Electronic Supplementary Material (ESI) for Dalton Transactions.


**Supporting information**

**1.** EDX measurement of crystals of $[\{(TsiGe)_2GeSe_4\}_2(\mu^2\text{-}Se)_2]$ **1**

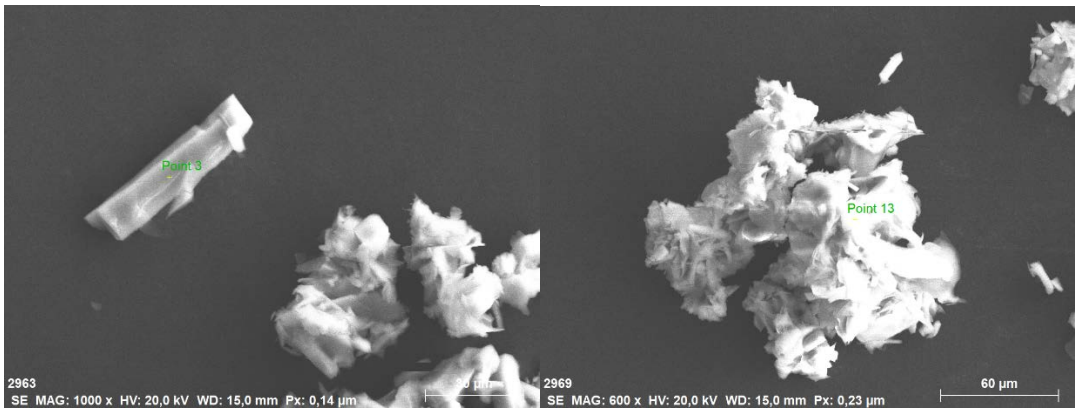


**Fig. S1**: SEM images of a **1** crystallite with the positions 7, 10 where the EDX measurements were performed. **Device:** HITACHI SU8030 scanning electron microscope with Bruker-EDX.

Table S1: Results of the EDX measurement of the crystals at point 3 (fig. S1)

| *ELEMENT* | *NORM. WT. %* | *NORM. WT. % CALCULATED* | *NORM. AT. %* | *NORM. AT. % CALCULATED* |
|---|---|---|---|---|
| ***GE*** | 26.3 | 27.9 | 20.2 | 21.4 |
| ***SE*** | 51.9 | 50.5 | 36.6 | 35.7 |
| ***SI*** | 21.8 | 21.6 | 43.2 | 42.9 |

Table S2: Results of the EDX measurement of the crystals at point 13 (fig. S1)

| *ELEMENT* | *NORM. WT. %* | *NORM. WT. % CALCULATED* | *NORM. AT. %* | *NORM. AT. % CALCULATED* |
|---|---|---|---|---|
| ***GE*** | 28.4 | 27.9 | 21.5 | 21.4 |
| ***SE*** | 48.8 | 50.5 | 34.0 | 35.7 |
| ***SI*** | 22.8 | 21.6 | 44.6 | 42.9 |

Table S3: Average results of the EDX measurement of the crystals

| *ELEMENT* | *Ø NORM. WT. %* | *NORM. WT. % CALCULATED* | *Ø NORM. AT. %* | *NORM. AT. % CALCULATED* |
|---|---|---|---|---|
| ***GE*** | 26.8 | 27.9 | 20.4 | 21.4 |
| ***SE*** | 51.0 | 50.5 | 35.8 | 35.7 |
| ***SI*** | 22.2 | 21.6 | 43.8 | 42.9 |

**2.** EDX measurement of crystals of $Ge_2(\mu^2\text{-}Te)_2(Tsi)_2(TeH)_2$ **2**

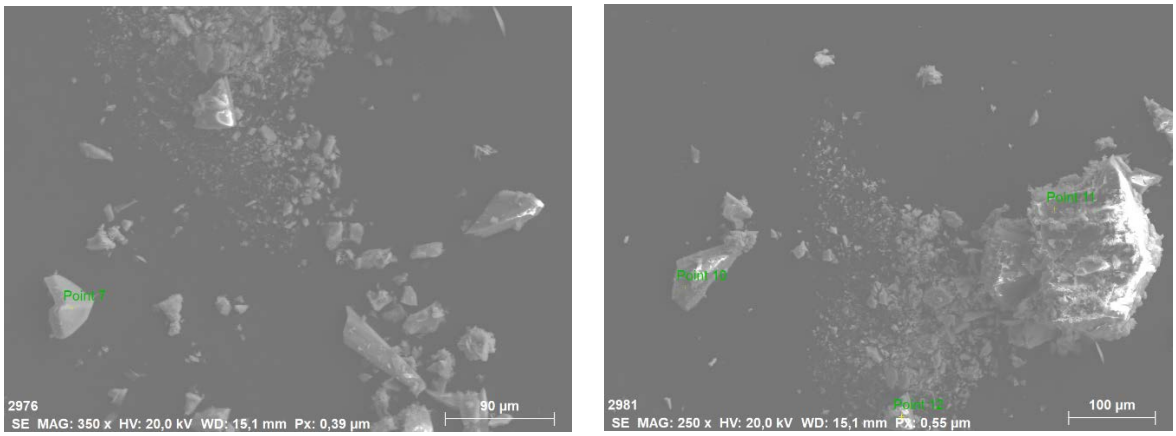


**Fig. S2**: SEM images of a **2** crystallite with the positions 7, 10 where the EDX measurements were performed. **Device:** HITACHI SU8030 scanning electron microscope with Bruker-EDX.

Table S4: Results of the EDX measurement of the crystals at point 7 (Fig. S2)

| *ELEMENT* | *NORM. WT. %* | *NORM. WT. % CALCULATED* | *NORM. AT. %* | *NORM. AT. % CALCULATED* |
|---|---|---|---|---|
| ***GE*** | 16.7 | 17.6 | 15.9 | 16.7 |
| ***TE*** | 62.9 | 61.9 | 34.0 | 33.3 |
| ***SI*** | 20.4 | 20.4 | 50.1 | 50.0 |

Table S5: Results of the EDX measurement of the crystals at point 10 (Fig. S2)

| *ELEMENT* | *NORM. WT. %* | *NORM. WT. % CALCULATED* | *NORM. AT. %* | *NORM. AT. % CALCULATED* |
|---|---|---|---|---|
| ***GE*** | 16.6 | 17.6 | 15.8 | 16.7 |
| ***TE*** | 62.5 | 61.9 | 34.2 | 33.3 |
| ***SI*** | 20.9 | 20.4 | 50.1 | 50.0 |

Table S6: Average results of the EDX measurement of the crystals at points 1-10

| *ELEMENT* | *Ø NORM. WT. %* | *NORM. WT. % CALCULATED* | *Ø NORM. AT. %* | *NORM. AT. % CALCULATED* |
|---|---|---|---|---|
| ***GE*** | 16.8 | 17.6 | 15.5 | 16.7 |
| ***TE*** | 62.5 | 61.9 | 33.6 | 33.3 |
| ***SI*** | 20.9 | 20.4 | 50.9 | 50.0 |

**3.** EDX-measurement of crystals of $[Li(Et_2O)(OC_4H_7)Ge_3Te_4(Tsi)_2]_2$ **3**

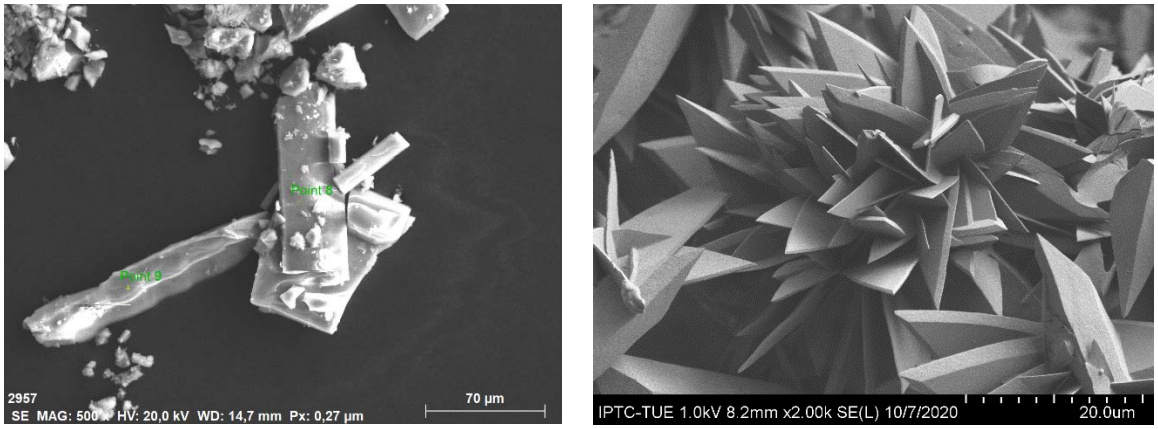


**Fig. S3**: SEM image of a **3** crystallite with the positions 7, 8 where the EDX measurements were performed (left side). SEM image of crystalline **3** with 2000x magnitude (right side). **Device:** HITACHI SU8030 scanning electron microscope with Bruker-EDX.

Table S7: Results of the EDX measurement of the crystallite at point 7 (Fig. S3)

| *ELEMENT* | *NORM. WT. %* | *NORM. WT. % CALCULATED* | *NORM. AT. %* | *NORM. AT. % CALCULATED* |
|---|---|---|---|---|
| ***GE*** | 23.6 | 24.3 | 22.4 | 23.1 |
| ***TE*** | 57.3 | 56.9 | 30.9 | 30.8 |
| ***SI*** | 19.1 | 18.8 | 46.7 | 46.2 |

Table S8: Results of the EDX measurement of the crystallite at point 8 (Fig. S3)

| *ELEMENT* | *NORM. WT. %* | *NORM. WT. % CALCULATED* | *NORM. AT. %* | *NORM. AT. % CALCULATED* |
|---|---|---|---|---|
| ***GE*** | 24.4 | 24.3 | 22.9 | 23.1 |
| ***TE*** | 56.2 | 56.9 | 30.0 | 30.8 |
| ***SI*** | 19.4 | 18.8 | 47.0 | 46.2 |

Table S9: Average results of the EDX measurement of the crystallite at points 1-10

| *ELEMENT* | *Ø NORM. WT. %* | *NORM. WT. % CALCULATED* | *Ø NORM. AT. %* | *NORM. AT. % CALCULATED* |
|---|---|---|---|---|
| ***GE*** | 23.9 | 24.3 | 22.5 | 23.1 |
| ***TE*** | 56.8 | 56.9 | 30.4 | 30.8 |
| ***SI*** | 19.4 | 18.8 | 47.1 | 46.2 |

**4.** NMR measurements of compounds **1** – **3**

**4.1** [{$(TsiGe)_2GeSe_4$}$_2$($\mu^2$-Se)$_2$] **1**

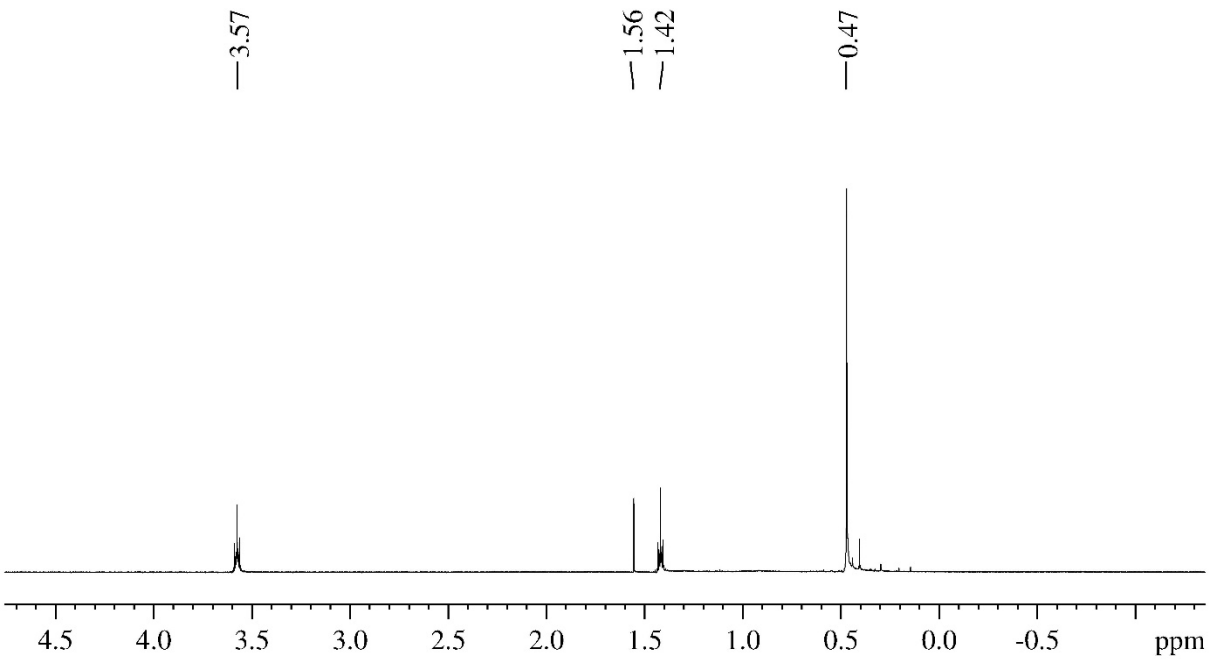


**Fig. S4**: $^1$H NMR measurement of dissolved crystals of [{$(TsiGe)_2GeSe_4$}$_2$($\mu^2$-Se)$_2$] **1**. **Device:** Bruker AVII+500 spectrometer, External standard $SiMe_4$.

$^1$H NMR (500 MHz, $C_6D_6$) at 25°C: δ (ppm): 0.47 (s, C(Si*Me*$_3$)$_3$)
1.42 (t, *thf*)
1.56 (s, *acetone*)
3.57 (t, *thf*)

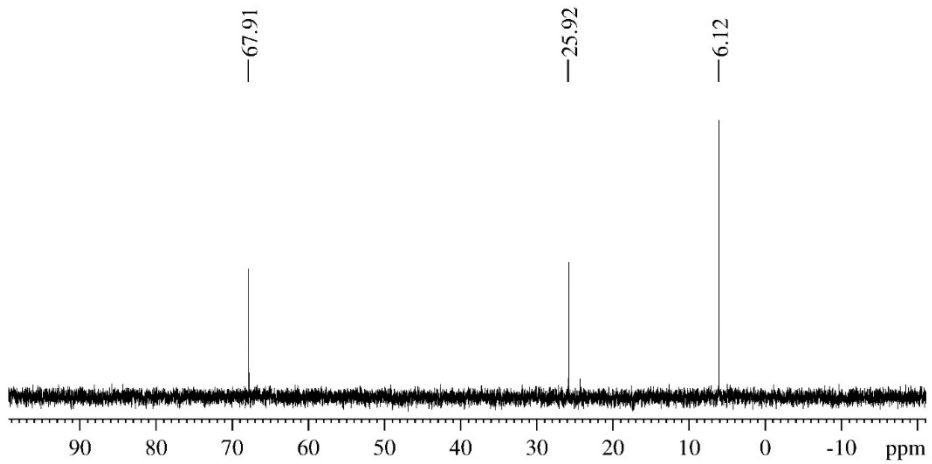


**Fig. S5**: $^{13}$C NMR measurement of dissolved crystals of [{(TsiGe)$_2$GeSe$_4$}$_2$(μ$^2$-Se)$_2$] **1**. **Device:** Bruker AVII+500 spectrometer, External standard SiMe$_4$.

$^{13}$C NMR (125.8 MHz, $C_6D_6$) at 25°C: δ (ppm): 6.12 (s, C(Si*Me*$_3$)$_3$)
25.92 (s, *thf*)
67.91 (s, *thf*)

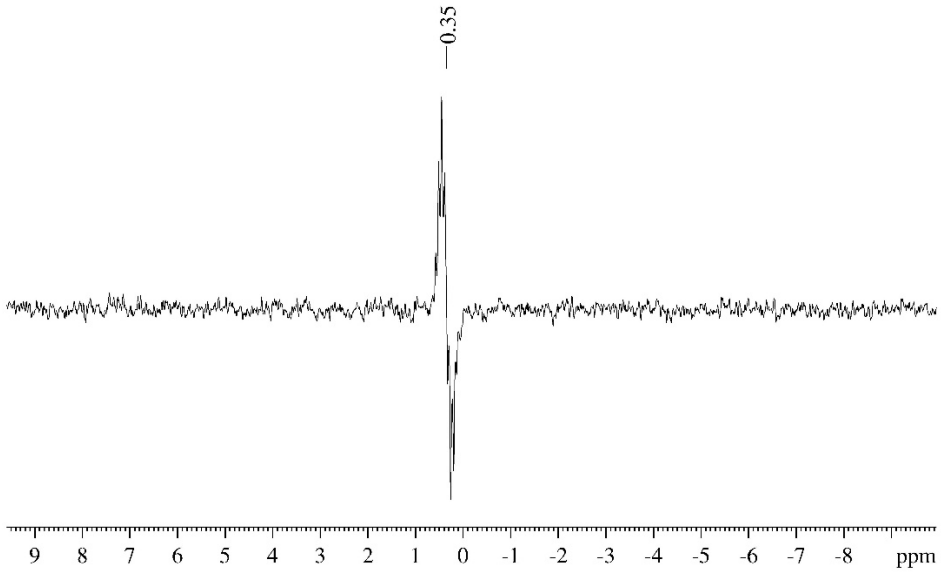


**Fig. S6**: $^{29}$Si NMR (INEPT pulse program) measurement of dissolved crystals of [{(TsiGe)$_2$GeSe$_4$}$_2$(μ$^2$-Se)$_2$] **1**. **Device:** Bruker AVII+500 spectrometer, External standard SiMe$_4$.

$^{29}$Si NMR (99.4 MHz, $C_6D_6$) at 25°C: δ (ppm): 0.35 (decet, C(*Si*Me$_3$)$_3$)

**4.2** $Ge_2(\mu^2\text{-}Te)_2(Tsi)_2(TeH)_2$ **2**

Crystals of **2** are bad soluble in any kind of solvents. Heating it in thf-$D_8$ to 60°C in an ultrasonic bath leads to a slightly red colored solution with red precipitate. It is unclear, if **2** undergoes a decomposition in this case and if only decomposition products are visible via NMR spectroscopy, as the hydrogen atoms of the Te-H groups cannot be identified exactly.

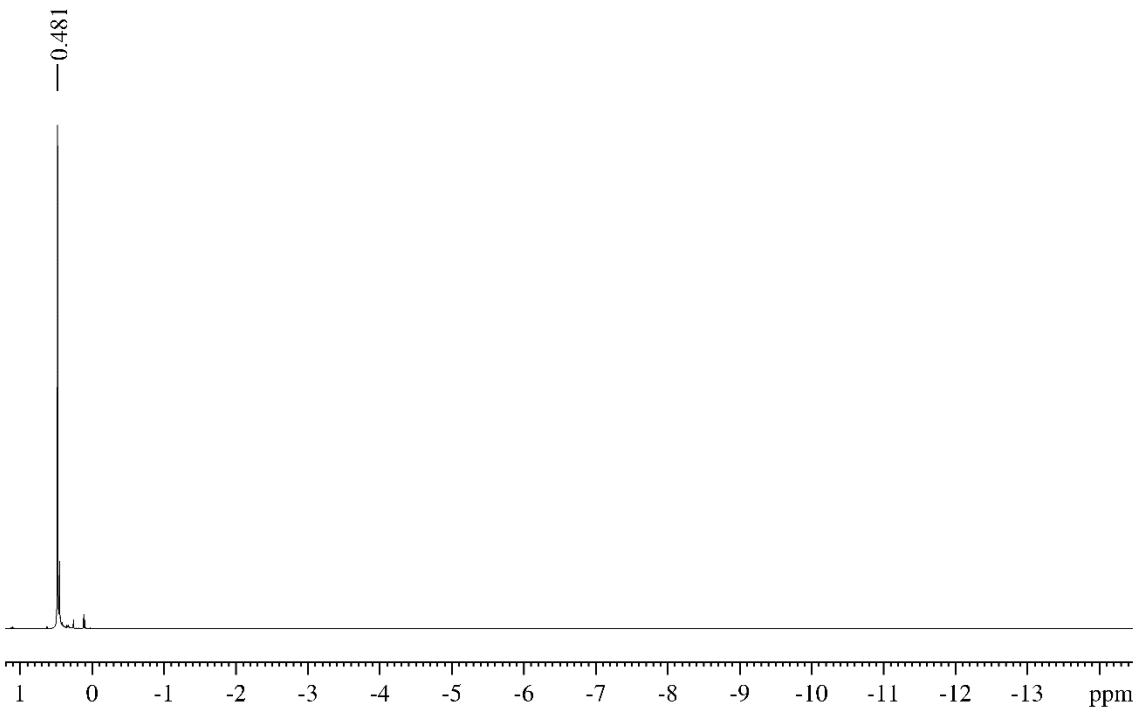


**Fig. S7**: $^1$H NMR measurement of dissolved crystals of $Ge_2(\mu^2\text{-}Te)_2(Tsi)_2(TeH)_2$ **2**. **Device:** Bruker AVIIIHD-300 spectrometer, External standard $SiMe_4$.

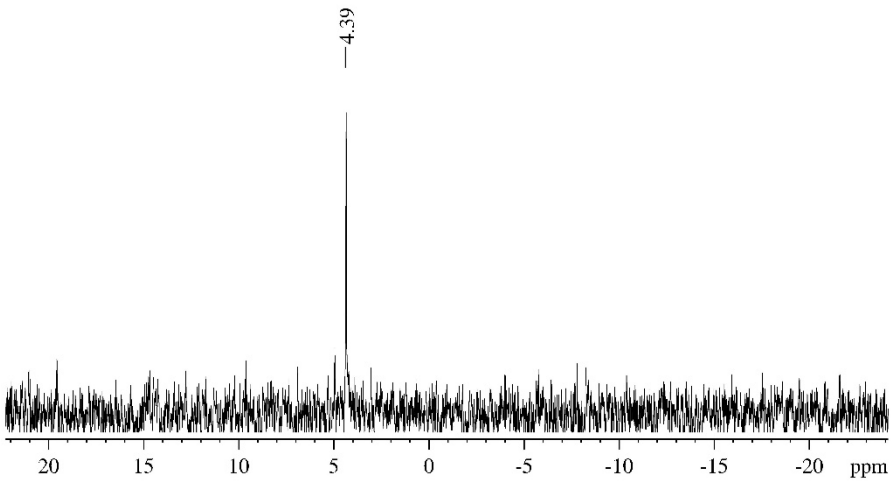


**Fig. S8**: $^{13}C$ NMR measurement of dissolved crystals of $Ge_2(\mu^2\text{-}Te)_2(Tsi)_2(TeH)_2$ **2**. **Device:** Bruker AVIIIHD-300 spectrometer, External standard $SiMe_4$.

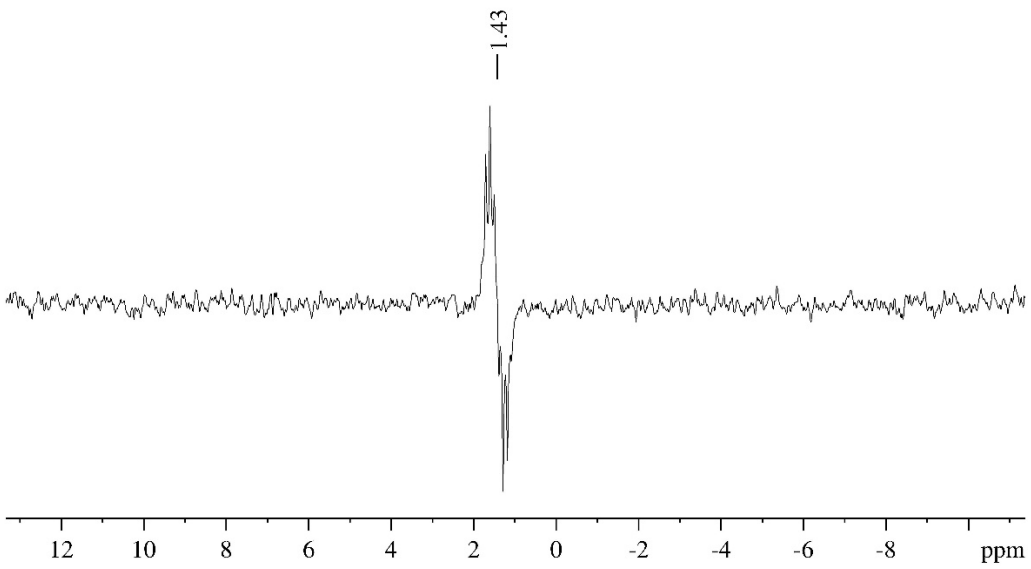


**Fig. S9**: $^{29}Si$ NMR (INEPT pulse program) measurement of dissolved crystals of $Ge_2(\mu^2\text{-}Te)_2(Tsi)_2(TeH)_2$ **2**. **Device:** Bruker AVIIIHD-300 spectrometer, External standard $SiMe_4$.

**4.3** $[Li(Et_2O)(OC_4H_7)Ge_3Te_4(Tsi)_2]_2$ **3**

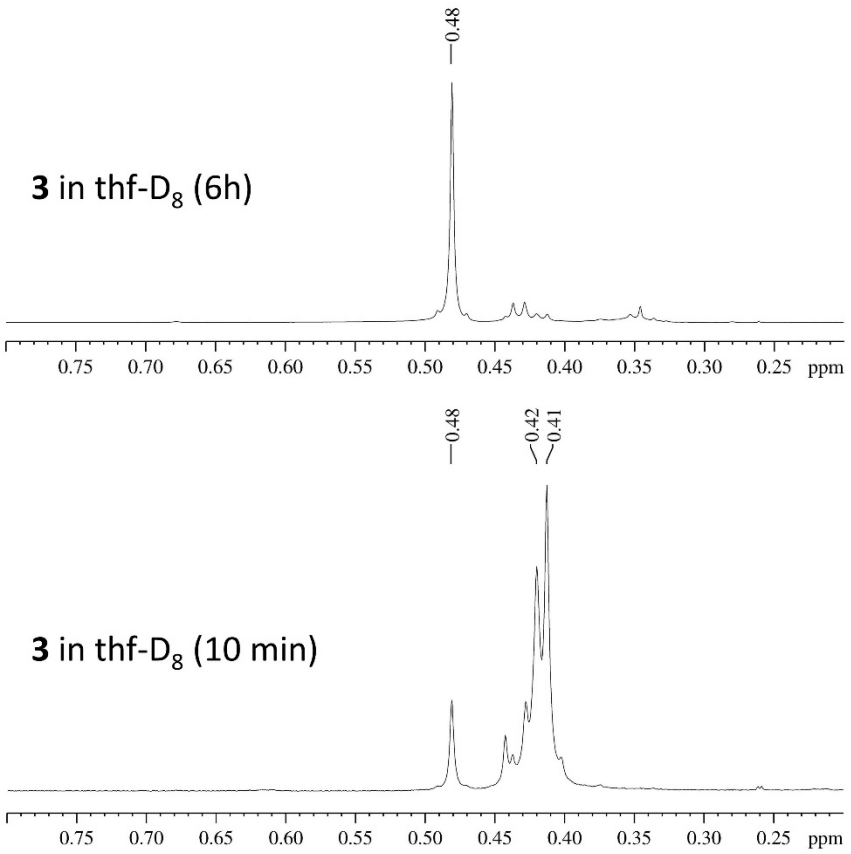


**Fig. S10**: $^1$H NMR measurement of dissolved crystals of $[Li(Et_2O)(OC_4H_7)Ge_3Te_4(Tsi)_2]_2$ **3** after 10 minutes and 6 hours in thf-$D_8$. **Device:** Bruker AVIIIHD-300 spectrometer, External standard $SiMe_4$.

**5.**NMR measurement of reaction mixture $GeCl_2$·dioxane/LiSeTsi

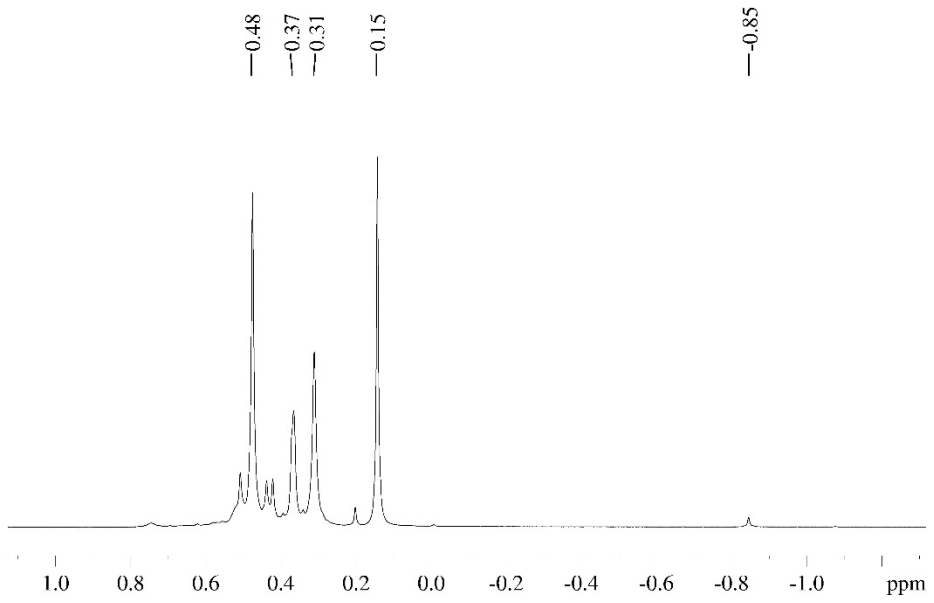


**Fig. S11**: $^1$H NMR measurement of the reaction mixture $GeCl_2$·dioxane/LiSeTsi after stirring at 0°C for 1h. **Device:** Bruker AVII+400 spectrometer, External standard $SiMe_4$.

$^1$H NMR (400 MHz, $C_6D_6$) at 25°C: δ (ppm): −0.85 (s, 1H, *H*C($SiMe_3$)$_3$)

0.15 (s, 27H, HC(Si*Me*$_3$)$_3$)

0.31 (s, (*Me*$_3$Si)$_3$C-Se-Se-Se-C(Si*Me*$_3$)$_3$)

0.37 (s, (*Me*$_3$Si)$_3$C-Se-Se-C(Si*Me*$_3$)$_3$)

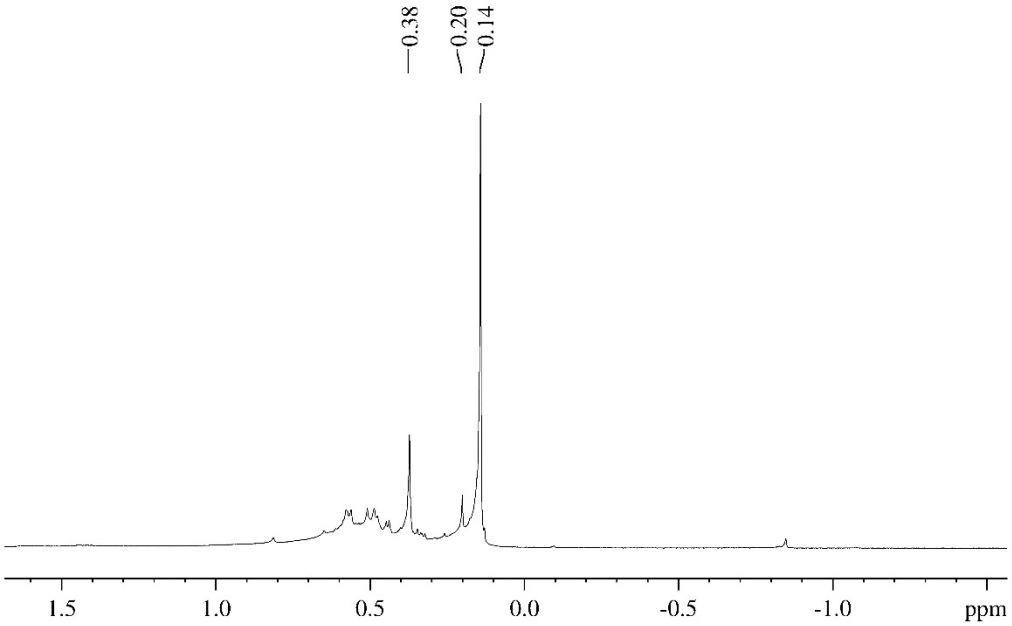


**Fig. S12**: $^{1}$H NMR measurement of the reaction mixture $GeCl_2$·dioxane/LiSeTsi after stirring at RT for 12h. **Device:** Bruker DRX-250 spectrometer, External standard $SiMe_4$.

$^{1}$H NMR (250 MHz, $C_6D_6$) at 25°C: δ (ppm)

−0.85 (s, 1H, *H*C(SiMe$_3$)$_3$)

0.15 (s, 27H, HC(Si*Me$_3$*)$_3$)

0.20 (s, HSeC(Si*Me$_3$*)$_3$)

0.38 (s, (*Me$_3$*Si)$_3$C-Se-Se-C(Si*Me$_3$*)$_3$)

## **6.** Characterization of Tsi-Te-Te-Tsi

### **6.1** Synthesis

**Synthesis of Tsi-Te-Te-Tsi as a byproduct:** $(thf)_2LiTeC(SiMe_3)_3$ (2.33 g, 4.57 mmol) was dissolved in thf and cooled to −78°C and $GeCl_2$·dioxane (0.529 g, 2.28 mmol) was given to the solution while stirring. The solution was allowed to reach room temperature and was stirred overnight to give a dark red reaction solution. After that, all volatiles were removed in vacuum and the remaining solid was extracted with toluene. Tsi-Te-Te-Tsi was obtained as blue crystals at −28°C. **$^{1}$H NMR** (300 MHz, thf-$D_8$): δ = 0.39 (s, Si*Me*$_3$) ppm. **$^{13}$C{$^{1}$H} NMR** (75.5 MHz, thf-$D_8$): δ = 4.90 (s, Si*Me*$_3$) ppm. **$^{29}$Si NMR** (59.6 MHz, thf-$D_8$): δ = 5.27 (decet, *Si*Me$_3$) ppm.

**6.2** Molecular structure

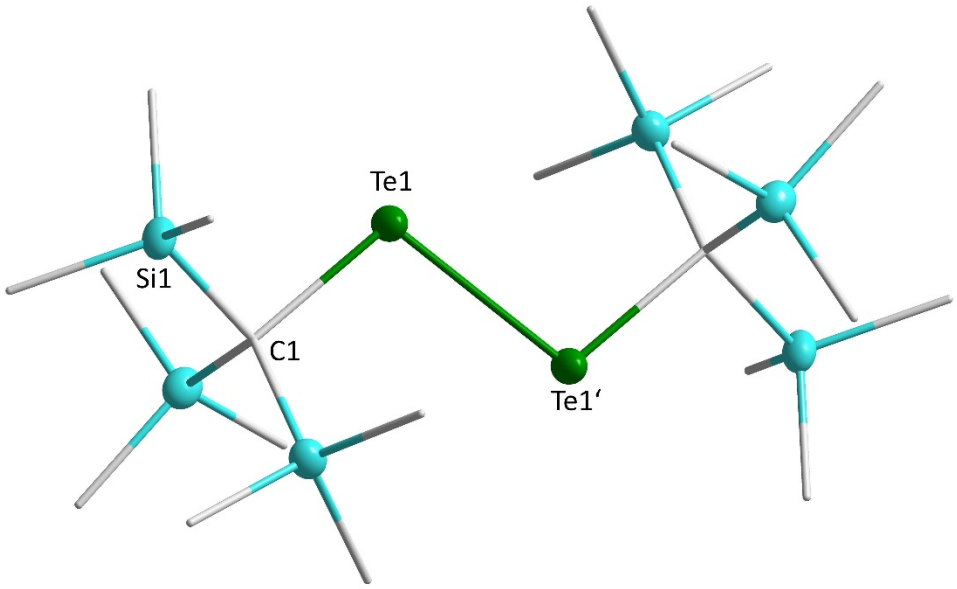


**Figure S13**: Molecular structure of Tsi-Te-Te-Tsi in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond lengths [pm], angles [°]: Te1-Te1’ 277.84(4), Te1-C1 220.2(2); C1-Te1-Te1’ 103.69(7).

**6.3** NMR measurements

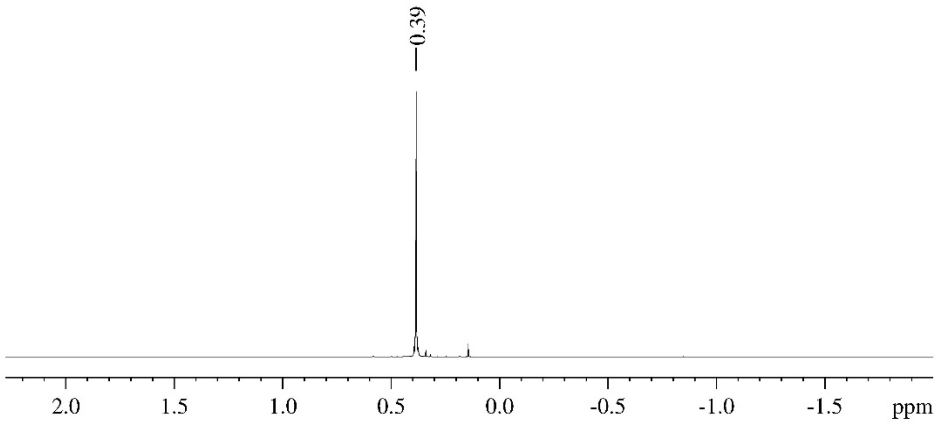


**Fig. S14**: $^{1}$H NMR measurement of dissolved crystals of Tsi-Te-Te-Tsi. **Device:** Bruker AVIIIHD-300 spectrometer, External standard $SiMe_4$.

$^{1}$H NMR (300 MHz, $C_6D_6$) at 25°C: δ (ppm): 0.39 (s, $(Me_3Si)_3C$-Te-Te-$C(SiMe_3)_3$)

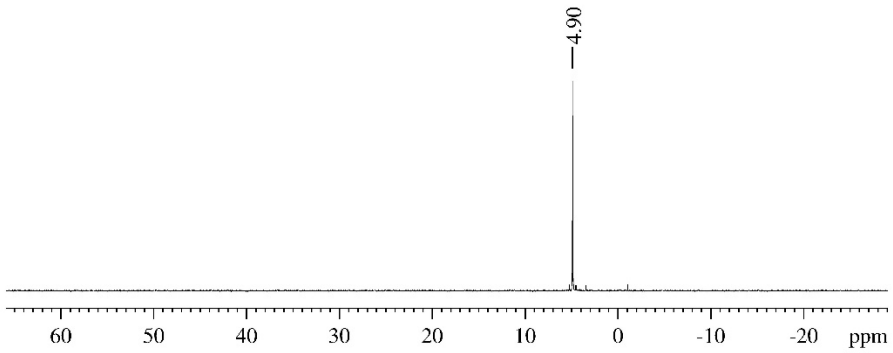


**Fig. S15**: $^{13}$C NMR measurement of dissolved crystals of Tsi-Te-Te-Tsi. **Device:** Bruker AVIIIHD-300 spectrometer, External standard $SiMe_4$.

$^{13}$C NMR (75.5 MHz, $C_6D_6$) at 25°C: δ (ppm): 4.90 (s, $(Me_3Si)_3C$-Te-Te-$C(SiMe_3)_3$)

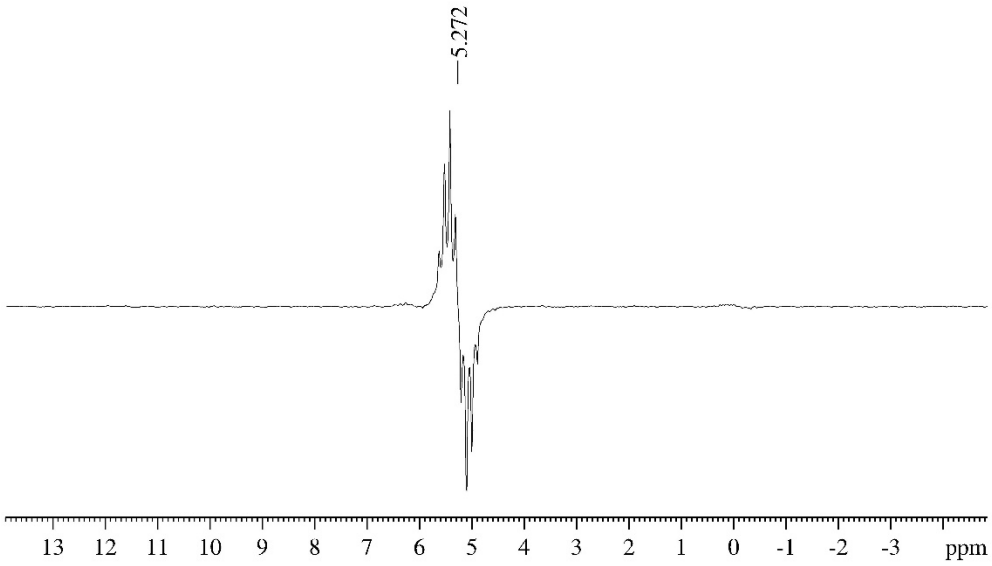


**Fig. S16**: $^{29}$Si NMR (INEPT pulse program) measurement of dissolved crystals of Tsi-Te-Te-Tsi. **Device:** Bruker AVIIIHD-300 spectrometer, External standard $SiMe_4$.

$^{29}$Si NMR (59.6 MHz, $C_6D_6$) at 25°C: δ (ppm): 5.27 (decet, $(Me_3\mathit{Si})_3$C-Te-Te-C($\mathit{Si}Me_3)_3$)

**7.** Crystallographic data of Tsi-Te-Te-Tsi:

Table S10: Crystallographic details for Tsi-Te-Te-Tsi

| | **Tsi-Te-Te-Tsi** |
|---|---|
| Empirical formula | $C_{20}H_{54}Si_6Te_2$ |
| Formula weight | 718.37 |
| T [K] | 150 |
| Crystal system | monoclinic |
| Space group | *C*2/c |
| a [pm] | 1618.91(11) |
| b [pm] | 893.21(5) |
| c [pm] | 2314.04(14) |
| α [°] | 90 |
| β [°] | 98.483(2) |
| γ [°] | 90 |
| V [Å³] | 3309.6(4) |
| Z | 4 |
| $\rho_{calc}$ [g/cm³] | 1.442 |
| μ [$mm^{-1}$] | 1.987 |
| F(000) | 1448 |
| Crystal size [mm³] | 0.225x0.076x0.037 |
| 2θ [°] | 5.088 – 52.95 |
| Index range | $-20 \leq h \leq 20$, $-11 \leq k \leq 11$,$-28 \leq l \leq 28$ |
| Reflections collected | 46797 |
| Independent reflections | 3433 [Rint = 0.0537] |
| Data/restraints/parameters | 3433/0/136 |
| GooF | 1.102 |
| R [$I \geq 2\sigma(I)$] | R1 = 0.0266, wR2 = 0.0619 |
| R [all data] | R1 = 0.0316, wR2 = 0.0644 |
| Largest peak/hole [e/Å³] | 0.84/-0.58 |
| CCDC | 2049718 |

# **8.** Quantum chemical calculations

## **8.1.** General Information

Quantum-chemical calculations were carried out with the RI-DFT version of the Turbomole program package by employing the BP86-functional. The basis sets were of SVP quality. Thermodynamic properties were calculated using correction was applied using Grimme's DFT-D3-BJ damping correction.[1]

## **8.2.** $Ge_2Se_2(SeTsi)_4$

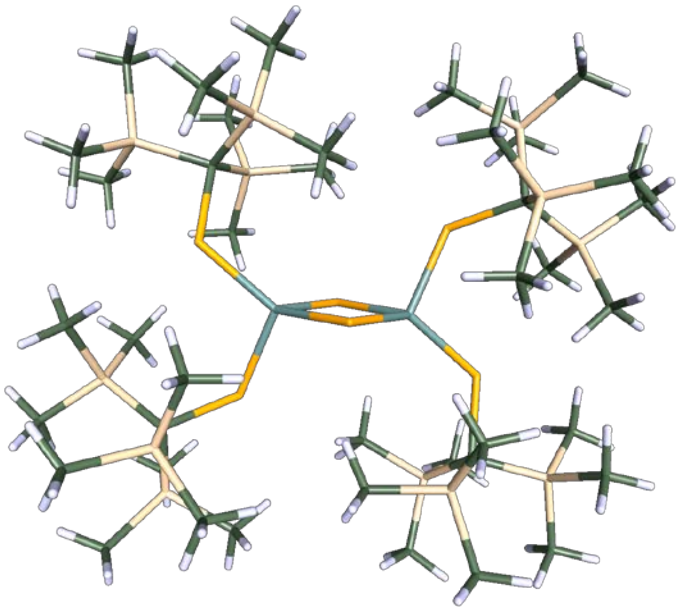

Figure S17: Geometry optimized structure

| | |
|---|---|
| Point group: | $C_1$ |
| Energy: | -23625.6849176667 Hartree |
| Enthalpy: | 3824.13 kJ $mol^{-1}$ |
| Entropy: | 2.31 kJ $mol^{-1}$ $K^{-1}$ |
| Lowest vibrational eigenvalue: | 10.45 $cm^{-1}$ |
| HOMO-LUMO-gap: | 2.074 eV |

Atom coordinates:

```
Se -2.729624 -1.146638 -0.933962  C 1.127705 -6.550441 1.296045     H -3.467568 -4.649890 -0.713243
Ge -1.436954 0.466206 0.263515    C 1.758288 -3.877108 2.692277     H -4.030803 -5.061591 -2.370360
Se -2.799569 2.345773 0.830603    C -0.635067 -4.132264 0.851356    H 0.785359 -7.072101 0.377538
C -2.010333 4.196997 0.618832     C 2.585079 -4.227051 -3.574653    H 0.400442 -6.786598 2.105992
Se 0.321054 0.554551 -1.350051    H -3.044170 7.201819 2.008625     H 2.107463 -6.980400 1.593359
Ge 1.607805 -0.492782 0.404993    H -4.315205 7.594909 0.805921     H -1.164679 -4.404714 1.791484
Se -0.138586 -0.564641 2.057378   H -2.595404 7.510305 0.293768     H -0.758890 -3.037857 0.715136
Se 2.983771 -2.296694 -0.302058   H -5.808742 5.314932 1.825730     H -1.145911 -4.648347 0.012580
C 2.273112 -4.184536 -0.423187    H -5.290311 3.603222 1.724347     H 1.480529 -2.803069 2.733957
Se 3.155602 1.327568 0.480426     H -4.538188 4.695947 2.933741     H 1.246709 -4.382695 3.542711
C 4.827912 1.247257 1.624839      H -4.737384 3.952512 -1.307308    H 2.851973 -3.951882 2.851959
C -4.675619 -1.443369 -0.457990   H -4.040373 5.491225 -1.925850    H 4.001036 -5.926298 2.066865
Si -3.671205 5.209811 0.590001    H -5.570931 5.512666 -0.987634    H 4.844266 -4.350605 1.845494
Si -0.949410 4.565858 2.178794    H 0.516280 6.421239 2.958112      H 5.628364 -5.870931 1.310163
Si -1.045030 4.431470 -1.036845   H -0.704930 7.073670 1.815386     H 3.509225 -6.869712 -2.193920
Si 3.952405 -5.159296 -0.372900   H 0.737659 6.198785 1.195704      H 2.951822 -7.487976 -0.599374
Si 1.373445 -4.357628 -2.117452   H -2.667436 5.569640 3.781104     H 4.705345 -7.443869 -0.986183
Si 1.166075 -4.659334 1.073128    H -1.319502 4.744202 4.629670     H 5.655131 -3.346665 -0.890341
Si 4.409712 0.800902 3.443170     H -2.629969 3.768037 3.884830     H 6.205421 -4.977660 -1.395189
Si 5.375672 3.104304 1.450959     H 1.024749 3.015309 1.690874      H 5.036011 -4.068728 -2.413055
Si 6.145282 0.054121 0.866392     H 0.883581 3.494716 3.412271      H 0.590192 -2.001579 -2.520207
Si -5.759018 0.094792 -0.904487   H -0.195389 2.232028 2.740244     H -0.491637 -3.208896 -3.292457
Si -5.038534 -2.898143 -1.698633  H -1.757049 2.284831 -2.196948    H -0.605310 -2.886051 -1.531479
Si -4.851921 -2.001155 1.368147   H -1.132425 3.511122 -3.345226    H 1.998448 -4.224713 -4.521353
C -3.356358 7.047536 0.953283     H -2.800785 3.652178 -2.685436    H 3.311955 -5.064927 -3.632097
C -4.572895 5.025717 -1.070506    H -0.676690 6.930103 -0.837195    H 3.152444 -3.271599 -3.530344
C -4.927017 4.637094 1.897932     H -2.128095 6.612651 -1.854609    H 1.127270 -6.899453 -2.084963
C 0.302117 3.198768 2.511449      H -0.484841 6.340061 -2.519214    H -0.379729 -6.092142 -1.525613
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C -2.005030 4.678186 3.754372     H 1.260310 4.105611 -1.888580     H 7.018261 2.906462 -0.503457
C -1.109985 6.249890 -1.601623    H 1.025272 3.070939 -0.453412     H 5.331712 3.187155 -1.062291
C -1.757905 3.369724 -2.435062    H -4.032074 1.620627 -1.867255    H 6.286701 4.541593 -0.370167
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C -7.509109 -0.405753 -1.471685   H -4.641775 0.518510 -3.145897    H 7.551024 2.909695 2.773140
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C -4.941109 1.122484 -2.264724    H -7.543732 -1.014219 -2.398816   H 4.352518 5.349498 1.734947
C -6.663293 -3.784389 -1.270463   H -8.050009 -0.956360 -0.671837   H 3.302202 4.127891 2.535661
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**8.3.** Compound C

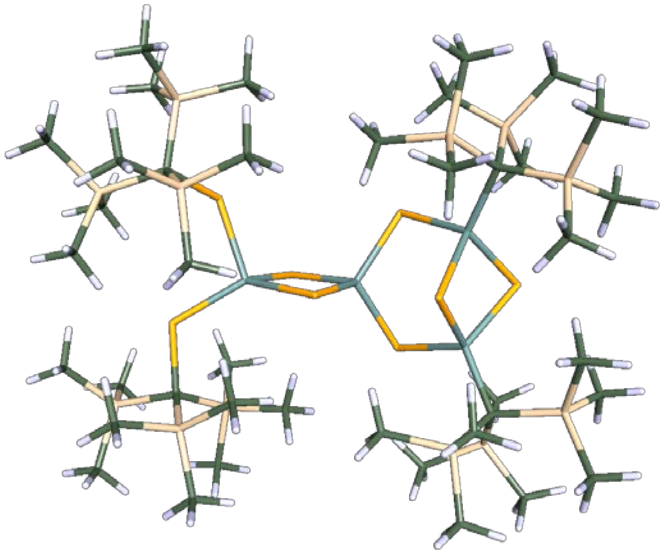

Figure S18: Geometry optimized structure

Point group: $C_1$

Energy: -32583.1360890315 Hartree

Enthalpy: 3856.92 kJ $mol^{-1}$

Entropy: 2.44 kJ $mol^{-1}$ $K^{-1}$

Lowest vibrational eigenvalue: 9.10 $cm^{-1}$

HOMO-LUMO-gap: 2.156 eV

Atom coordinates:

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Se -1.245478 -0.787109 -5.861965  Se -3.260373 -1.886288 0.357801   C -0.011239 -3.430900 3.770120
Se -3.167264 0.386732 -2.713335   C -0.506214 -4.715281 -5.659266   C -2.522479 2.386405 3.750372
C -1.714754 2.857997 -4.888560    C 2.409514 -5.612304 -5.995193    Si -0.394046 -4.152922 5.529659
Se -1.052601 -2.907603 -2.599548  C 1.203334 -5.511665 -3.242572   Si -0.590230 -4.643573 2.392821
C 1.807105 -2.739405 -4.784960    C 2.496485 -2.552240 -1.686092   Si 1.816514 -2.852602 3.606115
Ge -1.864227 -1.055208 -1.370126  C 4.509015 -3.873428 -3.577291   Si -0.787030 3.067360 3.306897
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Si -0.526606 3.258504 -6.370138   C 4.156194 -2.720132 -6.921257   C -0.555216 -2.797801 6.855511
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**8.4.** Compound 1

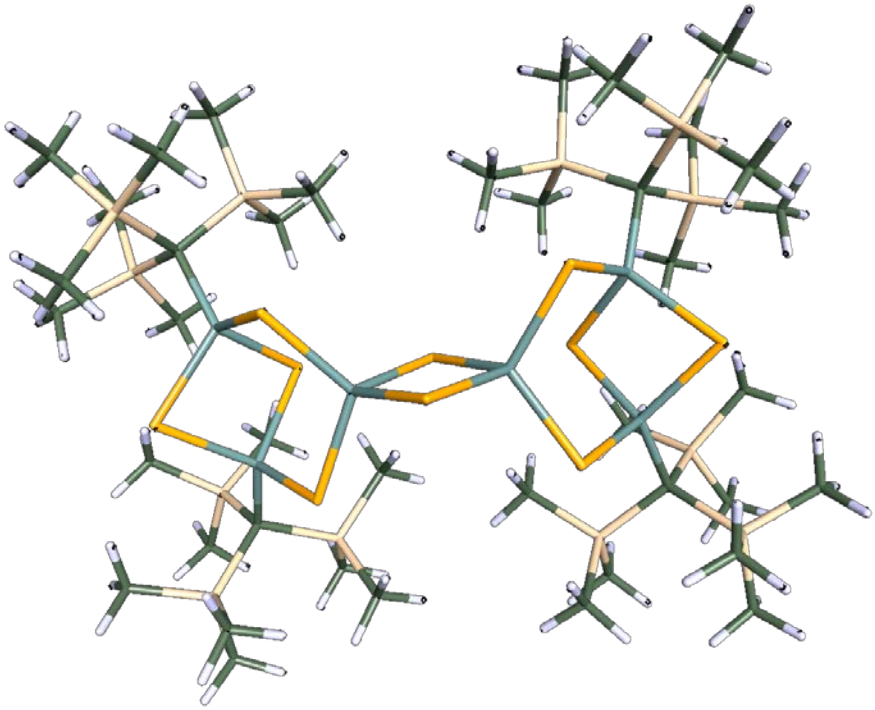

Figure S19: Geometry optimized structure

| | |
|---|---|
| Point group: | $C_1$ |
| Energy: | -41540.582933927Hartree |
| Enthalpy: | 3889.95 kJ $mol^{-1}$ |
| Entropy: | 2.56 kJ $mol^{-1}$ $K^{-1}$ |
| Lowest vibrational eigenvalue: | 9.04 $cm^{-1}$ |
| HOMO-LUMO-gap: | 2.519 eV |

Atom coordinates:

```
Se 0.379321 0.194701 -3.054100    Si -3.080141 3.205370 -5.954422   C 1.394287 -3.652953 -1.766669
Ge -1.584964 1.054531 -4.194500   Si 0.077347 3.411027 -5.606993    C 3.467696 -4.817659 -3.687981
Ge -0.250223 -1.783566 -4.297107  Si 0.434689 -4.543991 -5.607251   C 3.517047 -1.864891 -2.924281
Se -1.568431 -0.604991 -5.943864  Si 2.358647 -3.308052 -3.357223   C 2.731056 -0.229251 -5.802708
Se -3.423820 0.582895 -2.720335   Si 2.261554 -2.005804 -6.267916   C 3.924012 -2.866505 -6.608811
C -1.597167 2.959013 -4.737200    Se -0.657702 -0.623007 -0.019206  C 1.322584 -1.916057 -7.915983
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Ge -2.399747 -1.215034 -1.562276  C 1.602282 -5.470712 -6.785298    Se -3.226903 0.757628 2.600195
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H -4.451225 3.150556 3.765128
H -4.457019 1.830896 4.985590
H -2.963188 5.860158 4.544894
H -3.634483 5.741200 6.202808
H -1.864878 5.930513 5.965242
H -2.484562 1.864804 7.438870
H -1.928478 3.483070 7.994208
H -3.681163 3.157695 7.790442
H 1.606487 1.997231 7.585067
H 0.305900 0.915502 6.972583
H -0.107840 2.305731 8.018041
H 2.934446 2.977262 5.411631
H 2.211772 3.642781 3.908816
H 2.120745 1.877862 4.249318
H 1.544470 4.926470 7.030529
H -0.228479 5.015938 7.256059
H 0.526206 5.706608 5.775524

**8.5.** Tsi-Se-Se-Tsi

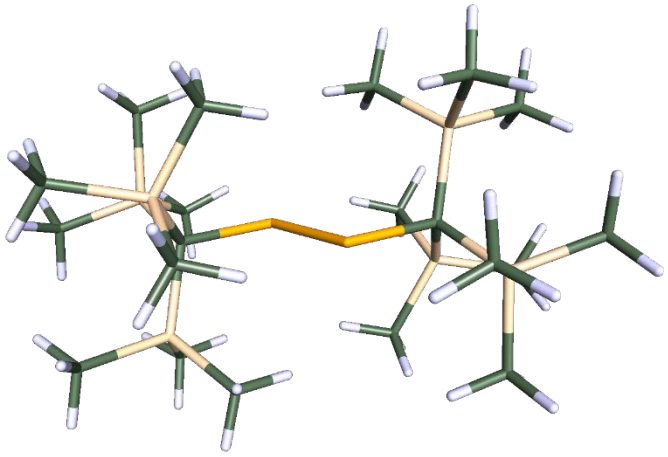

Figure S20: Geometry optimized structure

Point group: $C_1$

Energy: -7334.11988754679 Hartree

Enthalpy: 1892.03 kJ $mol^{-1}$

Entropy: 1.19 kJ $mol^{-1}$ $K^{-1}$

Lowest vibrational eigenvalue: 3.61 $cm^{-1}$

HOMO-LUMO-gap: 2.064 eV

Atom coordinates:

```
C -2.559387 0.199551 0.441736     C 5.572810 0.400606 0.863281      H 2.257685 2.495572 2.932522
Si -3.860679 1.305411 -0.479661   C -3.466284 1.476923 -2.335857    H 5.659296 1.367460 1.403567
Si -2.764507 -1.675290 0.053899   C -3.891597 3.090641 0.165251     H 6.289735 -0.311100 1.332188
Si -2.546431 0.613336 2.324793    C -5.606784 0.572346 -0.343837    H 5.891566 0.560899 -0.187295
Se -0.901631 0.824950 -0.497168   C -1.682772 -0.730048 3.359843    H 2.510753 -1.106953 3.031327
Se 0.867988 0.138340 1.011304     C -4.324394 0.702074 2.999405     H 3.319598 0.461086 3.376725
C 2.525425 0.768313 0.074955      C -1.649818 2.237861 2.707796     H 4.276346 -1.059766 3.327796
Si 3.827919 -0.335713 0.996955    C -4.207014 -2.425297 1.046046    H 4.568681 -2.705475 0.983671
Si 2.727042 2.643267 0.464039     C -3.104433 -1.973401 -1.791243   H 4.197033 -2.215952 -0.703117
Si 2.514800 0.355323 -1.808286    C -1.212904 -2.687326 0.454939    H 2.858656 -2.587290 0.444655
C 4.293393 0.269717 -2.481617     H 0.295368 3.299340 0.639681      H 4.245023 0.132510 -3.585855
C 1.649762 1.697801 -2.843350     H 1.372270 4.713951 0.341552      H 4.855785 1.207141 -2.284632
C 1.620719 -1.270379 -2.192276    H 0.902164 3.630042 -1.013142     H 4.879025 -0.577657 -2.066552
C 3.064215 2.940805 2.309781      H 3.973172 3.390092 -1.619973     H 2.163087 2.681438 -2.791690
C 4.169563 3.395947 -0.526072     H 5.132759 2.873642 -0.348857     H 0.588337 1.846209 -2.550669
C 1.174732 3.653575 0.061454      H 4.299746 4.458579 -0.218866     H 1.660126 1.367903 -3.907452
C 3.431886 -0.509137 2.852625     H 3.070485 4.038096 2.498966      H 1.765111 -1.515858 -3.269242
C 3.862933 -2.120496 0.351001     H 4.039567 2.535503 2.653808      H 0.530290 -1.154654 -2.007268
```

```
H 1.985054 -2.126364 -1.590483    H -4.310010 2.029265 -2.810343    H -1.692379 -0.399855 4.423862
H -4.009462 -2.419270 2.139733    H -3.356883 0.506165 -2.859582    H -0.621619 -0.879805 3.066886
H -4.339300 -3.487841 0.739442    H -2.543976 2.072507 -2.515940    H -2.013180 3.094223 2.105964
H -5.169534 -1.901464 0.869615    H -5.695466 -0.394719 -0.883394   H -1.793364 2.483850 3.784758
H -0.938169 -2.662788 1.528964    H -5.924865 0.413302 0.707130     H -0.559677 2.120368 2.522329
H -0.334200 -2.335023 -0.125528   H -6.322892 1.284989 -0.812570    H -4.274899 0.839566 4.103560
H -1.412352 -3.747806 0.176605    H -2.886421 3.555303 0.070589     H -4.908844 1.550365 2.584540
H -3.112722 -3.070805 -1.979711   H -4.224742 3.187367 1.219556     H -4.888592 -0.234417 2.803184
H -4.079556 -1.566748 -2.134326   H -4.596595 3.676713 -0.467239
H -2.297935 -1.529869 -2.415233   H -2.197345 -1.713051 3.308619
```

**8.6.** Double-decker $Ge_4Se_6Tsi_4$

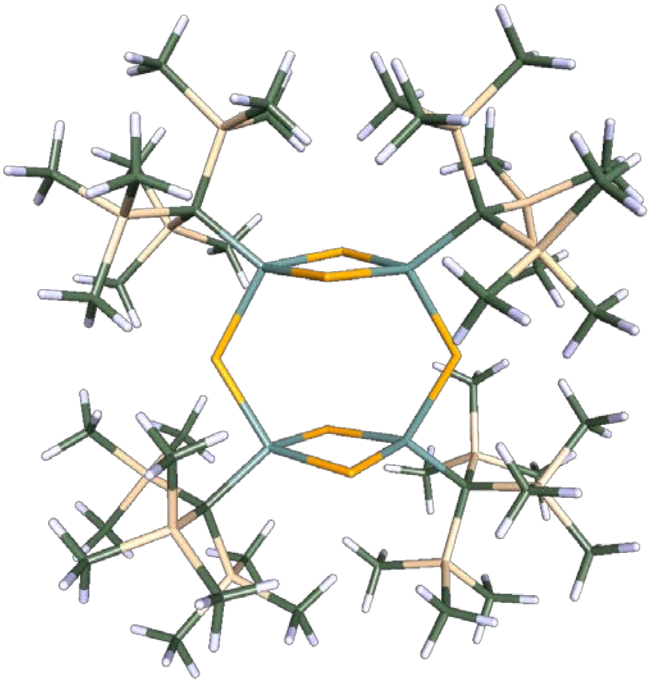

Figure S21: Geometry optimized structure

| | |
|---|---|
| Point group: | $C_1$ |
| Energy: | -27779.9324360766 Hartree |
| Enthalpy: | 3850.59 kJ $mol^{-1}$ |
| Entropy: | 2.28 kJ $mol^{-1}$ $K^{-1}$ |
| Lowest vibrational eigenvalue: | 9.30 $cm^{-1}$ |
| HOMO-LUMO-gap: | 2.588 eV |

Atom coordinates:

170

```
Ge 1.337983 2.239984 0.182790     C -5.195841 -4.104020 2.366747    H 2.585227 4.264177 -2.673920
Se -0.661631 2.156390 1.556567    C -3.565897 -1.533508 2.714677    H 3.413657 5.795827 -2.209620
Ge -1.827383 1.863645 -0.531928   C -5.515967 -2.308268 -0.542112   H 3.621591 -5.045286 -3.016131
Se 0.150798 2.166925 -1.906255    C -3.339740 -3.088591 -2.637728   H 2.259634 -3.867020 -3.085027
Se -2.745298 -0.338341 -0.45150   C -5.077838 -5.144642 -1.247413   H 3.708505 -3.637999 -4.122413
Ge -1.357092 -2.221543 0.101146   H -1.726721 6.468759 0.101460     H 6.288961 -4.318600 -1.366913
Se 0.267159 -2.022847 1.870855    H -2.828478 5.498983 1.118653     H 6.358099 -3.513690 -2.968263
Ge 1.847931 -1.892038 0.044459    H -1.264934 4.808526 0.616018     H 6.749294 -2.585137 -1.486858
Se 2.751984 0.316493 0.186846     H -2.460763 5.023745 -3.758958    H 4.577600 -1.189349 -3.620725
Se 0.249649 -2.350212 -1.699966   H -1.496075 6.176883 -2.779144    H 3.098598 -0.753973 -2.694089
C 3.534578 -3.004158 -0.040687    H -0.997471 4.454954 -2.884202    H 4.717174 -0.379013 -2.023213
C -2.743387 -3.651201 0.426342    H -5.035570 6.084894 -0.553183    H 3.209690 -0.933345 2.701107
C -3.449485 2.945650 -1.103993    H -5.094760 5.793743 -2.331522    H 4.640830 -1.489427 3.629855
C 2.692876 3.680596 0.639008      H -3.973152 7.015661 -1.651845    H 3.283533 -2.623635 3.312687
Si 4.247343 -2.863300 -1.844656   H -3.624276 3.637941 2.186214     H 5.449519 -0.212008 0.054153
Si 4.792428 -2.355243 1.299324    H -5.392636 3.545324 2.484625     H 6.797662 -1.396803 0.121784
Si 3.174986 -4.871970 0.334609    H -4.710592 4.960816 1.622651     H 6.363819 -0.447575 1.576436
Si -1.994836 -5.436172 0.354561   H -6.365802 1.299313 1.368895     H 6.712080 -3.991821 1.024796
Si -3.454868 -3.357150 2.212277   H -5.575301 0.412055 0.018857     H 6.721580 -3.137832 2.598752
Si -4.111163 -3.528235 -0.95578   H -4.651630 0.776773 1.512952     H 5.646112 -4.552269 2.365810
Si -2.950600 4.816442 -1.288419   H -6.934579 2.800279 -1.396588    H 0.895677 -4.959333 -0.789349
Si -4.930071 2.871469 0.152123    H -7.298527 3.569734 0.177771     H 1.504272 -6.581888 -0.305109
Si -4.010364 2.251987 -2.836283   H -6.472353 4.511038 -1.105347    H 2.143400 -5.774976 -1.766619
Si 3.436054 3.217266 2.380524     H -4.653505 -0.130184 -2.325412   H 1.990948 -4.408786 2.533092
Si 4.105755 3.855146 -0.684647    H -6.101934 0.928722 -2.182153    H 3.665037 -4.992319 2.819312
Si 1.806811 5.407061 0.763300     H -5.459336 0.499649 -3.802484    H 2.381124 -6.147004 2.330249
C -4.423798 6.011132 -1.476889    H -2.931770 1.375581 -4.889211    H 4.817422 -6.069303 -1.176707
C -2.107105 5.441870 0.282287     H -2.004019 0.827376 -3.457673    H 5.596222 -5.774781 0.418783
C -1.874112 5.131229 -2.822120    H -1.801037 2.509352 -4.075620    H 4.337356 -7.039815 0.247052
C -4.621173 3.861547 1.746431     H -5.274400 3.034991 -4.803112    H -3.958527 -1.501393 3.756898
C -6.542160 3.510889 -0.638082    H -5.916300 3.854608 -3.343174    H -4.252906 -0.953671 2.070026
C -5.410998 1.168315 0.808538     H -4.403548 4.442622 -4.118295    H -2.582885 -1.012630 2.709085
C -4.983155 3.535757 -3.851631    H 0.167218 4.947421 -1.123202     H -5.954452 -3.542041 1.784800
C -5.169435 0.750793 -2.756612    H 0.187200 6.674804 -0.623717     H -5.494842 -4.061654 3.438788
C -2.538399 1.698300 -3.898233    H 1.493657 6.017222 -1.647292     H -5.230107 -5.166673 2.049576
C 0.701536 5.535912 2.303478      H 1.301780 5.586483 3.236403      H -2.857361 -3.741013 4.568294
C 2.991293 6.896642 0.869059      H 0.107056 6.474027 2.233106      H -2.465129 -5.231728 3.654459
C 0.819274 5.780674 -0.803320     H -0.009477 4.689701 2.396693     H -1.359784 -3.808329 3.579090
C 2.141377 2.396978 3.500922      H 3.717215 6.864352 1.705232      H 0.245255 -4.840028 1.381443
C 4.910839 2.025007 2.335904      H 3.546745 7.061744 -0.078223     H -0.778057 -5.737063 2.532017
C 4.108745 4.735514 3.312824      H 2.339423 7.787486 1.024836      H 0.014497 -6.613734 1.190503
C 3.536832 4.696087 -2.293318     H 1.243211 3.030310 3.660354      H -0.948588 -6.851966 -1.414963
C 4.900708 2.262488 -1.322095     H 1.809516 1.409727 3.109189      H -0.916502 -5.132052 -1.921573
C 5.572042 4.851815 0.012828      H 2.608746 2.215009 4.495504      H -2.435045 -6.081136 -2.061251
C 3.365478 -3.969586 -3.115905    H 3.349069 5.507543 3.549718      H -4.168682 -6.826344 0.493418
C 4.140430 -1.129478 -2.597324    H 4.944224 5.222447 2.767846      H -2.678627 -7.742392 0.886800
C 6.081158 -3.368798 -1.899178    H 4.514687 4.359679 4.279694      H -3.386243 -6.635717 2.100827
C 6.065013 -3.657537 1.863138     H 5.298718 1.937495 3.376549      H -2.555410 -3.815929 -2.935094
C 5.943825 -0.970199 0.689276     H 5.749101 2.363471 1.692436      H -2.894371 -2.071313 -2.656571
C 3.883744 -1.798711 2.874101     H 4.600543 1.016762 2.001404      H -4.141877 -3.118491 -3.409918
C 1.794395 -5.598492 -0.731376    H 5.764949 2.573243 -1.954042     H -5.645905 -5.456191 -0.345421
C 2.768911 -5.115972 2.175960     H 4.206023 1.675988 -1.955437     H -4.478992 -6.005904 -1.605752
C 4.639418 -6.018266 -0.081251    H 5.283550 1.601337 -0.520950     H -5.824092 -4.903556 -2.039683
C -3.194359 -6.762480 1.014078    H 6.126264 4.281624 0.788448      H -5.766068 -1.701017 -1.437807
C -1.538800 -5.909046 -1.429400   H 5.300723 5.836761 0.437840      H -5.273729 -1.605782 0.277032
C -0.486454 -5.662466 1.467430    H 6.276714 5.029199 -0.831538     H -6.431250 -2.871031 -0.255036
C -2.424517 -4.123393 3.615708    H 4.322596 4.506257 -3.059144
```

**8.7.** Adamantane $Ge_4Se_6Tsi_4$

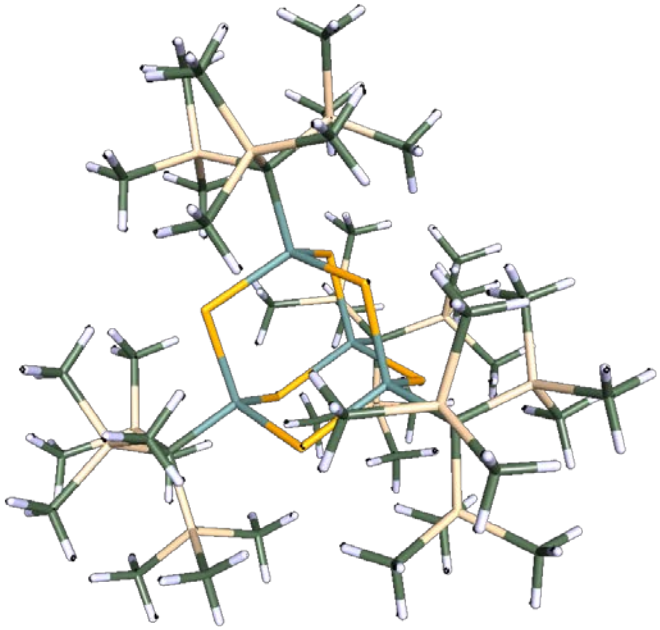

Figure S22: Geometry optimized structure

Point group: $C_1$

Energy: -27780.0072549071 Hartree

Enthalpy: 3840.76 kJ $mol^{-1}$

Entropy: 2.31 kJ $mol^{-1}$ $K^{-1}$

Lowest vibrational eigenvalue: 22.08 $cm^{-1}$

HOMO-LUMO-gap: 3.163 eV

Atom coordinates:

```
170
Ge 0.115500 1.614713 1.627718     C -3.829931 0.343850 -2.063520    Si -0.817897 2.450743 4.580475
Se -2.007769 1.841024 0.579262    C 0.245323 3.010228 3.052495      Si 2.108309 3.205368 3.571445
Ge -2.073347 0.181065 -1.123694   Si 2.755009 -0.435381 -4.494524   C 3.216790 -2.905649 2.540683
Se -1.950135 -2.006391 -0.197051  Si 3.371285 2.433702 -3.253485    C 1.168121 -3.152452 4.774828
Ge 0.139462 -2.118313 0.933750    Si 4.828276 -0.149693 -2.090977   C 2.299819 -5.647307 3.536221
Se 0.295759 -0.511589 2.679196    Si -1.412483 -4.375010 2.595832   C 0.319572 -7.004083 0.934624
Se 1.931267 -1.883063 -0.613065   Si 0.713013 -5.225260 0.379501    C 2.556580 -5.276532 -0.097110
Ge 1.697156 0.286210 -1.557795    Si 1.696899 -3.893887 3.101608    C -0.239841 -4.922539 -1.232973
Se 1.904135 1.975911 0.103741     Si -3.726136 -0.604447 -3.756757  C -2.728104 -5.022685 1.380503
Se -0.356557 0.530755 -2.733087   Si -5.215052 -0.436067 -0.945282  C -2.201633 -2.899707 3.491927
C 3.184790 0.537634 -2.868533     Si -4.203608 2.225596 -2.373801   C -1.226551 -5.771866 3.876656
C 0.286534 -3.930046 1.764698     Si -0.431723 4.688720 2.345737    C -1.224837 3.915109 5.728062
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C 0.050918 1.190219 5.713965
C -2.468784 1.659975 4.081284
C 2.281210 4.058187 5.265492
C 3.017386 1.543758 3.689552
C 3.137707 4.291924 2.392986
C 0.157956 6.177114 3.376970
C -2.330984 4.829174 2.358517
C 0.109238 5.004104 0.554074
C 6.367376 0.535413 -2.979204
C 5.009020 0.281805 -0.251845
C 5.019745 -2.041042 -2.214511
C 4.334857 2.731528 -4.868951
C 4.346954 3.403339 -1.935760
C 1.702543 3.318960 -3.430248
C 1.969248 -2.128817 -4.152549
C 4.301683 -0.743323 -5.561968
C 1.555127 0.480548 -5.655831
C -4.911313 3.139240 -0.859828
C -2.667648 3.202685 -2.909161
C -5.520142 2.468189 -3.728287
C -5.000888 -0.016551 0.892810
C -5.320473 -2.335118 -1.046102
C -6.950488 0.159277 -1.455730
C -2.872598 0.376823 -5.148185
C -5.455292 -0.998285 -4.451031
C -2.791958 -2.250599 -3.622524
H -2.772814 4.760928 3.374047
H -2.587359 5.832483 1.947846
H -2.827278 4.072970 1.715998
H 1.211096 5.001960 0.426127
H -0.271688 6.007320 0.253977
H -0.315608 4.254676 -0.147869
H 1.256286 6.330898 3.351135
H -0.157788 6.111178 4.438395
H -0.315002 7.086927 2.941819
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H -2.324434 0.700161 3.540664
H -3.092586 2.317985 3.442331
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H 0.988640 1.574081 6.166233
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H 1.906370 4.374861 -3.722054
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H 1.048966 2.867947 -4.204686
H 4.390255 4.463059 -2.276612
H 3.858590 3.397084 -0.939386
H 5.391200 3.050393 -1.808821
H 3.814278 2.355891 -5.773789
H 4.448800 3.833485 -4.985275
H 5.352429 2.290517 -4.846577
H 6.380249 0.288400 -4.060615
H 7.257017 0.052829 -2.513911
H 6.492952 1.632496 -2.872829
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H 5.996892 -2.300644 -1.746673
H -7.683915 -0.373288 -0.808226
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H -2.183550 2.790451 -3.818051
H -1.900225 3.244810 -2.106757
H -2.987037 4.246879 -3.131162
H 3.224067 -5.554053 0.744738
H 2.668200 -6.056563 -0.884603
H 2.922970 -4.320679 -0.525483
H 0.009526 -5.749854 -1.936530
H 0.052527 -3.965954 -1.716534
H -1.340219 -4.909062 -1.093880
H -0.760696 -7.188426 1.107470
H 0.644943 -7.683686 0.114219
H 0.871843 -7.297392 1.850857
H 3.994835 -2.996680 3.333153
H 2.987385 -1.826031 2.412492
H 3.649504 -3.276872 1.589212
H 0.345610 -3.712244 5.266209
H 0.864991 -2.087408 4.704903
H 2.054902 -3.201041 5.447346
H 3.060842 -5.542431 4.342862
H 2.785650 -6.174912 2.689889
H 1.486239 -6.292998 3.925921
H -3.016549 -4.275408 0.612816
H -3.639808 -5.252720 1.977897
H -2.427204 -5.954057 0.857824
H -0.816998 -6.702987 3.434019
H -0.598182 -5.497338 4.748687
H -2.245959 -6.003046 4.261526
H -2.480056 -2.085224 2.789146
H -1.545277 -2.464053 4.272869
H -3.134109 -3.258729 3.985084

**8.8.** Tsi-Se-Se-Se-Tsi

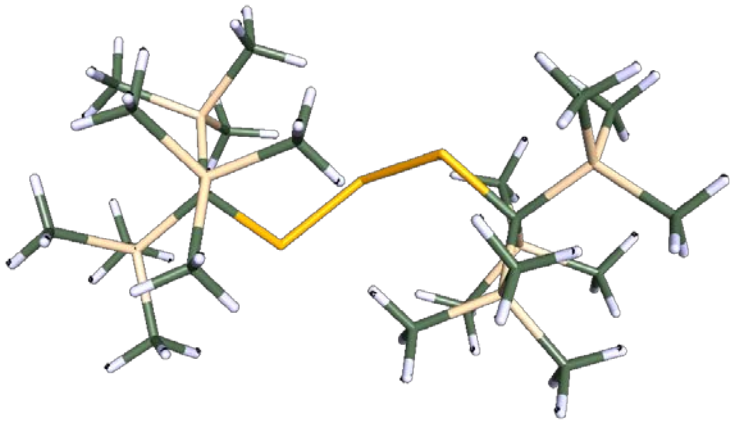


Figure S23: Geometry optimized structure

Point group: $C_1$

Energy: -9735.7083828508 Hartree

Enthalpy: 1899.92 kJ $mol^{-1}$

Entropy: 1.24 kJ $mol^{-1}$ $K^{-1}$

Lowest vibrational eigenvalue: 6.59 $cm^{-1}$

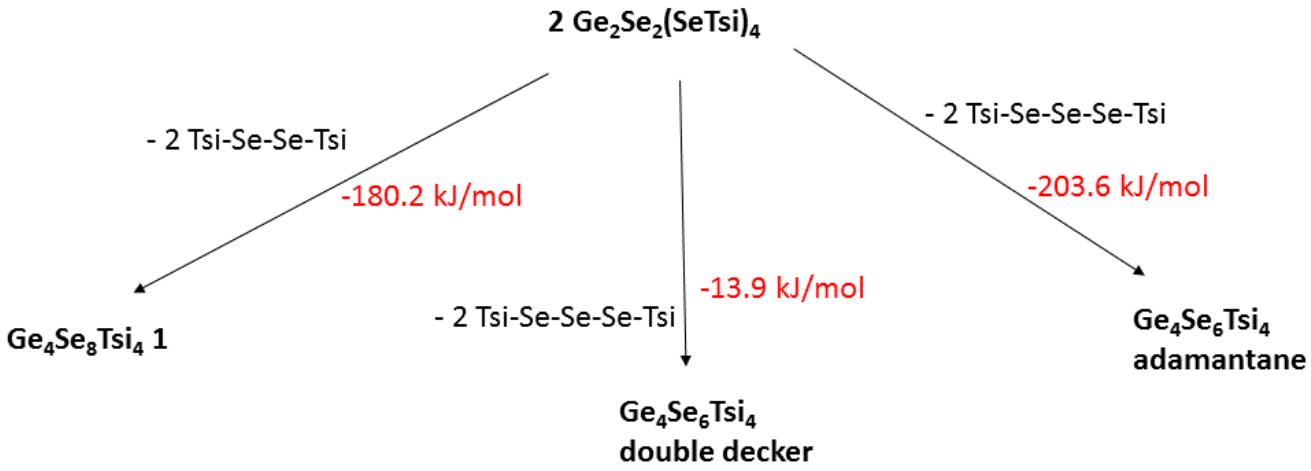
HOMO-LUMO-gap: 2.426 eV

Atom coordinates:

```
83
Se -2.900857 1.907201 -0.684172    C -6.232523 0.698220 0.829385     H -8.195321 0.862928 -1.660038
Se -0.787091 0.963244 -0.188113    C 3.718157 4.380183 0.445042      H -7.151149 0.933224 -3.117184
C -4.098370 0.530983 -1.544923     C 2.446584 1.700134 1.261303      H -7.241456 -0.579240 -2.148227
Se 0.803038 1.227006 -1.921311     C 0.740116 4.207581 1.038874      H -6.320338 -0.395743 0.996127
C 1.883437 2.905711 -1.635203      C -0.849998 4.450774 -2.095058    H -5.462237 1.097222 1.524320
Si 0.979291 4.331298 -2.558891     C 1.779333 6.017032 -2.182025     H -7.207280 1.161207 1.105169
Si 2.183356 3.273726 0.232141      C 0.995952 4.074940 -4.442142     H -5.667193 3.528097 -1.963066
Si 3.536296 2.395145 -2.513864     C 4.621647 1.265814 -1.441044     H -6.990493 3.364635 -0.758531
Si -3.768938 -1.246315 -0.877614   C 4.555642 3.919313 -3.008399     H -5.295400 3.542266 -0.205046
Si -3.866931 0.683901 -3.449577    C 3.225435 1.390452 -4.101980     H -4.322985 -1.709606 -4.158134
Si -5.832956 1.177401 -0.963540    H -3.425857 -2.329549 1.333567    H -4.674494 -0.537265 -5.467355
C -3.354513 -1.276974 0.975012     H -4.037842 -0.658081 1.589806    H -5.851943 -0.765809 -4.131228
C -5.297569 -2.348128 -1.152381    H -2.315247 -0.931503 1.164152    H -4.024283 3.195440 -3.587412
C -2.329921 -2.106399 -1.768955    H -6.175191 -2.037105 -0.545977   H -5.617241 2.464618 -4.011062
C -4.517263 2.344135 -4.106727     H -5.036495 -3.387875 -0.849994   H -4.263227 2.419710 -5.188406
C -2.049005 0.626835 -3.968143     H -5.607175 -2.376004 -2.218208   H -1.487441 1.502188 -3.577685
C -4.770041 -0.714729 -4.371958    H -1.388473 -1.526651 -1.665036   H -1.518831 -0.284977 -3.626449
C -5.937426 3.079180 -0.986039     H -2.170377 -3.101526 -1.293700   H -1.994318 0.656749 -5.080496
C -7.221781 0.528344 -2.085020     H -2.525426 -2.277603 -2.848921   H 3.638159 5.320708 -0.139194
```

```
H 4.664324 3.874261 0.156893      H 5.509436 0.963366 -2.042209     H -1.027153 4.570558 -1.006966
H 3.802979 4.657309 1.520456      H 4.073526 0.339372 -1.163247     H -1.411124 3.550312 -2.424564
H -0.205940 3.631701 0.959010     H 4.205175 1.256323 -4.616249     H 2.008655 4.135316 -4.893961
H 0.971334 4.334743 2.121283      H 2.533473 1.884110 -4.813556     H 0.370484 4.867566 -4.912233
H 0.577980 5.219360 0.609148      H 2.827437 0.375605 -3.881952     H 0.548784 3.092726 -4.711404
H 3.164525 0.990108 0.804866      H 4.050109 4.524703 -3.790807     H 1.657407 6.305230 -1.115292
H 2.840007 1.994811 2.261291      H 4.783749 4.583478 -2.149362     H 1.272532 6.796243 -2.795725
H 1.489291 1.159764 1.427271      H 5.523101 3.565095 -3.431414     H 2.862073 6.048920 -2.423310
H 4.992490 1.744430 -0.510609     H -1.289994 5.333866 -2.612243
```

## **8.9.** Competing reactions

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[1] Turbomole: O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346 – 354; BP86 functional: J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822 – 88824; A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098 – 3100; RI-DFT: K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *240*, 283 – 290; SVP: A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571 – 2577. TmoleX client: C. Steffen, K. Thomas, U. Huniar, A. Hellweg, O.Rubner, A. Schroer, *J. Comput. Chem.* **2010**, *31*, 2967 – 2970. DFT-D3 BJ damping: S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456-1465