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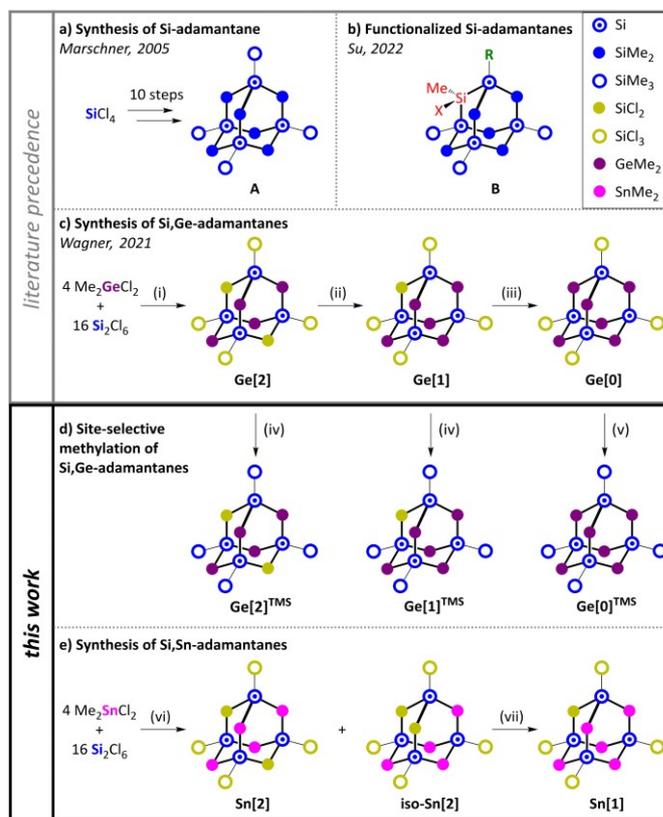
COMMUNICATION

Group IV heteroadamantanes: synthesis of Si₆Sn₄ and site-selective derivatization of Si₆Ge₄Received 00th January 20xx,
Accepted 00th January 20xxBenedikt Köstler,^a Jannik Gilmer,^a Michael Bolte,^a Alexander Virovets,^a Hans-Wolfram Lerner,^a Philipp Albert,^b Felipe Fantuzzi,^c and Matthias Wagner*^a

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The mixed heteroadamantanes Si₆Ge₄ and Si₆Sn₄ are readily accessible from Me₂ECl₂/Si₂Cl₆/cat. Cl⁻ (4 × EMe₂, 2 × SiCl₂, 4 × Si–SiCl₃ vertices; E = Ge, Sn). Different from Si₆Ge₄, two skeletal isomers are formed in the case of Si₆Sn₄. Site-selective SiCl₃-methylation of Si₆Ge₄ was achieved, leaving the SiCl₂ groups untouched.

In the last decades, homonuclear Si-,^{1–3} Ge-,^{4–7} and Sn-containing^{4,8} oligomers have been intensely studied. One reason for this continued interest is the substantial delocalization of the skeletal σ electrons along the oligomer backbones. This σ delocalization⁹ is of fundamental interest for a comprehensive understanding of chemical bonding in general and the rich photochemistry of oligotetrelanes in particular,¹⁰ but may also lead to potentially useful optoelectronic properties.^{2,11} In stark contrast to the homonuclear group IV oligomers, there are far fewer reports on well-defined heteronuclear E_nE'_m oligomers (E, E' = Si, Ge, Sn). Among these, a considerable number of examples feature 'core-shell' architectures in which a homonuclear E_n ring or cluster (E ≠ Si) is surrounded, e.g., by supersilyl substituents for kinetic protection.^{12–15} We argue, however, that 'truly mixed' oligomers¹⁶ with both E and E' in their backbones also deserve thorough investigation, because here a particularly pronounced effect of the different properties of E and E' on the electronic structure of the oligomeric scaffold can be anticipated.¹⁷ Recently, our group has shown that the Si₂Cl₆/[nBu₄N]Cl silylation system,¹⁸ which generates [SiCl₃]⁻ as the reactive



Scheme 1. a) Marschner's route to Si-adamantane **A**. b) Functionalization of Si-adamantane **A** in 2- (X = Cl; R = SiMe₃) or 1-position (X = Me, R = GeMe₃, SnMe₃, SiMe₂Cl) to give **B**-type compounds. c) Synthesis of Si,Ge-adamantane **Ge[2]** and its Cl⁻-induced rearrangement to **Ge[1]** and **Ge[0]**. d) Site-selective methylation leads to **Ge[2]TMS**, **Ge[1]TMS**, and **Ge[0]TMS**, leaving all SiCl₂ groups intact. e) Synthesis of Si,Sn-adamantanes **Sn[2]** and **iso-Sn[2]**; Cl⁻-induced rearrangement of **Sn[2]**/**iso-Sn[2]** to **Sn[1]**. (i) 0.8 eq. [nBu₄N]Cl, CH₂Cl₂, room temperature, 13 d; (ii) 1 eq. [nBu₄N]Cl, CH₂Cl₂, room temperature, 6 d; (iii) 1 eq. [nBu₄N]Cl, CH₂Cl₂, 60 °C, 2 d; (iv) exc. MeMgBr, Et₂O, 60 °C, 1 d, >80% yield; (v) exc. MeMgBr, THF/Et₂O, room temperature, 1 d, 51% yield; (vi) 0.8 eq. [nBu₄N]Cl, CH₂Cl₂, room temperature, 3 d, 37% yield; (vii) 0.1 eq. [nBu₄N]Cl, CH₂Cl₂, 60 °C, 1 d, 23% yield.

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intermediate,^{19,20} can be used in combination with R_2GeCl_2 for the efficient synthesis of mixed Si,Ge oligomers. Specifically, we prepared open-chain species $(Cl_3Si)_4Ge^{21,22}$ or $Cl_3Si-(R_2Ge)_n-SiCl_3$ ($n = 1, 2$; $R = Ph, nBu$) and applied them as precursors in the chemical vapor deposition (CVD) of Si_xGe_{1-x} alloys after hydrogenation.²³ The use of Me_2GeCl_2 gave access to $(Cl_2Si)_5(Me_2Ge)$ monocycles²⁴ and even the tricyclic heteroadamantane **Ge[2]**, which contains two $SiCl_2$ units together with four $GeMe_2$ and four $Si-SiCl_3$ vertices in the cluster core (Scheme 1; general formula **E[X]**: Si,E-adamantane with "X" $SiCl_2$ groups in the cluster core).²⁵ A Cl^- ion-induced rearrangement reaction leads from **Ge[2]** to **Ge[1]** (one remaining $SiCl_2$), and **Ge[0]** (zero remaining $SiCl_2$) at room temperature and 60 °C, respectively. Apart from Marschner's iconic sila-adamantane **A** (Scheme 1)^{26,27} and its recently published derivatives **B**,²⁸ **Ge[2]-Ge[0]** are the only adamantane frameworks realized so far with heavier group IV elements. To advance this as-yet underexplored chemistry, three key questions need to be addressed: 1) How can we achieve site-selective derivatization of specific $Si-Cl$ bonds in **Ge[2]** and **Ge[1]**? 2) Is there a profound reason why we exclusively obtain the 2,6- $(SiCl_2)_2$ -isomer **Ge[2]**? 3) Besides Si,Ge-, are Si,Sn-adamantanes also accessible via our protocol?²⁹ Answers to these questions are provided herein. Before turning to question 1), we emphasize that a major advantage of our protocol to **Ge[0]-Ge[2]** is that the obtained heteroadamantanes offer multiple options for further derivatization, oligomerization, and crosslinking. In this context, it should be noted that the currently thriving field of carbonaceous adamantanes began to flourish only after convenient functionalization methods had been developed.^{30,31} The presence of reactive $Si-Cl$ bonds in **Ge[0]-Ge[2]** is therefore a clear asset. However, their number of 12–16 is quite high, and it would be practical to reduce them to a smaller, more manageable quantity, which presents the following challenge: the need to accomplish both a site-selective (e.g., $SiCl_3$ vs. $SiCl_2$) and a quantitative substitution (e.g., all 12 silyl-Cl atoms). To first address the latter issue, we selected **Ge[0]** as substrate and methylation as derivatization mode: on the one hand, the resulting $SiMe_3$ (TMS) groups should be inert toward most chemicals, on the other hand, they could be exchangeable for other substituents in the future by applying Marschner's^{32,33} KO^tBu -induced $Si-Si$ bond-cleavage reaction.²⁸ In a series of NMR-scale experiments, we tested various methylation reagents/solvents and found that an excess of $MeMgBr$ in THF/ Et_2O quantitatively converts **Ge[0]** to permethylated **Ge[0]^{TMS}** already at room temperature (Scheme 1). After upscaling, **Ge[0]^{TMS}** was isolated in 51% yield. Unfortunately, this optimized protocol was not directly applicable to the synthesis of **Ge[1]^{TMS}** and **Ge[2]^{TMS}**, since the starting material **Ge[2]** in particular degrades under these conditions. The problem was finally solved by switching to pure Et_2O as solvent (without added THF) and increasing the reaction temperature to 60 °C. In this way, **Ge[1]^{TMS}** and **Ge[2]^{TMS}** were obtained with excellent yields of 82 and 86%, respectively.³⁴ Selective methylation exclusively at the silyl groups was achieved in both cases. The unreacted $SiCl_2$ moieties proved to

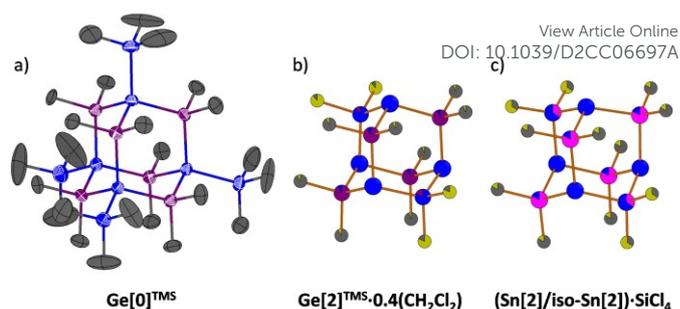


Figure 1. a) Molecular structure of the permethylated heteroadamantane **Ge[0]^{TMS}** in the solid state; H atoms omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. b), c) Disorder schemes of **Ge[2]^{TMS}·0.4(CH₂Cl₂)** and **(Sn[2]/iso-Sn[2])·SiCl₄** in the solid state; partial site-occupancy factors by sectors. Co-crystallized CH_2Cl_2 and $SiCl_4$ as well as the four exohedral $SiCl_3$ substituents are omitted for clarity. Gray: C, yellow: Cl, blue: Si, purple: Ge, pink: Sn.

be remarkably inert toward H_2O ,³⁵ but can be converted to $SiMe_2$ units by using $AlMe_3$ in toluene (200 °C, 3 d, sealed glass ampoule; see ESI for details). This proof-of-principle experiment demonstrates that late-stage derivatization at the $SiCl_2$ positions is indeed feasible and can be further exploited in the future.

The proposed molecular structure of **Ge[0]^{TMS}**, notably its exhaustive methylation, was confirmed by X-ray crystallography (Figure 1); all metric parameters of the cluster core are very similar to those of **Ge[0]**. In the solid state, the **Ge[1]^{TMS}** molecules have C_{2v} point symmetry (Figure S39).³⁶ Due to disorder, all three crystallographically unique $GeMe_2$ positions are shared to varying degrees with $SiCl_2$. Refinement gave the best figures-of-merit when the sum of site-occupancy factors was constrained to 5 $GeMe_2$ and 1 $SiCl_2$ groups. For **Ge[2]^{TMS}**, two solvatomorphs were obtained with and without co-crystallized CH_2Cl_2 . We here refer to **Ge[2]^{TMS}·0.4(CH₂Cl₂)**, because its heteroadamantane core, located on a mirror plane, is less affected by disorder and has 4 and 2 positions preferentially occupied by $GeMe_2$ and $SiCl_2$, respectively (Figure 1).

Each of the 1H , $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectra of **Ge[0]^{TMS}** contains two signals, indicating high (T_d) molecular symmetry. Moreover, the proton integrals confirm a $GeMe_2:SiMe_3$ ratio of 6:4. In **Ge[2]^{TMS}** the $GeMe_2:SiMe_3$ ratio decreases to 4:4 and a third ^{29}Si resonance appears at 50.9 ppm, which can be assigned to the pristine $SiCl_2$ groups. Compared to **Ge[0]^{TMS}** and **Ge[2]^{TMS}**, **Ge[1]^{TMS}** gives rise to the most NMR signals, consistent with its proposed low symmetry. A $GeMe_2:SiMe_3$ ratio of 5:4 is confirmed and an $SiCl_2$ resonance is visible at $\delta(^{29}Si) = 52.9$. Full assignment of all resonances of **Ge[0]^{TMS}-Ge[2]^{TMS}** was achieved by 2D NMR experiments (see ESI). Table S1 summarizes the experimentally determined and computed ^{29}Si chemical shift values, which agree very well.

The second question we asked in the introduction was why our synthesis leads exclusively to the 2,6- $(SiCl_2)_2$ -isomer **Ge[2]**, whereas the 2,4- $(SiCl_2)_2$ -isomer **iso-Ge[2]**, in which both $SiCl_2$ moieties are attached to the same $Si-SiCl_3$ vertex, has never been observed. Potential structure-determining factors are (i) the choice of substituents R and (ii) the nature of the group IV

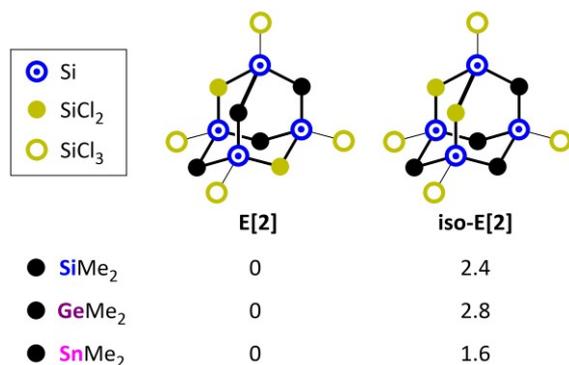


Figure 2. Relative free energies (ΔG in kcal mol⁻¹) of the two isomers **E[2]** and **iso-E[2]** computed for E = Si, Ge, Sn. Level of theory: SMD(CH₂Cl₂)/MN15/def2-TZVP//SMD(CH₂Cl₂)/MN15/def2-SVP (H, C, Cl, Si); def2-TZVP (Ge, Sn(ECP)).

element E in the R₂E unit. Since it is known that the reaction of R₂GeCl₂ with Si₂Cl₆/Cl⁻ (R = Ph, *n*Bu) furnishes chain-like oligomers Cl₃Si-(R₂Ge)_{*n*}-SiCl₃ (*n* = 1, 2)²³ instead of heteroadamantanes, we focus here on the use of Me₂ECl₂ (E = Si, Sn): while Me₂SiCl₂ proved inert toward Si₂Cl₆/Cl⁻, Me₂SnCl₂ gave an inseparable 1:1 mixture of heteroadamantanes **Sn[2]** and **iso-Sn[2]** (Scheme 1). This result is relevant beyond the actual question of isomer distribution as it answers our third question by proving that our synthesis approach to rare mixed Si,Ge oligomers also opens the gate to corresponding Si,Sn compounds. To substantiate this claim, we next demonstrated that **Sn[1]** is readily prepared through Cl⁻-mediated conversion of **Sn[2]/iso-Sn[2]** (Scheme 1); the identical reactivity of both isomers in this case is remarkable. Compared to **Ge[2]**, however, the behavior of **Sn[2]/iso-Sn[2]** toward Cl⁻ ions differs in subtle details: the **Ge[2]** → **Ge[1]** transformation was previously performed using 1 eq. of Cl⁻ at room temperature. Under these conditions, **Sn[2]/iso-Sn[2]** decomposes to a complex mixture of products. For the synthesis of **Sn[1]**, we therefore had to reduce the amount of added Cl⁻ to 0.1 eq. and in turn increase the reaction temperature to 60 °C. After 1 d, an approximate 2:1:1 mixture of **Sn[1]:Sn[2]:iso-Sn[2]** had formed; longer reaction times led to a gradual degradation of **Sn[1]** (unknown products; no **Sn[0]**). Finally, taking advantage of the higher solubility of **Sn[1]** compared to **Sn[2]/iso-Sn[2]** in *n*-hexane, a 90% enriched sample of **Sn[1]** was isolated in 23% yield (see ESI for analytical details).

Sn[2] and **iso-Sn[2]** crystallize as a solid solution together with one molecule of SiCl₄ per heteroadamantane cluster (Figure 1). Due to disorder, **Sn[2]** and **iso-Sn[2]** cannot be distinguished, but unconstrained refinement of the site-occupancy factors gives the chemical composition Si₁₀Sn₄. Four positions of the Si₆Sn₄ cluster core are mainly occupied by SnMe₂ and two mainly by SiCl₂, whereas the four remaining Si-SiCl₃ positions are not shared with Sn.

In solution, the D_{2d}-symmetric **Sn[2]** generates one ¹H and one ¹³C as well as one ¹¹⁹Sn NMR signal (at -139.9 ppm); the three chemically unique ²⁹Si nuclei resonate at 36.0 (SiCl₂), 15.1 (SiCl₃), and -103.9 ppm (Si-SiCl₃). Only the latter signal is significantly shifted relative to the corresponding resonance in **Ge[2]**, which is likely due to the fact that only the Si-SiCl₃ atom is directly bonded to the EMe₂ groups. The direction of the shift

(upfield by 22.9 ppm) can be explained by a more pronounced magnetic anisotropy effect of the larger Sn atom and by its lower electronegativity (1.72 for Sn vs. 2.02 for Ge on the Allred-Rochow scale).³⁷ In line with this interpretation, the signals of the three inequivalent Si-SiCl₃ atoms in the C_s-symmetric **iso-Sn[2]** appear in the order -87.1, -104.3, and -129.7 ppm, matching one, two (cf. **Sn[2]**), and three neighboring SnMe₂ groups, respectively. The three ¹¹⁹Sn resonances of **iso-Sn[2]** are detected at -121.4, -126.0, and -155.0 ppm. As in the cases of **Ge[0]**^{TMS}-**Ge[2]**^{TMS}, the experimental NMR data of **Sn[2]**, **iso-Sn[2]**, and **Sn[1]** are consistent with the computed ones (²⁹Si: Table S1, ¹¹⁹Sn: Table S2).

The relative energies of the two isomers **E[2]** and **iso-E[2]** were computed for E = Si, Ge, Sn at the SMD(CH₂Cl₂)/MN15/def2-TZVP//SMD(CH₂Cl₂)/MN15/def2-SVP (H, C, Cl, Si); def2-TZVP (Ge, Sn(ECP)) level of theory (Figure 2). In all three cases, **E[2]** is thermodynamically more stable than **iso-E[2]**, with the smallest difference in free energy between the isomers for E = Sn. Interestingly, our calculated free energy trends are consistent with the fact that we have been unable to detect any **iso-Ge[2]** so far, while **Sn[2]** and **iso-Sn[2]** are reproducibly formed in an equimolar mixture. However, since in all cases the energy differences are quite small, we conclude that the observed variations in the product yields are not primarily driven by thermodynamic reasons.

In summary, site-selective methylation of their four SiCl₃ substituents was achieved for the Si₆Ge₄ and Si₅Ge₅ heteroadamantanes **Ge[2]** and **Ge[1]** by using an excess of MeMgBr. The two unaffected SiCl₂ sites in the resulting **Ge[2]**^{TMS} and the one SiCl₂ vertex in **Ge[1]**^{TMS} are still available for further functionalization. The synthesis protocol for **Ge[2]** was successfully adapted for the preparation of the corresponding Si₆Sn₄ heteroadamantane, which was isolated as a 1:1 mixture of the 2,6-(SiCl₂)₂-isomer **Sn[2]** and the 2,4-(SiCl₂)₂-isomer **iso-Sn[2]**. Elemental Si, Ge, and Sn all crystallize in the cubic diamond lattice, which in turn is composed of adamantane substructures. While Si_{*x*}Ge_{1-*x*} alloys exist with any molar ratio *x* = 0–1, the fabrication of Si_{*x*}Sn_{1-*x*} is impeded by the ~20% mismatch between the atomic radii of Si and Sn and the low thermal equilibrium solubility of Sn in Si (0.1% at 1066 °C).³⁸ We therefore consider **Sn[2]/iso-Sn[2]** as valuable model systems for experimentally gauging the lattice strain as well as the chemical and physical behavior of elusive Si_{*x*}Sn_{1-*x*} samples, for which exciting optoelectronic properties have been predicted.^{38,39}

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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 **Ge[0]**^{TMS}, **Ge[1]**^{TMS}, **Ge[2]**^{TMS}, and **Ge[2]**^{Me}.

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- In our hands, methylation in THF/Et₂O at room temperature is nevertheless superior for the synthesis of Ge[0]^{TMS}.
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