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Dope it with germanium: selective access to functionalized Si_5Ge heterocycles

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Benedikt Köstler,[a] Hyunwoo Bae,[a] Jannik Gilmer,[a] Alexander Virovets,[a] Hans-Wolfram Lerner,[a] Philipp Albert,[b] Felipe Fantuzzi,[c] and Matthias Wagner*[a]

The Cl^- diadduct $[n\text{Bu}_4\text{N}]_2[\text{A}\cdot 2\text{Cl}]$ of the mixed cyclohexatetrelane $(SiCl_2)_5(GeMe_2)$, A, is accessible from Me_2GeCl_2, 6 eq. Si_2Cl_6, and 2 eq. $[n\text{Bu}_4\text{N}]Cl$ in one step (96%). Free, tenfold functionalized A can be released from the primary product by decomplexation with $AlCl_3$ (78%). Insight into the assembly mechanism of $[n\text{Bu}_4\text{N}]_2[\text{A}\cdot 2\text{Cl}]$ and the reactivity of A is provided.

Oligomers of the heavier group 14 elements are relatives of the alkanes. However, unlike the alkanes, their skeletal σ electrons are significantly delocalized along the oligomer backbones.[1] This σ delocalization is fundamentally interesting and may lead to potentially useful optoelectronic properties, especially in oligosilanes and –germanes.[2,3] Given this background, the synthesis and properties of homonuclear Si-[2,4] and Ge-containing[3,5–7] oligomers and polymers have been thoroughly studied. In stark contrast, structurally well-defined heteronuclear oligomers containing both Si and Ge atoms in their backbones have received much less attention, although the targeted doping of an oligosilane chain with more electronegative Ge atoms should provide an efficient means of tuning the oligomer's electronic structure (Allred-Rochow electronegativities:[8] Si = 1.74, Ge = 2.02). In addition, volatile Si_xGe_y species are promising single-source precursors for the deposition of mixed (hexagonal) Si_xGe_y alloys,[9–12] which not only have important applications in high-speed microelectronic devices,[13] but also possess potential as direct band-gap emitters, making them "an ideal material system in which to combine electronic and optoelectronic functionalities on a single chip".[14]

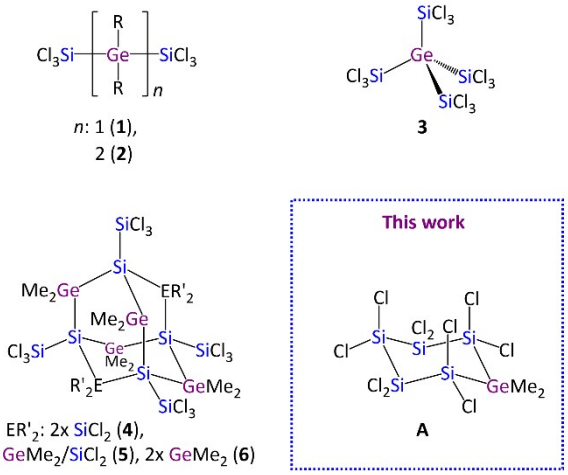

Figure 1. Selected examples of Si_xGe_y structural motifs realized by using the $Si_2Cl_6/[n\text{Bu}_4\text{N}]Cl$ silylation system and R_2GeCl_2 (**1**, **2**; R: *n*Bu, Ph), $GeCl_4$ (**3**) or Me_2GeCl_2 (**4**, **5**, **6**, **A**).

Single-source Si_xGe_y precursors not only allow better control over the composition of the deposited semiconductor film, but also require the adjustment of only a single kinetic parameter, i.e., the flow rate of the precursor at the specified temperature.[13] Despite these obvious advantages, suitable heterooligotetrelanes combining Si and Ge atoms are rare, mainly because of a lack of universally applicable synthesis protocols. Since the established Wurtz-type coupling and nucleophilic substitution reactions possess a very limited functional group tolerance, most of the known Si_xGe_y species carry organyl substituents at their peripheries.[15] For several years, our group has been developing the $Si_2Cl_6/[n\text{Bu}_4\text{N}]Cl$ silylation system[16] for the synthesis of novel organosilanes[17] and oligosilanes.[18–20] Recently, we have also adapted it successfully for the preparation of mixed chlorosilane-organogermane oligomers, such as the tri- (**1**),[12] tetra- (**2**),[12] and *neo*-pentatetrelanes (**3**),[21] or the heteroadamantanes **4**–**6** (Figure 1).[22]

[a] Institute for Inorganic and Analytical Chemistry, Goethe University Frankfurt, Max-von-Laue-Straße 7, 60438 Frankfurt am Main, Germany. E-mail: matthias.wagner@chemie.uni-frankfurt.de
[b] Smart Materials, Evonik Operations GmbH, Untere Kanalstraße 3, 79618 Rheinfelden, Germany.
[c] School of Chemistry and Forensic Science, University of Kent, Park Wood Road, Canterbury CT2 7NH, UK.

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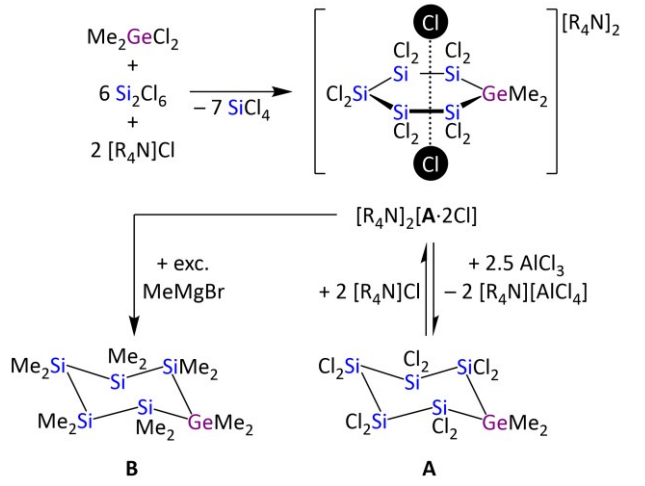
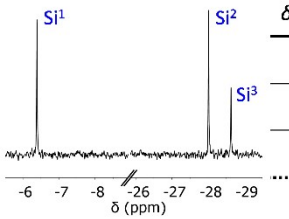
Herein, we present the high-yield synthesis of the Lewis-acidic six-membered heterocycle $(SiCl_2)_5(GeMe_2)$, **A** (Figure 1), its Cl^- diadduct $[n\mathrm{Bu_4N}]_2[\mathbf{A}\cdot 2\mathrm{Cl}]$, and its permethylated derivative $(SiMe_2)_5(GeMe_2)$, **B** (Scheme 1). Due to its inert and NMR-active Me groups, **B** is particularly well suited to conclusively confirm the proposed Si_5Ge scaffold. Unlike **B** and most other oligotetrelanes, **A** still possesses ten functionalizable Si–Cl bonds; a first reactivity screening showed interrelations between the chain-like species **1** and **2** (R = Me), the monocycle **A**, and the polycyclic heteroadamantanes **4**, **5**, and **6**.

The primary product $[n\mathrm{Bu_4N}]_2[\mathbf{A}\cdot 2\mathrm{Cl}]$ was synthesized from 6 eq. Si_2Cl_6, 2 eq. $[n\mathrm{Bu_4N}]Cl$, and 1 eq. Me_2GeCl_2 at room temperature in CH_2Cl_2 (Scheme 1). After 3 d, all volatiles were evaporated and the residue was washed with *n*-hexane to afford $[n\mathrm{Bu_4N}]_2[\mathbf{A}\cdot 2\mathrm{Cl}]$ in 96% yield. To rationalize the applied stoichiometry by formal electron bookkeeping, we assume that Cl^- ions induce the disproportionation of Si_2Cl_6 to $SiCl_4$ and $SiCl_2$.[17,23] Of the latter, 5 eq. are incorporated into the Si_5Ge ring, while the 6th eq. serves to reduce Me_2GeCl_2 to the Me_2Ge stage. Similar to $(SiCl_2)_6$,[24] $(SiCl_2)_5(GeMe_2)$ is apparently a strong Lewis acid that traps 2 Cl^- ions, so stoichiometric amounts of $[n\mathrm{Bu_4N}]Cl$ are required. Permethylation of $[n\mathrm{Bu_4N}]_2[\mathbf{A}\cdot 2\mathrm{Cl}]$ with MeMgBr in Et_2O reduces the Lewis acidity of the resulting $(SiMe_2)_5(GeMe_2)$, **B** (72% yield), to the point where it no longer binds Cl^- ions. Alternatively, decomplexation of $[n\mathrm{Bu_4N}]_2[\mathbf{A}\cdot 2\mathrm{Cl}]$ with $AlCl_3$ in C_6H_6 at room temperature can be achieved. Free **A** was isolated by extraction into *n*-hexane (78% yield).

The ^{1}H NMR spectrum[25] of $[n\mathrm{Bu_4N}]_2[\mathbf{A}\cdot 2\mathrm{Cl}]$ shows the counter-cation signals and a singlet at 0.53 ppm for the $GeMe_2$ moiety. In the spectrum of **B**, the $[n\mathrm{Bu_4N}]^+$ signals have disappeared, the $GeMe_2$ resonance shifts to 0.21 ppm (6H), and three more singlets, assignable to $SiMe_2$ groups, appear at 0.18 (12H), 0.14 (12H), and 0.13 (6H) ppm. Free **A** gives rise to a $GeMe_2$ singlet at 0.84 ppm. Each of the ^{29}Si{^{1}H} NMR spectra of $[n\mathrm{Bu_4N}]_2[\mathbf{A}\cdot 2\mathrm{Cl}]$, **A**, and **B** is characterized by three signals with approximate integral ratios of 2:2:1 (Figure 2). In all three cases, the signal with the lowest intensity is assigned to the unique Si^3 atom; only the signals attributed to Si^1 atoms show cross peaks with the $GeMe_2$ resonances in the ^{29}Si/^{1}H HMBC experiments (Figures S8, S12, and S16). Likely due to the higher electronegativity of Ge relative to Si, the Si^1 nuclei consistently are the most deshielded ones (Figure 2). In line with the smaller coordination numbers of c.n. = 4, all ^{29}Si resonances of **A** are shifted downfield by >20 ppm relative to those of $[\mathbf{A}\cdot 2\mathrm{Cl}]^{2-}$. Compared to **A**, Cl/Me exchange in **B** results in pronounced upfield shifts of >40 ppm (Figure 2). These shielding trends in the Si_5Ge heterocycles match those in comparable Si_6 analogues.[18,24,26]



Scheme 1. Synthesis of the mixed Si_5Ge heterocycle **A** as its Cl^- diadduct $[R_4N]_2[\mathbf{A}\cdot 2\mathrm{Cl}]$ (96%; CH_2Cl_2, 3 d). Reversible release of **A** by decomplexation with $AlCl_3$ (78%; C_6H_6, 1 d). Synthesis of **B** by tenfold methylation of $[R_4N]_2[\mathbf{A}\cdot 2\mathrm{Cl}]$ using exc. MeMgBr (72%; Et_2O, 1 d). R = *n*Bu.



$\delta(^{29}Si)$	$[\mathbf{A}\cdot 2\mathrm{Cl}]^{2-}$	**A**	**B**
Si^1	–6.4	15.9	–34.8
Si^2	–28.0	–0.4	–41.6
Si^3	–28.6	–0.6	–42.3
cf.	–21.7[a]	–3.0[b]	–41.7[c]

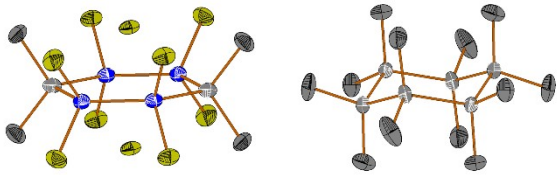


Figure 2. Top: ^{29}Si{^{1}H} NMR spectrum of $[n\mathrm{Bu_4N}]_2[\mathbf{A}\cdot 2\mathrm{Cl}]$ in CD_2Cl_2 (left; Si^1, Si^2, and Si^3 are the Si atoms in α, β, and γ positions relative to the Ge atom, respectively). ^{29}Si chemical shift values of $[n\mathrm{Bu_4N}]_2[\mathbf{A}\cdot 2\mathrm{Cl}]$, **A**, and **B** (right); reference compounds: $[n\mathrm{Bu_4N}]_2[(SiCl_2)_6\cdot 2\mathrm{Cl}]$ (*a*),[18] $(SiCl_2)_6$ (*b*),[26] $(SiMe_2)_6$ (*c*).[24] Bottom: X-ray crystallographically determined solid-state structures of $[n\mathrm{Bu_4N}]_2[\mathbf{A}\cdot 2\mathrm{Cl}]$ (left) and **A** (right). Counter cations and H atoms are omitted for clarity. In $[\mathbf{A}\cdot 2\mathrm{Cl}]^{2-}$, $GeMe_2$ is equally disordered over two sites; in **A**, $GeMe_2$ is disordered to varying degrees over all sites. Si: blue, Cl: yellow-green, disordered $SiCl_2/GeMe_2$: gray.

Single crystals of $[n\mathrm{Bu_4N}]_2[\mathbf{A}\cdot 2\mathrm{Cl}]$ were grown from *n*-hexane/CH_2Cl_2. X-ray analysis revealed an inverse sandwich complex with 2 Cl^- ions residing above and below a planarized Si_5Ge ring (Figure 2). The complex $[\mathbf{A}\cdot 2\mathrm{Cl}]^{2-}$ has an inversion center with mutual disorder of $GeMe_2$ and the $SiCl_2$ group opposite it. The intramolecular distance between the two coordinating Cl^- ions amounts to Cl···Cl = 3.9083(9) Å, which is 0.073 Å longer than in the case of $[n\mathrm{Bu_4N}]_2[(SiCl_2)_6\cdot 2\mathrm{Cl}]$ (3.8357(6) Å).[27] We therefore conclude that the energy gained by Lewis pairing with **A** is somewhat smaller than in the case of the $(SiCl_2)_6$ ring with 12 (instead of 10) electron-accepting Si–Cl σ* orbitals, but still large enough to flatten the Si_5Ge ring by suppressing the pseudo-Jahn-Teller effect.[28] Compound **A** crystallizes from CH_2Cl_2 as a solid solution with 8 mol% of $(SiCl_2)_6$ (according to the unconstrained refinement of the corresponding site occupancy factors). **A** adopts a puckered chair conformation in the solid state and lies on an inversion center (Figure 2); due to disorder, all three crystallographically unique $SiCl_2$ positions are shared to varying degrees with $GeMe_2$.[23] Permethylated **B** is isostructural to **A** and suffers from comparable $GeMe_2/SiMe_2$ disorder (Figure S29). Nevertheless, the six-membered ring motif is undoubtedly still present after tenfold nucleophilic Cl/Me substitution.

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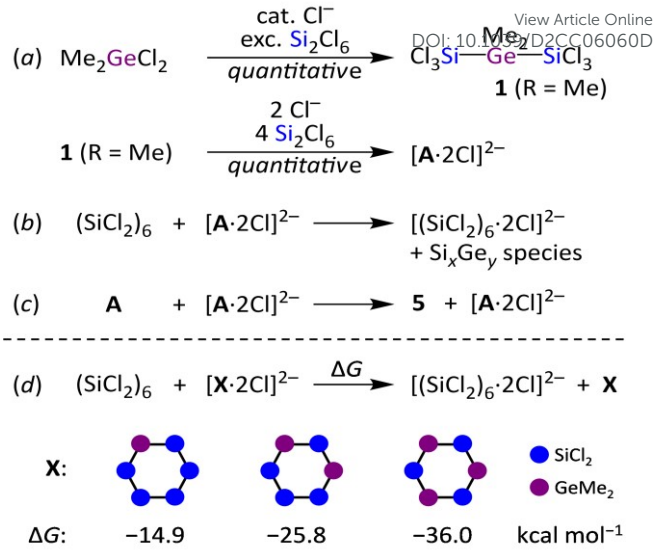
At this point, the following questions arise: Why is **A** a six-membered ring and what is the reason for the selective incorporation of exactly one $GeMe_2$ group? Cl^--induced heterolysis of Si_2Cl_6 leads to $SiCl_4$ and the primary reactive species $[SiCl_3]^-$.[18,29] In the present case, $[SiCl_3]^-$ can target either Si_2Cl_6 or Me_2GeCl_2, with the attack on the dichlorogermane apparently being preferred: Analogous to the synthesis of **1** (R = Ph, *n*Bu; Figure 1),[12] we converted Me_2GeCl_2 quantitatively and instantaneously to $Cl_3Si–Me_2Ge–SiCl_3$ (**1**, R = Me) by adding exc. Si_2Cl_6 and cat. $[nBu_4N]Cl$.[23,30] In a quantitative yet much slower follow-up reaction, $[nBu_4N]_2[\mathbf{A}\cdot 2Cl]$ is subsequently accessible from $Cl_3Si–Me_2Ge–SiCl_3$, 4 eq. Si_2Cl_6, and 2 eq. $[nBu_4N]Cl$ (Scheme 2a).[23] NMR monitoring of this second step showed the appearance and disappearance of several (unknown) intermediates over the course of 3 d, eventually leading solely to $[nBu_4N]_2[\mathbf{A}\cdot 2Cl]$. Based on these overall findings, we propose that also in the one-pot synthesis of $[nBu_4N]_2[\mathbf{A}\cdot 2Cl]$ (Scheme 1), $Cl_3Si–Me_2Ge–SiCl_3$ is formed as a key intermediate. Its silyl substituents then grow by further reaction with $[SiCl_3]^-$ until the oligotetrelane chain becomes sufficiently long to cyclize via established ring-closing mechanisms.[18,31] The early incorporation of $GeMe_2$ into the $Cl_3Si–Me_2Ge–SiCl_3$ tritetrelane is likely essential for $GeMe_2$ to be found in the final $[\mathbf{A}\cdot 2Cl]^{2-}$ product as well. Even if different ring sizes were initially formed, Cl^--catalyzed rearrangement equilibria should provide some "self-healing effect", eventually establishing the thermodynamically most favorable cyclohexatetrelane diadduct (note that $(SiCl_2)_5$ undergoes ring expansion to $(SiCl_2)_6$ diadducts in the presence of 2 eq. Cl^-).[27] The important role of Cl^--diadduct stability could finally explain why not more than one $GeMe_2$ group is incorporated into the heterocycle: Any exchange of $SiCl_2$ for $GeMe_2$ leads to the loss of strongly electron-accepting Si–Cl σ* orbitals, which should decrease the Lewis acidity of the ring and thereby reduce the thermodynamic thrust toward the formation of a corresponding inverse sandwich complex. To validate this assumption, we performed a competition experiment between $[nBu_4N]_2[\mathbf{A}\cdot 2Cl]$ and free $(SiCl_2)_6$ in CD_2Cl_2 and detected the intense ^{29}Si resonance of the newly formed diadduct $[(SiCl_2)_6\cdot 2Cl]^{2-}$ (Scheme 2b). Vice versa, $[(SiCl_2)_6\cdot 2Cl]^{2-}$ persists in a mixture with free **A**. Quantum-chemical calculations also confirm that the transfer of two Cl^- ions from $[\mathbf{A}\cdot 2Cl]^{2-}$ to $(SiCl_2)_6$ is exergonic by –14.9 kcal mol^{-1} and becomes even more exergonic upon going to the higher doped 1,3- and 1,3,5-$GeMe_2$ derivatives (Scheme 2d).[23] In other words, the thermodynamic stability of the respective diadducts indeed decreases upon stepwise incorporation of $GeMe_2$.

One remarkable fact, however, is still puzzling: Cl_3Si-substituted derivatives of **A** do not seem to be generated, although oligochlorosilanes have a pronounced tendency to build neo-substructures with formal Si(0)/Si(III) centers. For example, the reaction between 6 eq. Si_2Cl_6 and 2 eq. $[nBu_4N]Cl$ furnishes substantial amounts of $[(SiCl_2)_5(Si(SiCl_3)_2)\cdot 2Cl]^{2-}$ and its positional isomers. Conversion of this product mixture to $[(SiCl_2)_6\cdot 2Cl]^{2-}$ requires additional $SiCl_2$ extrusion by thermolysis at 85 °C in CH_2Cl_2.[18] Although the question of why incorporated $GeMe_2$ suppresses the formation of branched final products



Scheme 2. (*a*) Synthesis of $Cl_3Si–Me_2Ge–SiCl_3$ and its subsequent conversion to the Cl^- diadduct of $(SiCl_2)_5(GeMe_2)$, $[\mathbf{A}\cdot 2Cl]^{2-}$. (*b*) Abstraction of Cl^- ions from $[\mathbf{A}\cdot 2Cl]^{2-}$ by $(SiCl_2)_6$; the released **A** is not stable under these conditions, but rearranges mainly to **1**, **2** (R = Me),[23] and **5**. (*c*) Conversion of **A** to the heteroadamantane **5** in the presence of 1 eq. $[\mathbf{A}\cdot 2Cl]^{2-}$. Counter cations: $[nBu_4N]^+$. (*d*) Theoretical study on the thermodynamics of the competition reaction between $(SiCl_2)_6$ and its 1-, 1,3-, and 1,3,5-$GeMe_2$-doped congeners; the tendency to form Cl^- diadducts decreases with increasing $GeMe_2$ content. SMD(DCM)/MN15/6-311++G**//SMD(DCM)/MN15/6-31+G*.

already at room temperature remains to be explored, we take this observation as an indicator of how significantly the incorporation of $GeMe_2$ can perturb the electronic structure of cyclooligosilanes (a second indicator being the influence of the $GeMe_2$ dopant on Lewis acidity).

Having achieved a basic understanding of the assembly mechanism of **A**, we finally attempted to contextualize this monocyclic compound with the open-chain molecule **1** (R = Me) and the polycyclic heteroadamantanes **4**–**6**. In a series of NMR-scale experiments (CD_2Cl_2, room temperature), **A** was treated with varying amounts of Cl^- ions: (i) Addition of 2 eq. $[nBu_4N]Cl$ takes **A** back to the $[\mathbf{A}\cdot 2Cl]^{2-}$ diadduct state, thereby demonstrating that decomplexation is fully reversible (Scheme 1). (ii) Addition of 1 eq. $[nBu_4N]Cl$ to **A** formally leads to $[nBu_4N][\mathbf{A}\cdot Cl]$. The same stoichiometry can be obtained by mixing equimolar amounts of **A** and $[nBu_4N]_2[\mathbf{A}\cdot 2Cl]$, which is more practical and therefore the way we performed the experiment. After 1 d, the solution contained heteroadamantane **5** and $[\mathbf{A}\cdot 2Cl]^{2-}$ as only $GeMe_2$-containing species (Scheme 2c). To a good approximation, the proton integral values indicated a ratio of **5** to $[\mathbf{A}\cdot 2Cl]^{2-}$ = 1:5. (iii) Decreasing the amount of added $[nBu_4N]Cl$ further to 0.1 eq., yielded a complex product mixture that showed the characteristic ^1H NMR signal of **1** (R = Me) next to a broad, undiagnostic hump. Notably, even after six weeks, the reaction had not proceeded further to the stage of heteroadamantanes, although pure samples of **1** (R = Me) in the presence of 0.1 eq. $[nBu_4N]Cl$ give **5** and **2** (R = Me).[23]

In summary, we succeeded in the high-yield synthesis of the heteronuclear cyclohexatetrelane $(SiCl_2)_5(GeMe_2)$, **A**, from Me_2GeCl_2, 6 eq. Si_2Cl_6, and 2 eq. $[nBu_4N]Cl$. The primary product is the Cl^- diadduct $[nBu_4N]_2[\mathbf{A}\cdot 2Cl]$; here, the Cl^- ions play a

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decisive role in templating the six-membered ring and protecting it from further rearrangement or degradation. Key factors for the selective incorporation of precisely one $GeMe_2$ group into $[\mathbf{A}\cdot 2Cl]^{2-}$ have been identified. Decomplexation of $[n Bu_4N]_2[\mathbf{A}\cdot 2Cl]$ was achieved by means of $AlCl_3$ (to give free **A**). Treatment with MeMgBr gave free $(SiMe_2)_5(GeMe_2)$, **B**. This successful tenfold methylation reaction makes us optimistic that other nucleophilic late-stage derivatizations will lead to a broad scope of other mixed cyclohexatetrelanes in the future. Of particular interest is $(SiH_2)_5(GeMe_2)$, a promising single-source precursor for the deposition of Ge-doped silicon semiconductor materials.

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Conflicts of interest

B.K., H.-W.L., and M.W. are inventors on patent application WO2021244705A1 submitted by the Goethe University Frankfurt, which covers the synthesis and use of **1** and **2** (R = Me).

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31 In a second conceivable scenario, Si_2Cl_6 remaining after the formation of $Cl_3Si–Me_2Ge–SiCl_3$ could undergo the well-known Cl^--induced conversion to $[(SiCl_2)_6\cdot 2Cl]^-$ (Ref[18]), which then reacts with $Cl_3Si–Me_2Ge–SiCl_3$ to give $[\mathbf{A}\cdot 2Cl]^-$. However, this alternative pathway can be ruled out since we found that a 1:1-mixture of $[(SiCl_2)_6\cdot 2Cl]^-$ and $Cl_3Si–Me_2Ge–SiCl_3$ in CD_2Cl_2 remains unchanged for several days (NMR-spectroscopic control; cf. the Supporting Information).