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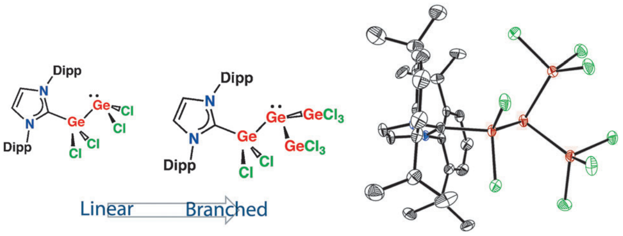

To branch or not to branch: A mild stepwise route to various linear and branched $(GeCl_2)_x$ oligogermylenes supported by Lewis bases is reported, including the carbene-bound Ge_4 complex $NHC{\cdot}GeCl_2Ge(GeCl_3)_2$ (see picture). Dipp = 2,6-$i$$Pr_2C_6H_3$, NHC = N-heterocyclic carbene.

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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 $(\mathrm{R_2E})_n$ (E = Si, Ge, Sn, and Pb); these materials display novel optoelectronic properties as a result of increasing σ–σ* 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 $(\mathrm{R_2E})_n$ 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 $(\mathrm{SiCl_2})_n$ and $(\mathrm{GeCl_2})_n$ in the solid state,[6] we focused our efforts towards developing an efficient bottom–up synthesis of related oligomers and polymers $(\mathrm{ECl_2})_x$ ($x \geq 2$) in the presence of Lewis basic (LB) hosts. This strategy is predicated on the propensity of strong electron-pair donors to bind/stabilize $\mathrm{SiCl_2}$ and $\mathrm{GeCl_2}$ in the form of stable molecular adducts $\mathrm{LB{\cdot}ECl_2}$ (E = Si and Ge).[7] It is hoped that by forming well-defined higher oligomers of $(\mathrm{ECl_2})_x$ ($x \geq 2$) that productive halide replacement chemistry could later afford substituted $(\mathrm{R_2E})_x$ 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 $(\mathrm{GeCl_2})_x$ ($x \geq 2$) 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, $\mathrm{EH_2}$ and $\mathrm{H_2EE'H_2}$ (E and E′ = Si, Ge, and/or Sn), complexes.[10,11] Knowing that the $\mathrm{Ge^{II}}$ adduct $\mathrm{IPrGeCl_2}$ (IPr = $[(\mathrm{HCNDipp})_2\mathrm{C}{:}]$; Dipp = 2,6-$i\mathrm{Pr_2C_6H_3}$) contains a nucleophilic lone pair at Ge,[10a] we decided to explore whether this complex would interact with further equivalents of Lewis acidic $\mathrm{GeCl_2}$ as a method to gain access to new carbene-stabilized oligomers $\mathrm{IPr{\cdot}(GeCl_2)}_x$ ($x \geq 2$). We began our studies by combining $\mathrm{IPr{\cdot}GeCl_2}$ with $\mathrm{Cl_2Ge{\cdot}dioxane}$ (1 equiv) in toluene, resulting in the formation of a sparingly soluble colorless solid [Eq. (1)]. This product was recrystallized from $\mathrm{CH_2Cl_2}$ to give the linear tetrachlorodigermene adduct $\mathrm{IPr{\cdot}GeCl_2GeCl_2}$ (**1**) as pale yellow crystals in a 75% yield (Figure 1).[12,13]

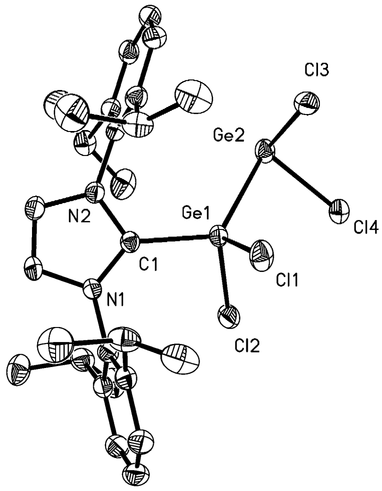
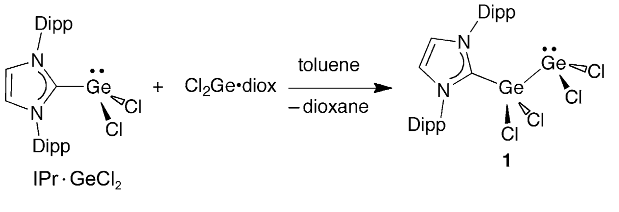


Figure 1. Thermal ellipsoid plot (30% probability level) of $\mathrm{IPr{\cdot}GeCl_2GeCl_2}$ (**1**); all hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–Ge(1) 2.032(5), Ge(1)–Ge(2) 2.6304(9), Ge(1)–Cl(1) 2.1811(16), Ge(1)–Cl(2) 2.1780(15), Ge(2)–Cl(3) 2.2568(16), 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).

The $\mathrm{C_{IPr}}$–Ge bond length in $\mathrm{IPr{\cdot}GeCl_2GeCl_2}$ (**1**) is 2.032(5) Å, which is shorter than the related distance in $\mathrm{IPr{\cdot}GeCl_2}$ (2.112(2) Å),[10a] whereas the two $\mathrm{GeCl_2}$ units in **1** are linked in nearly eclipsed arrangements when viewed down the Ge–Ge bond vector (for example, Cl1-Ge1-Ge2-Cl3



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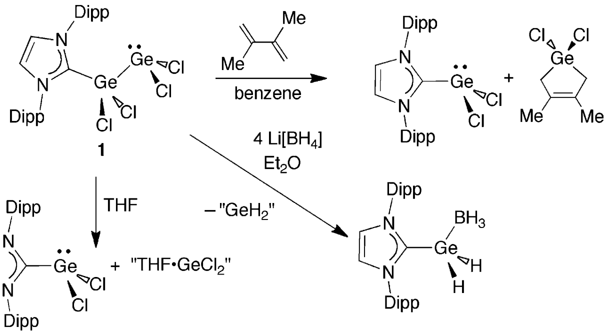
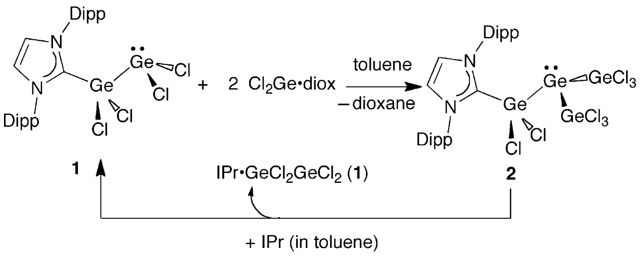
torsion angle = 22.85(7)°). The Ge–Ge bond distance in **1** is 2.6304(9) Å and longer than most typical Ge–Ge single bonds (ca. 2.40–2.50 Å);[14] moreover, the germanium atom within the terminal $GeCl_2$ group contains a lone pair (bond angle sum at Ge = 276.36(9)°). The Cl3-Ge2-Cl4 angle [96.22(6)°] 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 $GeCl_2$ group, reaction of **1** with 2,3-dimethyl-1,3-butadiene cleanly afforded the cycloadduct $Cl_2Ge(CH_2CMe)_2$ and $IPr{\cdot}GeCl_2$ (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.



Scheme 1. Representative chemistry of $IPr{\cdot}GeCl_2GeCl_2$ (**1**). Dipp = 2,6-$iPr_2C_6H_3$.

Given the successful synthesis of a carbene-supported $GeCl_2$–$GeCl_2$ array,[13,18] we decided to investigate the synthesis of higher germanium dichloride oligomers using a similar strategy. When $IPr{\cdot}GeCl_2GeCl_2$ (**1**) was combined with either one or two additional equivalents of $GeCl_2{\cdot}dioxane$ in toluene, the branched Ge_4 adduct, $IPr{\cdot}GeCl_2Ge(GeCl_3)_2$ (**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 $Cl_2GeGe(GeCl_3)_2$.



Scheme 2. Synthesis of $IPr{\cdot}GeCl_2(GeCl_3)_2$ (**2**) and carbene-induced reversion to $IPr{\cdot}GeCl_2GeCl_2$ (**1**). Dipp = 2,6-$iPr_2C_6H_3$, IPr = $[(HCNDipp)_2C\!:]$.

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 C_{IPr}–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 the Ge–Ge bond found in $IPr{\cdot}GeCl_2GeCl_2$ (**1**; 2.6304(9) Å) and are approaching the Ge–Ge distances present in the neopentyl-shaped species $(Cl_3Ge)_4Ge$ (avg. of 2.420(6) Å).[19d] The central germanium atom of the Ge_4 branch in **2** (Ge2) adopts a significantly pyramidalized geometry (Σ°Ge(2) = 271.71(3)°) due to the presence of a lone pair, while the average Ge-Ge-Ge angles at Ge2 (90.46(3)°) indicate that a very high degree of p character resides in these bonds.

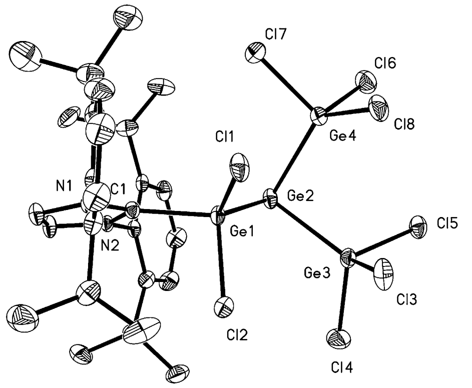
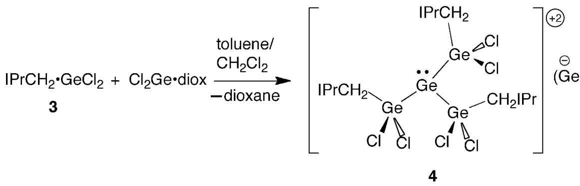


Figure 2. Thermal ellipsoid plot (30% probability level) of $IPr{\cdot}GeCl_2Ge(GeCl_3)_2$ (**2**); all hydrogen atoms and CH_2Cl_2 solvate have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–Ge(1) 2.0024(5), Ge(1)–Cl(1) 2.1506(15), Ge(1)–Cl(2) 2.1734(16), Ge(1)–Ge(2) 2.4983(8), Ge(2)–Ge(3) 2.4870(8), Ge(3)–Ge(4) 2.4987(8), Ge(3)–Cl(3-5) 2.1549(18) to 2.1792(15), Ge(4)-Cl(6-8) 2.1525(19) to 2.1675(17); C(1)-Ge(1)-Ge(2) 117.46(14), Ge(1)-Ge(2)-Ge(3) 90.90(3), Ge(1)-Ge(2)-Ge(4) 91.27(3), Ge(3)-Ge(2)-Ge(4) 89.20(3).

Treatment of **2** with IPr, a strong σ-donor, instigated an unusual halide migration/Ge–Ge bond cleavage reaction to regenerate $IPr{\cdot}GeCl_2GeCl_2$ (**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 $IPr{\cdot}(GeCl_2)_4$, might be feasible. Attempts to further grow the Ge chain by combining **2** with additional equivalents of $Cl_2Ge{\cdot}dioxane$ 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 $Li[BH_4]$ led to the formation of $IPr{\cdot}GeH_2{\cdot}BH_3$[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 IPrCH$_2$·GeCl$_2$ (**3**),[22] we targeted the preparation of higher polygermanes by the addition of Cl$_2$Ge·dioxane to **3**. Instead of isolating the expected tetrachlorodigermene adduct, IPrCH$_2$·GeCl$_2$GeCl$_2$, the unusual donor-capped Ge$_4$ dication [(IPrCH$_2$·GeCl$_2$)$_3$Ge]$^{2+}$ was formed as part of the bis(trichlorogermate) salt **4** in 97% yield [Eq. (2)].



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As illustrated in Figure 3,[12] the dicationic [(IPrCH$_2$·GeCl$_2$)$_3$Ge]$^{2+}$ portion of compound **4** has a trigonal pyramidal geometry at the central Ge1 atom derived from three capping IPrCH$_2$·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 [(Me$_3$Ge)$_3$Ge]$^-$ were found to average 2.4412(12) Å.[23] The C$_{\mathrm{IPrCH_2}}$–Ge bonds in **4** average to 2.001(4) Å and are slightly shorter than the respective C$_{\mathrm{IPrCH_2}}$–Ge distance in IPrCH$_2$·GeCl$_2$·W(CO)$_5$ (2.056(3) Å).[21] The less-hindered donor site in IPrCH$_2$ relative to IPr enables three IPrCH$_2$·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.

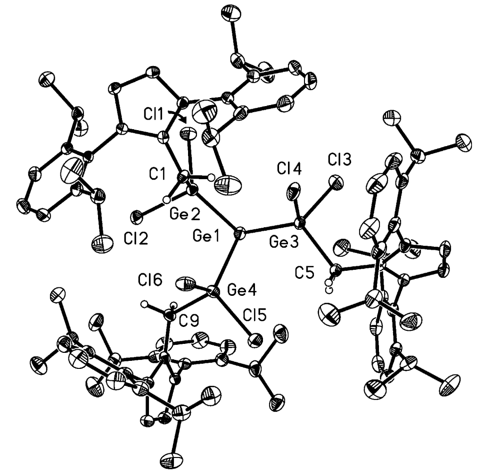

Figure 3. Thermal ellipsoid plot (30% probability level) of the [(IPrCH$_2$·GeCl$_2$)$_3$Ge]$^{2+}$ dication in **4**; selected hydrogen atoms, the [GeCl$_3$]$^-$ anions, and CH$_2$Cl$_2$ solvate have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–Ge(2) 2.004(4), C(5)–Ge(3) 1.996(4), C(9)–Ge(4) 2.004(4), Ge(1)–Ge(2) 2.4899(6), Ge(1)–Ge(3) 2.4743(6), Ge(1)–Ge(4) 2.5005(6); Ge(2)-Ge(1)-Ge(3) 98.75(2), Ge(2)-Ge(1)-Ge(4) 88.38(2), Ge(3)-Ge(1)-Ge(4) 95.61(2).

The above chemistry implies that, as the Ge content is increased, branched (GeCl$_2$)$_x$ structures become more stable relative to linear systems. Given the wealth of data that supports the thermodynamic preference for branching in extended hydrocarbons,[9] we were eager to further explore our Ge systems theoretically. We initiated our computational studies by determining the relative energies of a series of carbene-capped linear and branched oligomers, IPr·(GeCl$_2$)$_x$ ($x = 2$–4), both in the gas phase and with a CH$_2$Cl$_2$ solvation model.[22] The results are summarized in Figure 4; in each instance, there is a clear energetic preference for forming branched structures once three Ge atoms are bound in sequence.

As noted above, the Ge–Ge linkage in IPr·GeCl$_2$GeCl$_2$ (**1**; 2.6304(9) Å) is much longer than the Ge-Ge bonds in IPr·GeCl$_2$Ge(GeCl$_3$)$_2$ (**2**; avg. of 2.4947(14) Å). Accordingly, natural bond orbital (NBO) analysis shows that the Wiberg bond index (WBI) for the Ge–Ge bond in **1** is 0.69, whereas much higher indices (0.90 to 0.92) are found in the branched Ge$_4$ array in **2**; thus, branching appears to be partially driven by the formation of stronger Ge–Ge bonds. In both adducts, the C$_{\mathrm{IPr}}$–Ge bonds have similar WBI values (0.55 and 0.59,

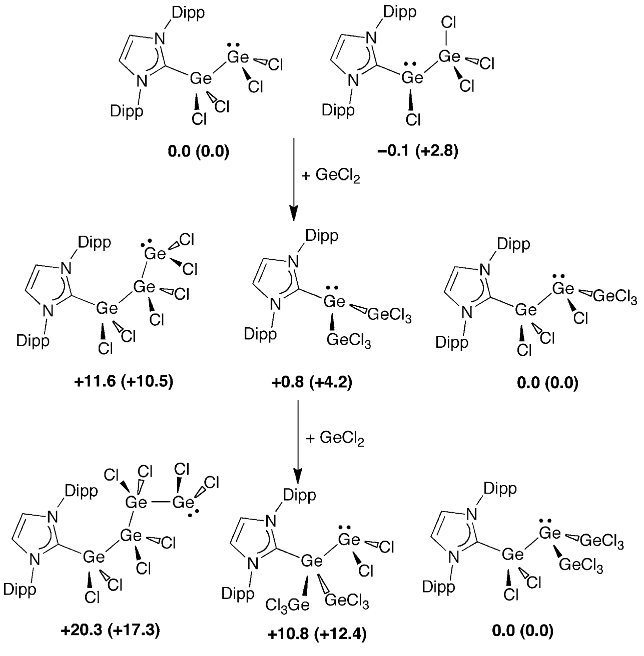

Figure 4. Computed [M06-2X/cc-pVDZ] relative electronic energies (kcal mol^{-1}) for a series of carbene-bound (GeCl$_2$)$_x$ oligomers ($x = 2$–4) showing a preference for Ge-chain branching at higher Ge content; values in parentheses have been determined using a CH$_2$Cl$_2$ solvation model.[22]

respectively) and similar bond polarities (ca. 80% electron density towards the donor C atoms), which is consistent with dative C_{IPr}–Ge interactions. In line with the data shown, a high degree of p character is present within the Ge–Ge bonds in **1**, **2**, and $[(IPrCH_2{\cdot}GeCl_2)_3Ge]^{2+}$ leading to the narrow bond angles observed.

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**, $IPr{\cdot}GeCl_2GeCl_2GeCl_2GeCl_2$, 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 digermane, $H_3Ge–GeH_3$ 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 $ImMe_2{\cdot}GeCl_2GeCl_2$ to its germylene–germane isomer, $ImMe_2{\cdot}GeCl–GeCl_3$ ($ImMe_2 = [(HCNMe)_2C\!:]$; 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 $(GeCl_2)_x$ oligomers through halide migration chemistry.[7f,18,25]

In summary, the stepwise synthesis of a series of donor-capped dichlorgermylene oligomers $(GeCl_2)_x$ ($x \geq 2$) 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.

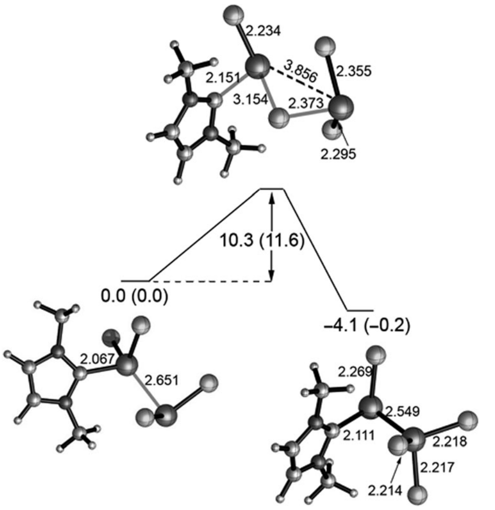

Figure 5. Computed [M06-2X/cc-pVDZ] free energy barrier of halide migration/isomerization involving $ImMe_2{\cdot}GeCl_2GeCl_2$ in the gas phase, with values in parentheses obtained using a CH_2Cl_2 solvation model.

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Keywords: carbenes · density functional calculations · germanium · main group elements · oligomerization

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