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## Tris(trichlorosilyl)tetrelide Anions and a Comparative Study of Their Donor Qualities

Julian Teichmann,<sup>[a]#</sup> Chantal Kunkel,<sup>[a]#</sup> Isabelle Georg,<sup>[a]</sup> Maximilian Moxter,<sup>[a]</sup> Tobias Santowski,<sup>[a]</sup> Michael Bolte,<sup>[a]</sup> Hans-Wolfram Lerner,<sup>[a]</sup> Stefan Bade,<sup>[b]</sup> Matthias Wagner\*<sup>[a]</sup>

**Abstract:** Trichlorosilylated tetrelides  $[(Cl_3Si)_3E]^-$  have been prepared by adding 1 equiv of a soluble CI<sup>-</sup> salt to  $(Cl_3Si)_4Si$  (E = Si) or 4 Si<sub>2</sub>Cl<sub>6</sub>/GeCl<sub>4</sub> (E = Ge). To assess their donor qualities, the anions  $[(Cl_3Si)_3E]^-$  (E = C, Si, Ge) have been treated with BCl<sub>3</sub>, AlCl<sub>3</sub>, and GaCl<sub>3</sub>. BCl<sub>3</sub> and GaCl<sub>3</sub> give 1:1 adducts with the anionic centers. AlCl<sub>3</sub> leads to Cl<sup>-</sup> abstraction from  $[(Cl_3Si)_3E]^-$  with formation of  $(Cl_3Si)_4E$  (E = Si or Ge).  $(Cl_3Si)_4Ge$  is cleanly converted to the perhydrogenated (H<sub>3</sub>Si)<sub>4</sub>Ge by use of Li[AlH<sub>4</sub>]. Another case of Cl<sup>-</sup> abstraction was observed for  $[(Cl_3Si)_3Ge-GaCl_3]^-$ , which reacts with GaCl<sub>3</sub> to afford the neutral dimer  $((Cl_3Si)_3Ge-GaCl_2)_2$ .

Oligosilanes are precursors in the chemical vapor deposition (CVD) of amorphous Si-based materials for use in thin-film solar cells. The spectrum of absorbed light can be widened to shorter or longer wavelengths through the incorporation of C or Ge atoms, respectively.<sup>[11]</sup> Yet, the simultaneous deposition of individual silanes and germanes suffers from separation effects, which lead to Si- and Ge-enriched areas and thereby reduce the photovoltaic efficiency of the device. Mixed-element precursors containing Si and Ge covalently linked to each other offer a solution to the problem, but the number of available compounds is very limited.<sup>[2–5]</sup> Future progress in the field will therefore depend on the development of additional access routes to well-defined Si-Ge oligomers.<sup>[6]</sup>

Oligotetrels are also interesting in their own right, because of the  $\sigma\text{-}\sigma^{*}$  conjugation along the oligomer backbones^{[7]} and a tendency for skeletal rearrangements. To manipulate the electronic structures and reactivities of oligotetrels, one can decorate the chains with strongly electron-withdrawing substituents or incorporate low-valent, lone-pair bearing tetrel centers. Still today, most oligotetrels carry hydrogen or organyl substituents.<sup>[8]</sup> Far fewer examples are known of perhalogenated derivatives,<sup>[9]</sup> which means lost opportunities given that already the simplest member of the family, Si<sub>2</sub>Cl<sub>6</sub>, reacts substantially different from its methylated relative Si<sub>2</sub>Me<sub>6</sub>: (i) Tertiary amines suffice to catalyze the disproportionation of Si<sub>2</sub>Cl<sub>6</sub> according to 4  $Si_2Cl_6 \rightarrow (Cl_3Si)_4Si + 3 SiCl_4$  and thereby open an access route to the perchlorinated *neo*-pentasilane.<sup>[10,11]</sup> (ii) In the presence of soluble chloride salts,  $Si_2CI_6$  undergoes heterolytic cleavage of its Si-Si bond to form SiCl<sub>4</sub> and the [SiCl<sub>3</sub>]<sup>-</sup> anion, [12,13] a versatile intermediate for the in situ generation of higher oligoand organosilanes.<sup>[14]</sup> (iii) The challenging activation of Si<sub>2</sub>Me<sub>6</sub>, on the other hand, requires the presence of powerful transitionmetal catalysts.<sup>[15]</sup> Representatives of exhaustively Cl<sub>3</sub>Sisubstituted tetrelides are the methanide [(Cl<sub>3</sub>Si)<sub>3</sub>C]<sup>-</sup> ([**1**]<sup>-</sup>)<sup>[16-18]</sup> and the silanide [(Cl<sub>3</sub>Si)<sub>3</sub>Si]<sup>-</sup> ([**2**]<sup>-</sup>).<sup>[19,20]</sup> A corresponding uncharged species **A** also exists (Figure 1).<sup>[21]</sup> The related

 [a] [\*] M. Sc. J. Teichmann, M. Sc. C. Kunkel, M. Sc. I. Georg, Dr. M. Moxter, M. Sc.T Santowski, Dr. M. Bolte, Dr. H.-W. Lerner, Prof. Dr. M. Wagner
Institut für Anorganische Chemie
Goethe-Universität Frankfurt
Max-von-Laue-Strasse 7, 60438 Frankfurt (Main) (Germany)
E-mail: Matthias.Wagner@chemie.uni-frankfurt.de

- [b] Dr. S. Bade Evonik Resource Efficiency GmbH, Untere Kanalstraße 3, 79618 Rheinfelden, Germany
- # These authors contributed equally

germanium compound was obtained through catenation of the Ge(II) adducts GeCl<sub>2</sub>(IDipp) and GeCl<sub>2</sub>(dioxane), which stops at the stage of ((IDipp)Cl<sub>2</sub>Ge)Ge(GeCl<sub>3</sub>)<sub>2</sub> (**B**; IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene).<sup>[22]</sup> A comparable compound, [(Cl<sub>3</sub>Si)<sub>2</sub>P]<sup>-</sup> ([**C**]<sup>-</sup>), has also been reported for the pnictogens.<sup>[23]</sup>





Beckmann, Ketkov, and Mebs characterized the silanide [2] - as weakly coordinating anion with an inert lone pair. Likewise, Rivard's GeCl<sub>2</sub> catenation does not proceed beyond B, which indicates a low nucleophilicity of this compound, too. Considering the fundamental importance of such low-valent Si and Ge species, a more thorough assessment of their Lewis basicities is nevertheless worthwhile. Herein, we first extend the series of tetrelides  $[(Cl_3Si)_3E]^-$  (E = C, Si) to the germanide  $[(Cl_3Si)_3Ge]^-$  ([3]<sup>-</sup>). We then show that all three anions [1]<sup>-</sup>-[3]<sup>-</sup> are surprisingly reactive toward various electrophiles and structurally characterize their adducts  $[(Cl_3Si)_3E \cdot GaCl_3]^-$  (E = C, Finally, we disclose Si. Gel. the neutral species ((Cl<sub>3</sub>Si)<sub>3</sub>Ge-GaCl<sub>2</sub>)<sub>2</sub> and (Cl<sub>3</sub>Si)<sub>4</sub>Ge, which are relevant for the preparation of single-source, mixed-element CVD precursors such as (H<sub>3</sub>Si)<sub>4</sub>Ge.

The methanide [1]<sup>-</sup> is accessible in >90% yield from CCl₄ and in situ-generated [SiCl<sub>3</sub>]<sup>-</sup> (Scheme 1).<sup>[18]</sup> The silanide [2]<sup>-</sup> was first identified on the basis of <sup>29</sup>Si NMR spectroscopy<sup>[13]</sup> and later structurally characterized by Beckmann, Ketkov, and Mebs.<sup>[19]</sup> who isolated [2] as a side product of the synthesis of SiCl<sub>2</sub>(IDipp).<sup>[24]</sup> Their subsequent targeted protocol involves two steps: (i) (Cl<sub>3</sub>Si)<sub>4</sub>Si in SiCl<sub>4</sub> is subjected to a protodesilylation reaction using 1 equiv of ethereal HCI.[25] (ii) The obtained (Cl<sub>3</sub>Si)<sub>3</sub>SiH is then deprotonated with PMP to obtain [PMP-H][2] in yields of 96% (PMP = 1,2,2,6,6-pentamethylpiperidine; less bulky, more nucleophilic amines were found not suitable for this reaction).<sup>[19]</sup> To save the deprotonation step, we performed the desilvlation of (Cl<sub>3</sub>Si)₄Si using Cl<sup>-</sup> ions without H<sup>+</sup> present: The reaction of 1 equiv of [R<sub>4</sub>N]Cl with (Cl<sub>3</sub>Si)<sub>4</sub>Si resulted in the heterolytic cleavage of one Si-Si bond and directly furnished the silanide salts [R<sub>4</sub>N][2] (R = Et, nBu).<sup>[9,20]</sup> The germanide salt [nBu<sub>4</sub>N][3] was prepared by adding 4 equiv of Si<sub>2</sub>Cl<sub>6</sub> to an equimolar mixture of GeCl<sub>4</sub> and [nBu<sub>4</sub>N]Cl in CH<sub>2</sub>Cl<sub>2</sub>.<sup>[26]</sup> A 1:1:1 mixture of Si<sub>2</sub>Cl<sub>6</sub>, GeCl<sub>4</sub>, and [nBu<sub>4</sub>N]Cl in CH<sub>2</sub>Cl<sub>2</sub> cleanly gave SiCl<sub>4</sub> and [*n*Bu<sub>4</sub>N][GeCl<sub>3</sub>] (Scheme 1), as proven by X-ray crystallography.<sup>[26,27]</sup> Treatment of [nBu<sub>4</sub>N][GeCl<sub>3</sub>] in CH<sub>2</sub>Cl<sub>2</sub> with 3 equiv of  $Si_2Cl_6$  again resulted in the formation of  $[nBu_4N][3]$ , which confirmed the role of [GeCl<sub>3</sub>]<sup>-</sup> as the first intermediate of

the reaction cascade leading to [3]-: analogous to the case of CCl<sub>4</sub>,<sup>[18]</sup> chlorophilic attack of [SiCl<sub>3</sub>]<sup>-</sup> on GeCl<sub>4</sub> removes a Cl<sup>+</sup> cation. However, while [CCl3]<sup>-</sup> is nucleophilic enough to bite back into SiCl<sub>4</sub> and form Cl<sub>3</sub>C-SiCl<sub>3</sub>,<sup>[18]</sup> [GeCl<sub>3</sub>]<sup>-</sup> behaves inert toward SiCl<sub>4</sub>.<sup>[28]</sup> Toward the more reactive Si<sub>2</sub>Cl<sub>6</sub>,  $[GeCl_3]^-$  likely acts as a Cl<sup>-</sup> donor to afford GeCl<sub>2</sub> and [SiCl<sub>3</sub>]<sup>-</sup>/SiCl<sub>4</sub>, which subsequently combine to establish a first Ge-Si bond in a putative [Cl<sub>2</sub>GeSiCl<sub>3</sub>]<sup>-</sup> anion. A repetition of analogous steps ultimately furnishes the anion  $[(Cl_3Si)_3Ge]^-$  ([3]<sup>-</sup>). [R<sub>4</sub>N][1] and [R<sub>4</sub>N][3] are stable over the long term under inert conditions, whereas [R<sub>4</sub>N][2] decomposes in CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature over a period of several days to give the cyclohexasilane-chloride diadduct [R<sub>4</sub>N]<sub>2</sub>[1,1-(Cl<sub>3</sub>Si)<sub>2</sub>Si<sub>6</sub>Cl<sub>10</sub>·2Cl]<sup>[12]</sup> as the main product.

Scheme 1 compiles the solid-state structures of the anions [1]<sup>-</sup>–[3]<sup>-</sup>. For a discussion of the trigonal-planar [1]<sup>-</sup>, see references<sup>[17,18]</sup> and the Supporting Information of this paper. The Si and Ge centers in [2]<sup>-</sup> and [3]<sup>-</sup> are strongly pyramidalized ( $\Sigma$ (SiSiSi) = 290.0°,  $\Sigma$ (SiGeSi) = 285.5°). The average Si–Si (2.321 Å) and Ge–Si (2.373 Å) bond lengths are alike those in the permethylated analogs [(Me<sub>3</sub>Si)<sub>3</sub>Si]<sup>-</sup> (2.331 Å) and [(Me<sub>3</sub>Si)<sub>3</sub>Ge]<sup>-</sup> (2.384 Å).<sup>[29,30]</sup> Contrary to the sp<sup>2</sup>-hybridized C atom of [1]<sup>-</sup> with its  $\pi$ -donation into the  $\sigma^*$ (Si–Cl) bonds,<sup>[31]</sup> the anionic centers of [2]<sup>-</sup>/[3]<sup>-</sup> avoid hybridization and keep their lone pairs essentially localized in 3s/4s orbitals.<sup>[32]</sup>



 $\label{eq:Scheme 1. Synthesis of [Ph_4P][1], [Et_4N][2], and [Et_4N][3] in CH_2Cl_2 solutions. Solid-state structures of [Ph_4P][1], [Et_4N][2], and [Et_4N][3] (shown as ball-and-stick models; for ORTEP plots, see the ESI). \\$ 







**Scheme 2.** Adduct formation of  $[1]^-[3]^-$  with GaCl<sub>3</sub> (rt, CH<sub>2</sub>Cl<sub>2</sub>). Solid-state structures of [Ph<sub>4</sub>P][1·GaCl<sub>3</sub>], [*n*Bu<sub>4</sub>N][2·GaCl<sub>3</sub>].0.5 SiCl<sub>4</sub>, and [Ph<sub>4</sub>P][3·GaCl<sub>3</sub>] (shown as ball-and-stick models; for ORTEP plots, see the ESI; [Ph<sub>4</sub>P]<sup>+</sup>[*n*Bu<sub>4</sub>N]<sup>+</sup> cations and co-crystallized SiCl<sub>4</sub> molecules are omitted for clarity).

It is known that [1]<sup>-</sup> and [2]<sup>-</sup> accept protons to afford H[1] and H[2].<sup>[18,19]</sup> We now disclose that they also react with the group III Lewis acids  $E'Cl_3$  (E' = B, AI, Ga). Of those, only  $GaCl_3$  (1 equiv) gave adducts with all three anions that were sufficiently stable and well-ordered in the solid state to allow X-ray crystallography  $([Ph_4P][\mathbf{1}\cdot GaCl_3], [nBu_4N][\mathbf{2}\cdot GaCl_3], [Ph_4P][\mathbf{3}\cdot GaCl_3]; Scheme$ 2).<sup>[33]</sup> We observe fully pyramidalized GaCl<sub>3</sub> moieties, indicating strong donor-acceptor interactions (CI-Ga-CI = 107.5(1)° -110.8(3)°). Also the [1]<sup>-</sup> moiety is no longer planar (av. Si-C-Si = 110.9°), because the lone pair is now localized between the C and Ga atoms. In contrast, the Si-Si-Si and Si-Ge-Si angles in [2·GaCl<sub>3</sub>]<sup>-</sup> (av. 106.0°) and [3·GaCl<sub>3</sub>]<sup>-</sup> (av. 106.1°) are wider than those of the free Lewis bases [2]<sup>-</sup> (av. 96.7°) and [3]<sup>-</sup> (av. 95.2°) and approach the value of the ideal tetrahedral angle (109.5°; cf. Bent's rule<sup>[34]</sup>).<sup>[27]</sup> The C-Ga, Si-Ga, and Ge-Ga bond lengths amount to 2.094(9) Å,[35] av. 2.422 Å,[36] and 2.460(4) Å, respectively. The first value is larger by 0.09 Å than that of the corresponding bond in  $[Li(thf)_2][(PhMe_2Si)_3C\cdot GaCl_3]$  (2.00(1) Å),[37] which contains a more Lewis basic methanide donor. The length of the dative Si-Ga bond in [2·GaCl3] compares well to that of the covalent Si-Ga bond in the sterically crowded dimer (tBu<sub>3</sub>Si-GaCl<sub>2</sub>)<sub>2</sub> (av. 2.413 Å).<sup>[36,38]</sup> Suitable systems for comparison with  $[\mathbf{3} \cdot GaCl_3]^-$  are lacking.<sup>[27]</sup>

Differences in the bond orders between the C–Si bond and the (Si/Ge)–Si bonds of [1]<sup>-</sup>–[3]<sup>-</sup> also become evident from the SiCl<sub>3</sub> NMR resonances: [1]<sup>-</sup> resonates at  $\delta$ <sup>(29</sup>Si) = –10.9 ppm, whereas the signals of [2]<sup>-</sup> and [3]<sup>-</sup> are detected at lower field

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strengths with almost identical chemical shift values of  $\delta$ <sup>(29</sup>Si) = 29.5 and 29.7 ppm, respectively. In the case of  $[1 \cdot \text{GaCl}_3]^- \text{ vs.}$ [1]<sup>-</sup>, the SiCl<sub>3</sub> resonance undergoes a downfield shift to  $\delta$ <sup>(29</sup>Si) = -3.4 ppm (*cf.* H[1]: -2.6 ppm).<sup>[18]</sup> The resonances of the other two adducts experience almost identical upfield shifts to  $\delta$ <sup>(29</sup>Si) = 11.9 ppm ([2 \cdot \text{GaCl}\_3]^-; *cf.* H[2]: 5.5 ppm)<sup>[19]</sup> and 11.3 ppm ([3 \cdot \text{GaCl}\_3]^-). The smaller spread in the chemical shift values of the three adducts compared to the free anions reflects a smaller difference in the bond orders between the respective central atom and its SiCl<sub>3</sub> substituents.

Compounds of the type  $[2 \cdot GaCl_3]^-$  and  $[3 \cdot GaCl_3]^-$  are promising precursors for the fabrication of Ga-doped Si and Si/Ge layers. However, the gas-phase deposition of such materials requires uncharged, volatile species. Taking  $[3 \cdot GaCl_3]^-$  as a representative example, we tested whether one Cl<sup>-</sup> ion is abstracted by excess GaCl\_3. Indeed, the neutral dimer ((Cl\_3Si)\_3Ge-GaCl\_2)\_2, (4)\_2, forms in a one-pot reaction from a mixture of [Et\_4N][3] and 2 equiv of GaCl\_3 in CH\_2Cl\_2. After extraction with *n*-hexane, (4)<sub>2</sub> crystallized from the extract in 40% yield. The centrosymmetric solid-state structure features a Ga\_2Cl\_2 ring with tetracoordinate Ga atoms (Scheme 3).



Scheme 3. Cl<sup>-</sup> abstraction reactions of [3]<sup>-</sup> with GaCl<sub>3</sub> and AlCl<sub>3</sub> (rt, CH<sub>2</sub>Cl<sub>2</sub>) and hydrogenation reaction of 5 to give 5<sup>H</sup>. Solid-state structures of the neutral products (4)<sub>2</sub> and 5 (shown as ball-and-stick models; for ORTEP plots, see the ESI).

The covalent Ge–Ga bond (2.4071(6) Å) is shorter by 0.053 Å than the related dative bond in  $[3 \cdot GaCl_3]^-$  and the Si–Ge–Si bond angle (av. 109.9°) is expanded a little further compared to the situation in the adduct. The <sup>29</sup>Si NMR signal of the dimer appears at 7.8 ppm, and is even more upfield-shifted than the signal of  $[3 \cdot GaCl_3]^-$ .

Different from the cases of  $BCl_3^{[33]}$  and  $GaCl_3$ , no adducts of  $[1]^--[3]^-$  with the stronger Lewis acid AlCl<sub>3</sub> could be isolated so far. The <sup>29</sup>Si NMR spectrum of equimolar mixtures of AlCl<sub>3</sub> and  $[nBu_4N][2]$  in CH<sub>2</sub>Cl<sub>2</sub> rather showed two resonances assignable to (Cl<sub>3</sub>Si)<sub>4</sub>Si (3.5, -80.9 ppm),<sup>[11]</sup> which was obtained in 36%

yield. The analogous experiment repeated with [Ph<sub>4</sub>P][**3**] led to <sup>29</sup>Si NMR signals at 14.2 and 3.8 ppm. The first signal possesses a similar chemical shift value as the corresponding resonances of [**3**·BCl<sub>3</sub>]<sup>-</sup> and [**3**·GaCl<sub>3</sub>]<sup>-</sup> and is thus tentatively assigned to a Ge $\rightarrow$ Al adduct [**3**·AlCl<sub>3</sub>]<sup>-</sup>. The signal at 3.8 ppm arises from the previously unknown compound (Cl<sub>3</sub>Si)<sub>4</sub>Ge (**5**). Removal of all volatiles under reduced pressure and extraction of the solid residue with *n*-hexane ultimately gave single crystals of (Cl<sub>3</sub>Si)<sub>4</sub>Ge in 24% yield (unoptimized; Scheme 3). Compound **5** possesses a tetrahedral structure with an average Ge–Si bond length of 2.366 Å<sup>[36]</sup> (*cf.* (Me<sub>3</sub>Si)<sub>4</sub>Ge: av. Ge–Si = 2.371 Å<sup>[39]</sup>).

With regard to the mechanism underlying the assembly of **5**, the following facts are important: (i) A conversion of the putative  $[\mathbf{3} \cdot \text{AlCl}_3]^-$  adduct to **5** was never observed, even at 50 °C (sealed NMR tube). It thus seems unlikely that  $[\mathbf{3} \cdot \text{AlCl}_3]^-$  plays a significant role for product formation. (ii)  $[\text{Ph}_4\text{P}][\text{AlCl}_4]$  was repeatedly isolated as byproduct of **5**, thereby indicating that AlCl<sub>3</sub> abstracts one  $[\text{Cl}]^-$  ion directly from  $[\mathbf{3}]^-$  to generate  $(\text{Cl}_3\text{Si})_2\text{Ge}=\text{SiCl}_2$ . (iii) The yield of **5** is not increased by added SiCl<sub>4</sub>, which rules out a mere "chlorosilylation" of the Ge=Si double bond. We rather envisage a more complex scenario involving oligomers of  $(\text{Cl}_3\text{Si})_2\text{Ge}=\text{SiCl}_2$  and their subsequent rearrangement to afford **5**. A propensity of the Ge atom to occupy the central position of Si/Ge *neo*-structures is obvious from the AlCl<sub>3</sub>-catalyzed rearrangement of (Me<sub>3</sub>Si)<sub>3</sub>Si(GeMe<sub>3</sub>) to give (Me<sub>3</sub>Si)<sub>4</sub>Ge.<sup>[40]</sup>

Quantitative CI/H exchange to furnish (H<sub>3</sub>Si)<sub>4</sub>Ge (5<sup>H</sup>; Scheme 3) occurred upon treatment of 5 with Li[AlH<sub>4</sub>] (<sup>1</sup>H and <sup>29</sup>Si NMR spectroscopy, GC/MS). The only alternative route to 5<sup>H</sup> available to-date uses finely dispersed Na metal together with pyrophoric and toxic SiH<sub>4</sub>/GeH<sub>4</sub> to produce silylgermanides NaGeH<sub>n</sub>(SiH<sub>3</sub>)<sub>3-n</sub> (n = 0-2; 4h, 100 °C). After silvlation with C<sub>4</sub>F<sub>9</sub>SO<sub>3</sub>SiH<sub>3</sub>, 5<sup>H</sup> was isolated from the resulting mixture  $GeH_n(SiH_3)_{4-n}$  (*n* = 0-2) by fractionating condensation and subsequent preparative gas chromatography.<sup>[2]</sup> Our new threestep process  $\text{GeCl}_4 \rightarrow [3]^- \rightarrow 5 \rightarrow 5^H$  is more practical than the previous protocol and thus represents a major advance toward the development of mixed oligotetrels.

In summary, we have disclosed a facile protocol for the synthesis of the germanide [(Cl<sub>3</sub>Si)<sub>3</sub>Ge]<sup>-</sup> ([3]<sup>-</sup>) and thereby extended the homologous series of trichlorosilylated tetrelides  $[(Cl_3Si)_3E]^-$  (E = C, Si, Ge;  $[1]^--[3]^-$ ). Contrary to a priori expectations, the anions readily form 1:1 adducts with BCl3 and GaCl<sub>3</sub>. The addition of 2 equiv of GaCl<sub>3</sub> to [3]<sup>-</sup> results in Cl<sup>-</sup>-ion abstraction from the primary product  $[\mathbf{3} \cdot GaCl_3]^-$  and generates the neutral dimer ((Cl<sub>3</sub>Si)<sub>3</sub>Ge-GaCl<sub>2</sub>)<sub>2</sub>, (4)<sub>2</sub>. Cl<sup>-</sup> abstraction (this time from an SiCl<sub>3</sub> substituent) is also key to the reactivity of AICl<sub>3</sub> toward [2]<sup>-</sup> and [3]<sup>-</sup>. Here, skeletal rearrangements afford the neo-pentatetrels (Cl<sub>3</sub>Si)<sub>4</sub>Si and (Cl<sub>3</sub>Si)<sub>4</sub>Ge (5), respectively. Compound 5 can quantitatively be transformed into its perhydrogenated congener 5<sup>H</sup>, a promising precursor for the deposition of Si/Ge-based thin films. As an outlook, we emphasize that [nBu<sub>4</sub>N][2] reacts with C<sub>2</sub>Cl<sub>6</sub> to give the ethylenedianion salt [nBu<sub>4</sub>N]<sub>2</sub>[(Cl<sub>3</sub>Si)<sub>2</sub>C-C(SiCl<sub>3</sub>)<sub>2</sub>].<sup>[18]</sup> The scope of this Si-C bond-forming reaction, which is conceptually similar to the use of [(Cl<sub>3</sub>Si)<sub>2</sub>P]<sup>-</sup> and chloroalkanes for the formation of P-C bonds,<sup>[23]</sup> will be explored in the future.

Competing interests: J.T., H.-W.-L. and M.W. are inventors on patent applications EP 17173940.2, EP 17173959.2, EP 18206148.1, and EP 18206150.7 submitted by Evonik Industries AG, which cover the synthesis and use of  $[3]^-$ ,  $[3\cdot GaCl_3]^-$ ,  $(4)_2$ , and 5.

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- [28] An independent sample, prepared from [*n*Bu<sub>4</sub>N][GeCl<sub>3</sub>] and SiCl<sub>4</sub> in CD<sub>2</sub>Cl<sub>2</sub>, showed exclusively the <sup>29</sup>Si NMR signal of SiCl<sub>4</sub>, even after prolonged storage and heating to 120 °C.
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### COMMUNICATION

#### Entry for the Table of Contents

#### COMMUNICATION



Julian Teichmann,<sup>[a]#</sup> Chantal Kunkel,<sup>[a]#</sup> Isabelle Georg,<sup>[a]</sup> Maximilian Moxter,<sup>[a]</sup> Tobias Santowski,<sup>[a]</sup> Michael Bolte,<sup>[a]</sup> Hans-Wolfram Lerner,<sup>[a]</sup> Stefan Bade,<sup>[b]</sup> Matthias Wagner<sup>\*[a]</sup>

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## Tris(trichlorosilyl)tetrelide Anions and a Comparative Study of Their Donor Qualities

**Cornerstone added:** The trichlorosilylated germanide  $[(Cl_3Si)_3Ge]^$ readily accessible from GeCl<sub>4</sub> and Si<sub>2</sub>Cl<sub>6</sub>/Cl<sup>-</sup>. All tetrelides  $[(Cl_3Si)_3E]^-$ .<sup>(r)</sup> = C, Si, Ge) were found surprisingly nucleophilic and form adducts vith BCl<sub>3</sub> and GaCl<sub>3</sub>. The unique  $(Cl_3Si)_4Ge$  was obtained through an Alc<sub>13</sub>induced rearrangement of  $[(Cl_3Si)_3Ge]^-$ .

- [a] [\*] M. Sc. J. Teichmann, M. Sc. C. Kunkel, M. Sc. I. Georg, Dr. M. Moxter, M. Sc.T Santowski, Dr. M. Bolte, Dr. H.-W. Lerner, Prof. Dr. M. Wagner Institut für Anorganische Chemie Goethe-Universität Frankfurt Max-von-Laue-Strasse 7, 60438 Frankfurt (Main) (Germany) E-mail: Matthias.Wagner@chemie.uni-frankfurt.de
- [b] Dr. S. Bade Evonik Resource Efficiency GmbH, Untere Kanalstraße 3, 79618 Rheinfelden, Germany
- # These authors contributed equally

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