observed at 1.41 ppm, showing a slight deshielding compared with tmp_2AlCl (0.08 ppm). Only one ^{1}H NMR signal is observed for

Table 1. Structural data for $Ph_3AlGeMe_2(OEt_2)$, **4**, and calculated values (B3LYP [21]) for the model compound $Me_3Ge\text{-}AlMe_2(OMe_2)$.

Bond lengths (Å)	$Ph_3GeAlMe_2$ OEt_2	$Me_3GeAlMe_2$ OMe_2	Bond angles (deg)	$Ph_3GeAlMe_2$ OEt_2	$Me_3GeAlMe_2$ OMe
Ge–Al	2.515(2)	2.542	C–Al–C	114.1(2)	116.9
Al–C	1.952(2)	1.992	C–Al–Ge	113.4(2)	116.2
Al–O	1.903(2)	2.071	C–Ge–C	103.5(1)	104.6
Ge–C	1.968(3)	2.014			

the Ge-bonded methyl groups in **9**. This signal, however, splits into two signals on cooling below −15 °C. Compound **9** was also characterized by its mass spectrum which shows two typical fragments for tmp_2Al^+ as well as $(tBu_3Si)Me_2Ge^+$.

X-Ray structures of the germyl-alanes and germyl-aluminates

The germyl-alane ether adduct **4** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$. As shown in Fig. 4, its Al atom is tetra-coordinated. The Ge–Al bond length, determined as 2.515(1) Å, is about the same as for $[(Ph_3Ge)_3AlMe]^-$ (2.520(2) Å) [13]. It is longer than expected from the covalent radii of Al and Ge (1.25 and 1.22 Å) but is much shorter than the sum of the atomic radii (Al = 1.432, Ge = 1.225 Å) and agrees better with the Al–Si bond lengths in tri-coordinated $tmp_2Al\text{-}Si(SiMe_3)_3$ [25]. The Ge–C bonds are slightly shorter than in compound **3**. In contrast the Al–O bond length is comparatively long with 1.903(2) Å (usually only 1.725 to 1.852 Å [26]). The bond angles at the Al atom vary from 103.7(2) to 112.9(1)°. This is not at all unusual for tetra-coordinated Al atoms carrying three different substituents. The calculated bond length for the model compound $Me_3Ge\text{-}AlMe_2(OEt_2)$ (Fig. 5) are slightly longer than the experimental value for **4** while the bond angles deviate only by about 3°, as shown in Table 1.

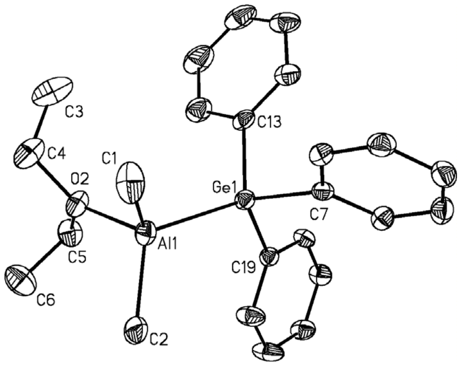

Fig. 4. Molecular structure of $Ph_3Ge\text{-}AlMe_2(OEt_2)$, **4**. Selected bond lengths (Å) and angles (deg.): Ge1–Al1 2.515(1), Al1–C1 1.949(4), Al1–C2 1.954(4), Al1–O2 1.903(2), Ge1–C7 1.964(3), Ge1–C13 1.970(3), Ge1–C19 1.971(3); C1–Al1–O2 103.7(2), C2–Al1–O2 106.2(2), C1–Al1–C2 114.1(2), C1–Al1–Ge1 113.8(2), C2–Al1–Ge1 112.9(1), O2–Al1–Ge1 104.7(9), C7–Ge1–C13 102.13(1), C13–Ge1–C19 103.2(1), C7–Ge1–C19 105.2(1), C7–Ge1–Al1 109.6(1), C13–Ge1–Al1 118.7(1), C19–Ge1–Al1 116.2(1).

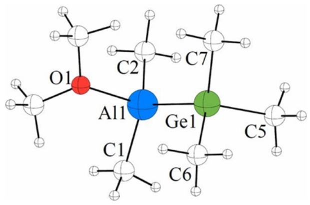

Fig. 5. The calculated structure (B3LYP [21]) of the model compound $Me_3Ge\text{-}AlMe_2(OMe_2)$. Calculated bond lengths (Å) and angles (deg): Al1–Ge1 2.542, Al1–C1 1.992, Al1–O1 2.071, Ge1–C7 2.018, Ge1–C5 2.012, Ge1–C6 2.012; C1–Al1–C2 116.9, C1–Al1–O1 101.3, C2–Al1–O1 100.8, C2–Al1–Ge1 117.3, C1–Al1–Ge1 115.0, C5–Ge1–C6 105.1, C5–Ge1–C7 104.2, C6–Ge1–C7 104.6, C5–Ge1–Al1 112.0, C6–Ge1–Al1 113.8, C7–Ge1–Al1 116.1.

Crystals of the germylalanate $[(Ph_3Ge)_3AlH]Li(THF)_3$, **5**, are monoclinic, space group $P2_1/c$. There are two benzene molecules and one uncoordinated THF molecule besides one molecule of **5** in the asymmetric unit. The molecular structure is shown in Fig. 6. The Al–Ge bond lengths span the range from 2.532(2) to 2.548(2) Å (average 2.540 Å). They are significantly longer than in compound $[(Ph_3Ge)_3AlMe]Li(THF)_3$ with 2.520(4) Å [13]. The Li–H bond of 1.54(4) Å is shorter than the 1.83(7) Å observed in $(THF)_3Li[HAl(OCPh_3)_3]$ [26], and the Al–H bond length is longer (1.63(2) *versus* 1.50(7) Å). While the Li–H–Al bond angle in **5** is 168.3(1)° the corresponding angle in $(THF)_3LiHAl(OCPh_3)_3$ is 180°. The C–Ge–C bond angles are more acute (101.3(2) to 104.6(3)°) than the Ge–Al–Ge bond angles (110.2(8)° to 112.2(8)°). The arrangement of the atoms around the Li atom is rather asymmetric with the H–Li–O bond angles close to 120° and O–Li–O bond angles ranging from 95.6(1)° to 102.8(1)°.

In contrast to the observed structure of **5**, calculations for the model anion $[(Me_3Ge)_3AlH]^-$ (Fig. 7) result in a more symmetric array of the atoms, *i. e.* the Ge–Al–Ge bond angles are very close to the tetrahe-

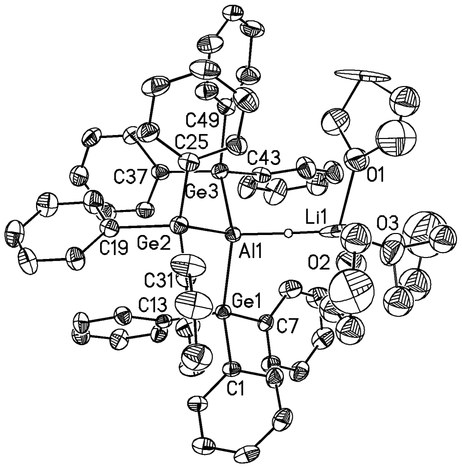

Fig. 6. The molecular structure of $[(Ph_3Ge)_3AlH]Li(THF)_3$, **5**. Displacement ellipsoids are shown at the 30 % probability level. The CH_2 groups of the THF molecules are omitted for the sake of clarity. Two of the coordinated THF molecules are disordered. Selected bond lengths (Å) and angles (deg): Al1–H1 1.63(2), Al1–Ge1 2.532(2), Al1–Ge2 2.539(2), Al1–Ge3 2.548(2), Ge1–C1 1.987(7), Ge1–C7 1.964(6), Ge1–C13 1.955(7), Ge2–C19 1.974(8), Ge2–C25 1.987(7), Ge2–C31 1.977(8), Ge3–C37 1.983(8), Ge3–C43 2.005(7), Ge3–C49 1.979(8), Li–H1 1.54(4), Li1–O1 2.09(2), Li1–O2 2.13(3), Li1–O3 1.90(2); H1–Al1–Ge1 104(2), H1–Al1–Ge2 109(2), H1–Al1–Ge3 112.1(8), Ge1–Al1–Ge2 112.2(8), Ge1–Al1–Ge3 110.2(8), Ge2–Al1–Ge3 112.1(8), C1–Ge1–C17 101.3(3), C1–Ge1–C13 103.3(3), C7–Ge1–C13 104.6(3), Li1–H1–Al1 168.3(1), H1–Li1–O1 112.3(4), H1–Li1–O2 120.3(4), H1–Li1–O3 121.3(4), O1–Li1–O2 95.6(1), O1–Li1–O3 101.9(1), O2–Li1–O3 102.8(1).

dral angle including also the Ge–Al–H bond angles. However, the C–Ge–C bond angles deviate with values close to 102° from the tetrahedral angle. The Al–Ge bond lengths turn out to be longer (2.555 to 2.558 Å) than those determined for **5**.

Compound **9** is the first germyl-alane to be studied by X-ray crystallography (Fig. 8). There are two independent molecules in the asymmetric unit of the monoclinic unit cell, space group $P2_1/c$. Since the molecular parameters for bond lengths and bond angles are similar for both molecules, only the data of one molecule will be described in more detail. It shows a tri-coordinated planar Al center, *i. e.* the sum of bonds angles is 359.7°. Its Ge–Al bond length is 2.545(1) Å which is slightly but significantly longer than the Ge–Al bonds in the germyl aluminates **4** and **5** with tetra-coordinated Al atoms. As expected, the Ge–C bonds are also slightly longer than in **3**, and they are of course also longer than the Al–N bonds.

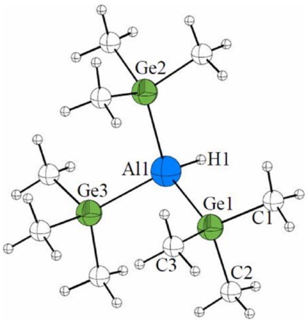

Fig. 7. Calculated structure (B3LYP [21]) for the anion $[(Me_3Ge)_3AlH]^-$. Selected calculated bond lengths (Å) and angles (deg): Al1–H1 1.626, Al1–Ge1 2.557, Al1–Ge2 2.555, Al1–Ge3 2.558, Ge1–C1 2.026, Ge1–C2 2.027, Ge1–C3 2.024; Ge1–Al1–Ge2 109.6, Ge1–Al1–Ge3 109.3, Ge2–Al1–Ge3 109.9, Ge1–Al1–H1 109.4, Ge2–Al1–H1 109.4, Ge3–Al1–H1 109.3, C1–Ge1–C2 102.6, C1–Ge1–Al1 115.4, C2–Ge1–Al1 115.1, C2–Ge1–C3 103.0, C3–Ge1–Al1 116.1, C1–Ge1–C3 102.9.

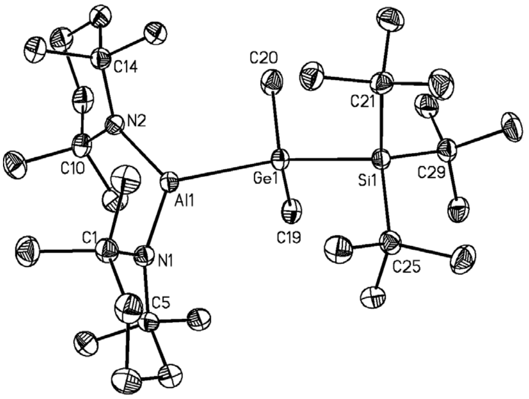

Fig. 8. Molecular structure of $tmp_2Al–GeMe_2SiMe_3$, **9**. Selected bond lengths (Å) and lengths (deg): Al1–Ge1 2.545(1), Al1–N1 1.833(4), Al1–N2 1.830(4), Ge1–C20 1.987(5), Ge1–C19 1.994(5), Ge1–Si1 2.461(1), Si1–C21 1.949(4), Si1–C25 1.933(5), Si1–C29 1.954(5); N1–Al1–N2 123.8(1), N1–Al1–Ge1 123.8(1), N2–Al1–Ge1 112.0(1), C19–Ge1–C20 98.5(2), C19–Ge1–Al1 106.5(1), C19–Ge1–Si1 108.1(1), C20–Ge1–Al1 104.0(1), C20–Ge1–Si1 109.4(1), Si1–Ge1–Al1 126.5(5), C1–N1–C5 116.1(4), C10–N2–C14 115.5(4).

The N atoms of the tetramethylpiperidine units are planar. This has also been observed in several $(tmp)_2AlX$ compounds [22, 24], and both molecules **9** show the same Al–N bond lengths of 1.830(2) Å. The N–Ge–Al bond angles are different with 112.0(1)° for N2 and 123.8(1)° for N1. This is due to the interaction of the tmp group of N1 with the Me_3Si group which leads to an interplanar angle between the C_2N planes of N1 and N2 of 107.1°. It is also interesting to note that the angle

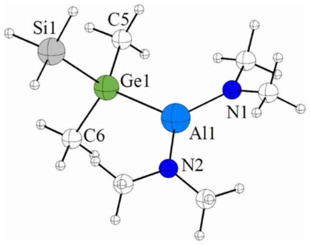

Fig. 9. Calculated (B3LYP [21]) bond lengths (Å) and angles (deg) for the model compound $(H_3Si)Me_2Ge\text{-}Al(NH_2)_2$: Al1–Ge1 2.516, Al1–N1 1.804, Al1–N2 1.804, Ge1–C5 2.009, Ge1–C6 2.010, Ge1–Si1 2.433; N1–Al1–N2 119.4, N1–Al1–Ge1 121.8, N2–Al1–Ge1 118.8, C6–Ge1–C6 106.6, Si1–Ge1–C5 106.3, Si1–Ge1–C6 106.9, Si1–Ge1–Al1 110.1, C5–Ge1–Al1 114.4, C6–Ge1–Al1 112.7.

Si1–Ge1–Al is blunt with 126.5(3)°. For the model compound $(Me_2N)_2AlGeMe_2SiMe_3$ (Fig. 9) calculations resulted in an Al–Ge bond length of 2.516 Å which is shorter than found for **9**. Moreover, all bond angles are closer to 120° (at Al and N) or to the tetrahedral angles at Ge and Si, and these differences are most likely due to the different state of the two molecules.

Discussion and Conclusions

Four new compounds with Al–Ge bonds have been structurally characterized, amongst them the first monomeric germyl-alane **9** with a tri-coordinated planar aluminum atom. This compound has a longer Al–Ge bond than the tetra-coordinated germyl-aluminates with tetra-coordinated Al atoms. Usually the bond lengths E–X increase as the coordination number increases. Typical examples are BCl_3 with (d(B–Cl) = 1.73 Å [26] *versus* 1.837 Å for d(B–Cl) in $pyBCl_3$ [27], or d(Al–Cl) in monomeric tmp_2AlCl with 2.144 Å *versus* the tetra-coordinated THF adduct, $tmp_2AlCl(THF)$, with 2.227 Å [25, 28]. The Al–Si bond in the tri-coordinated alane derivative $tmp_2AlSi(SiMe_3)_3$ of 2.514(1) Å [28] is longer than the Al–Si bond lengths of 2.456(2) Å in the tetra-coordinate Al species $[Cl_3Al\text{-}Si(SiMe_3)_3]^-$. Habereder [13] also showed that $R_3Sn\text{-}BX_2$ compounds have longer Sn–B bonds than observed in the respective stannylborates $R_3Sn\text{-}BX_3^-$ [13]. This suggests that the E–X bond lengths of compounds EX_n with E–X bonds between elements with large electronegativity differences behave differently compared with those of similar electronegativity. Table 2 gives an overview of bond order and bond polarity for three germyl-aluminates/alanes.

Table 2. Calculated bonding parameters (B3LYP [21]) for tri- and tetra-coordinated germyl-aluminum compounds. Influence of partial charges at the Al and Ge atoms.

	$[(Me_3Ge)_3AlH]^-$	$Me_3GeAl\text{-}Me_2(OEt_2)$	$(H_3Si)Me_2\text{-}GeAl(NMe_2)_2$
Bond order Ge–Al	0.71	0.64	0.70
Bond polarity at Al	0.35	0.33	0.34
Charge difference $\Delta = \delta Al - \delta Ge$	−0.35	+0.53	+1.07
d(Al–Ge), Å	2.557	2.542	2.516

As shown in Table 2, the strongest influence results from large charge differences. However, according to these calculations, the tri-coordinated germyl alane has a shorter Ge–Al bond than the tetra-coordinated germyl aluminates. But experimentally, the Ge–Al bond length in $tmp_2AlGeMe_2(SiMe_3)$ is the longest observed so far. This is most likely due to steric effects.

Experimental Section

Dimethyl[tri(tert-butyl)silyl]germyllithium

To a mixture of Li powder (40 mg, 6.0 mmol) and naphthalene (40 mg, 0.033 mmol) was added tetrahydrofuran (30 mL). After stirring for 6 h a green suspension had formed to which $Me_2(tBu_3Si)GeCl$ (1.09 g, 3.25 mmol), dissolved in THF (20 mL), was added dropwise at −78 °C. The mixture was then stirred for 12 h at ambient temperature followed by removal of the insoluble material by filtration. The filtrate was checked by NMR data (see below) and was used directly assuming a 90 % conversion. – NMR (in THF/C_6D_6): $\delta^{27}Si$ = 16.6 ppm; $\delta^{7}Li$ = 3.3 ppm; $\delta^{1}H$ = 0.51 (s, 6H $GeCH_3$), 1.31 ppm (s, 27 H, CMe_3); $\delta^{13}C$ = 1.7 ($GeMe_2$), 30.4 (Me_3), 32.4 ppm (CMe_3).

Attempt to prepare lithium triphenylgermyl-trimethylaluminate

To a stirred solution of $LiGePh_3$ in diethyl ether (33.0 mL, 0.18 M, 5.40 mmol) was added at −78 °C a solution of $(Me_3Al)_2$ (0.46 g, 6.38 mmol, 1 M in hexane). After warming to ambient temperature a yellow solution resulted. The ^{27}Al NMR spectrum of this solution showed no change in the ^{27}Al chemical shift. Therefore, one equivalent of tetramethylethylenediamine (6.42 mmol, 1.20 g) was added for complexation of the Li cation in order to increase the base strength of the Ge atom. At −40 °C moisture-sensitive crystals separated which according to their crystal structure turned out not to be the expected $(Ph_3GeAlMe_3)Li(THF)TMEDA$ but the triphenylgermyl lithium complex $Ph_3GeLi(THF)TMEDA$; yield: 800 mg (29 %), m. p. > 130 °C (dec). The solution showed the ^{27}Al signal of Al_2Me_6 at 158 ppm ($h_{1/2}$ 1340 Hz). – NMR (THF/C_6D_6) of $Ph_3GeLi(THF)(TMEDA)$,

3: δ^7Li = 3.6 ppm; δ^{14}N = −66.7 ppm; δ^1H = 2.04 (s, 12 H, C*H*$_3$), 2.19 (m, 4H CH$_2$), 7.01 – 7.74 ppm (m, 15 H, Ar); δ^{13}C = 45.7 (4 C, *C*H$_3$), 57.7 (*C*H$_2$), 124.3, 126.7, 135.1, 136.4, 158.8 ppm (*C*$_{ar}$). – MS: *m/z* (%) = 608 (1) [Ph$_6$Ge$_2$]$^+$, 545 (1) [Ph$_5$Ge$_2$Me]$^+$, 305 (35) [Ph$_3$Ge]$^+$, 228 (100) [Ph$_2$Ge]$^{2+}$, 151 (42) [PhGe]$^+$, 115 (1) [C$_6$H$_{15}$N$_2$]$^+$, 77 (4) [Ph]$^+$, 74 (2) [Ge]$^+$, 58 (9) [C$_3$H$_8$N]$^+$. – C$_{29}$H$_{39}$N$_2$OGeLi (499.82): calcd. C 67.37, H 7.88, N 5.26; found C 66.32, H 7.04, N 5.04.

*Triphenylgermyl-dimethylalane diethyl ether, **4***

To a stirred solution of Me$_2$AlCl (5.0 mL, 1.0 M solution, 5.0 mmol) in hexane was added at −78 °C a solution of Ph$_3$GeLi in hexane/diethyl ether (30 mL, 0.18 M, 5.4 mmol). A solid precipitate formed on warming to ambient temperature which was removed by filtration. From the filtrate moisture-sensitive crystals separated within a week on storing the filtrate at −40 °C. Yield: 360 mg of **4** (20 %), m. p. 78 °C. – NMR (THF/C$_6$D$_6$): δ^{27}Al = 160 ppm ($h_{1/2}$ = 3800 Hz); δ^1H = −0.43 (s, 6 H, Al*Me*), 1.07 (t, ^3J(H,H) = 7.0 Hz, 6 H, *Me*CH$_2$), *3.25* (q, ^3J(H,H) = 7.0 Hz, 4 H), 7.1 – 7.64 ppm (m, 15 H, Ar); $\delta^{13}C$ = −7.6 (AlMe), 15.2 (Me$_2$CH$_2$), 65.6 (Me*C*H$_2$), 127.1, 127.8, 128.3, 135.3, 145.1, 194.5 ppm (Ar). – IR (KBr): ν (cm^{-1}) = 2964 m, 2901 w, 2827 w, 1416 w, 1260 st, 1091 st, 1018 st, 871 w, 798 st, 734 w, 463 w, 390 w. – Raman: ν (cm^1) = 3136 w, 3048 m, 2981 w, 2939 m, 2887 m, 2819 w, 2681 m, 1569 sh, 1482 w, 1451 w, 1324 w, 1188 w, 1159 w, 1085 w, 1028 m, 663 m, 619 m, 569 w, 228 st, 167 w. – C$_{20}$H$_{21}$AlGe (360.96): calcd. C 66.55, H 5.86, Al 7.47, Ge 20.11; found C 64.86, H 5.08, Al 6.97, Ge 20.93.

*Tetrakis(tetrahydrofuran)lithium-(triphenylgermyl)-trihydridoaluminate, **7***

A solution of Ph$_3$GeH (590 mg, 1.92 mmol) in diethyl ether (40 mL) was cooled to 0 °C. Then a solution of LiBu (1.6 M, 1.2 mL) was added. After 1 h this solution was cooled to −78 °C before adding AlH$_3$NMe$_3$ (170 mg, 1.02 mmol), suspended in diethyl ether (20 mL). When the mixture had attained r. t. a turbid suspension was present. THF (20 mL) was added which resulted in the formation of a clear solution. Its ^{27}Al NMR spectrum showed a signal at 103.7 ppm ($h_{1/2}$ = 800 Hz) besides a small signal at 98.9 ppm ($h_{1/2}$ = 300 Hz). The solution was then cooled to −30 °C. Under these conditions polycrystalline **7** separated. Yield 800 mg (67 %), m. p. 250 °C. – NMR (C$_6$D$_6$): δ^1H = 1.30 (s, br. 16 H, OCH$_2$C*H*$_2$), 3.44 (s, br, 16 H, OC*H*$_2$), 7.24 (m, 3H, *m*-PhH). 7.79 (m, 6H, *p*-PhH), 7.97 ppm (m, 6H, *o*-PhH); δ^{13}C = 25.2 (OCH$_2$*C*H$_2$), 68.2 (O*C*H$_2$), 126.7, 127.6, 136.4, 146.2 ppm (C$_{ar}$); δ^{27}Al = 109.2 ppm ($h_{1/2}$ = 1400 Hz). – IR (Hostaflon): ν (AlH, cm^1) = 1727 st, 1683 vst. – C$_{34}$H$_{50}$AlGeLi (630.3): calcd. C 64.90, H 8.01; found C 63.57, H 7.97.

*Tris(tetrahydrofuran)lithium tris(triphenylgermyl)hydridoaluminate), **6***

To a stirred solution of AlHCl$_2$(THF)$_2$ (250 mg, 1.02 mmol), dissolved in toluene (20 mL), was added at −78 °C a solution of LiGePh$_3$ in diethyl ether (10 mL, 3.0 mmol). On warming the mixture to ambient temperature a white solid (LiCl) precipitated which was removed by filtration after stirring the suspension for 24 h. The filtrate was then cooled to −40 °C. The solvent was stepwise removed *in vacuo* until crystals of **6** separated. The yield was not determined, m. p. 175 °C. – NMR (THF/C$_6$D$_6$): δ^{27}Al = 71 ppm ($h_{1/2}$ = 5350 Hz); δ^7L*i* = −0.1 ppm; δ^1H = 7.15 – 7.40 ppm (H$_{ar}$), AlH could not be detected; δ^{13}C = 128.2, 129.0, 134.9, 135.5, 152.7, 194.5 ppm (C$_{ar}$). – IR (KBr): ν (cm^{-1}) = 3049 m, 2830 m, 1930 w, 1600 br, 1380 w, 1255 m, 1182 m, 1083 m, 984 br, st, 855 m, 782 st, 729 st, 706 st, 691 st, 682 st, 501 sh, 463 w, 456 w, 440 w, 373 w, 355 w. – Raman: ν (cm^{-1}) = 3050 st, 2961 m, 2907 m, 1581 st, 1569 st, 1027 st, 668 m, 617 m, 448 br, 228 m, 172 m. – C$_{34}$H$_{50}$O$_4$AlGeLi (630.3): calcd. C 64.90, H 8.0; found C 62.57, H 7.97.

*Bis(2,2,6,6-tetramethyl)piperidino-triphenylgermylalane, **8***

To a stirred solution of triphenylgermane (580 mg, 1.92 mmol) in diethyl ether (40 mL) was added a solution of LiBu (1.2 mL, 1.6 M). After stirring for 1 h the solution was cooled to −78 °C. Then a hexane solution (10 mL) of bis(tetramethylpiperidino)aluminum bromide (740 mg, 1.92 mmol) was added. After the mixture had attained r. t. stirring was continued for 2 h. All volatiles were removed *in vacuo*. The solid residue was treated with hexane (30 mL), and the insoluble material was removed by filtration. The filtrate was concentrated and cooled to 4 °C. Within a week thin colorless platelets of **8** separated. Yield: 280 mg, 51 %. – NMR (C$_6$D$_6$): δ^1H = 1.24 (m, 8H, CC*H*$_2$), 1.34 (s 24 H, C*H*$_3$), 1.39 (m, 14H C*H*$_2$), 7.20 (m, 9H, *p*-PhH), 7.90 ppm (m, 6H, *o*-PhH); δ^{27}Al: only a very broad peak. – C$_{30}$H$_{51}$N$_2$AlGe (612.3): calcd. C 70.72, H 8.41, N 4.51; found C 69.35, H 8.23, N 4.87.

*Bis(2,2,6,6-tetramethylpiperidino) (tert-butyl(dimethylsilyl)-germylalane, **9***

As described for **8** a solution of LiGe(Me$_2$)Si(*t*Bu)$_3$ (310 mg, 1.0 mmol) in THF (10 mL) was dropped into a solution of tmp$_2$AlCl (340 mg, 1.0 mmol) in toluene (20 mL). The solution turned slightly yellow, and a colorless precipitate formed on warming to ambient temperature. The filtrate was cooled to 40 °C. Colorless crystals of **9** separated within a few days. Yield: 30 mg, m. p. 145 °C. – NMR (THF/C$_6$D$_6$): δ^{27}Al = 60 ppm ($h_{1/2}$ = 8700 Hz); δ^{29}Si = 23.3 ppm; δ^{14}N: no detectable signal; δ^1H = 0.75 (s, 6H, Ge*Me*), 1.30 (m, 8 H, β-C*H*$_2$), 1.31 (s, 27 H, C*Me*$_3$), 1.47 (s, 24 H, tmp-

Table 3. Crystal data and parameters pertinent to data collection and refinement of **3**–**5** and **9**.

Compound	**3**	**4**	**5**	**9**
Chem. formula	$C_{28}H_{39}N_2OLiGe$	$C_{48}H_{62}O_2Al_2Ge_2$	$C_{76}H_{84}O_4AlGe_3Li$	$C_{64}H_{138}N_4Al_2Ge_2Si_2$
Mr	499.14	870.12	1313.12	1219.10
Crystal size, mm^3	$0.2 \times 0.2 \times 0.3$	$0.2 \times 0.2 \times 0.2$	$0.2 \times 0.2 \times 0.2$	$0.2 \times 0.2 \times 0.3$
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	Pn	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a, Å	8.7719(6)	10.0856(9)	13.186(1)	13.910(1)
b, Å	10.0658(7)	11.338(1)	20.687(2)	8.7015(8)
c, Å	15.493(1)	11.496(1)	26.149(2)	59.366(5)
α, deg	90	98.670(1)	90	90
β, deg	93.148(1)	90.819(2)	100.568(2)	90.933(2)
γ, deg	90	115.935(2)	90	90
V, $Å^3$	1365.9(2)	1163.9(2)	7011(1)	7184(1)
Z	2	2	4	8
$\rho_{calcd.}$, Mg m^{-3}	1.21	1.24	1.24	1.13
$\mu(MoK_\alpha)$, mm^{-1}	1.1	1.4	1.4	0.9
$F(000)$, e	528	456	2736	2672
Index range hkl	$-11 \le h \le 11$	$-9 \le h \le 13$	$-14 \le h \le 14$	$-15 \le h \le 15$
	$-13 \le k \le 13$	$-15 \le k \le 14$	$-22 \le k \le 22$	$-11 \le k \le 11$
	$-16 \le l \le 21$	$-14 \le l \le 14$	$-28 \le l \le 24$	$-77 \le l \le 77$
$2\,\theta_{max}$, deg	58.36	57.58	44.92	55.34
T, K	293(2)	193(2)	193(2)	193(2)
Refl. collected	7779	6838	28352	37624
Refl. unique	4919	3593	8517	11945
R_{int}	0.0281	0.0230	0.0647	0.0797
Refl. observed (4 σ)	4347	2935	6154	7038
Refined param.	302	248	767	706
Final R^a (4 σ)	0.0359	0.0352	0.0684	0.0550
Final $wR2^a$ (all data)	0.0855	0.10832	0.1430	0.1270
Wght., scheme^a x/y	0.0510 / 0.2431	0.0388 / 0.7226	0.0543 / 16.8437	0.0754 / 0.000
GoF^b (F^2)	1.034	1.070	1.121	1.004
$\Delta\rho_{fin}$ (max), e $Å^{-3}$	0.364	0.295	0.538	0.555

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (xP)^2 + yP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; [b] GoF = $[\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

CH_3), 1.66 ppm (m, 4 H, tmp-γ-CH_2); $\delta^{13}C$ = 3.8 (Ge*C*), 18.6 (γ-CH_2), 30.7 (Si*C*), 32.0 (tmp-*Me*), 32.5 (SiC*Me*), 40.8 (β-CH_2), 52.1 ppm (N*C*). – MS: *m/z* (%) = 307 (10) $[tmp_2Al]^+$, 303 (9) $[Me_2GeSi(t\mathrm{Bu})_3]^+$, 278 (5) $[303\text{–Me}]^+$; 277 (3) $[tmpAl\text{–}2Me]^+$; 245 (2) $[303\text{–}t\mathrm{Bu}]^+$, 230 (2) $[245\text{–}CH_3]^+$, 166 (8) $[tmpAl\text{–}H]^+$, 156 (21) $[MeSit\mathrm{Bu}_2]^+$, 140 (13) $[tmp]^+$, 135 (2) $[tmp\text{–}Me]^+$, 111 (8) $[tmp\text{–}2Me]^+$, 101 (8) $[GeSi]^+$, 81 (11) $[tmp\text{–}4Me]^+$, 73 (100) $[Ge]^+$, 69 (77) $[SiC_3H_5]^+$, 57 (36) $[CMe_3]^+$.

X-Ray structure analyses

Single crystals suitable for X-ray diffraction were covered with perfluoro ether oil and selected under a cover of cold nitrogen gas (−20 °C). The selected specimen were then placed on the tip of a glass fiber and mounted on the goniometer head of a Bruker P4 four circle diffractometer equipped with a low-temperature device and an area detector. Graphite-monochromatized MoK_α radiation was used. Data collections were performed with samples cooled to −80 °C. The unit cell parameters were calculated from the reflections collected on 5 sets of 15 frames each (changes in ω by 3°) which were taken at different settings of θ and χ by using the program SMART [29]. Data collections were performed in the hemisphere mode, and the data were reduced by using the program SAINT [30]. The structures were solved with the programs SHELXTL or SHELX-93 [31]. Empirical absorption corrections (min./max. for **3**: 0.5315/0.6946; for **4**: 0.7528/0.8252, for **6**: 0.7056/0.8623, and for **9**: 0.4661/0.8608) were applied. Relevant crystallographic information and data referring to the structure solution and refinement are summarized in Table 3.

CCDC 751080 (**3**), 751081 (**4**), 751082 (**5**), and 751083 (**9**) contain 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.

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