# Supporting Information for

# Chlorine-35 Solid-State NMR Spectroscopy as an Indirect Probe of Germanium Oxidation State and Coordination Environment in Germanium Chlorides

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**Low Field SSNMR Spectra**



**Figure S1.** Partial $^{35}$Cl WURST-QCPMG NMR spectrum of **2** at 9.4 T. * indicates an impurity of the hydrochloride salt of the carbene while # indicates a spectrometer artefact. The blank region from -20000 to -35000 ppm is due to limitations of the probe electronics.



**Figure S2.** Partial $^{35}$Cl WURST-QCPMG NMR spectrum of **4** at 9.4 T. The low frequency edge of the spectrum was not acquired due to tuning limitations of the probe. The signal to high frequency of the fitted edge is due to contamination by $GeCl_2 \cdot$dioxane.

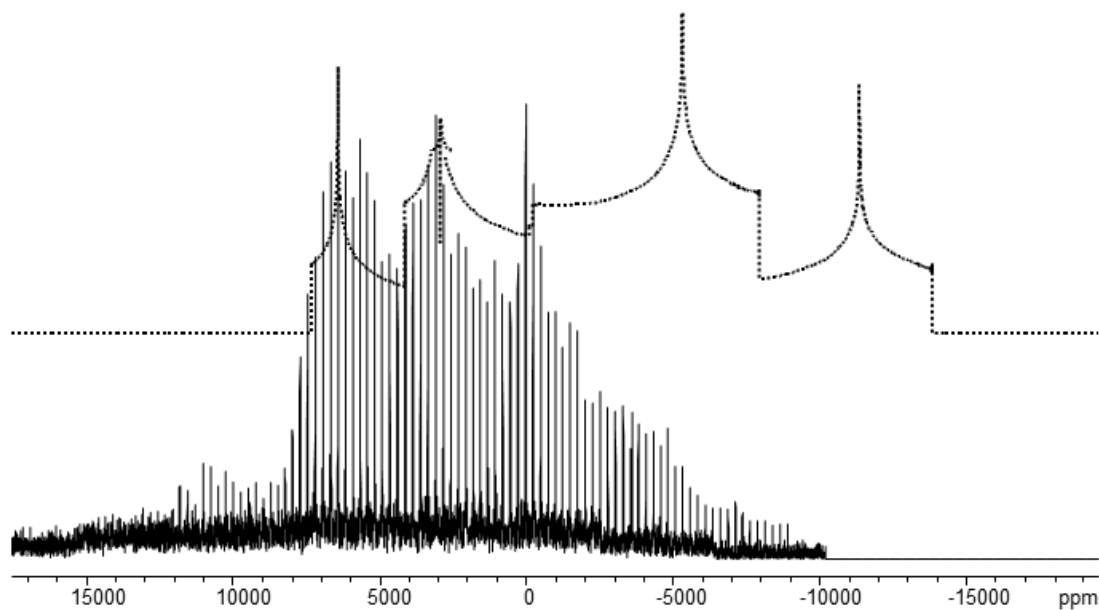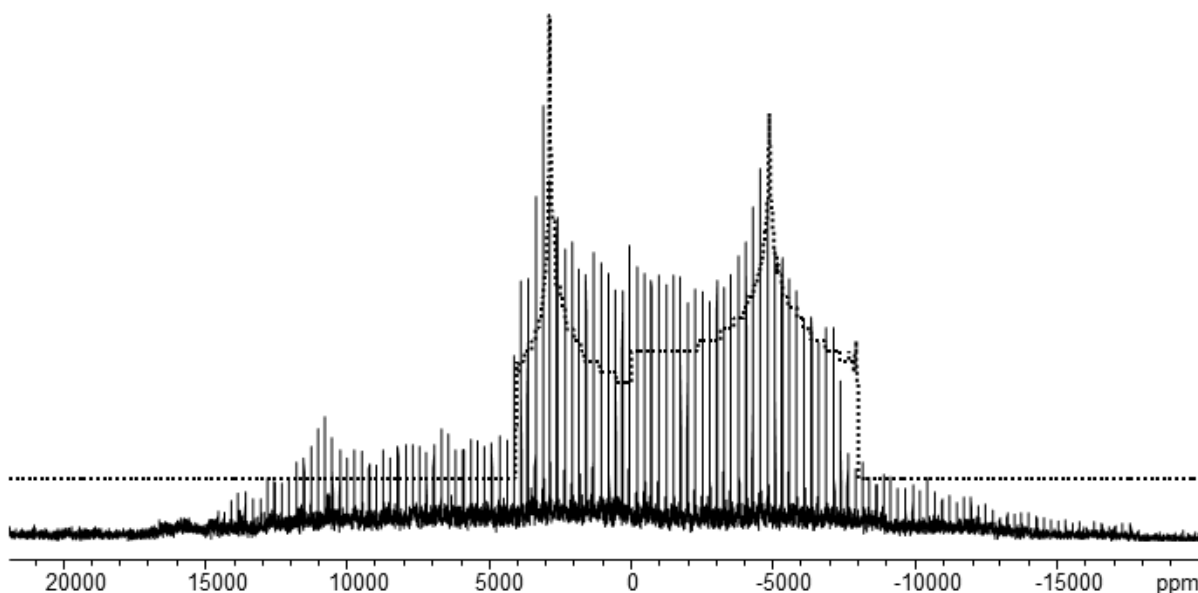**Figure S3.** $^{35}$Cl WURST-QCPMG NMR spectrum of **5** at 9.4 T. Part of the second signal can be observed

## Optimization of Computational Methodology

The calculations of NMR parameters for **1** using CASTEP gave values for $^{35}$Cl parameters that were in excellent agreement with the experimental results (calculated: $C_Q = 27.6$, $\eta_Q = 0.04$). In order to account for long range order in *Gaussian* 09, a series of clusters of increasing complexity were constructed (**Figure S**). Initial calculations were performed on the isolated monomer (**1**). Cluster **I** took into account the polymeric nature of the system by adding two repeat units. Cluster **II** was used to investigate the importance of long range Ge–Cl interactions by adding two adjacent GeCl$_2$ units. Cluster **III** is, effectively, a combination of clusters **I** and **II**, accounting for both the extended chain and the adjacent units. Finally, cluster **IV** extended the network in three dimensions. In all cases the calculated $^{35}$Cl NMR parameters are for the chlorines bound to the central germanium as circled in **Figure S**.
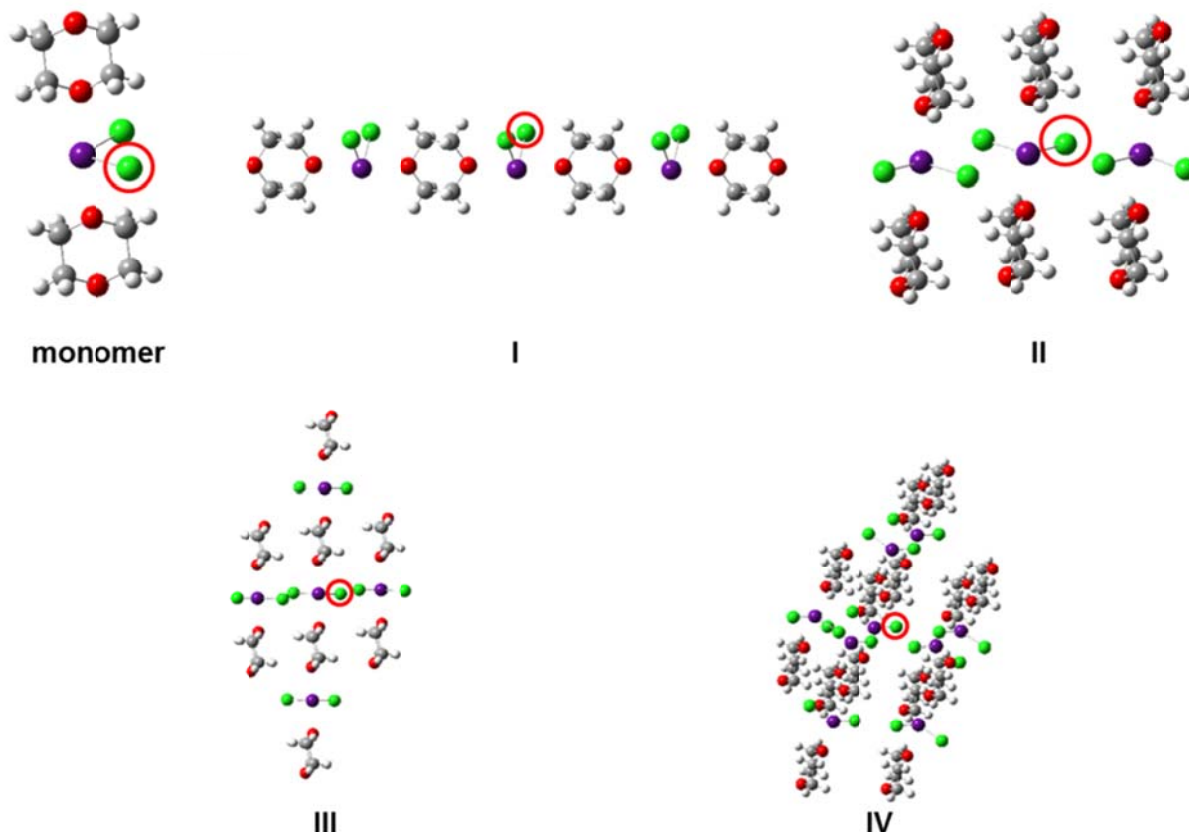
**Figure S4.** Clusters employed in the calculation of the $^{35}$Cl NMR parameters for GeCl$_2$·dioxane in *Gaussian* 09. The chlorine center for which the parameters were determined is indicated with a circle.

We systematically examined several different density functionals and basis sets in order to best approximate the experimental values. B3LYP is a very popular functional which has been previously employed for the calculation of $^{35}$Cl SSNMR parameters.[1] PBE1PBE and TPSSTPSS have not been employed for chlorine, but have been shown to reproduce the SSNMR parameters of $^{73}$Ge.[2] The results of these calculations are summarized in Table S1. Cluster **IV** was not calculated at the PBE1PBE/6-311+G** level as it was not possible to complete the calculation within the time constraints of the available computational resources. For clusters **II-IV**, the 6-311+G** basis set gave values in better agreement with experiment than 6-31G* across all functionals. The relatively recent TPSSTPSS[3] functional gave better agreements than the

PBE1PBE[4] functional in a shorter time. The popular B3LYP[5] functional was also investigated but was abandoned when it became apparent that it gave results very similar to PBE1PBE.

**Table S1.** Assessment of computational methodology using **1**

| Cluster | Functional | Basis Set | $C_Q$ [$^{35}$Cl] (MHz) | $\eta_Q$ [$^{35}$Cl] |
|---|---|---|---|---|
| **Experimental** | | | 28.3 | 0.055 |
| **monomer** | PBE1PBE | 6-31G* | 33.1 | 0.13 |
| | | 6-311+G** | 34.2 | 0.11 |
| | TPSSTPSS | 6-31G* | 32.3 | 0.12 |
| | | 6-311+G** | 33.1 | 0.11 |
| | B3LYP | 6-31G* | 32.3 | 0.12 |
| | | 6-311+G** | 34.0 | 0.10 |
| **I** | PBE1PBE | 6-31G* | 33.5 | 0.14 |
| | | 6-311+G** | 34.6 | 0.12 |
| | TPSSTPSS | 6-31G* | 32.7 | 0.15 |
| | | 6-311+G** | 33.5 | 0.12 |
| **II** | PBE1PBE | 6-31G* | 27.9 | 0.07 |
| | | 6-311+G** | 29.4 | 0.12 |
| | TPSSTPSS | 6-31G* | 27.0 | 0.12 |
| | | 6-311+G** | 28.5 | 0.11 |
| **III** | PBE1PBE | 6-31G* | 26.6 | 0.06 |
| | | 6-311+G** | 29.7 | 0.13 |
| | TPSSTPSS | 6-31G* | 27.3 | 0.14 |
| | | 6-311+G** | 27.9 | 0.10 |
| **IV** | PBE1PBE | 6-31G* | 26.6 | 0.06 |
| | | 6-311+G** | N/A[a] | N/A[a] |
| | TPSSTPSS | 6-31G* | 25.8 | 0.05 |
| | | 6-311+G** | 27.8 | 0.10 |

[a] *N/A = not applicable (job did not complete after 1 week)*

Not surprisingly, the isolated monomer gave results in poor agreement with experiment regardless of the functional or basis set employed, greatly overestimating $C_Q$. Extending the linear chain (cluster **I**) offered very little improvement over the calculations on the monomer. However, the addition of the adjacent $GeCl_2$ unit on either side of the fragment (cluster **II**) offered a dramatic improvement in the calculated value of $C_Q$ for the chloride attached to the central germanium atom, bringing it into excellent agreement with experiment. This suggests that

the long range contact between the terminal chlorine and the adjacent germanium atom is of importance to the overall EFG of the complex. Further elaboration (clusters **III** and **IV**) did not offer any notable improvement in the calculated values. In light for these results, the TPSSTPSS/6-311+G** model chemistry was used for the calculation of $^{35}$Cl NMR parameters for compounds **2**-**9**. All compounds were modelled with the inclusion of long distance contacts which fell within the sum of the van der Waals radii.
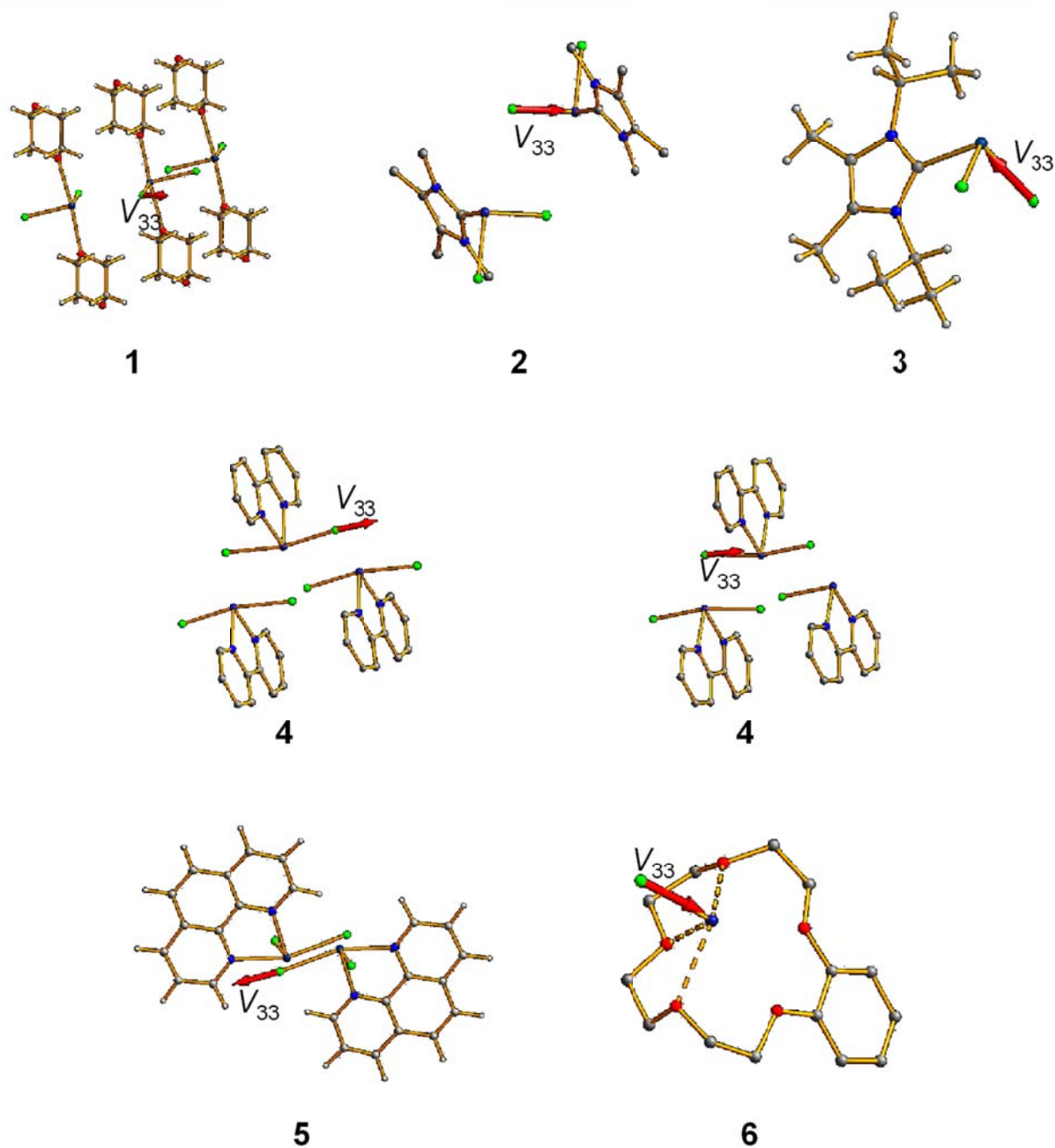
**Figure S5.** Orientation of the $V_{33}$ component of the EFG for compounds **1**-**6** calculated at the TPSSTPSS/6-311+G** level. Hydrogen atoms have been omitted for clarity.
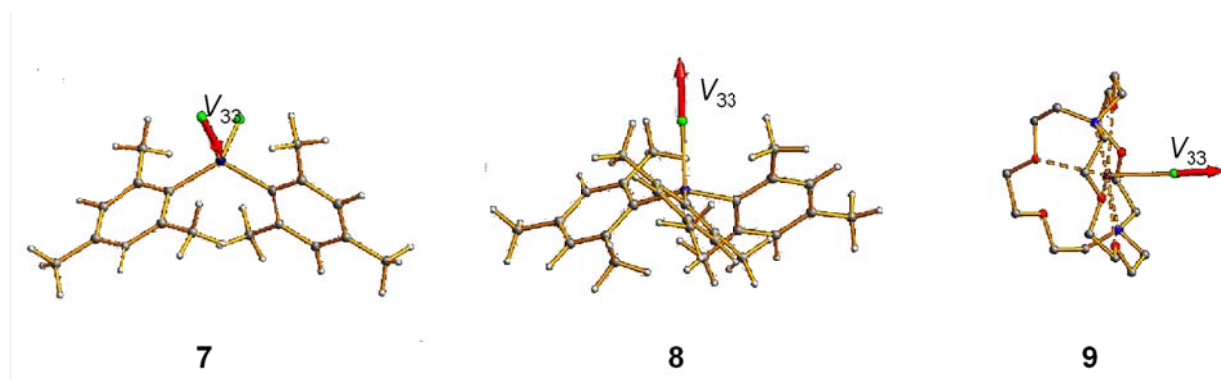
**Figure S6.** Orientation of the $V_{33}$ component of the EFG for compounds **7-9**. Compounds **7** and **8** were geometry optimized at the TPSSTPSS/6-31G* level. Hydrogen atoms and the $SnCl_3^-$ anion are omitted for clarity.

**Table S2.** $^{35}$Cl NMR acquisition parameters for **1-9**

| Compound | # of Subspectra | Subspectra Offset (kHz) | Transients per Subspectrum | # Echoes | Recycle Delay (s) |
|---|---|---|---|---|---|
| **1** (QCPMG) | 13 | 200 | 512 | 64 | 5 |
| **1** (WURST-QCPMG) | 2 | 200 | 256 | 64 | 5 |
| **2** | 9 | 200 | 1024 | 128 | 2 |
| **3** | 9$^a$ | 200 | 4096 | 128 | 2 |
| **4** (WURST-QCPMG) | 3 | 250 | 1024 | 128 | 1 |
| **4** (WURST-Echo) | 3 | 250 | 73 728 | N/A | 1 |
| **5** | 5 | 500 | 128 | 128 | 4 |
| **6** | 1 | N/A | 12 288 | 96 | 2 |
| **7** | 17 | 200 | 512 | 128 | 2 |
| **8** | 8 | 200 | 2048 | 64 | 1 |
| **9** | 2 | 200 | 81 920 | 32 | 1 |

$^a$ *An additional subspectrum was acquired over 28 762 transients to confirm the position of the low frequency edge of the spectrum*

**References**

(1) Perras, F. A.; Bryce, D. L. *Angew. Chem. Int. Ed.* **2012**, *51*, 4227.

(2) Hanson, M. A.; Sutrisno, A.; Terskikh, V. V.; Baines, K. M.; Huang, Y. *Chem. - Eur. J.* **2012**, *18*, 13770.

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