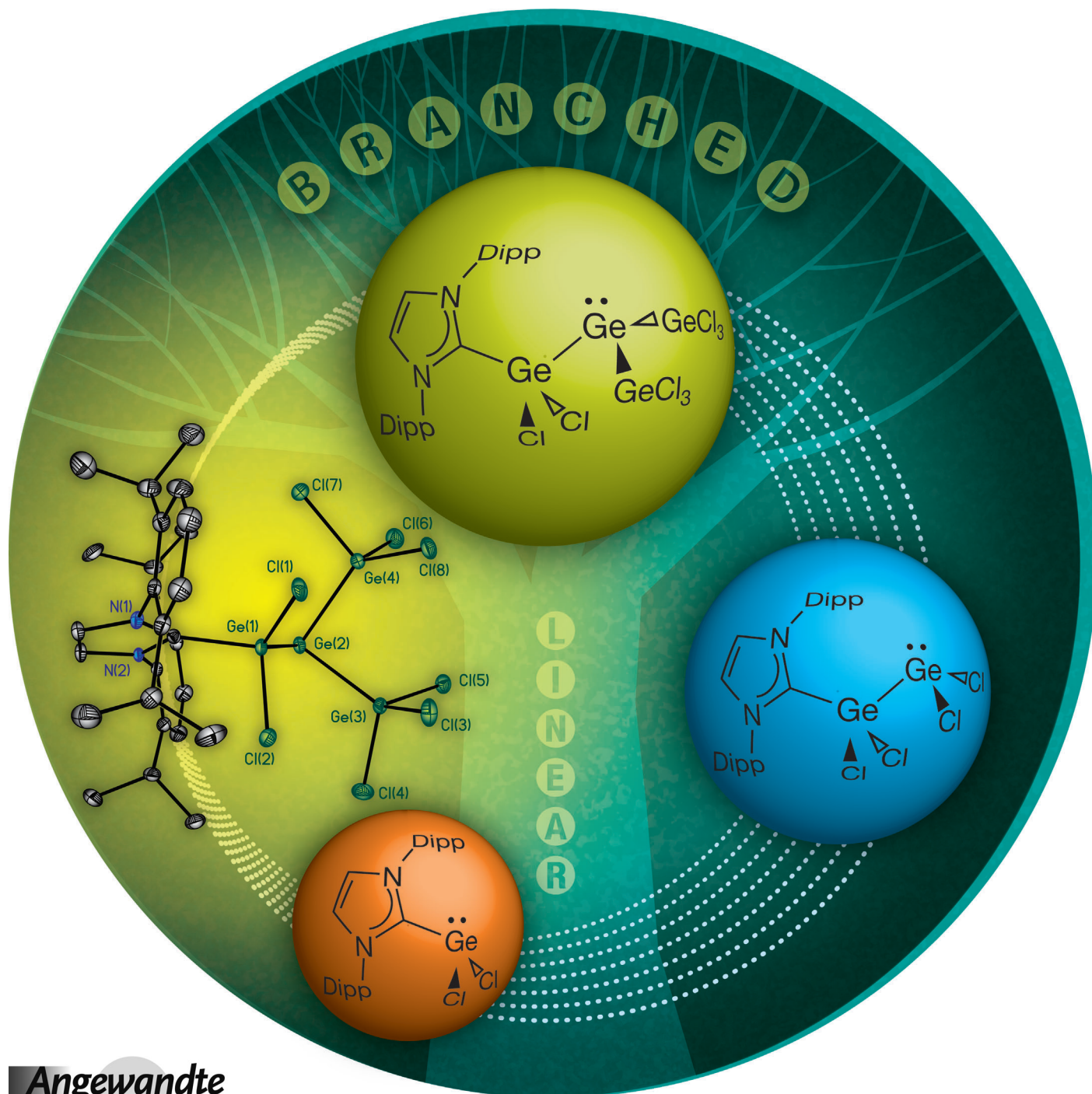


Controlled Growth of Dichlorogermanium Oligomers from Lewis Basic Hosts**

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The concept of catenation is widely exploited by synthetic chemists to construct new polymeric/oligomeric materials with desirable properties. As illustrated by the polyolefin industry, control over macromolecular topology (for example, branching vs. linear) is a key design criterion for the development of advanced materials.^[1] Amongst the inorganic Group 14 tetrel elements, it has been shown that catenation leads to species of the general form $(R_2E)_n$ ($E = Si, Ge, Sn$, and Pb); these materials display novel optoelectronic properties as a result of increasing $\sigma-\sigma^*$ conjugation, both as the length of the chains is extended and as the core element becomes heavier.^[2] Consequently, polysilanes and their heavier element congeners are now being actively explored as photoresist materials.^[3]

In general, polytetrelanes $(R_2E)_n$ are synthesized under harsh reducing conditions, such as Wurtz coupling, which leads to uncontrolled polymer growth.^[4,5] Drawn by this challenge and the uncertainty associated with the structures of the metastable halides $(SiCl_2)_n$ and $(GeCl_2)_n$ in the solid state,^[6] we focused our efforts towards developing an efficient bottom-up synthesis of related oligomers and polymers $(ECl_2)_x$ ($x \geq 2$) in the presence of Lewis basic (LB) hosts. This strategy is predicated on the propensity of strong electron-pair donors to bind/stabilize $SiCl_2$ and $GeCl_2$ in the form of stable molecular adducts $LB \cdot ECl_2$ ($E = Si$ and Ge).^[7] It is hoped that by forming well-defined higher oligomers of $(ECl_2)_x$ ($x \geq 2$) that productive halide replacement chemistry could later afford substituted $(R_2E)_x$ analogues with tailored optoelectronic properties,^[2] as well as generating precursors with suitable decomposition kinetics for chemical deposition processes.^[8] In pursuit of this goal, we herein report the mild and sequential synthesis of Lewis base supported germanium dichloride oligomers $(GeCl_2)_x$ ($x \geq 2$) that form thermodynamically favored branched structures upon increasing Ge content (a principle that is well known for hydrocarbons).^[9]

Our group reported the use of N-heterocyclic carbenes (NHCs) to facilitate the isolation of the parent inorganic methylene and ethylene, EH_2 and $H_2EE'H_2$ (E and $E' = Si, Ge$, and/or Sn), complexes.^[10,11] Knowing that the Ge^{II} adduct $IPrGeCl_2$ ($IPr = [(HCNDipp)_2C]$; $Dipp = 2,6-iPr_2C_6H_3$) contains a nucleophilic lone pair at Ge,^[10a] we decided to explore whether this complex would interact with further equivalents of Lewis acidic $GeCl_2$ as a method to gain access to new carbene-stabilized oligomers $IPr \cdot (GeCl_2)_x$ ($x \geq 2$). We began our studies by combining $IPr \cdot GeCl_2$ with $Cl_2Ge \cdot$ dioxane (1 equiv) in toluene, resulting in the formation of a sparingly soluble colorless solid [Eq. (1)]. This product was recrystal-

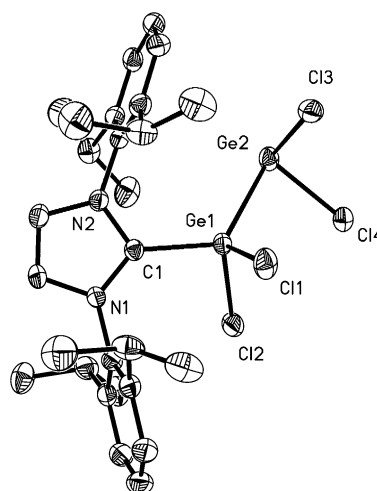
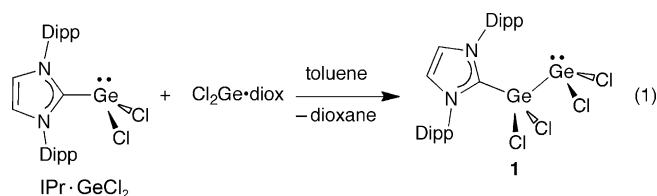


Figure 1. Thermal ellipsoid plot (30% probability level) of $IPr-GeCl_2GeCl_2$ (**1**); all hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: $C(1)-Ge(1)$ 2.032(5), $Ge(1)-Ge(2)$ 2.6304(9), $Ge(1)-Cl(1)$ 2.1811(16), $Ge(1)-Cl(2)$ 2.1780(15), $Ge(2)-Cl(3)$ 2.2568(16), $Ge(2)-Cl(4)$ 2.2844(15); $C(1)-Ge(1)-Ge(2)$ 125.04(14), $Cl(1)-Ge(1)-Cl(2)$ 103.38(7), $Cl(3)-Ge(2)-Cl(4)$ 96.22(2); torsion angle = $Cl(1)-Ge(1)-Ge(2)-Cl(3)$ 22.85(7).

lized from CH_2Cl_2 to give the linear tetrachlorodigermene adduct $IPr \cdot GeCl_2GeCl_2$ (**1**) as pale yellow crystals in a 75% yield (Figure 1).^[12,13]

The $C_{IPr}-Ge$ bond length in $IPr \cdot GeCl_2GeCl_2$ (**1**) is 2.032(5) Å, which is shorter than the related distance in $IPr \cdot GeCl_2$ (2.112(2) Å),^[10a] whereas the two $GeCl_2$ units in



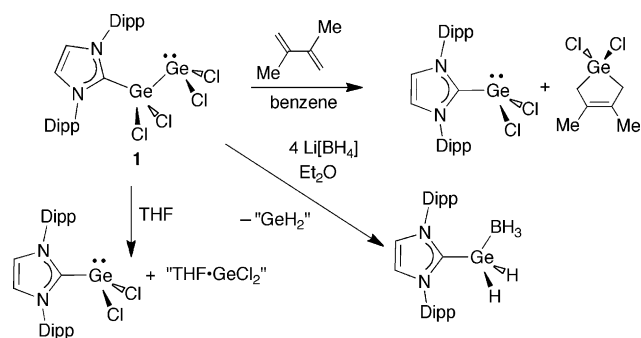
1 are linked in nearly eclipsed arrangements when viewed down the $Ge-Ge$ bond vector (for example, $Cl1-Ge1-Ge2-Cl3$ torsion angle = 22.85(7)°). The $Ge-Ge$ bond distance in **1** is 2.6304(9) Å and longer than most typical $Ge-Ge$ single bonds (ca. 2.40–2.50 Å);^[14] moreover, the germanium atom within the terminal $GeCl_2$ group contains a lone pair (bond angle sum at $Ge = 276.36(9)^\circ$). The $Cl3-Ge2-Cl4$ angle [96.22(6)°] is appreciably narrower than the related $Cl-Ge-Cl$ angle at the four-coordinate $Ge(1)$ center [103.39(7)°], and is consistent with the presence of a high degree of p character in the terminal $Ge-Cl$ bonds.

In accordance with the lengthened $Ge-Ge$ bond in $IPr \cdot GeCl_2GeCl_2$ (**1**), compound **1** decomposes in THF solvent by $Ge-Ge$ bond scission to give $IPr \cdot GeCl_2$ and presumably $Cl_2Ge \cdot THF$ (Scheme 1).^[15] Attempts to prepare the donor-acceptor digermene adduct $IPr \cdot GeH_2GeH_2 \cdot BH_3$ through treatment of **1** with $Li[BH_4]$, gave the known Ge^{II} dihydride adduct $IPr \cdot GeH_2 \cdot BH_3$ ^[10a] as the only soluble product.^[16] In a further demonstration of the lability of the terminal $GeCl_2$

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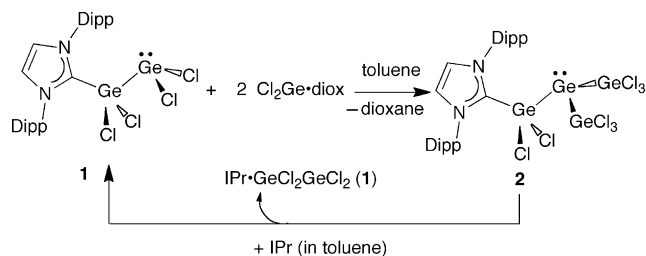
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Scheme 1. Representative chemistry of $\text{IPr-GeCl}_2\text{GeCl}_2$ (**1**). Dipp = 2,6- $i\text{Pr}_2\text{C}_6\text{H}_3$.

group, reaction of **1** with 2,3-dimethyl-1,3-butadiene cleanly afforded the cycloadduct $\text{Cl}_2\text{Ge}(\text{CH}_2\text{CMe})_2$ and IPr-GeCl_2 (Scheme 1).^[17] Despite the tendency of the Ge–Ge bond in **1** to cleave in solution, compound **1** is stable in the solid state under N_2 up to ca. 130 °C.

Given the successful synthesis of a carbene-supported $\text{GeCl}_2\text{–GeCl}_2$ array,^[13,18] we decided to investigate the synthesis of higher germanium dichloride oligomers using a similar strategy. When $\text{IPr-GeCl}_2\text{GeCl}_2$ (**1**) was combined with either one or two additional equivalents of GeCl_2 -dioxane in toluene, the branched Ge_4 adduct, $\text{IPr-GeCl}_2\text{Ge}(\text{GeCl}_3)_2$ (**2**) was isolated in low to moderate yield as a pale yellow solid (Scheme 2). Notably, compound **2** features Ge centers in formal oxidation states of 0, +2, and +3 and can be regarded as an adduct between IPr and the perhaloisobutylene congener $\text{Cl}_2\text{GeGe}(\text{GeCl}_3)_2$.



Scheme 2. Synthesis of $\text{IPr-GeCl}_2(\text{GeCl}_3)_2$ (**2**) and carbene-induced reversion to $\text{IPr-GeCl}_2\text{GeCl}_2$ (**1**). Dipp = 2,6- $i\text{Pr}_2\text{C}_6\text{H}_3$, IPr = $[(\text{HCN-Dipp})_2\text{C}]$.

Compound **2** is a rare example of a species containing an extended perhalogermane moiety^[19] and is, to our knowledge, the first polygermane synthesized through the controlled sequential addition of germanium halides. X-ray crystallography^[12] (Figure 2) revealed that the dative $\text{C}_{\text{IPr}}\text{–Ge}$ interaction in **2** is quite similar in length (2.0024(5) Å) to that found in the digermene adduct **1**, wherein all three core Ge–Ge bond lengths in **2** lie in the narrow range of 2.4870(8) to 2.4987(8) Å. These latter distances are significantly contracted with respect to the Ge–Ge bond found in $\text{IPr-GeCl}_2\text{GeCl}_2$ (**1**; 2.6304(9) Å) and are approaching the Ge–Ge distances present in the neopentyl-shaped species $(\text{Cl}_3\text{Ge})_4\text{Ge}$ (avg. of 2.420(6) Å).^[19d] The central germanium

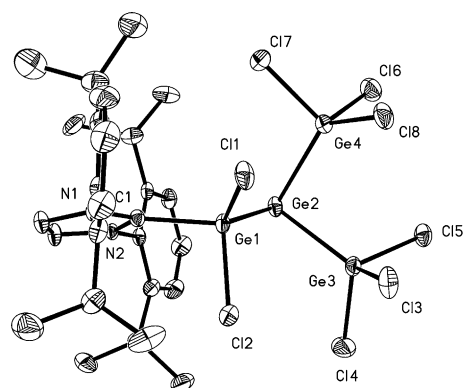


Figure 2. Thermal ellipsoid plot (30% probability level) of $\text{IPr-GeCl}_2\text{Ge}(\text{GeCl}_3)_2$ (**2**); all hydrogen atoms and CH_2Cl_2 solvate have been omitted for clarity. Selected bond lengths [Å] and angles [°]: $\text{C}(1)\text{–Ge}(1)$ 2.0024(5), $\text{Ge}(1)\text{–Cl}(1)$ 2.1506(15), $\text{Ge}(1)\text{–Cl}(2)$ 2.1734(16), $\text{Ge}(1)\text{–Ge}(2)$ 2.4983(8), $\text{Ge}(2)\text{–Ge}(3)$ 2.4870(8), $\text{Ge}(3)\text{–Ge}(4)$ 2.4987(8), $\text{Ge}(3)\text{–Cl}(3-5)$ 2.1549(18) to 2.1792(15), $\text{Ge}(4)\text{–Cl}(6-8)$ 2.1525(19) to 2.1675(17); $\text{C}(1)\text{–Ge}(1)\text{–Ge}(2)$ 117.46(14), $\text{Ge}(1)\text{–Ge}(2)\text{–Ge}(3)$ 90.90(3), $\text{Ge}(1)\text{–Ge}(2)\text{–Ge}(4)$ 91.27(3), $\text{Ge}(3)\text{–Ge}(2)\text{–Ge}(4)$ 89.20(3).

atom of the Ge_4 branch in **2** ($\text{Ge}2$) adopts a significantly pyramidalized geometry ($\Sigma^\circ\text{Ge}(2) = 271.71(3)^\circ$) due to the presence of a lone pair, while the average Ge–Ge–Ge angles at $\text{Ge}2$ ($90.46(3)^\circ$) indicate that a very high degree of p character resides in these bonds.

Treatment of **2** with IPr, a strong σ -donor, instigated an unusual halide migration/Ge–Ge bond cleavage reaction to regenerate $\text{IPr-GeCl}_2\text{GeCl}_2$ (**1**; Scheme 2). The detailed mechanism of this transformation is unknown at this time, but our preliminary theoretical investigations (see below) suggest that isomerization of **2** to form related species, such as the linear isomer $\text{IPr}(\text{GeCl}_2)_4$, might be feasible. Attempts to further grow the Ge chain by combining **2** with additional equivalents of $\text{Cl}_2\text{Ge-dioxane}$ failed to yield any discernable reaction. Our efforts to install hydride functionality onto the Ge chain in **2** (to form germanium polyhydrides and/or clusters)^[8,20] by treatment with $\text{Li}[\text{BH}_4]$ led to the formation of $\text{IPr-GeH}_2\text{–BH}_3$ ^[10a] and germanium metal. We are currently exploring related hydride transfer chemistry, as our prior experiences have shown that the nature of the hydride source has a profound impact in dictating the success of E–H bond formation.^[10,11]

Another dimension of reactivity to explore would be the role of the Lewis base in directing Ge oligomer growth; accordingly, we investigated germylene oligomerization in the presence of the nucleophilic olefin IPr=CH_2 .^[21] Starting from the new adduct $\text{IPrCH}_2\text{–GeCl}_2$ (**3**),^[22] we targeted the preparation of higher polygermanes by the addition of $\text{Cl}_2\text{Ge-dioxane}$ to **3**. Instead of isolating the expected tetrachlorodigermene adduct, $\text{IPrCH}_2\text{–GeCl}_2\text{GeCl}_2$, the unusual donor-capped Ge_4 dication $[(\text{IPrCH}_2\text{–GeCl}_2)_3\text{Ge}]^{2+}$ was formed as part of the bis(trichlorogermate) salt **4** in 97% yield [Eq. (2)].

As illustrated in Figure 3,^[12] the dicationic $[(\text{IPrCH}_2\text{–GeCl}_2)_3\text{Ge}]^{2+}$ portion of compound **4** has a trigonal pyramidal geometry at the central $\text{Ge}1$ atom derived from three capping $\text{IPrCH}_2\text{–GeCl}_2$ groups and a lone pair. The



empirical formula of **4** consists of one IPrCH_2 unit per two GeCl_2 fragments, and thus **4** can be considered a structural isomer of **1** with the IPr donor replaced by IPrCH_2 . The constituent Ge–Ge bond lengths within the Ge_4 core are nearly equivalent (avg. of 2.488(6) Å) and similar in length to the Ge–Ge distances in **2** (avg. of 2.4947(14) Å); for comparison, the Ge–Ge lengths in the hindered germyl anion $[(\text{Me}_5\text{Ge})_3\text{Ge}]^-$ were found to average 2.4412(12) Å.^[23] The $\text{C}_{\text{IPrCH}_2}$ –Ge bonds in **4** average to 2.001(4) Å and are slightly shorter than the respective $\text{C}_{\text{IPrCH}_2}$ –Ge distance in $\text{IPrCH}_2\text{GeCl}_2\text{W}(\text{CO})_5$ (2.056(3) Å).^[21] The less-hindered donor site in IPrCH_2 relative to IPr enables three $\text{IPrCH}_2\text{GeCl}_2$ units to bind to a single Ge center, with added stabilization in the form of lattice enthalpy resulting from the formation of a salt. The formation of **4** shows that the Lewis basic scaffold has an important role in dictating the outcome of germylene oligomerization.

We further analyzed **1**, **2**, and the dication in **4** by AIM (atoms in molecules). A nice correlation between the higher WBI values noted for the Ge–Ge bonds in **2** with an increase in the value of $\rho(r)$, which corresponds to the minimum electron density along a bond path, was noted (Supporting Information, Figure S6).^[22] Moreover, a noticeable increase in covalent character of the Ge–Ge bonds, which is related to negative Laplacian $\nabla^2\rho(r)$ values in AIM,^[24] was detected upon going from **1** (+0.004) to the branched species **2** (−0.006 to −0.035). The calculated linear isomer of **2**, IPr-

·GeCl₂GeCl₂GeCl₂GeCl₂, displayed a less covalent and weaker terminal Ge–Ge bond in relation to the internal bonds (Figure S6), and thus partially explains the lower stability of this isomer relative to **2**.^[22] For comparison, the digermene, H₃Ge–GeH₃ species was analyzed by AIM at the same M06-2X/cc-pVDZ level of theory and $\nabla^2\rho(r)$ was determined to be –0.085 for the covalent Ge–Ge bond.

Furthermore, we computed the free energy barrier for the isomerization of the model system ImMe₂·GeCl₂GeCl₂ to its germylene–germane isomer, ImMe₂·GeCl–GeCl₃ (ImMe₂ = [(HCNMe)₂C]; Figure 5), and noted a small free-energy barrier of 10.3 kcal mol^{–1}. Thus it appears that rich isomerization chemistry could be available to these (GeCl₂)_x oligomers through halide migration chemistry.^[7f,18,25]

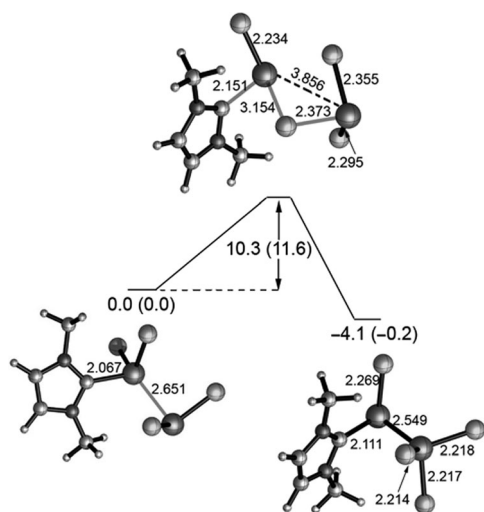


Figure 5. Computed [M06-2X/cc-pVDZ] free energy barrier of halide migration/isomerization involving ImMe₂·GeCl₂GeCl₂ in the gas phase, with values in parentheses obtained using a CH₂Cl₂ solvation model.

In summary, the stepwise synthesis of a series of donor-capped dichlorgermylene oligomers (GeCl₂)_x ($x \geq 2$) has been reported. Detailed theoretical studies revealed a thermodynamic preference for branching structures, which matches what is observed for their ubiquitous hydrocarbon analogues. The ability to readily form polyhalogermane structures in a controlled fashion should pave the way for the future development of novel Group 14 materials through bottom–up methods.

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