Electronic Supplementary Information

Group IV heteroadamantanes: synthesis of Si₆Sn₄ and site-selective derivatization of Si₆Ge₄

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1. Experimental Details and Characterization Data

1.1. General Considerations

All reactions were carried out under an inert-gas atmosphere (dry argon or nitrogen) using standard Schlenk or glove-box techniques. Commercially available starting materials were used as received. Heteroadamantanes Ge[2], Ge[1], and Ge[0] were prepared according to literature.^{S1} THF, Et₂O, toluene, and *n*-hexane were dried over Na metal; CH₂Cl₂ was dried over CaH₂. All solvents were freshly distilled prior to use. CD₂Cl₂ was stored over molecular sieves (3 Å). NMR spectra were recorded at 298 K on a Bruker Avance III HD 500 spectrometer equipped with a Prodigy BBO 500 S1 probe. ¹H/¹³C{¹H} NMR spectra were referenced against (residual) solvent signals (CD₂Cl₂: 5.32 ppm/53.84 ppm;^{S2} s = singlet). ²⁹Si{¹H} NMR spectra were calibrated against external SiMe₄ (δ (²⁹Si) = 0); whenever present, SiCl₄ (δ (²⁹Si) = -18.9 ppm) was used as internal standard. Resonance assignments were supported by twodimensional ¹³C/¹H HSQC, ¹³C/¹H HMBC, ²⁹Si/¹H HSQC, ²⁹Si/¹H HMBC, and ¹¹⁹Sn/¹H HMBC spectra. ^{117/119}Sn satellites are observed in most cases where they are expected; the corresponding coupling constants ${}^{n}J({}^{117/119}Sn/X)$ are given only if they could be determined unambiguously. Elemental analyses were performed at the microanalytical laboratory Pascher, Remagen, Germany (Sn[2]/iso-Sn[2]) and at the Institute of Organic Chemistry, Justus-Liebig-University Gießen, Germany (Ge[0]^{TMS} and Ge[2]^{TMS}).

1.2. Synthesis of the two isomers Sn[2] and iso-Sn[2]



A solution of $[nBu_4N]Cl$ (0.253 g, 0.910 mmol) and Me₂SnCl₂ (1.00 g, 4.55 mmol) in CH₂Cl₂ (20 mL) was prepared in a screw-cap Schott glass bottle. After addition of neat Si₂Cl₆ (4.90 g, 18.2 mmol) at room temperature, the bottle was closed and stored for 3 d. During this time, colorless, X-ray quality crystals formed, which contained 1 eq. SiCl₄ per heteroadamantane unit.^{*)} The crystals were isolated by filtration, washed with CH₂Cl₂ (3 mL), and identified as a 1:1-mixture of the two isomers **Sn**[2] and **iso-Sn**[2] by means of NMR spectroscopy. Since the separation of the two isomers was not possible, the isomer mixture **Sn**[2]/iso-**Sn**[2] was further investigated to characterize both compounds. Yield: 0.614 g (0.426 mmol, 37%).

Note: The corresponding reaction of Me_2SiCl_2 with Si_2Cl_6/Cl^- did not lead to the formation of analogous Si-adamantanes. NMR spectroscopy showed unconsumed Me_2SiCl_2 along with the products that are usually obtained from mixtures of Si_2Cl_6 and Cl^- in the absence of additional reaction partners.

*) *Note:* To exclude any risk of hydrolysis, the crystals were used directly for NMR analysis. Therefore, the ²⁹Si NMR spectrum shows the signal of SiCl₄. If the substance is to be used for further reactions, the crystals can be dissolved in CH₂Cl₂ beforehand and the solution subsequently evaporated in vacuo, which easily and quantitatively removes the volatile SiCl₄.

Elemental analysis: Calculated for $C_8H_{24}Cl_{16}Si_{10}Sn_4$ (1443.17): C 6.66; H 1.68. Found: C 6.11;

H 1.58.

Sn[2]:

¹H NMR (500.2 MHz, CD₂Cl₂): $\delta = 0.86$ (s, ²*J*(^{117/119}Sn,¹H) = 52, 54 Hz, 24H; SnMe₂). ¹³C{¹H} NMR (125.8 MHz, CD₂Cl₂): $\delta = -6.5$ (SnMe₂).

²⁹Si{¹H} NMR (99.4 MHz, CD₂Cl₂): $\delta = 36.0 ({}^{2}J({}^{117/119}Sn, {}^{29}Si) = 19 \text{ Hz}, \text{ SiCl}_{2}), 15.1 (SiCl_{3}), -103.9 ({}^{1}J({}^{119}Sn, {}^{29}Si) = 142 \text{ Hz}, {}^{1}J({}^{117}Sn, {}^{29}Si) = 136 \text{ Hz}; Si-SiCl_{3}).$

¹¹⁹Sn{¹H} NMR (186.5 MHz, CD₂Cl₂): $\delta = -139.9 ({}^{1}J({}^{119}Sn, {}^{29}Si) = 142 \text{ Hz}; SnMe_2).$

iso-Sn[2]:

¹**H NMR (500.2 MHz, CD₂Cl₂):** $\delta = 0.97$ (s, 3H; Me¹), 0.88 (s, ²*J*(^{117/119}Sn, ¹H) = 52, 54 Hz, 12H; Me² and Me³), 0.79 (s, 3H; Me^{1'}), 0.79 (s, 6H; Me^{2'}).

¹³C{¹H} NMR (125.8 MHz, CD₂Cl₂): $\delta = -5.4$ (Me² or Me³), -5.6 (Me¹), -5.8 (Me² or Me³), -6.0 (Me^{2'}), -8.3 (Me^{1'}).

²⁹Si{¹H} NMR (99.4 MHz, CD₂Cl₂): δ = 33.1 (Si⁴Cl₂), 21.6 (Si⁶Cl₃), 14.8 (Si⁵Cl₃), 9.4 (Si⁷Cl₃), -87.1 (Si³), -104.3 (Si¹), -129.7 (Si²).

¹¹⁹Sn{¹H} NMR (186.5 MHz, CD₂Cl₂): $\delta = -121.4$ (Sn²), -126.0 (Sn³), -155.0 (Sn¹).

Note: Based on their relative signal intensities in combination with HSQC/HMBC experiments, it was possible to unequivocally assign all resonances of Sn[2] and iso-Sn[2] – the only exception being the SiCl₂ resonances. These were tentatively assigned based on the following considerations: (i) Only in Sn[2] all four $SnMe_2$ groups are strictly equivalent, should thus show precisely the same coupling to ²⁹SiCl₂, and in turn give the more pronounced satellite signals. (ii) Quantum-chemical calculations predict that the ²⁹SiCl₂ signal of Sn[2] appears downfield-shifted relative to the corresponding signal of iso-Sn[2] (see Table S1).



Figure S1. *Left:* Numbering scheme used for the NMR characterization of **iso-Sn[2]**. *Right:* Analogous to the case of **Ge[2]**, the NMR spectrum of the highly symmetric **Sn[2]** shows only one signal each for CH_3 , CH_3 , Si, SiCl₂, SiCl₃, and Sn.



Figure S2. The X-ray powder diffractogram of the bulk product (top; room temperature) agrees very well with the reference diffractogram simulated from the single-crystal data of the isomer mixture **Sn[2]/iso-Sn[2]** (bottom; -100 °C). Measured at a *STOE-STADI-P* diffractometer.

1.3. Synthesis of Sn[1]



A glass ampoule was charged with single crystals of the isomer mixture Sn[2]/iso-Sn[2] (0.500 g, 0.346 mmol), [*n*Bu₄N]Cl (0.010 g, 0.035 mmol), and CH₂Cl₂ (15 mL). The ampoule was flame-sealed and heated to 60 °C for 24 h. After cooling to room temperature, the ampoule was opened, and the reaction solution was transferred to a Schlenk tube. All volatiles were removed under reduced pressure and the yellow residue was extracted into *n*-hexane (4×5 mL). All volatiles were removed from the extract to obtain Sn[1] as a colorless solid. Yield: 0.094 g (0.063 mmol, 23%).

Note: (i) Monitoring of the above reaction by NMR spectroscopy (CD_2Cl_2) shows a conversion to **Sn[1]** of about 50% next to unreacted **Sn[2]/iso-Sn[2]** after 3 d (longer reaction times slowly lead to a higher degree of conversion, no detectable side products); yield losses occur during workup. (ii) Treatment of the isomer mixture **Sn[2]/iso-Sn[2]** with 1.0 eq. [*n*Bu₄N]Cl led to unselective decomposition already at room temperature (sealed NMR tube; CD_2Cl_2). This contrasts with the case of **Ge[2]**, which is selectively transformed into **Ge[1]** under the same conditions. (iii) Heating of the isomer mixture **Sn[2]/iso-Sn[2]** to 60 °C in the absence of [*n*Bu₄N]Cl resulted in no reaction (sealed NMR tube; CD_2Cl_2).

¹**H** NMR (500.2 MHz, CD₂Cl₂): $\delta = 0.85$ (s, ²*J*(^{117/119}Sn,¹H) = 51, 53 Hz, 12H; Sn¹Me₂), 0.78 (s, 6H; Sn²Me₂), 0.77 (s, ²*J*(^{117/119}Sn,¹H) = 50, 52 Hz, 12H; Sn¹Me₂).

¹³C{¹H} NMR (125.8 MHz, CD₂Cl₂): $\delta = -5.2$ (Sn²Me₂), -5.6 (Sn¹Me₂), -6.2 (Sn¹Me₂).

²⁹Si{¹H} NMR (99.4 MHz, CD₂Cl₂): $\delta = 37.0$ (Si³Cl₂), 21.5 (Si⁵Cl₃), 15.4 (Si⁴Cl₃), -104.1 (Si¹), -130.1 (Si²).

¹¹⁹Sn{¹H} NMR (186.5 MHz, CD₂Cl₂): $\delta = -107.5 ({}^{2}J({}^{119}Sn, {}^{117/119}Sn) = 54 \text{ Hz}; \text{ Sn}{}^{2}\text{Me}_{2}),$ -119.5 (${}^{2}J({}^{119}Sn, {}^{117/119}Sn) = 54 \text{ Hz}, {}^{1}J({}^{119}Sn, {}^{29}Si) = 132 \text{ Hz}; \text{ Sn}{}^{1}\text{Me}_{2}).$

1.4. Synthesis of Ge[2]^{TMS}



A solution of Ge[2] (0.100 g, 0.0790 mmol) in Et₂O (3 mL) was prepared in a glass ampoule. MeMgBr (3.0 M in Et₂O, 1.1 mL, 3.3 mmol) was added dropwise with stirring via syringe at 0 °C. The ampoule was flame-sealed under vacuum and heated to 60 °C for 24 h. After opening the ampoule, the reaction solution was transferred to a Schlenk flask. To ensure complete transfer, the ampoule was rinsed with Et₂O (1 mL). The excess MeMgBr was quenched with MeOH (0.3 mL) at 0 °C. After stirring at room temperature for 10 min, all volatiles were removed under reduced pressure and the colorless residue was extracted into *n*-hexane (4×5 mL). All volatiles were removed from the extract under reduced pressure to obtain Ge[2]^{TMS} as a colorless solid. Yield: 0.069 g (0.068 mmol, 86%).

Single crystals of $Ge[2]^{TMS}$. 0.4(CH₂Cl₂) suitable for X-ray analysis were grown by slow evaporation of a CH₂Cl₂ solution. The solvatomorph $Ge[2]^{TMS}$ without co-crystallized solvent molecules was obtained by slow evaporation of an *n*-hexane solution.

Elemental analysis: Calculated for $C_{20}H_{60}Cl_4Ge_4Si_{10}$ (1013.87): C 23.69; H 5.97. Found: C 23.71; H 6.09. ¹H NMR (500.2 MHz, CD₂Cl₂): $\delta = 0.70$ (s, 24H; GeMe₂), 0.37 (s, 36H; SiMe₃). ¹³C{¹H} NMR (125.8 MHz, CD₂Cl₂): $\delta = 3.7$ (SiMe₃), 2.5 (GeMe₂). ²⁹Si{¹H} NMR (99.4 MHz, CD₂Cl₂): $\delta = 50.9$ (SiCl₂), -2.0 (SiMe₃), -92.3 (*Si*-SiMe₃).

1.5. Synthesis of Ge[1]^{TMS}



A solution of **Ge**[1] (0.100 g, 0.0790 mmol) in Et₂O (3 mL) was prepared in a glass ampoule. MeMgBr (3.0 M in Et₂O, 1.1 mL, 3.3 mmol) was added dropwise with stirring via syringe at 0 °C. The ampoule was flame-sealed under vacuum and heated to 60 °C for 24 h. After opening the ampoule, the reaction solution was transferred to a Schlenk flask. To ensure complete transfer, the ampoule was rinsed with Et₂O (1 mL). The excess MeMgBr was quenched with MeOH (0.3 mL) at 0 °C. After stirring at room temperature for 10 min, all volatiles were removed under reduced pressure and the colorless residue was extracted into *n*-hexane (4×5 mL). All volatiles were removed from the extract under reduced pressure to obtain **Ge**[1]^{TMS} as a colorless solid. Yield: 0.066 g (0.065 mmol, 82%). Single crystals of **Ge**[1]^{TMS} suitable for X-ray analysis were grown by slow evaporation of a CH₂Cl₂ solution.

¹H NMR (500.2 MHz, CD₂Cl₂): $\delta = 0.66$ (s, 12H; Ge¹Me₂), 0.61 (s, 12H; Ge¹Me₂), 0.59 (s, 6H; Ge²Me₂), 0.35 (s, 18H; Si⁴Me₃), 0.27 (s, 18H; Si⁵Me₃).

¹³C{¹H} NMR (125.8 MHz, CD₂Cl₂): $\delta = 4.1$ (Si⁵Me₃), 3.8 (Si⁴Me₃), 3.6 (Ge²Me₂), 3.3 (Ge¹Me₂), 2.9 (Ge¹Me₂).

²⁹Si{¹H} NMR (99.4 MHz, CD₂Cl₂): $\delta = 52.9$ (Si³Cl₂), -2.6 (Si⁴Me₃), -3.5 (Si⁵Me₃), -91.9 (Si¹), -97.6 (Si²).

1.6. Synthesis of Ge[0]^{TMS}



A suspension of Ge[0] (0.200 g, 0.158 mmol) in THF (10 mL) was prepared in a Schlenk flask. MeMgBr (3.0 M in Et₂O, 2.1 mL, 6.3 mmol) was added dropwise with stirring via syringe at 0 °C. Stirring was continued at room temperature for 24 h. Excess MeMgBr was quenched with MeOH (0.7 mL) at 0 °C. After stirring at room temperature for 10 min, all volatiles were removed under reduced pressure and the colorless residue was extracted into *n*-hexane (2×10 mL). All volatiles were removed from the extract under reduced pressure to obtain $Ge[0]^{TMS}$ as a colorless solid. Yield: 0.082 g (0.080 mmol, 51%). Single crystals of $Ge[0]^{TMS}$ suitable for X-ray analysis were grown by slow evaporation of a CH₂Cl₂ solution.

Note: Incomplete methylation of **Ge[0]** was observed when the reaction was performed in Et₂O at 60 °C (as in the cases of **Ge[1]**^{TMS} and **Ge[2]**^{TMS}). Formation of permethylated **Ge[0]**^{TMS} was achieved only when THF was added to the reaction mixture (but then already at room temperature). In turn, **Ge[2]** showed significant decomposition under the reaction conditions applied for the synthesis of **Ge[0]**^{TMS}.

Elemental analysis: Calculated for C₂₄H₇₂Ge₆Si₈ (1021.30): C 28.23; H 7.11. Found: C 27.92; H 7.15. ¹H NMR (500.2 MHz, CD₂Cl₂): $\delta = 0.57$ (s, 36H; GeMe₂), 0.25 (s, 36H; SiMe₃). ¹³C{¹H} NMR (125.8 MHz, CD₂Cl₂): $\delta = 4.2$ (SiMe₃), 3.7 (GeMe₂). ²⁹Si{¹H} NMR (99.4 MHz, CD₂Cl₂): $\delta = -3.9$ (SiMe₃), -97.7 (*Si*-SiMe₃).

1.7. Synthesis of permethylated Ge[2]^{Me}



A solution of **Ge[2]**^{TMS} (0.149 g, 0.148 mmol) in toluene (6 mL) was prepared in a glass ampoule. AlMe₃ (2.0 M in toluene, 0.74 mL, 1.5 mmol) was added via syringe. The ampoule was flame-sealed under vacuum and heated to 200 °C for 3 d. After opening the ampoule, the yellow reaction solution was transferred to a Schlenk flask. Upon addition of Et₂O (20 mL), a colorless precipitate formed. The excess AlMe₃ was quenched with aqueous HCl (20 mL), which was added slowly with stirring at 0 °C. After aqueous workup, all volatiles were removed from the organic phase under reduced pressure to obtain the permethylated **Ge[2]**^{Me} as a colorless solid. Yield: 0.111 g (0.119 mmol, 80%).

Note: The product contains about 10-20% of an unknown impurity, which is assumed to be the heteroadamantane bearing one SiMe₂ and one SiMeCl group as a result of incomplete methylation of one SiCl₂ group.

¹H NMR (500.2 MHz, CD₂Cl₂): $\delta = 0.57$ (s, 24H; GeMe₂), 0.46 (s, 12H; SiMe₂). 0.25 (s, 36H; SiMe₃).

¹³C{¹H} NMR (125.8 MHz, CD₂Cl₂): $\delta = 4.5$ (SiMe₃), 3.9 (SiMe₂), 3.6 (GeMe₂). ²⁹Si{¹H} NMR (99.4 MHz, CD₂Cl₂): $\delta = -4.3$ (SiMe₃), -23.3 (SiMe₂), -105.3 (*Si*-SiMe₃).

2. NMR Spectroscopy

2.1. Compilation of ²⁹Si NMR chemical shift values

Table S1.²⁹Si NMR chemical shift values $\delta_{exp}(^{29}Si)$ of Si,Sn-adamantanes (**iso-Sn[2]**, **Sn[2]**, and **Sn[1]**) and methylated Si,Ge-adamantanes (**Ge[2]**^{TMS}, **Ge[1]**^{TMS}, and **Ge[0]**^{TMS}). The published chemical shift values of the Si,Ge-adamantanes (**Ge[2]**, **Ge[1]**, and **Ge[0]**) are provided for comparison.^{S1} Calculated chemical shift values $\delta_{calc}(^{29}Si)$ are given in parentheses.

$ \begin{array}{c} \delta_{exp}(^{29}{\rm Si}) \\ \delta_{calc}(^{29}{\rm Si}) \end{array} $	Si	Si	Si	SiCl ₃	SiCl ₃	SiCl ₃	SiCl ₂
iso-Sn[2]	-129.6 (-129.6)	-104.2 (-99.9)	-87.0 (-79.9)	21.6 (22.5)	14.8 (18.1)	9.4 (13.4)	33.1 (22.6)
Sn[2]		-103.8 (-95.9)			15.1 (19.5)		36.0 (27.1)
Sn[1]	-130.1 (-126.2)	-104.1 (-97.8)		21.5 (23.5)	15.4 (18.6)		37.0 (27.4)
Ge[2] ^{<i>a</i>}		-81.0 (-75.9)			11.9 (16.8)		29.6 (22.4)
Ge[1] ^a	-83.3 (-80.7)	-80.7 (-76.6)		16.2 (20.0)	12.1 (17.1)		31.0 (23.0)
Ge[0] ^a	-83.4 (-81.0)			16.2 (20.5)			
	Si	Si	Si	SiMe ₃	SiMe ₃	SiMe ₃	SiCl ₂
Ge[2] ^{TMS}		-92.2 (-91.5)			-2.0 (-12.4)		50.9 (41.8)
Ge[1] ^{TMS}	-97.6 (-98.5)	-91.9 (-91.7)		-3.5 (-13.0)	-2.6 (-12.5)		52.9 (43.2)
Ge[0] ^{TMS}	-97.7 (-99.6)			-3.9 (-13.0)			



Table S1 compiles the experimentally determined and the computed (in parentheses) ²⁹Si NMR chemical shift values of the heteroadamantanes. It is seen that (i) the experimental and calculated values (see 'Computational Details') agree very well supporting the assignment and (ii) corresponding chemical shift values of comparable compounds are consistent (cf. colors).

2.2. Compilation of ¹¹⁹Sn NMR chemical shift values

Table S2. ¹¹⁹Sn NMR chemical shift values $\delta_{exp}(^{119}Sn)$ of Si,Sn-adamantanes **iso-Sn[2]**, **Sn[2]**, and **Sn[1]**. Calculated chemical shift values $\delta_{calc}(^{119}Sn)$ are given in parentheses.



Table S2 compiles the experimentally determined ¹¹⁹Sn NMR chemical shift values of the Si,Sn-adamantanes **iso-Sn[2]**, **Sn[2]**, and **Sn[1]**; the calculated values are given in parentheses (see 'Computational Details').

2.3. Plots of NMR Spectra (${}^{1}H$, ${}^{13}C{}^{1}H$, ${}^{29}Si{}^{1}H$, ${}^{29}Si-DEPT$, ${}^{29}Si/{}^{1}H$ HMBC, ${}^{119}Sn{}^{1}H$, and ${}^{119}Sn/{}^{1}H$ HMBC)



Figure S3. ¹H NMR spectrum (500.2 MHz, CD_2Cl_2) of the isomer mixture **Sn[2]/iso-Sn[2]** (containing trace amounts of **Sn[1]**). ¹¹⁹Sn and ¹¹⁷Sn satellites are marked with asterisks.



220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 δ (ppm)

Figure S4. ¹³C{¹H} NMR spectrum of the isomer mixture Sn[2]/iso-Sn[2] (125.8 MHz, CD_2Cl_2).



Figure S5. ²⁹Si{¹H} NMR spectrum of the isomer mixture Sn[2]/iso-Sn[2] (99.4 MHz, CD_2Cl_2).



Figure S6. ²⁹Si-DEPT NMR spectrum (99.4 MHz, CD_2Cl_2) of the isomer mixture Sn[2]/iso-Sn[2] (containing trace amounts of Sn[1]).



Figure S7. ²⁹Si/¹H HMBC NMR spectrum of the isomer mixture Sn[2]/iso-Sn[2].



Figure S8. ¹¹⁹Sn{¹H} NMR spectrum of the isomer mixture Sn[2]/iso-Sn[2] (186.5 MHz, CD_2Cl_2).



Figure S9. ¹¹⁹Sn/¹H HMBC NMR spectrum of the isomer mixture Sn[2]/iso-Sn[2].



Figure S10. ¹H NMR spectrum of **Sn[1]** (500.2 MHz, CD₂Cl₂). ¹¹⁹Sn and ¹¹⁷Sn satellites are marked with asterisks.



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 δ (ppm)

Figure S11. ${}^{13}C{}^{1}H$ NMR spectrum of Sn[1] (125.8 MHz, CD₂Cl₂).



-70

-90

-110

Figure S12. ²⁹Si{¹H} NMR spectrum of **Sn[1]** (99.4 MHz, CD₂Cl₂).

-30



Figure S13. ²⁹Si/¹H HMBC NMR spectrum of Sn[1].



400 350 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 -400 -450 -500 δ (ppm)

Figure S14. ¹¹⁹Sn{¹H} NMR spectrum of Sn[1] (186.5 MHz, CD_2Cl_2). Satellites are marked with asterisks.



Figure S15. ¹¹⁹Sn/¹H HMBC NMR spectrum of Sn[1].



Figure S16. ¹H NMR spectrum of Ge[2]^{TMS} (500.2 MHz, CD₂Cl₂).



220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 δ (ppm)

Figure S17. ${}^{13}C{}^{1}H$ NMR spectrum of Ge[2]^{TMS} (125.8 MHz, CD₂Cl₂).



Figure S18. ²⁹Si{¹H} NMR spectrum of Ge[2]^{TMS} (99.4 MHz, CD_2Cl_2).



Figure S19. ²⁹Si/¹H HMBC NMR spectrum of Ge[2]^{TMS}.



Figure S20. ¹H NMR spectrum of Ge[1]^{TMS} (500.2 MHz, CD₂Cl₂).



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 δ (ppm)

Figure S21. ¹³C{¹H} NMR spectrum of **Ge[1]**^{TMS} (125.8 MHz, CD₂Cl₂).





Figure S22. ²⁹Si{¹H} NMR spectrum of **Ge[1]**^{TMS} (99.4 MHz, CD₂Cl₂).



Figure S23. ²⁹Si/¹H HMBC NMR spectrum of Ge[1]^{TMS}.



Figure S24. ¹H NMR spectrum of Ge[0]^{TMS} (500.2 MHz, CD₂Cl₂).



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 δ (ppm)

Figure S25. ¹³C{¹H} NMR spectrum of Ge[0]^{TMS} (125.8 MHz, CD₂Cl₂).



Figure S26. ²⁹Si{¹H} NMR spectrum of Ge[0]^{TMS} (99.4 MHz, CD_2Cl_2).



Figure S27. ²⁹Si/¹H HMBC NMR spectrum of Ge[0]^{TMS}.



Figure S28. ¹H NMR spectrum of $Ge[2]^{Me}$ (500.2 MHz, CD_2Cl_2).



220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 δ (ppm)

Figure S29. ${}^{13}C{}^{1}H$ NMR spectrum of Ge[2]^{Me} (125.8 MHz, CD₂Cl₂).



Figure S30. ²⁹Si-DEPT NMR spectrum of Ge[2]^{Me} (99.4 MHz, CD₂Cl₂).



Figure S31. ²⁹Si/¹H HMBC NMR spectrum of Ge[2]^{Me}.

3. Computational details

All geometry optimizations and Hessian calculations were performed applying the MN15^{S3} functional in combination with the functionals def2-SVP^{S4} (H, C, Si, Cl) and def2-TZVP^{S4,S5} (Ge, Sn (ECP)). Solvation corrections were incorporated with the solvent model based on density (SMD; solvent = CH₂Cl₂).^{S6} Optimized geometries were confirmed to be the desired minimum energy structures by the absence of imaginary frequencies ($i\omega < 15 \text{ cm}^{-1}$) in the harmonic vibrational frequency calculation. Single point calculations were performed at the SMD(CH₂Cl₂)/MN15/def2-TZVP level of theory to get final energy values. All free energy (*G*₂₉₈) values were calculated for the corresponding experimental temperature at 298 K.

All ²⁹Si and ¹¹⁹Sn NMR isotropic shielding tensors (IST) were computed using the gaugeinvariant atomic orbital (GIAO)^{S7} method with the SMD(CH₂Cl₂)/PBE0/x2c-TZVPall-s level of theory,^{S8,S9} as this combination was shown to deliver reliable results in recent benchmark studies.^{S10} Since the experimentally observed NMR chemical shift values are a result of a dynamic process, the computed ISTs were averaged over all symmetry-related positions of the nuclei under consideration in each molecule. ²⁹Si and ¹¹⁹Sn NMR resonances were referenced against SiMe₄ (IST = 340.3300 ppm) and SnMe₄ (IST = 2463.7378 ppm), respectively, for which optimization and chemical shielding were calculated in the same manner.

The calculated NMR chemical shift values $\delta(E)$ were further corrected by applying a compensating linear scaling approach using the general formula (1). The correction factors α and β were determined from a benchmark set consisting of constitutionally comparable compounds (all structures were optimized with the method described above): Me₃SnCl,^{S11} Me₃SnCl₂,^{S11} Me₃SnSiCl₃,^{S12} Me₃SnSi(SiMe₃)₃,^{S13} (Me₃Sn)₂Si(SiCl₃)₂,^{S12} Me₃GeSiCl₃,^{S12} (Me₃Ge)₂Si(SiCl₃)₂.^{S12} Figure S32 and Figure S33 show the calculated uncorrected ²⁹Si and ¹¹⁹Sn NMR chemical shift values of the benchmark set (x-axis) plotted against the experimentally observed NMR chemical shift values (y-axis) published in the literature. The linear regressions derived from these plots for ²⁹Si and ¹¹⁹Sn have the formulas (2) and (3), respectively, and can be used directly to correct the calculated NMR chemical shift values in the heteroadamantanes.

General:	$\delta_{corr}(E) = \alpha \cdot \delta(E) + \beta$	(1)
²⁹ Si:	$f(x) = 0.7336 \cdot x - 9.1031$	(2)
¹¹⁹ Sn:	$f(x) = 0.8038 \cdot x + 1.7162$	(3)

All DFT calculations were performed using Gaussian 16, Revision B.01.^{S14} Graphical representations of molecular geometries were produced with the *CYLview20* software.^{S15}

3.1. Linear scaling approach for ²⁹Si and ¹¹⁹Sn NMR calculations

Table S3. Calculated isotropic shielding tensors (IST; top), calculated NMR chemical shift values δ_{calc} (middle), and experimental NMR chemical shift values δ_{exp} (bottom) in ppm for all ²⁹Si and ¹¹⁹Sn nuclei of the benchmark set.

$egin{array}{l} \mathbf{avg. IST} \ \delta_{ ext{calc}}(^{29} ext{Si}) \ \delta_{ ext{exp}}(^{29} ext{Si}) \ [ppm] \end{array}$	<i>Si</i> (SiR ₃) ₃	SiR3	Sn
Me ₃ SnCl	-	-	2277.1979 186.5 164.2
Me2SnCl2	-	_	2285.6384 178.1 137
EtSnCl ₃	-	-	2442.7389 21.0 6
Me3SnSiCl3	294.0166 46.3	-	2547.4573 -83.7 -70
Me3SnSi(SiMe3)3	515.7489 -175.4 -136.6	352.2391 -11.9 -6.1	2554.7869 -91.0 -69.4
(Me3Sn)2Si(SiCl3)2	466.6837 -126.4 -106.4	300.1247 40.2 19.6	2547.3272 -83.6 -55.2
Me3GeSiCl3	-	296.7357 43.6 17.8	-
(Me3Ge)2Si(SiCl3)2	441.6128 -101.3 -84.2	302.226 38.1 17.2	-



Figure S32. Plot of the calculated ²⁹Si NMR chemical shift values (x-axis, ppm) of the benchmark set against the corresponding experimentally determined chemical shift values (y-axis, ppm) reported in the literature. The linear regression is f(x) = 0.7336x - 9.1031 with a certainty of R² = 0.993.



Figure S33. Plot of the calculated ¹¹⁹Sn NMR chemical shift values (x-axis, ppm) of the benchmark set against the corresponding experimentally determined chemical shift values (y-axis, ppm) reported in the literature. The linear regression is f(x) = 0.8038x + 1.7162 with a certainty of R² = 0.991.

		Ĩ			Ĩ		
•	<i>C_s</i> : iso-Sn[2]	Sn[2],	D _{2d} : [2], [2] ^{™S}	C _{2v} : Sn[1], [1], [1] ^{TMS}	<i>T_d</i> : [0], [0]™s	•
avg. IST $\delta(^{29}\text{Si})$ $\delta_{\text{corr}}(^{29}\text{Si})$ [ppm]	Si	Si	Si	SiCl ₃	SiCl ₃	SiCl ₃	SiCl ₂
iso-Sn[2]	504.0768 -163.7 -129.2	464.0683 -123.7 -99.9	436.8397 -96.5 -79.9	297.2684 43.1 22.5	303.2810 37.0 18.1	309.7229 30.6 13.4	297.1239 43.2 22.6
Sn[2]		458.6170 -118.3 -95.9			301.4055 38.9 19.5		291.0349 49.3 27.1
Sn[1]	499.9728 -159.6 -126.2	461.1784 -120.8 -97.8		295.8489 44.5 23.5	302.5802 37.7 18.6		290.5912 49.7 27.4
Ge[2] ^a		431.4427 -91.1 -75.9			305.0311 35.3 16.8		297.3424 43.0 22.4
Ge[1] ^a	437.9177 -97.6 -80.7	432.2765 -91.9 -76.6		300.6709 39.7 20.0	304.6085 35.7 17.1		296.5132 43.8 23.0
Ge[0] ^a	438.2841 -98.0 -81.0			300.0299 40.3 20.5			
	Si	Si	Si	SiMe ₃	SiMe ₃	SiMe ₃	SiCl ₂
Ge[2] ^{TMS}		452.5883 -112.3 -91.5			344.8337 -4.5 -12.4		270.9810 69.3 41.8
Ge[1] ^{TMS}	462.1950 -121.9 -98.5	452.9534 -112.6 -91.7		345.6034 -5.3 -13.0	344.9370 -4.6 -12.5		269.0904 71.2 43.2
Ge[0] ^{TMS}	463.6663 -123.3 -99.6			345.6834 -5.4 -13.0			

3.2. Calculation of ²⁹Si NMR chemical shift values

Figure S34. *Top:* Schematic representation of the heteroadamantane scaffolds. *Bottom:* Calculated isotropic shielding tensors (IST in ppm; first value), calculated NMR chemical shift values δ ⁽²⁹Si) (second value), and the corrected NMR chemical shift values δ_{corr} ⁽²⁹Si) (corrected with formula (2); third value) in ppm for all ²⁹Si nuclei in the heteroadamantanes.

The calculated ²⁹Si NMR chemical shift values of the quaternary silicon atoms variate on average by ± 3.4 ppm from the experimentally determined chemical shift values. A similar but systematic deviation is found for all calculated values of *Si*Cl₃ atoms, whose chemical shift values are overestimated by an average of 3.6 ppm. Somewhat larger discrepancies are observed for the *Si*Cl₂ atoms of the adamantane backbone, whose NMR chemical shift values are underestimated by 9.0 ppm on average. The NMR chemical shift values of the *Si*Me₃ atoms are also underestimated by 9.7 ppm on average. This slightly larger deviation can be explained by the choice of the benchmark set, since SiCl₃ groups are mostly present here instead of SiMe₃ groups.



3.3. Calculation of ¹¹⁹Sn NMR chemical shift values

Figure S35. *Top:* Schematic representation of the heteroadamantane scaffolds. *Bottom:* Calculated isotropic shielding tensors (IST in ppm; first value), calculated NMR chemical shift values δ (¹¹⁹Sn) (second value), and the corrected NMR chemical shift values δ_{corr} (¹¹⁹Sn) (corrected with formula (**3**); third value) in ppm for all Si,Sn-adamantanes.

The uncorrected calculated NMR chemical shift values $\delta(^{119}\text{Sn})$ systematically underestimate the experimentally determined chemical shift values by an average of 65 ppm, which is within a common error range for predicted ¹¹⁹Sn resonances.^{S10b} However, correction by the compensating linear scaling approach significantly improves the accuracy of the calculated NMR chemical shift values $\delta_{corr}(^{119}\text{Sn})$, underestimating the experimental values by only 26 ppm on average.

3.4. Comparison of the isomers E[2] and iso-E[2] (E = Si, Ge, Sn)

Table S4. Absolute (*G*₂₉₈) and relative (ΔG_{298}) free energies of the isomers **E**[2] and iso-**E**[2] for E = Si, Ge, Sn.

	Com / Hantman	$\Delta G_{298} = G_{298} (\text{iso-}$	$E[2]) - G_{298}(E[2])$	
	G298 / Hartree	ΔG_{298} / Hartree	ΔG_{298} / kcal mol $^{-1}$	
Si[2]	-11733.39265790	0.00282220	2.4	
iso-Si[2]	-11733.38883460	0.00382330		
Ge[2]	-18885.09987240	0.00447060	2.9	
iso-Ge[2]	-18885.09539280	0.00447900	2.8	
Sn[2]	-11431.15537390	0.00250620	16	
iso-Sn[2]	-11431.15277770	0.00259620	1.0	

3.5. Computed structures and free energy values

Si[2]		iso-Si[2]
$G_{298} =$	-11733.39265790 Hartree	$G_{298} =$

*G*298 =



Ge[0] *G*298 =

-20779.65042380 Hartree



Ge[2] *G*₂₉₈ =

-18885.09987240 Hartree





-19832.37681450 Hartree

-11733.38883460 Hartree





-18885.09539280 Hartree



Ge[2]^{TMS}

 $G_{298} =$





Sn[2]

G298 =

-11431.15537390 Hartree



Ge[1]^{TMS}

 $G_{298} =$

-14788.43390190 Hartree



Sn[1]

 $G_{298} =$

-10514.94266020 Hartree



iso-Sn[2]

$$G_{298} =$$

-11431.15277770 Hartree



4. Single-crystal X-ray analyses

Single-crystal diffraction data were collected at -100° C on *STOE IPDS II* two-circle diffractometer equipped with *Genix 3D HS* microfocus Mo K_{α} X-ray source ($\lambda = 0.71073$ Å). The finalization of the data, including empirical absorption corrections, were done using *CrysAlisPro* software v.1.171.42.43a (Rigaku Oxford Diffraction, 2022). The structures were solved by direct methods using the program SHELXS and refined against $|F|^2$ with full-matrix least-squares techniques using the program *SHELXL*-2018/3.^{S16,S17} All H atoms were located geometrically and refined riding on the pivot atom.

The crystal structure of **Ge[0]^{TMS}** does not show disorder. In the heteroadamantane core of **Sn[2]/iso-Sn[2]** all positions of SnMe₂ groups are shared with SiCl₂ groups with variable ratios (due to disorder). In the heteroadamantane cores of **Ge[2]^{TMS}** and **Ge[1]^{TMS}** all positions of GeMe₂ groups are shared with SiCl₂ groups with variable ratios (due to disorder). In these cases, both positions were taken into refinement assuming the same atomic coordinates and anisotropic replacement parameters (EXYZ and EADP instructions in *SHELXL-2018*). Moreover, because there is no chemical evidence for the existence of SiMe₂, SnCl₂, or GeCl₂ groups, the same occupancy factors were assigned to Si/Cl and Sn/Me pairs or Si/Cl and Ge/Me pairs.

CIF files containing the crystallographic information are deposited in the Cambridge Crystallographic Data Centre under the deposition codes CSD2223399 ((iso-)Sn[2]·SiCl4), CSD2223400 (Ge[2]^{TMS}), CSD2223401 (Ge[2]^{TMS}·0.4(CH₂Cl₂)), CSD2223402 ({Ge[1]^{TMS}}_{0.86}{Ge[2]^{TMS}}_{0.14}), and CSD2223403 (Ge[0]^{TMS}) and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif. Crystallographic data and parameters of the diffraction experiments are given in Table S6, Table S7, and Table S8.

The authors thank Dr. Matthias Meyer (Rigaku Oxford Diffraction) for his precious help with the implementation of the *CrysAlisPro* software for the *STOE IPDS II* diffraction data.

4.1. Single-Crystal X-ray Analysis of (iso-)Sn[2]·SiCl4

(iso-)Sn[2]·SiCl₄ crystallizes in the tetragonal space group *I*4*m*2 (No. 119) with both the Si₁₀Sn₄ heteroadamantane and SiCl₄ laying in different special positions with $4m^2$ (D_{2d}) point symmetry, close to ideal T_d . There are two crystallographically unique positions of SnMe₂ groups that are shared with SiCl₂ to varying degrees (due to disorder). The unconstrained refinement of the site occupancy factors results in a chemical composition statistically undistinguishable from Si₁₀Sn₄ and therefore the SUMP instruction was implemented at the final stage of the refinement. Due to disorder Sn[2] and iso-Sn[2] cannot be distinguished. Selected bond length [Å]: Si(3)–Si(4) = 2.319(4).



Figure S36. Molecular structure of (**iso-**)**Sn[2]·SiCl**⁴ in the solid state. *Left:* All SnMe₂ vertices of the heteroadamantane core depict positions shared with SiCl₂ and are therefore colored in light gray. The a.d.p. ellipsoids are shown at the 50% probability level. All H atoms and the cocrystallized SiCl₄ molecule are omitted for clarity. *Right:* Schematic representation of partial site occupancy factors by means of sectors. Blue: Si, pink: Sn, yellow: Cl, dark gray: C.

4.2. Single-Crystal X-ray Analysis of Ge[2]^{TMS}

Molecular compound $Ge[2]^{TMS}$ was obtained in two distinct crystalline phases: A ($Ge[2]^{TMS}$) and B ($Ge[2]^{TMS}$ ·0.4(CH_2Cl_2)) by the crystallization from *n*-hexane and CH_2Cl_2 , respectively.

Structure **A** crystallizes in the orthorhombic space group *Pbca* (No. 61) with **Ge[2]**^{TMS} lying in the general position (Z = 8). All six positions of GeMe₂ groups are shared with SiCl₂ to varying degrees (due to disorder). An unconstrained refinement of the site occupancy factors of GeMe₂/SiCl₂ resulted in a chemical composition being statistically undistinguishable from Ge₄Si₁₀ and therefore the occupancy factors were restrained to give this exact composition by using the SUMP instruction. Selected bond lengths [Å]: Si(1)–Si(5) = 2.363(2), Si(2)–Si(6) = 2.360(2), Si(3)–Si(7) = 2.380(2), Si(4)–Si(8) = 2.364(2).



Figure S37. Molecular structure of $Ge[2]^{TMS}$ in the solid state. *Left:* All GeMe₂ vertices of the heteroadamantane core depict positions shared with SiCl₂ and are therefore colored in light gray. The a.d.p. ellipsoids are shown at the 50% probability level. All H atoms are omitted for clarity. *Right*: Schematic representation of partial site occupancy factors by means of sectors. Blue: Si, purple: Ge, yellow: Cl, dark gray: C.

Structure **B** crystallizes in the orthorhombic space group *Pnma* (No. 62) with **Ge[2]**^{TMS} lying on the mirror plane. In addition, the crystal contains 0.4 equivalents of severely disordered CH₂Cl₂ per formula unit. All six positions of GeMe₂ groups are shared with SiCl₂ to varying degrees (due to disorder). An unconstrained refinement of the GeMe₂/SiCl₂ site occupancy factors resulted in a chemical composition being statistically undistinguishable from Ge₄Si₁₀ and therefore in the final refinement step the SUMP instruction was implemented. Selected bond lengths [Å]: Si(1)–Si(4) = 2.3632(12), Si(2)–Si(5) = 2.3749(17), Si(3)–Si(6) = 2.3644(16).



Figure S38. Molecular structure of $Ge[2]^{TMS} \cdot 0.4(CH_2Cl_2)$ in the solid state. *Left:* All GeMe₂ vertices of the heteroadamantane core depict positions shared with SiCl₂ and are therefore colored in light gray. The a.d.p. ellipsoids are shown at the 50% probability level. All H atoms are omitted for clarity. *Right*: Schematic representation of partial site occupancy factors by means of sector. Blue: Si, purple: Ge, yellow: Cl, dark gray: C.

4.3. Single-Crystal X-ray Analysis of {Ge[1]^{TMS}}0.86{Ge[2]^{TMS}}0.14

The molecular compound $Ge[1]^{TMS}$ is isostructural to $Ge[0]^{TMS}$. It crystallizes in the orthorhombic space group *Cmcm* (No. 63) with the molecule lying on the position m2m ($C_{2\nu}$ point symmetry). The terminal SiMe₃ groups are affected by the rotational disorder around Si-Si axis that was approximated with the anisotropic ellipsoids of carbon atoms. All three crystallographically unique positions of GeMe₂ groups are shared with SiCl₂ to varying degrees (due to disorder).

Therefore, the crystal selected for the SC-XRD is a solid solution with the average formula $\{Ge[1]^{TMS}\}_{0.86}\{Ge[2]^{TMS}\}_{0.14}$, similar to the structure of Sn[1] being mixed with Sn[2]. Selected bond lengths [Å]: Si(1)–Si(3) = 2.357(2), Si(2)–Si(4) = 2.358(2).



Figure S39. Molecular structure of $\{Ge[1]^{TMS}\}_{0.86}\{Ge[2]^{TMS}\}_{0.14}$ in the solid state. *Left:* All GeMe₂ vertices of the heteroadamantane core depict positions shared with SiCl₂ and are therefore colored in light gray. The a.d.p. ellipsoids are shown at the 50% probability level. All H atoms are omitted for clarity. *Right*: Schematic representation of partial site occupancy factors by means of sectors. Blue: Si, purple: Ge, yellow: Cl, dark gray: C.

4.4. Single-Crystal X-ray Analysis of Ge[0]^{TMS}

The molecular compound $Ge[0]^{TMS}$ crystallizes in the orthorhombic space group *Cmcm* (No. 63) with the molecule lying on the position m2m ($C_{2\nu}$ point symmetry). The terminal SiMe₃ groups are affected by the rotational disorder around Si–Si axis that was approximated with the anisotropic ellipsoids of carbon atoms. Analysis of the atomic displacement parameters and the residual density gives no evidence for a possible GeMe₂/SiCl₂ disorder; this is in agreement with the expected absence of SiCl₂ moleties in compound Ge[0]^{TMS}. For selected bond lengths [Å] and bond angles [°] see Table S5.



Figure S40. Molecular structure of $Ge[0]^{TMS}$ in the solid state. The a.d.p. ellipsoids are shown at the 50% probability level. All H atoms are omitted for clarity; blue: Si, purple: Ge, dark gray: C.

Table S5. Ranges of selected bond lengths [Å] and bond angles [°] of **Ge[0**]^{TMS}.

bond length/	minimal value	maximal value	average
angle			
Ge–Si	Ge(3)-Si(2) = 2.3904(12)	Ge(2)-Si(2) = 2.3947(7)	2.392
Si–Si	Si(2)-Si(4) = 2.3561 (17)	Si(1)-Si(3) = 2.3581 (16)	2.357
Ge–Si–Ge	Ge(2)-Si(1)-Ge(2) = 107.81(5)	Ge(2)-Si(2)-Ge(2) = 110.06(5)	108.70
Si–Si–Ge	Si(4)-Si(2)-Ge(2) = 109.75(4)	Si(4)-Si(2)-Ge(3) = 111.18(6)	110.36

	(iso-)Sn[2]·SiCl4
Crystal data	2223399
Chemical formula	$C_8H_{24}Cl_{16}Si_{10}Sn_4\cdot Cl_4Si$
M _r	1613.02
Crystal system, space group	Tetragonal, <i>I</i> 4m2
Temperature (K)	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	15.4337 (3),
	15.4337 (3),
	10.8282 (4)
α, β, γ (°)	90, 90, 90
$V(\text{\AA}^3)$	2579.26 (12)
Z	2
F(000)	1532
Radiation type	Μο Κα
μ (mm ⁻¹)	3.22
Crystal shape	Block
Color	Colorless
Crystal size (mm)	$0.21\times0.14\times0.12$
T_{\min}, T_{\max}	0.588, 1.000
No. of measured, independent and observed $[I > 2s(I)]$	6111, 1288, 1251
reflections	
R _{int}	0.057
Θ values (°), max, min	25.7, 4.2
Range of h, k, l	$h = -18 \rightarrow 18,$
	$k = -18 \rightarrow 12,$
	$l = -13 \rightarrow 12$
$R[F^2 > 2s(F^2)], wR(F^2), S$	0.030, 0.068, 1.19
No. of reflections	1288
No. of parameters	65
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} \ (\text{e} \cdot \text{\AA}^{-3})$	0.43, -0.48
Absolute structure parameter	0.06 (7)

Table S6. Crystallographic data and details of the diffraction experiments for (iso-)Sn[2]·SiCl4.

	Ge[2] ^{TMS}	Ge[2] ^{TMS} ·0.4(CH ₂ Cl ₂)	
Deposition code	2223400	2223401	
Chemical formula	$C_{20}H_{60}Cl_4Ge_4Si_{10}$	$C_{20}H_{60}Cl_4Ge_4Si_{10} \cdot 0.4(CH_2Cl_2)$	
$M_{ m r}$	1013.74	1047.71	
Crystal system, space group	Orthorhombic, Pbca	Orthorhombic, Pnma	
Temperature (K)	173	173	
<i>a</i> , <i>b</i> , <i>c</i> (Å)	20.2374(4),	25.2179(4),	
	12.5486(3),	15.3306(2),	
	37.1944(9)	12.6825(2)	
α, β, γ (°)	90, 90, 90	90, 90, 90	
$V(\text{\AA}^3)$	9445.5 (4)	4903.14 (13)	
Z	8	4	
<i>F</i> (000)	4128	2131	
Radiation type	Μο <i>Κ</i> α	Μο <i>Κ</i> α	
$\mu (\mathrm{mm}^{-1})$	3.02	2.95	
Crystal shape	Needle	Plate	
Color	Colorless	Colorless	
Crystal size (mm)	$0.17 \times 0.09 \times 0.02$	$0.19 \times 0.14 \times 0.03$	
T_{\min}, T_{\max}	0.369, 1.000	0.607, 1.000	
No. of measured, independent and	74122, 8626, 5703	83027, 4829, 4159	
observed $[I > 2s(I)]$ reflections			
R _{int}	0.124	0.064	
Θ values (°), max, min	25.4, 3.8	25.7, 3.8	
Range of <i>h</i> , <i>k</i> , <i>l</i>	$h = -23 \rightarrow 24,$	$h = -30 \rightarrow 30,$	
	$k = -12 \rightarrow 15$,	$k = -18 \rightarrow 18$,	
	<i>l</i> = −44→44	$l = -15 \rightarrow 14$	
$R[F^2 > 2s(F^2)], wR(F^2), S$	0.053, 0.121, 1.06	0.033, 0.086, 1.04	
No. of reflections	8626	4829	
No. of parameters	373	225	
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e \cdot \text{\AA}^{-3})$	1.15, -0.47	0.89, -0.66	

Table S7.Crystallographicdataandexperimentaldetailsfor $Ge[2]^{TMS}$ and $Ge[2]^{TMS} \cdot 0.4(CH_2Cl_2).$

	$\{Ge[1]^{TMS}\}_{0.86}\{Ge[2]^{TMS}\}_{0.14}$	Ge[0] ^{TMS}
Deposition code	2223402	2223403
Chemical formula	$(C_{20}H_{60}Cl_4Ge_4Si_{10})_{0.142}$	$C_{24}H_{72}Ge_6Si_8$
	$(C_{22}H_{66}Cl_2Ge_5Si_9)_{0.858}$	
M _r	1016.83	1021.07
Crystal system, space group	Orthorhombic, Cmcm	Orthorhombic, Cmcm
Temperature (K)	173	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	17.1568(11),	17.4656(5),
	18.8562(10),	18.7853(6),
	15.1154(9)	15.0222(5)
α, β, γ (°)	90, 90, 90	90, 90, 90
$V(\text{\AA}^3)$	4890.0 (5)	4928.7 (3)
Z	4	4
<i>F</i> (000)	2071	2080
Radiation type	Μο <i>Κ</i> α	Μο <i>Κ</i> α
$\mu (\mathrm{mm}^{-1})$	3.32	3.82
Crystal shape	Plate	Block
Color	Colorless	Colorless
Crystal size (mm)	$0.18 \times 0.13 \times 0.05$	$0.18 \times 0.14 \times 0.12$
T_{\min}, T_{\max}	0.747, 1.000	0.404, 1.000
No. of measured, independent and	9822, 2490, 1674	35724, 2511, 2129
observed $[I > 2s(I)]$ reflections		
R _{int}	0.070	0.056
Θ values (°), max, min	25.7, 4.0	25.7, 4.3
Range of <i>h</i> , <i>k</i> , <i>l</i>	$h = -17 \rightarrow 20,$	$h = -21 \rightarrow 21,$
	$k = -22 \longrightarrow 22,$	$k = -22 \rightarrow 22,$
	$l = -15 \rightarrow 18$	$l = -18 \rightarrow 18$
$R[F^2 > 2s(F^2)], wR(F^2), S$	0.043, 0.100, 1.04	0.031, 0.071, 1.10
No. of reflections	2490	2511
No. of parameters	111	109
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e \cdot \text{\AA}^{-3})$	0.51, -0.46	0.44, 0.51

Table S8. Crystallographic data and details of the diffraction experiments for $Ge[0]^{TMS}$ and $\{Ge[1]^{TMS}\}_{0.86}\{Ge[2]^{TMS}\}_{0.14}$.

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