



## Theoretical investigation on structures and isomerizations of the aluminum chlorogermolenoid $\text{H}_2\text{GeClAlCl}_2$

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### ABSTRACT

The aluminum chlorogermolenoid  $\text{H}_2\text{GeClAlCl}_2$  was studied for the first time by using the DFT B3LYP and QCISD methods in gas phase and in  $\text{C}_6\text{H}_{12}$ , THF, DMSO, and  $\text{H}_2\text{O}$  solvents. The theoretical calculations predicted that  $\text{H}_2\text{GeClAlCl}_2$  has three equilibrium configurations, in which the *p*-complex is the lowest in energy and is the most stable structure. The isomerization reactions among the three complexes have been investigated. The *p*-complex is suggested to be the predominant form of  $\text{H}_2\text{GeClAlCl}_2$  in the gas phase and in solutions thermodynamically and kinetically.

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### 1. Introduction

The cyclopropanation reaction is an interesting topic [1–4] since many cyclopropane-containing molecules have been found to have biologic activity [5–11]. Many carbenoids such as Zn carbenoids [2,12–21], Li carbenoids [22], Sm carbenoids [23,24], and Al carbenoids [25–28] have been confirmed to be efficient cyclopropanating reagents. Germolenoid, analogous to carbenoid, which can be denoted as  $\text{R}_1\text{R}_2\text{GeMX}$ , has been suggested to be important active intermediate in many reactions [29–32]. If the germolenoid could promote analogous cyclopropanation reactions it would be used in the synthesis of new containing-germanium compounds. However, until now there are not any stable germolenoids being prepared by experiments and few theoretical studies have been carried out on germolenoid. Since Qiu et al. [33] firstly studied the isomeric structure of the simplest germolenoid  $\text{H}_2\text{GeLiF}$  by *ab initio* calculations, up to now, metal atoms in the germolenoids investigated are limited only to such metals as Li [34–37], Be [38], Na [39–41], and Mg [42]. Are other metal germolenoids exist? This is an interesting topic not only to experimental but also to theoretical workers. Recently, we performed theoretical investigation on the aluminum chlorogermolenoid  $\text{H}_2\text{GeClAlCl}_2$  and predicted its possible structures in gas phase and some solvents.

### 2. Computational details

All geometries were fully optimized by using the density functional theory (DFT) B3LYP (Becke's three-parameter hybrid function with the non-local correlation of Lee–Yang–Parr) [43,44] method. In the geometry optimization calculations the 6-311+G(d, p) [45] basis set has been used for all atoms. The geometries were first optimized and then the harmonic vibrational frequencies were calculated at the same level of theory to confirm the nature of the stationary points. The nature of a given transition state was analyzed by IRC (intrinsic reaction coordinate) [46] computations at the same level. The B3LYP/6-311+G(d, p) natural bond order analysis calculations were performed at the optimum geometries. In order to improve the treatment of electron correlation the single-point calculations were made at the QCISD level using the 6-311++G(d, p) basis set for all species. Unless otherwise noted, relative energies given in the text are those determined at QCISD/6-311++G(d, p)//B3LYP/6-311+G(d, p) and include vibrational zero-point energy (ZPE, without scale) corrections determined at B3LYP/6-311+G(d, p) level. To consider solvent effects on the structures and isomerization reactions, the polarized continuum model (PCM) was applied to the calculations. The solvents cyclohexane ( $\text{C}_6\text{H}_{12}$ ), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), and water ( $\text{H}_2\text{O}$ ) were used. All of the calculations were carried out using the GAUSSIAN 03 program suits [47].

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### 3. Results and discussion

Unlike the carbene  $H_2C$ : [48], the ground state of  $H_2Ge$ : is singlet [49].  $H_2GeClAlCl_2$  can be considered as complexes of the ground singlet germylene  $H_2Ge$ : with  $AlCl_3$ . We only calculated the singlet state of  $H_2GeClAlCl_2$ . Though the germynoid  $H_2GeClAlCl_2$  could be considered as the complex of  $H_2Ge$ : with  $AlCl_3$ , the reaction of  $GeH_2$  and  $AlCl_3$  is not easy and in fact it is not a feasible way to generating germynoid  $H_2GeClAlCl_2$  by using the reaction of  $GeH_2$  and  $AlCl_3$ . Therefore, in this work we did not study the reaction path of  $GeH_2$  and  $AlCl_3$ . The B3LYP/6-311+G(d, p) optimized stationary structures of  $H_2GeClAlCl_2$  in gas phase are shown in Fig. 1. The total energies, relative energies, dipole moments, and number of the imaginary frequency of each isomer in gas phase are given in Table 1.

#### 3.1. Equilibrium structures in gas phase

We performed the full search on the possible structures of  $H_2GeClAlCl_2$  and in the paper only the equilibrium structures will be reported. The B3LYP/6-311+G(d, p) calculations indicated that  $H_2GeClAlCl_2$  has three equilibrium structures (1–3 in Fig. 1) in gas phase. As displayed in Fig. 1, complex 1 is characterized by a three-membered ring structure, in which the Ge, Al, and Cl1 atoms combine with each other. Complex 1 is of  $C_s$  symmetry. Alkali metal germynoid  $R_2GeMX$  [34–37,39,40] and the beryllium chlorogermynoid  $H_2GeClBeCl$  [38] also have similar structures as complex 1. From the bond lengths, it can be seen that the Cl1–Al bond length of complex 1 is 0.213 Å longer than that of  $AlCl_3$  and the Ge–Cl1 bond length is 0.320 Å longer than that of  $H_3GeCl$ , indicating that the Cl1–Al and Ge–Cl1 bonds of complex 1 are weaker

than those corresponding monomer, respectively. The Ge–Al bond length of complex 1 is only 0.006 Å shorter than that of  $H_3GeAlCl_2$ , indicating that the interaction between Ge and Al in complex 1 is similar to that in  $H_3GeAlCl_2$ . Overall, the stability of complex 1 has been enhanced through the donating of  $\sigma$  electron of  $H_2Ge$ : toward Al atom and feedback of part of lone pair electrons of Cl1 atom to  $p$  orbital of Ge atom, resulting in the formation of the electron circle of  $Ge \rightarrow Al \rightarrow Cl1 \rightarrow Ge$ . The energy of complex 1 is 22.19 kcal/mol lower than the sum of energies of  $H_2Ge$ : and  $AlCl_3$ .

Complex 2 in Fig. 1, which is of  $C_1$  symmetry, is a  $p$ -complex formed by donating of electron of a Cl1 atom in  $AlCl_3$  molecule toward unoccupied  $p$  orbital of Ge atom in  $H_2Ge$ . There also exists interaction among Al atom with positive charge and two H atoms with negative charge (see Fig. 1), which may be a main reason for complex 2 to be very stable. The interaction among Al and H1 atoms makes the angle  $HGeH$  3.6° smaller and the Ge–H1 distance 0.146 Å longer than  $H_2Ge$ , respectively. The Al–Cl1 bond length of complex 2 is 0.142 Å longer than that of  $AlCl_3$  and the Ge–Cl1 bond length is 0.365 Å longer than that of  $H_3GeCl$ . Complex 2 is the lowest in energy among the three equilibrium structures of  $H_2GeClAlCl_2$ . The energy of complex 2 is 23.09 kcal/mol lower than the sum of energies of  $H_2Ge$ : and  $AlCl_3$ , and 0.90 kcal/mol lower than that of complex 1. Complex 2 is suggested to be experimentally detectable structure.

Complex 3 in Fig. 1, which is of  $C_s$  symmetry, is formed by insertion of  $H_2Ge$ : into a Al–Cl bond in  $AlCl_3$  molecule and complex 3 can be regarded as a “classical” tetrahedral structure. The Ge–Cl1 distance in complex 3 is 0.297 Å shorter than that in complex 1, indicating that the interaction between the Ge and Cl atoms in complex 3 is stronger than in complex 1, but still 0.023 Å longer than that in  $H_3GeCl$ . The energy of complex 3 is 20.15 kcal/mol

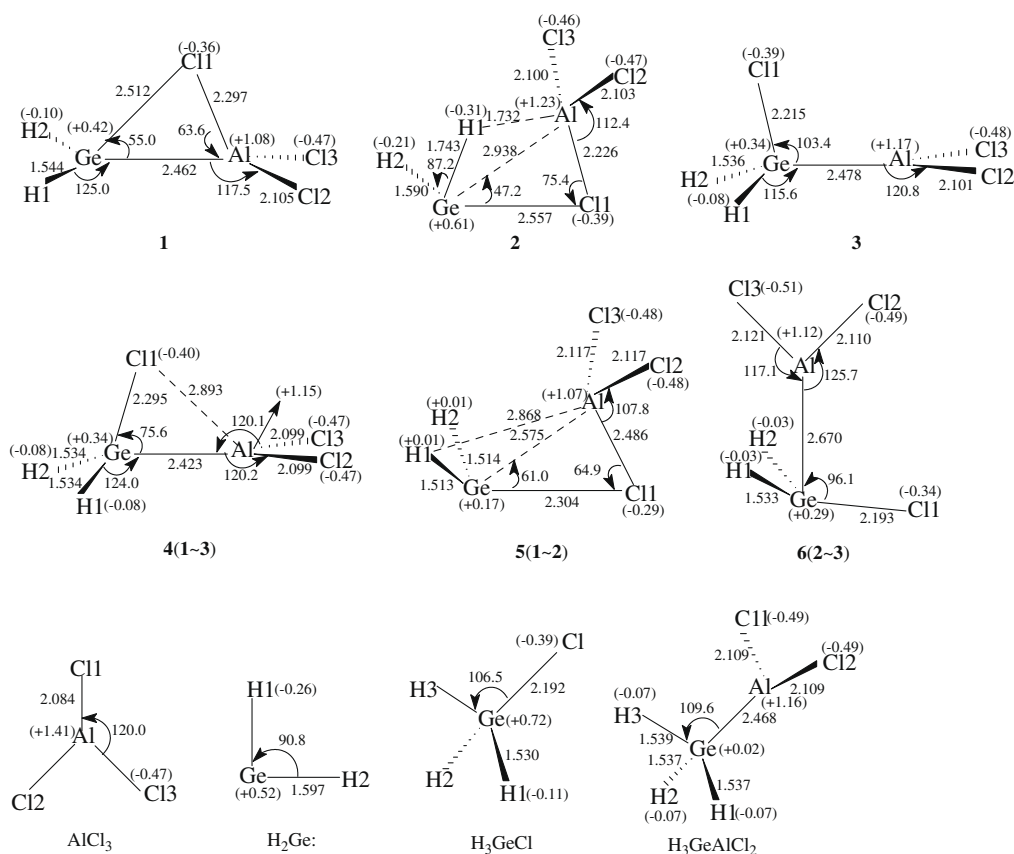


Fig. 1. The equilibrium configurations and the transition states for isomerization reactions of  $H_2GeClAlCl_2$  in gas phase calculated at B3LYP/6-311+G(d, p) level (bond lengths are given in angstroms and angles in degrees, values in parentheses are the natural charges).

**Table 1**  
The total energies ( $E_{\text{tot}}$ ), vibrational zero-point energies (ZPE), relative energies ( $E_{\text{rel}}$ ), dipole moments ( $\mu$ ), and number ( $N_{\text{imag}}$ ) of imaginary frequency of the geometries for  $\text{H}_2\text{GeClAlCl}_2$ .

Geometries	$E_{\text{tot}}^{\text{a}}$ (a.u.)	ZPE <sup>b</sup> (a.u.)	$E_{\text{rel}}$ (kcal/mol)	$\mu^{\text{b}}$ (Debye)	$N_{\text{imag}}$
<b>1</b>	−3697.7538928	0.020325	0.90	3.6730	0
<b>2</b>	−3697.7552586	0.020252	0.00	3.5651	0
<b>3</b>	−3697.7510661	0.020741	2.94	2.4056	0
<b>4</b>	−3697.7472626	0.020170	4.97	3.3017	1
<b>5</b>	−3697.6865299	0.018878	42.27	3.8985	1
<b>6</b>	−3697.6830332	0.018501	44.22	2.4874	1

<sup>a</sup> At the QCISD/6-311++G(d, p)//B3LYP/6-311+G(d, p) level.

<sup>b</sup> At the B3LYP/6-311+G(d, p) level.

lower than the sum of energies of  $\text{H}_2\text{Ge}$ : and  $\text{AlCl}_3$ , and 2.94 kcal/mol higher than that of complex **2**.

In a word, the germynoid  $\text{H}_2\text{GeClAlCl}_2$  has three equilibrium configurations in gas phase and according to the analysis on the energies (see Table 1), the order of the thermodynamic stability of the three complexes of  $\text{H}_2\text{GeClAlCl}_2$  should be **2** > **1** > **3**.

### 3.2. Isomerization reactions in gas phase

As displayed in Fig. 1, three transition-state structures **4**, **5**, and **6** have been located. Further IRC calculations suggest that they are the true transition states for the isomerization reactions between complexes **1** and **3**, **1** and **2**, and **2** and **3**, respectively. Vibration analysis calculations indicate that the unique imaginary frequencies of structures **4**, **5**, and **6** are 97.3i, 855.3i, and 902.8i, respectively, at the B3LYP/6-311+G(d, p) level.

As presented in Table 1, the potential barrier from complex **1** to complex **3** is 4.07 kcal/mol and the inverse is 2.03 kcal/mol, implying the easy isomerization from the latter to the former. The potential barrier from complex **1** to complex **2** is 41.37 kcal/mol and the inverse is 42.27 kcal/mol, so isomerization reaction between complex **1** and complex **2** is not easy. The potential barrier from complex **2** to complex **3** is 44.22 kcal/mol and the inverse is 41.28 kcal/mol,

so isomerization reaction between complex **2** and complex **3** is not easy too. Thus, complex **2** should be the predominant form of  $\text{H}_2\text{GeClAlCl}_2$  in the gas phase thermodynamically and kinetically and would be searched in future experiments. Complex **1** may also be existent structure.

### 3.3. The solvent effect

The geometry optimization calculations for  $\text{H}_2\text{GeClAlCl}_2$  in  $\text{C}_6\text{H}_{12}$ , THF, DMSO, and  $\text{H}_2\text{O}$  were performed at the same level as in the gas phase. The main geometric parameters of all stationary points calculated in various solvents are listed in Table 2. The calculations indicated that all the stationary points in gas phase can exist in a solution of various solvents. From Table 2 we find that the geometric parameters change little in solvents and in gas phase. For structure **1**, the Ge–Cl1 bond length value of 2.639 Å in  $\text{H}_2\text{O}$  is 0.127 Å larger than that in gas phase (2.512 Å). For other bond length values the changes in various solvents and in gas phase are smaller than 0.127 Å. For the bond angle values the changes in gas phase and in solutions are smaller than 3°. Therefore, it can be inferred that the solvent effect on the geometric parameters is not strong.

**Table 2**  
The main geometric parameters of configurations of  $\text{H}_2\text{GeClAlCl}_2$  in solvents (bond lengths in Å and angles in °).

Structure	GeAl	GeCl1	AlCl1	AlCl2	GeH1	Cl1GeAl	Cl1AlCl2	H1GeH2	Cl2AlGe
<i>C<sub>6</sub>H<sub>12</sub> (<math>\epsilon = 2.023</math>)</i>									
<b>1</b>	2.455	2.541	2.288	2.113	1.542	54.5	112.5	106.6	118.2
<b>2</b>	2.939	2.581	2.219	2.111	1.753	46.8	112.6	86.9	120.4
<b>3</b>	2.478	2.225		2.106	1.534	104.2		110.7	121.2
<b>4</b>	2.420	2.310	2.879	2.105	1.532	74.9	107.8	111.0	120.6
<b>5</b>	2.571	2.314	2.473	2.126	1.514	60.6	107.8	134.4	122.3
<b>6</b>	2.669	2.202		2.119	1.532	95.5		120.6	125.7
<i>THF (<math>\epsilon = 7.58</math>)</i>									
<b>1</b>	2.448	2.593	2.275	2.124	1.540	53.6	112.6	107.3	119.1
<b>2</b>	2.940	2.615	2.213	2.121	1.767	46.5	112.5	86.7	122.7
<b>3</b>	2.479	2.238		2.113	1.532	105.2		111.4	121.8
<b>4</b>	2.416	2.335	2.853	2.113	1.530	73.8	107.0	111.8	121.3
<b>5</b>	2.566	2.329	2.464	2.140	1.514	60.2	107.4	135.2	123.5
<b>6</b>	2.668	2.216		2.133	1.532	94.6		121.6	125.2
<i>DMSO (<math>\epsilon = 46.7</math>)</i>									
<b>1</b>	2.445	2.626	2.270	2.129	1.539	53.0	112.4	107.6	119.5
<b>2</b>	2.946	2.636	2.209	2.125	1.774	46.2	112.6	86.5	122.7
<b>3</b>	2.478	2.248		2.115	1.531	104.7		111.6	121.9
<b>4</b>	2.414	2.351	2.837	2.117	1.529	73.1	106.2	112.1	121.6
<b>5</b>	2.564	2.336	2.466	2.146	1.514	60.2	107.1	135.6	124.0
<b>6</b>	2.668	2.223		2.140	1.532	94.2		122.0	124.9
<i>H<sub>2</sub>O (<math>\epsilon = 78.39</math>)</i>									
<b>1</b>	2.445	2.639	2.267	2.131	1.539	52.8	112.6	107.6	119.8
<b>2</b>	2.943	2.631	2.211	2.127	1.774	46.3	112.6	86.6	123.0
<b>3</b>	2.477	2.250		2.118	1.532	105.4		111.4	122.4
<b>4</b>	2.413	2.355	2.834	2.119	1.530	72.9	106.7	111.9	122.0
<b>5</b>	2.563	2.338	2.467	2.148	1.514	60.2	107.2	135.5	124.2
<b>6</b>	2.665	2.225		2.142	1.531	94.3		122.3	124.7

**Table 3**The relative energy (in kcal/mol) of structures of  $\text{H}_2\text{GeClAlCl}_2$  in solvents.

	$\text{C}_6\text{H}_{12}$	THF	DMSO	$\text{H}_2\text{O}$
<b>1</b>	0.75	0.73	0.72	0.55
<b>2</b>	0.00	0.00	0.00	0.00
<b>3</b>	2.58	1.94	1.68	1.15
<b>4</b>	5.10	5.13	5.13	4.98
<b>5</b>	42.41	42.66	42.86	42.94
<b>6</b>	43.94	43.53	43.42	43.21

The relative energies of the structures of  $\text{H}_2\text{GeClAlCl}_2$  in the four solvents are given in Table 3. From Table 3, we can see that structure **2** is the lowest in energy and should be the most stable structure. When the polarity of the solvent increases, the relative energy of structure **1** and **3** decreases. Therefore, it can be deduced that the higher the polarity of the solvent is, the more stable structure **1** and **3** will be. From Table 3 we can calculate the potential barriers of the isomerization reactions for the structures of  $\text{H}_2\text{GeClAlCl}_2$ . Based on the calculated potential barriers we can conclude that when the polarity of the solvent increases, the potential barriers from complex **2** to complex **3** decrease, while other potential barriers increase. However, the difficulty of each isomerization reaction is the same whether the structures are in gas phase or in solvents.

#### 4. Conclusions

The aluminum chlorogermolenoid  $\text{H}_2\text{GeClAlCl}_2$  has been studied for the first time by using the DFT B3LYP and QCISD methods in gas phase and in  $\text{C}_6\text{H}_{12}$ , THF, DMSO, and  $\text{H}_2\text{O}$  solvents. Geometry optimization calculations indicate that  $\text{H}_2\text{GeClAlCl}_2$  has three equilibrium structures in gas phase. The three structures still exist in a solution of various solvents. Three transition states for isomerization reactions of  $\text{H}_2\text{GeClAlCl}_2$  are located and the energy barriers are calculated. The calculated results indicated that the *p*-complex has the lowest energy in the gas phase and in solvents and is the predominant form of  $\text{H}_2\text{GeClAlCl}_2$  thermodynamically and kinetically. We hope the results would be helpful for further experimental and theoretical studies on germolenoids.

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