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Selective One-Pot Syntheses of Mixed Silicon-Germanium Heteroadamantane Clusters

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Abstract: Si_xGe_y alloys are emerging materials for modern semiconductor technology. Well-defined model systems of the bulk structures aid in understanding their intrinsic characteristics. Three such model clusters have now been realized in the form of the Si_xGe_y heteroadamantanes **[0]**, **[1]**, and **[2]** through selective one-pot syntheses starting from Me_2GeCl_2, Si_2Cl_6, and [$n$$Bu_4$N]Cl. Compound **[0]** contains six $GeMe_2$ and four $SiSiCl_3$ vertices, whereas one and two of the $GeMe_2$ groups are replaced by $SiCl_2$ moieties in compounds **[1]** and **[2]**, respectively. Chloride-ion-mediated rearrangement quantitatively converts **[2]** into **[1]** at room temperature and finally into **[0]** at 60 °C, which is not only remarkable in view of the rigidity of these cage structures but also sheds light on the assembly mechanism.

Introduction

Bulk silicon is the materials basis of semiconductor technology. For the deposition of silicon thin films, oligosilanes have been intensively studied and used as volatile precursors.[1] Marschner's sila-adamantane **[A]** is a substructure of bulk cubic silicon and a particularly fine example of a large, monodisperse oligosilane (Figure 1a).[2] The incorporation of Ge atoms into bulk silicon can lead to Si_xGe_y alloys with unprecedented optoelectronic properties of exceptional promise.[3] To fully exploit the potential of this class of materials, deeper insight into fundamentally important phenomena, such as σ-electron conjugation,[4] would be desirable and can best be gained by studying well-defined molecular model systems. Apart from Kouvetakis' perhydrogenated single-source Si_xGe_y precursors, which have been successfully used for the CVD of corresponding mixed semiconductors,[5,6] only few examples of complex (polycyclic) Si_xGe_y oligomers are known to-date, making a systematic assessment of their properties difficult.[7–14] In this regard, the *neo*-Si_3Ge_2 structure **[B]** (Figure 1b) is noteworthy, which was obtained by the du Mont group from Me_3GeCl and $HSiCl_3/NEt_3$ (Benkeser reagent).[15,16] The analogous reaction with Me_2GeCl_2 led to the double silylation product $Me_2Ge(SiCl_3)_2$. Recently, our group succeeded in synthesizing germanide **[C]**$^-$ from $GeCl_4$ and the alternative trichlorosilylation system Si_2Cl_6/Cl^-,[17–20] which disproportionates into $SiCl_4$ and the actual reactive intermediate $[SiCl_3]^-$; treatment of **[C]**$^-$ with $AlCl_3$ gave the *neo*-Si_4Ge species **[D]**.[21]

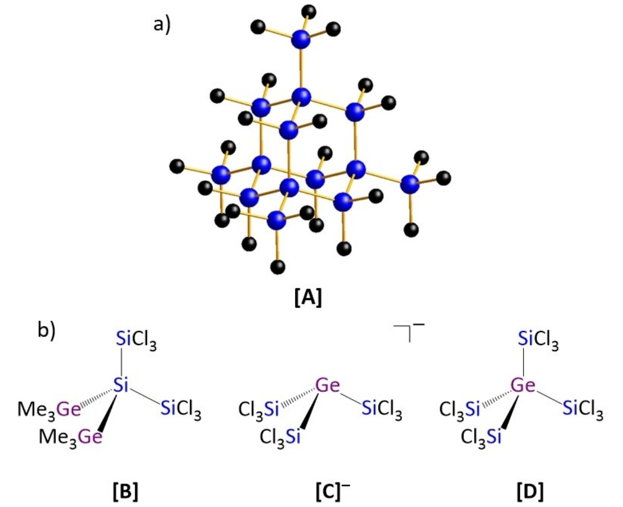

Figure 1. a) Solid-state structure of Marschner's sila-adamantane **[A]** (Si: blue, CH_3: black). b) Schematic representations of the Si_xGe_y oligomers **[B]**, **[C]**$^-$, and **[D]**.

Herein, we describe reactions of Me_2GeCl_2 with the Si_2Cl_6/Cl^- system and show that, in striking contrast to du Mont's results with the Benkeser reagent, three structurally defined Si_xGe_y heteroadamantanes, **[0]**, **[1]**, and **[2]**, become accessible in good yields, which can be regarded as long-sought model systems of Si_xGe_y alloys (see Figure 2 for the molecular structures and an explanation of the numbering scheme).

Results and Discussion

Syntheses and reactivities of the heteroadamantanes [0], [1], and [2]

All reactions were carried out in CH_2Cl_2 or CD_2Cl_2. Our initial experiments with Me_2GeCl_2, Si_2Cl_6, and cat. [$n$$Bu_4$N]Cl using the

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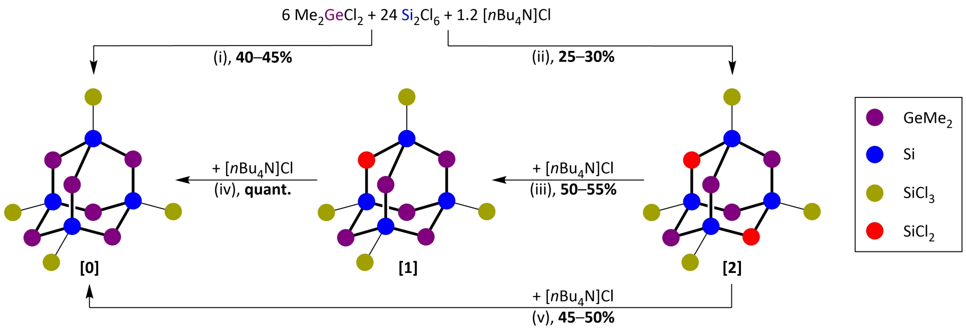

Figure 2. Syntheses of the Si_xGe_y heteroadamantanes **[0]**, **[1]**, and **[2]** from Me_2GeCl_2 and the Si_2Cl_6/Cl^- system in CH_2Cl_2. Note that the reactions are catalytic in [$n$$Bu_4$N]Cl; in practice ca. 1 equiv. was used. The compound numbers [X] refer to the number, X, of $SiCl_2$ vertices incorporated into the cluster core instead of $GeMe_2$ vertices (ideal number of the latter: 6 in **[0]**). (i) 1: room temperature, 4 h; 2: removal of $SiCl_4$; 3: 60 °C, 6 d. (ii) room temperature, 13 d, in-situ crystallization from an unstirred mixture. (iii) room temperature, 6 d, with stirring. (iv) 60 °C, 2 d. (v) 60 °C, 4.5 d.

theoretically required stoichiometry for the formation of the Si_8Ge_6 heteroadamantane **[0]** (i.e., Me_2GeCl_2/Si_2Cl_6 6:16; see Figure S1 in the Supporting Information for the atom and electron count) gave the target compound in 20% yield. Further optimization of the reaction conditions led to the following protocol for the synthesis of **[0]**: in a one-pot procedure, a Me_2GeCl_2/Si_2Cl_6 6:24 mixture was first stored at room temperature for 4 h, evaporated to remove the released $SiCl_4$, re-dissolved, and heated to 60 °C for 6 d.

Heteroadamantane **[0]** then crystallized from the solution and was isolated in 40–45% yield (see below for a rationale of the modified stoichiometry). Single crystals of a second heteroadamantane, the $Si_{10}Ge_4$ species **[2]**, grew and were isolated after 13 d in 25–30% yield, when a 6:24 mixture of Me_2GeCl_2/Si_2Cl_6 was stored at room temperature without stirring. Compared to **[0]**, in **[2]** two $GeMe_2$ vertices at opposite positions of the cluster are replaced by $SiCl_2$ groups. A further increase in the crystallization time caused an increasing contamination of the crystal crop by a third heteroadamantane, the Si_9Ge_5 derivative **[1]**, in which only one of the six $GeMe_2$ vertices of **[0]** is exchanged for $SiCl_2$. Marschner prepared sila-adamantane **[A]**, the close molecular relative to **[0]**, **[1]**, and **[2]**, in a fundamentally different way by a reaction inspired by Schleyer's adamantane synthesis (8 steps from $SiCl_4$ and Me_3SiLi, 17% overall yield).[2,9]

How are the formations of **[0]**, **[1]**, and **[2]** interrelated? While pure **[2]** is stable over weeks in CH_2Cl_2 at room temperature, NMR monitoring proved that a continuous conversion **[2]**→**[1]**→**[0]** is possible in the presence of [$n$$Bu_4$N]Cl (quantitative with respect to $GeMe_2$ fragments; Figure S2): Reaction **[2]**→**[1]** already takes place at room temperature, whereas reaction **[1]**→**[0]** requires prolonged heating at 60 °C. This temperature dependence allows the selective synthesis of **[1]** from **[2]** in 50–55% yield after workup (Figure 2). Isolation of **[2]** is thus only possible if **[2]** is allowed to escape rearrangement by crystallization. Upon going from **[2]** to **[1]** and **[0]**, dichlorosilylenes ($SiCl_2$) are extruded from the cluster cores and dimethylgermylenes ($GeMe_2$) are incorporated. Formal cyclocondensation of 6 $SiCl_2$ moieties would give perchlorinated cyclohexasilane, which was indeed detected by ^{29}Si NMR spectroscopy in the form of [*cyclo*-$Si_6Cl_{12}\cdot 2Cl]^{2-}$.[22–26] The $GeMe_2$ fragments, in turn, must originate from cannibalized heteroadamantanes **[2]** and **[1]**.

The following conclusions can be drawn: i) the assembly of **[0]** most likely involves Si-enriched **[2]** as a key intermediate, which explains why the best yields of **[0]** are obtained when the starting materials are combined in the stoichiometry theoretically required for the synthesis of **[2]** (Figure S1). ii) Since the sequence **[2]**→**[1]**→**[0]** cannot be reversed by heating of **[0]** with [$n$$Bu_4$N]Cl and $SiCl_4$ or Si_2Cl_6, it apparently represents the downhill pathway to the thermodynamically most favorable species. iii) The reaction critically depends on certain properties peculiar to Ge, because the use of Me_2SiCl_2 instead of Me_2GeCl_2 does not lead to the corresponding Si_{14} heteroadamantane (Me_2SiCl_2 rather behaved as an innocent bystander of the Cl^--induced Si_2Cl_6 disproportionation[17]).

X-ray crystal structure analysis of the heteroadamantanes [0], [1], and [2]

Compound **[0]** crystallizes from CH_2Cl_2 as C_1-symmetric solvate **[0]**$\cdot CH_2Cl_2$.[27] The heteroadamantane cluster core is built of six Ge and four Si vertices, arranged in a perfectly alternating manner (Figure 3a). The valences of each Ge or Si vertex are saturated by two Me groups or one $SiCl_3$ substituent, respectively. Thus, **[0]** combines the structural motifs of *neo*-pentatetrelanes and (fused) cyclohexatetrelanes, both of which are frequently encountered in products of Si_2Cl_6 disproportionation (e.g., [*cyclo*-$Si_6Cl_{12}\cdot 2Cl]^{2-}$ and $Si(SiCl_3)_4$).[23,28,29] The average Si–Ge bond length of **[0]** (2.395 Å) is essentially the same as that determined for SiGe alloy in the bulk phase (2.398 Å).[30]

In the solid state, the molecules of **[2]** and **[1]** are located on a threefold rotation axis and a mirror plane, respectively. The $GeMe_2$ groups are disordered with $SiCl_2$ moieties. Structure refinement gave the best figures-of-merit when the sum of site occupation factors of all $GeMe_2$ groups was constrained to 4 (rather than 5 or 6) in the case of **[2]** and 5 (rather than 4 or 6) in the case of **[1]** (see the Supporting Information for more details). X-ray analysis thus supports the proposed molecular

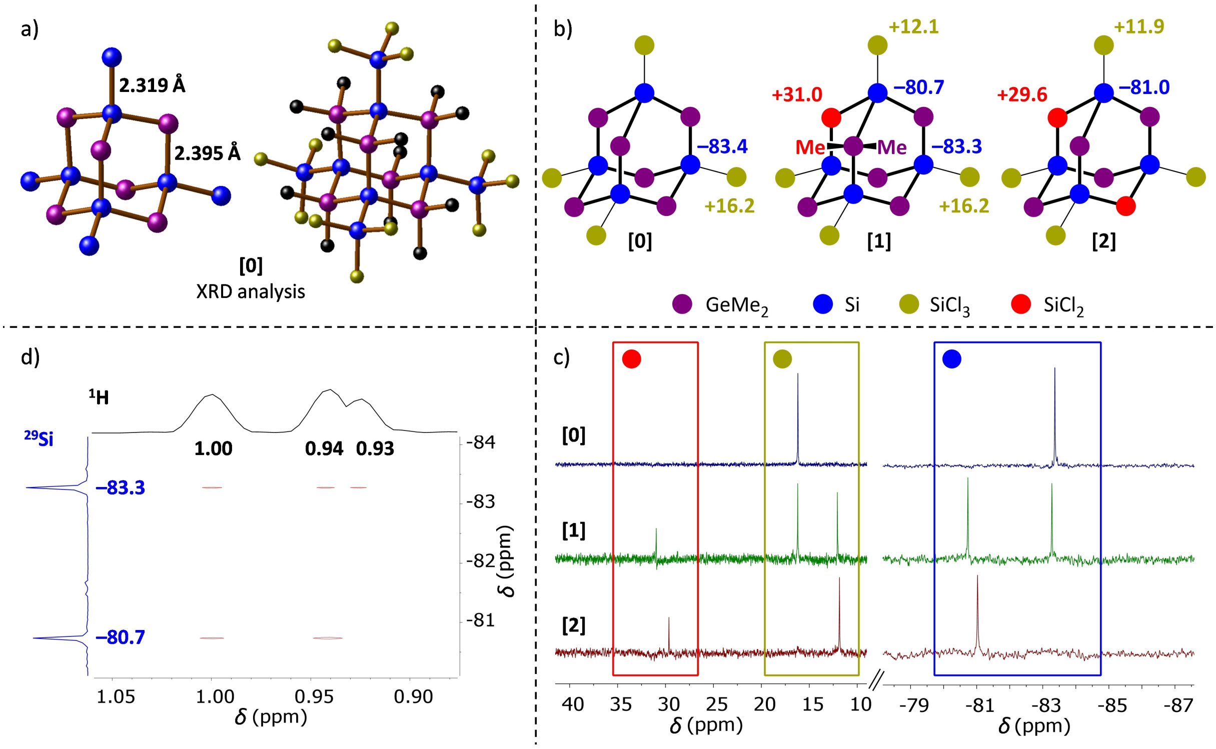

Figure 3. a) Solid-state structure of **[0]** (Si: blue, Ge: purple, Cl: yellow-green, CH$_3$: black); Si$_8$Ge$_6$ core (left), complete structure (right). b) Schematic representations of **[0]**, **[1]**, and **[2]** with ^{29}Si NMR chemical shift values given for comparison. c) Sections of the ^{29}Si{^{1}H} NMR spectra of **[0]**, **[1]**, and **[2]** in CD$_2$Cl$_2$. d) ^{29}Si/^{1}H HMBC NMR spectrum of **[1]** to prove the proposed structure containing 3 (2) magnetically inequivalent kinds of Me groups (quaternary Si vertices) in the molecule (CD$_2$Cl$_2$).

structures of **[1]** and **[2]**, but the proof could only be gained in combination with NMR spectroscopy.

NMR spectroscopic characterization of the heteroadamantanes [0], [1], and [2]

The Me groups of **[0]** give rise to one ^{1}H (0.91 ppm) and one ^{13}C NMR signal (2.6 ppm); the ^{29}Si{^{1}H} NMR spectrum is characterized by two resonances at −83.4 (*Si*SiCl$_3$) and 16.2 ppm (Si*Si*Cl$_3$; Figure 3b,c). The number of signals is in line with an average T_d symmetry of **[0]** in solution, and the ^{29}Si chemical shift values agree with those of the reference compounds **[B]** (−84.2 ppm, *Si*SiCl$_3$; 17.2 ppm, Si*Si*Cl$_3$)[15] and Si(SiCl$_3$)$_4$ (−80.9 ppm, *Si*SiCl$_3$; 3.5 ppm, Si*Si*Cl$_3$).[28] A ^{29}Si/^{1}H HMBC NMR experiment on **[0]** gave a pronounced crosspeak between the signals at −83.4 ppm (^{29}Si) and 0.91 ppm (^{1}H), in line with the direct Si(quart)–GeMe$_2$ bond that is the principal interaction within the heteroadamantane scaffold.

Compound **[2]** (point group D_{2d}) retains high symmetry and thus chemically equivalent Me groups, but the corresponding shift values, $\delta(^1\text{H}) = 1.03$ ppm and $\delta(^{13}\text{C}) = 1.6$ ppm, differ slightly from those of **[0]**. Three signals are detectable in the ^{29}Si{^{1}H} NMR spectrum, two of them (−81.0 ppm, *Si*SiCl$_3$; 11.9 ppm, Si*Si*Cl$_3$) appear in the same ranges as the two resonances of **[0]**, the third one is assignable to the SiCl$_2$ centers (29.6 ppm; Figure 3b, c). Crosspeaks are observed between the GeMe$_2$ and *Si*SiCl$_3$ as well as SiCl$_2$ signals in the ^{29}Si/^{1}H HMBC NMR spectrum of **[2]**.

Compound **[1]** (point group C_{2v}) shows three ^{1}H NMR resonances with integral values of 6H, 12H, and 12H. The five signals visible in the ^{29}Si{^{1}H} NMR spectrum can be assigned to two chemically inequivalent *Si*SiCl$_3$ units (−80.7, −83.3 ppm), two inequivalent Si*Si*Cl$_3$ moieties (16.2, 12.1 ppm), and one SiCl$_2$ vertex (31.0 ppm; Figure 3b,c). Importantly, the *Si*SiCl$_3$ signal at −80.7 ppm shows only crosspeaks to the two more intense proton resonances in the ^{29}Si/^{1}H HMBC NMR spectrum, whereas the signal at −83.3 ppm couples to all Me groups present in **[1]** and consequently corresponds to the two quaternary Si atoms that are linked to the unique GeMe$_2$ group (Figure 3d).

Conclusion

In summary, time- and cost-efficient one-pot syntheses of Si$_8$Ge$_6$, Si$_9$Ge$_5$, and Si$_{10}$Ge$_4$ heteroadamantanes **[0]**, **[1]**, and **[2]** from the simple, commercially available building blocks Me$_2$GeCl$_2$, Si$_2$Cl$_6$, and [*n*Bu$_4$N]Cl have been disclosed. The clusters obtained are subunits of bulk cubic Si$_x$Ge$_y$ alloys with the advantage of containing the two elements in different stoichiometries. Theory predicts that a Si$_{10}$ cluster is already large enough to exhibit representative features of Si nanoparticles.[31] We therefore conclude that our Si$_x$Ge$_y$ heteroadamantanes help to bridge the gap between small Si$_x$Ge$_y$

molecules, such as **[B]** and **[D]**, and more-extended Si_xGe_y nanoclusters. The effects of doping the adamantane scaffold with varying numbers of Si and Ge atoms have so far been studied only theoretically. Considerable consequences for the optoelectronic properties of the individual compounds have been predicted[32–34] and can now be experimentally confirmed (cf. optical band gaps of 4.35, 4.43, and 4.56 eV for **[0]**, **[1]**, and **[2]**, respectively; Table S2). According to works of Tamao et al.,[35] the all-*anti* conformation of pairs of $SiCl_3$ substituents in **[0]**, **[1]**, and **[2]** should result in pronounced σ-conjugation, thereby rendering our heteroadamantanes suitable building blocks for the fabrication of Si_xGe_y-based molecular wires.[36] The fact that **[0]**, **[1]**, and **[2]** carry exohedral $SiCl_3$ substituents should be of benefit in this context. Thus, similar to the discovery of carbonaceous diamondoids and the elaboration of their remarkably high application potential,[37–39] the successful synthesis of **[0]**, **[1]**, and **[2]** is expected to pave the way to novel and useful Si_xGe_y nanostructures.

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Conflict of Interests

B.K., H.-W.L., and M.W. are inventors on patent application PCT/DE2021 100470 submitted by Johann Wolfgang Goethe-Universität, which covers the synthesis and use of **[0]**, **[1]**, and **[2]**.

Keywords: cluster compounds · germanium · rearrangements · SiGe alloys · silicon

[1] M. A. Brook, *Silicon in Organic, Organometallic, and Polymer Chemistry*, Wiley, New York, **2000**.
[2] J. Fischer, J. Baumgartner, C. Marschner, *Science* **2005**, *310*, 825.
[3] E. M. T. Fadaly, A. Dijkstra, J. R. Suckert, D. Ziss, M. A. J. van Tilburg, C. Mao, Y. Ren, V. T. van Lange, K. Korzun, S. Kölling, M. A. Verheijen, D. Busse, C. Rödl, J. Furthmüller, F. Bechstedt, J. Stangl, J. J. Finley, S. Botti, J. E. M. Haverkort, E. P. A. M. Bakkers, *Nature* **2020**, *580*, 205–209.
[4] R. D. Miller, J. Michl, *Chem. Rev.* **1989**, *89*, 1359–1410.
[5] C. J. Ritter, C. Hu, A. V. G. Chizmeshya, J. Tolle, D. Klewer, I. S. T. Tsong, J. Kouvetakis, *J. Am. Chem. Soc.* **2005**, *127*, 9855–9864.
[6] A. V. G. Chizmeshya, C. J. Ritter, C. Hu, J. B. Tice, J. Tolle, R. A. Nieman, I. S. T. Tsong, J. Kouvetakis, *J. Am. Chem. Soc.* **2006**, *128*, 6919–6930.
[7] L. Klemmer, V. Huch, A. Jana, D. Scheschkewitz, *Chem. Commun.* **2019**, *55*, 10100–10103.
[8] V. Y. Lee, K. Takanashi, T. Matsuno, M. Ichinohe, A. Sekiguchi, *Appl. Organomet. Chem.* **2010**, *24*, 834–836.
[9] L. Albers, S. Rathjen, J. Baumgartner, C. Marschner, T. Müller, *J. Am. Chem. Soc.* **2016**, *138*, 6886–6892.
[10] A. Schnepf, *Chem. Commun.* **2007**, *4*, 192–194.
[11] K. M. Baines, K. A. Mueller, T. K. Sham, *Can. J. Chem.* **1992**, *70*, 2884–2886.
[12] S. M. I. Al-Rafia, A. C. Malcolm, R. McDonald, M. J. Ferguson, E. Rivard, *Angew. Chem. Int. Ed.* **2011**, *50*, 8354–8357; *Angew. Chem.* **2011**, *123*, 8504–8507.
[13] M. Waibel, C. B. Benda, B. Wahl, T. F. Fässler, *Chem. Eur. J.* **2011**, *17*, 12928–12931.
[14] H. Wagner, J. Baumgartner, T. Müller, C. Marschner, *J. Am. Chem. Soc.* **2009**, *131*, 5022–5023.
[15] L. Müller, W.-W. du Mont, F. Ruthe, P. G. Jones, H. C. Marsmann, *J. Organomet. Chem.* **1999**, *579*, 156–163.
[16] R. A. Benkeser, *Acc. Chem. Res.* **1971**, *4*, 94–100.
[17] J. Teichmann, M. Wagner, *Chem. Commun.* **2018**, *54*, 1397–1412.
[18] J. Teichmann, M. Bursch, B. Köstler, M. Bolte, H.-W. Lerner, S. Grimme, M. Wagner, *Inorg. Chem.* **2017**, *56*, 8683–8688.
[19] I. Georg, M. Bursch, J. B. Stückrath, E. Alig, M. Bolte, H.-W. Lerner, S. Grimme, M. Wagner, *Angew. Chem. Int. Ed.* **2020**, *59*, 16181–16187; *Angew. Chem.* **2020**, *132*, 16315–16321.
[20] I. Georg, J. Teichmann, M. Bursch, J. Tillmann, B. Endeward, M. Bolte, H.-W. Lerner, S. Grimme, M. Wagner, *J. Am. Chem. Soc.* **2018**, *140*, 9696–9708.
[21] J. Teichmann, C. Kunkel, I. Georg, M. Moxter, T. Santowski, M. Bolte, H.-W. Lerner, S. Bade, M. Wagner, *Chem. Eur. J.* **2019**, *25*, 2740–2744.
[22] S.-B. Choi, B.-K. Kim, P. Boudjouk, D. G. Grier, *J. Am. Chem. Soc.* **2001**, *123*, 8117–8118.
[23] J. Tillmann, L. Meyer, J. I. Schweizer, M. Bolte, H.-W. Lerner, M. Wagner, M. C. Holthausen, *Chem. Eur. J.* **2014**, *20*, 9234–9239.
[24] J. Tillmann, M. Moxter, M. Bolte, H.-W. Lerner, M. Wagner, *Inorg. Chem.* **2015**, *54*, 9611–9618.
[25] J. Teichmann, B. Köstler, J. Tillmann, M. Moxter, R. Kupec, M. Bolte, H.-W. Lerner, M. Wagner, *Z. Anorg. Allg. Chem.* **2018**, *644*, 956–962.
[26] J. Tillmann, F. Meyer-Wegner, A. Nadj, J. Becker-Baldus, T. Sinke, M. Bolte, M. C. Holthausen, M. Wagner, H.-W. Lerner, *Inorg. Chem.* **2012**, *51*, 8599–8606.
[27] Deposition Numbers 2091220 (for **[0]**), 2091221 (for **[1]**), and 2091222 (for **[2]**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.
[28] F. Meyer-Wegner, A. Nadj, M. Bolte, N. Auner, M. Wagner, M. C. Holthausen, H.-W. Lerner, *Chem. Eur. J.* **2011**, *17*, 4715–4719.
[29] J. Tillmann, J. H. Wender, U. Bahr, M. Bolte, H.-W. Lerner, M. C. Holthausen, M. Wagner, *Angew. Chem. Int. Ed.* **2015**, *54*, 5429–5433; *Angew. Chem.* **2015**, *127*, 5519–5523.
[30] J. P. Dismukes, L. Ekstrom, R. J. Paff, *J. Phys. Chem.* **1964**, *68*, 3021–3027.
[31] Y. Shiraishi, D. Robinson, Y. Ge, J. D. Head, *J. Phys. Chem. C* **2008**, *112*, 1819–1824.
[32] F. K. Fotooh, M. Atashparvar, *Russ. J. Phys. Chem. B* **2019**, *13*, 1–8.
[33] O. Lehtonen, D. Sundholm, *Phys. Rev. B* **2006**, *74*, 045433.
[34] F. Marsusi, K. Mirabbaszadeh, G. Ali Mansoori, *Physica E* **2009**, *41*, 1151–1156.
[35] H. Tsuji, M. Terada, A. Toshimitsu, K. Tamao, *J. Am. Chem. Soc.* **2003**, *125*, 7486–7487.
[36] F. Pichierri, *Chem. Phys. Lett.* **2006**, *421*, 319–323.
[37] V. Georgakilas, J. A. Perman, J. Tucek, R. Zboril, *Chem. Rev.* **2015**, *115*, 4744–4822.
[38] M. A. Gunawan, J. C. Hierso, D. Poinsot, A. A. Fokin, N. A. Fokina, B. A. Tkachenko, P. R. Schreiner, *New J. Chem.* **2014**, *38*, 28–41.
[39] H. Schwertfeger, A. A. Fokin, P. R. Schreiner, *Angew. Chem. Int. Ed.* **2008**, *47*, 1022–1036; *Angew. Chem.* **2008**, *120*, 1038–1053.

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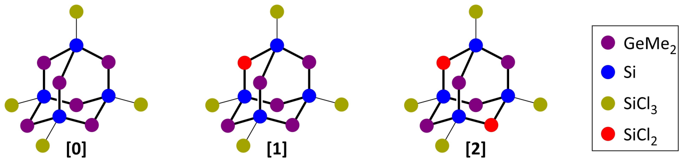

Toward novel nanoclusters: The fourfold $SiCl_3$-substituted Si_4Ge_6 ([**0**]), Si_5Ge_5 ([**1**]), and Si_6Ge_4 ([**2**]) heteroadamantane cores are accessible directly from Me_2GeCl_2 and Si_2Cl_6/Cl^- in a time- and cost-efficient synthesis. In a chloride ion-mediated rearrangement, [**2**] is converted into [**1**] at room temperature and into [**0**] at 60 °C.

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Selective One-Pot Syntheses of Mixed Silicon-Germanium Hetero-adamantane Clusters