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$GeCl_2$ cycloaddition reactions to unsaturated organic compounds taking ethylene, buta-1,3-diene, and hexa-1,3,5-triene as examples: a quantum chemical study*

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The cycloaddition reactions of dichlorogermylene $GeCl_2$ to ethylene, buta-1,3-diene, and hexa-1,3,5-triene were studied within the framework of the density functional theory (PBE and B3LYP density functionals) and by the *ab initio* CBS-QB3 method. The energy characteristics of the reaction of $GeCl_2$ with ethylene were refined and non-empirical quantum chemical calculations of reaction pathways in the $GeCl_2$ + buta-1,3-diene and $GeCl_2$ + hexa-1,3,5-triene systems were carried out for the first time. It was shown that the [2+1] cycloaddition reactions are kinetically hindered and thermodynamically unfavorable, while the [4+1] and [6+1] cycloaddition reactions are characterized by low barriers and result in thermodynamically favorable products. For the [4+1] cycloaddition to buta-1,3-diene and [6+1] cycloaddition to hexa-1,3,5-triene, the most energetically favorable reaction pathways involve a suprafacial and antarafacial approach of reactants, respectively.

Key words: dichlorogermylene, ethylene, buta-1,3-diene, hexa-1,3,5-triene, germiranes (germacyclopropanes), germacyclopent-3-enes, germacyclohepta-3,5-dienes, cycloaddition reactions, sigmatropic rearrangements, suprafacial processes, antarafacial processes, quantum chemical calculations, PBE density functional, *ab initio* quantum chemical calculations, CBS-QB3 method.

The ability of germylenes to enter cycloaddition reactions with unsaturated organic compounds is well known. To date, the [2+1], [4+1], and [6+1] cycloaddition reactions have been described,[1—4] although their mechanisms (especially in the two latter cases) are still to be clarified. Recent theoretical[5] and experimental[6] studies made it possible to revise the mechanisms of the reactions of germylenes ($GeMe_2$ and $GeAr_2$) with 1,3-dienes.

In the present work, we report a comprehensive PBE and B3LYP density functional and *ab initio* CBS-QB3

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* Dedicated to Academician of the Russian Academy of Sciences I. L. Eremenko on the occasion of his 60th birthday.

† Deceased.

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quantum chemical study of the potential energy surfaces (PES) of the reactions of dichlorogermylene ($GeCl_2$) cycloaddition to ethylene, buta-1,3-diene, and hexa-1,3,5-triene and compare our results with those obtained in previous experimental and theoretical investigations.

Calculation Procedure

Quantum chemical calculations with full geometry optimization were carried out using the PBE density functional[7] implemented in the "PRIRODA" Version 2.02 program,[8] the TZ2P basis set with two sets of polarization functions, namely,[9] H(5s2p)/[3s2p], C(11s6p2d)/[6s3p2d], Cl(15s11p2d)/[10s6p2d], Ge(18s14p9d)/[13s10p5d], and expansion of the electron density over an auxiliary uncontracted basis set[10]: H(5s2p), C(10s3p3d1f), Cl(14s3p3d1f1g), Ge(18s3p3d1f1g). The final energy values were corrected for the corresponding zero-point vibrational energies (ZPE). The character of the stationary points located was determined by calculating the eigenvalues of the Hessian. The PES topologies were determined by the intrinsic reaction coordinate (IRC) calculations for all transition states. Thermodynamic functions were calculated in the "harmonic oscillator—rigid rotator" approximation.

The B3LYP/6-311G(2*d*,*d*,*p*) method (with Opt = Tight and Int = Ultrafine keywords) was employed to search for the stationary points corresponding to those located by the PBE/TZ2P method with subsequent refinement of their energies by high-precision thermochemical method CBS-QB3[11,12] using the Gaussian-03 program.[13] The results of quantum chemical calculations were visualized using the "Chemcraft" program (http://www.chemcraftprog.com).

Results and Discussion

$GeCl_2$ reactions with ethylene and buta-1,3-diene

Based on the results of previous calculations of the PES of [2+1] cycloaddition reactions, it was established that the reactions of both the less reactive germylenes GeF_2 (see Refs 14 and 15) and $GeCl_2$ (see Ref. 15) and the much more reactive GeH_2 (see Refs 14—18) and $GeMe_2$ (see Refs 15 and 19 and notes in Ref. 17) proceed in a stepwise manner and begin with a barrierless formation of a π-complex, which then undergoes transformation to a germirane (germacyclopropane). The salient features of dihalogermylenes include a relatively low exothermicity of the formation of π-complexes, high activation energy of the reaction, and endothermicity of formation of the corresponding 1,1-dihalogermirane.[14,15] The results obtained in Ref. 15 revealed a low probability of the formation of 1,1-dichlorogermirane in the reaction of ethylene with $GeCl_2$ and suggested that it is π-complexes rather than 1,1-dichlorogermiranes that participate as intermediates in the reactions of $GeCl_2$ with alkenes.[2]

CBS-QB3 calculations of the system $GeCl_2 + C_2H_4$ (Scheme 1, Tables 1 and 2) predict that the energy released upon the formation of π-complex **3** ($\Delta E_0 = -25$ kJ mol^{-1}) does not compensate the corresponding decrease in entropy ($\Delta G°_{298} > 0$). Further transformation of **3** to 1,1-dichlorogermirane **4** is an endothermic process proceeding *via* a late transition state **TS1**, which requires the overcoming of a rather high activation barrier (94 kJ mol^{-1} relative to **3**). By and large, it should be noted that the energy parameters of the [2+1] cycloaddition reaction in the system $GeCl_2 + C_2H_4$ obtained from B3LYP/6-31G(d) calculations[15] are in reasonable agreement with the results of the CBS-QB3 calculations.

Yet another possible reaction pathway for germiranes and the corresponding π-complexes involves transfer of a substituent from the germanium atom to a carbon atom, thus resulting in a new germylene.[16,17,20] In the system $GeH_2 + C_2H_4$, transfer of a hydrogen atom from GeH_2 occurs with relative ease and is thermodynamically favorable.[17] However, in the reaction of $GeCl_2$ with ethylene a similar isomerization of **3** to **5** *via* **TS2** (Scheme 1 and Table 1) is not accompanied by a decrease in the energy of the system; rather, it leads to a considerable increase in the energy. The key factor determining the endothermicity of this reaction is that the dissociation energies of the

Table 1. Total[a] (E_0/au) and relative[b] energies (ΔE_0/kJ mol^{-1}), and the Gibbs free energies[c] (ΔG/kJ mol^{-1}) of the structures corresponding to stationary points on the PES of the reaction of $GeCl_2$ with C_2H_4

Structure	PBE/TZ2P			B3LYP/6-311G(2*d*,*d*,*p*)			CBS-QB3		
	$-E_0$	ΔE_0	ΔG	$-E_0$	ΔE_0	ΔG	$-E_0$	ΔE_0	ΔG
1+2	3075.35620	0	0	3076.11401	0	0	3073.72141	0	0
3	3075.36339	–19	22	3076.11898	–13	20	3073.73110	–25	7
TS1	3075.32317	87	137	3076.06767	122	167	3073.69517	69	114
4	3075.33429	58	107	3076.08087	87	133	3073.71017	30	76
TS2	3075.33623	52	101	3076.08179	85	128	3073.69498	69	113
5	3075.33700	50	98	3076.08502	76	118	3073.70505	43	85

[a] $E_0 = E + ZPE$.

[b] Relative to isolated $GeCl_2$ (**1**) and ethylene (**2**).

[c] For $T = 298$ K and $p = 1$ atm.

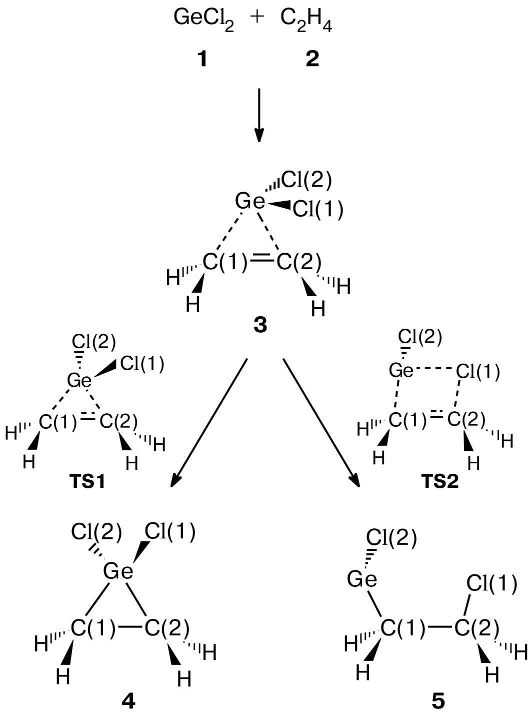
Table 2. Interatomic distances[a] in the structures corresponding to stationary points on the PES of the reaction of $GeCl_2$ with C_2H_4[b]

Structure	*d*/Å				
	C(1)—C(2)	Ge—C(1)	Ge—C(2)	Ge—Cl(1)	C(2)—Cl(1)
3	1.346 (1.336)	2.738 (3.011)	2.959 (3.120)	—	—
TS1	1.477 (1.467)	1.998 (2.009)	2.091 (2.090)	—	—
4	1.585 (1.583)	1.932 (1.926)	1.932 (1.926)	—	—
TS2	1.446 (1.442)	2.120 (2.126)	2.777 (2.795)	2.575 (2.590)	2.131 (2.168)
5	1.497 (1.508)	2.069 (2.054)	2.826 (2.886)	2.748 (2.944)	1.906 (1.871)

[a] Calculated by the PBE/TZ2P and B3LYP/6-311G(2*d*,*d*,*p*) methods (in parentheses).

[b] The numbering of the atoms is shown in Scheme 1.

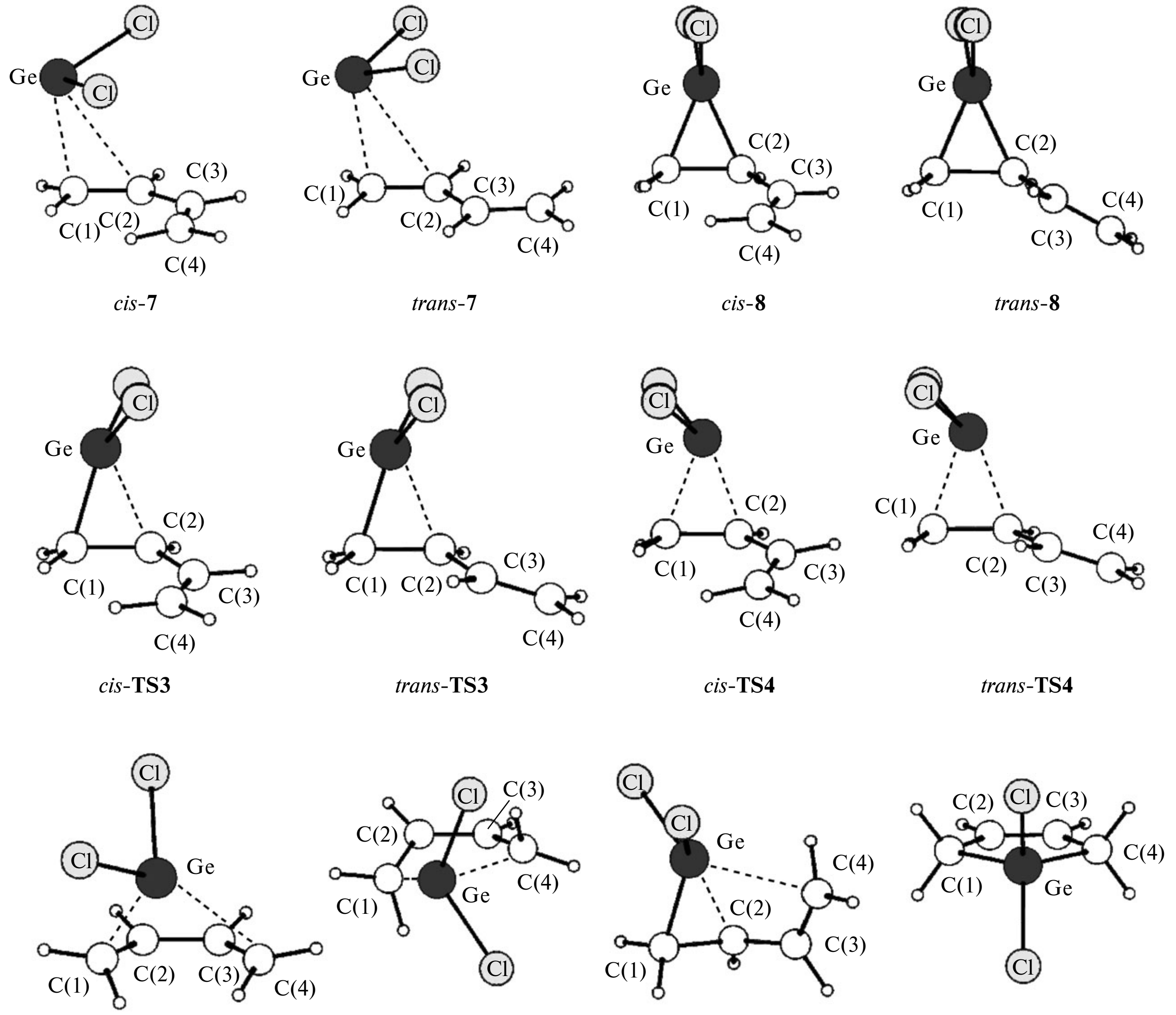
Scheme 1



ethylene π-bond and a strong Ge—Cl bond cannot be compensated by the energy of formation of a weaker C—Cl bond and the C—Ge bond. Since this consideration is also valid for the systems $GeCl_2 + C_4H_6$ and $GeCl_2 + C_6H_8$ (see below), similar reactions of Cl transfer in them will be left out of consideration.

The reaction of $GeCl_2$ with buta-1,3-diene (**6**) begins with a barrierless formation of π-complexes **7** (Fig. 1, Tables 3 and 4). The complex of *trans*-butadiene with $GeCl_2$ (*trans*-**7**) is 10 kJ mol^{-1} (CBS-QB3 calculations) more stable than the *cis*-butadiene complex (*cis*-**7**); this value is close to the value of 12 kJ mol^{-1} (CBS-QB3 calculations) equal to the energy difference between the *cis*- and *trans*-conformers of butadiene. Compared to **3**, the complexes *cis*-**7** (*trans*-**7**) are characterized by a shortened distance Ge—C(1) (by ~0.3 Å) and by a higher energy of stabilization relative to free compounds **1** and *cis*-**6** (*trans*-**6**). Nevertheless, the formation of π-complexes in the system $GeCl_2 + C_4H_6$ is also thermodynamically unfavorable under normal conditions ($\Delta G°_{298} \geq 0$). Subsequent transformation of π-complexes **7** to 1,1-dichloro-2-vinylgermirane **8** in the course of the [2+1] cycloaddition reaction (**TS3**, **TS4**) requires the overcoming of rather high activation barriers (see Table 3). Moreover, compound **8** is destabilized relative to the starting reactants similarly to germirane **4**.

In the study of the PES of the system $GeCl_2 + C_4H_6$, we located two transition states, **TS5** and **TS6** (see Fig. 1 and Table 4), of the [4+1] cycloaddition reactions, which connect the π-complex *cis*-**7** with 1,1-dichlorogermacyclopent-3-ene **9**. **TS5** corresponds to the suprafacial approach of reactants. Structurally, this is an early transition state similar to the π-complex *cis*-**7**. It is characterized by asymmetrical bonding of the germanium atom to the carbon atoms (Ge—C(1) and Ge—C(4) bond lengths differ by more than 0.4 Å) and a relatively small change in the carbon—carbon bond lengths compared to *cis*-**7**. The transition state **TS6** corresponds to antarafacial approach of reactants and is more similar to compound **9**, although a difference between the Ge—C(1) and Ge—C(4) bond lengths is retained. At the same time, in **TS6** both Ge—C bonds are shorter than in **TS5** (Ge—C(1) by ~0.15 Å and Ge—C(4) by ~0.3 Å). In addition, in **TS6** the C(1)—C(2) and C(3)—C(4) bonds are lengthened while the C(2)—C(3) bond is on the contrary shortened to a greater extent than in **TS5**; this enhances the similarity between **TS6** and **9** (see Fig. 1, Table 4). The transition state **TS6** was located only in the PBE/TZ2P calculations. Taking account of a large energy difference between **TS5** and **TS6** obtained from PBE/TZ2P calculations (145 kJ mol^{-1}), one can suggest that suprafacial [4+1] cycloaddition in the system in question is much more favorable than the antarafacial one. In addition, the energy of **TS5** is 4 kJ mol^{-1} lower than those of the starting reactants (CBS-QB3 calcula-



cis-**7** *trans*-**7** *cis*-**8** *trans*-**8**

cis-**TS3** *trans*-**TS3** *cis*-**TS4** *trans*-**TS4**

TS5 **TS6** **TS7** **9**

Fig. 1. Structures corresponding to stationary points on the PES of the system $GeCl_2 + C_4H_6$.

tions), which suggests that the [4+1] cycloaddition reaction can proceed quite easily. The formation of 1,1-dichlorogermacyclopent-3-ene **9** as a result of the [4+1] cycloaddition reaction is an exothermic process leading to a considerable decrease in the energy of the system, *viz.*, $\Delta E_0 = -147$ kJ mol^{-1} and $\Delta G°_{298} = -94$ kJ mol^{-1} (CBS-QB3 calculations). Nevertheless, the deactivating effect of chlorine atoms manifests itself when comparing the exothermicity of the formation of **9** and 1,1-dimethylgermacyclopent-3-ene, for which $\Delta E + ZPE = -240$ kJ mol^{-1} and $\Delta G°_{298} = -191$ kJ mol^{-1} (calculated by the CCSD(T, FC)/cc-pVTZ//B3LYP/[6-31G(d,p) for the H and C atoms and 6-311G(d,p) for the Ge atom] method).[5] It should be noted that in both cases the use of more precise methods (CBS-QB3 and CCSD(T)) allowed one to significantly correct the results of B3LYP calculations, which overestimate the relative energy of germacyclopent-3-enes by about 70 kJ mol^{-1} (compared to free germylene and *trans*-butadiene).

Particular attention should be paid to analysis of the possibility of direct rearrangement of **8** to **9**, which in essence represents a [1,3] sigmatropic shift. Only one transition state **TS7** was located for this reaction. It corresponds to an antarafacial rearrangement and requires the overcoming of a rather high activation barrier of 129 kJ mol^{-1}. A comparison of two transition states **TS6** and **TS7** found in the present work and corresponding to antarafacial approach of the germylene and butadiene fragments in the reaction resulting in **9** suggests that the energy of **TS7** is 35 kJ mol^{-1} higher (PBE/TZ2P calculations). This can be due to structural similarity of **TS7** to 1,1-dichloro-2-vinylgermirane **8**; as shown earlier,[14] a dis-

Table 3. Total[a] (E_0/au) and relative[b] energies (ΔE_0/kJ mol^{-1}), and the Gibbs free energies[c] (ΔG/kJ mol^{-1}) of the structures corresponding to the stationary points on the PES of reactions of GeCl$_2$ with C$_4$H$_6$

Structure	PBE/TZ2P			B3LYP/6-311G(2*d*,*d*,*p*)			CBS-QB3		
	$-E_0$	ΔE_0	ΔG	$-E_0$	ΔE_0	ΔG	$-E_0$	ΔE_0	ΔG
1+*trans*-**6**	3152.65260	0	0	3153.50456	0	0	3150.97171	0	0
1+*cis*-**6**	3152.64683	15	15	3153.49906	14	14	3150.96712	12	11
cis-**7**	3152.65858	−16	30	3153.50624	−4	35	3150.98291	−29	10
trans-**7**	3152.66363	−29	14	3153.51162	−19	20	3150.98654	−39	0
cis-**TS3**	3152.61545	98	150	3153.45326	135	184	3150.94527	69	119
trans-**TS3**	3152.61538	98	150	3153.45329	135	184	3150.94504	70	119
cis-**TS4**	3152.61744	92	145	3153.45594	128	177	3150.94544	69	118
trans-**TS4**	3152.61670	94	146	3153.45572	128	177	3150.94440	72	120
cis-**8**	3152.62488	73	124	3153.46484	104	152	3150.95790	36	84
trans-**8**	3152.62464	73	124	3153.46483	104	152	3150.95726	38	85
TS5	3152.65155	3	55	3153.49126	35	84	3150.97342	−4	44
TS6[d]	3152.59629	148	199	—	—	—	—	—	—
TS7	3152.58308	183	236	3153.41603	232	282	3150.90872	165	215
9	3152.69016	−99	−45	3153.53249	−73	−21	3151.02768	−147	−94

[a] $E_0 = E + ZPE$.

[b] Relative to isolated GeCl$_2$ (**1**) and *trans*-buta-1,3-diene (*trans*-**6**).

[c] For T = 298 K and p = 1 atm.

[d] Attempts to locate the corresponding transition state on the PES by the B3LYP/6-311G(2*d*,*d*,*p*) method have failed.

tinctive feature of the simplest germirane C$_2$H$_4$GeH$_2$ is high strain energy (156 kJ mol^{-1}), which increases by 90 kJ mol^{-1} upon replacement of GeH$_2$ by GeF$_2$. Attempts to locate a stationary point corresponding to the transition state of the suprafacial rearrangement of **8** to **9** by the density functional theory methods failed.

Thus, our quantum chemical study of the PES of the system GeCl$_2$ + C$_4$H$_6$ clearly demonstrates that the [2+1] cycloaddition reaction is kinetically inhibited and thermodynamically unfavorable and that 1,1-dichlorogermacyclopent-3-ene (**9**) is formed solely by the [4+1] cycloaddition (Fig. 2). This confirms the conclusion drawn earlier based on the results of semiempirical modeling of this reaction[21] and agrees with the results of a study[22] of competing cycloaddition of the complex of GeCl$_2$ with dioxane (GeCl$_2$·Diox) to buta-1,3-diene and 1,4-dideuteriobuta-1,3-diene.

An important stereochemical consequence of the established pathway of the formation of **9** *via* **TS5** is a disrotatory motion of methylene groups of the diene in the course of the reaction. Unfortunately, the stereochemistry of the addition of GeCl$_2$ to 1,3-diene is difficult to investi-

Table 4. Interatomic distances[a] in the structures corresponding to stationary points on the PES of the reaction of GeCl$_2$ with C$_4$H$_6$[b]

Structure	*d*/Å					
	C(1)—C(2)	C(2)—C(3)	C(3)—C(4)	Ge—C(1)	Ge—C(2)	Ge—C(4)
cis-**7**	1.374 (1.355)	1.446 (1.456)	1.350 (1.339)	2.447 (2.683)	2.991 (3.120)	—
trans-**7**	1.369 (1.354)	1.440 (1.446)	1.349 (1.339)	2.499 (2.711)	2.997 (3.133)	—
cis-**8**	1.576 (1.576)	1.467 (1.473)	1.344 (1.335)	1.934 (1.927)	1.976 (1.963)	—
trans-**8**	1.590 (1.590)	1.465 (1.471)	1.344 (1.335)	1.927 (1.921)	1.974 (1.962)	—
cis-**TS3**	1.490 (1.480)	1.458 (1.462)	1.348 (1.339)	1.973 (1.981)	2.123 (2.124)	—
trans-**TS3**	1.500 (1.488)	1.458 (1.462)	1.346 (1.337)	1.966 (1.975)	2.108 (2.109)	—
cis-**TS4**	1.479 (1.474)	1.460 (1.462)	1.347 (1.339)	2.071 (2.062)	2.073 (2.082)	—
trans-**TS4**	1.488 (1.482)	1.457 (1.458)	1.346 (1.338)	2.056 (2.048)	2.083 (2.093)	—
TS5	1.400 (1.405)	1.420 (1.406)	1.375 (1.381)	2.296 (2.287)	2.795 (2.794)	2.836 (2.697)
TS6	1.438	1.389	1.408	2.134	2.997	2.527
TS7	1.568 (1.561)	1.430 (1.421)	1.373 (1.368)	1.910 (1.907)	2.256 (2.317)	2.609 (2.694)
9	1.509 (1.512)	1.347 (1.339)	1.509 (1.512)	1.973 (1.969)	2.693 (2.695)	

[a] Calculated by the PBE/TZ2P and B3LYP/6-311G(2*d*,*d*,*p*) methods (in parentheses).

[b] The numbering of the atoms is shown in Fig. 1.

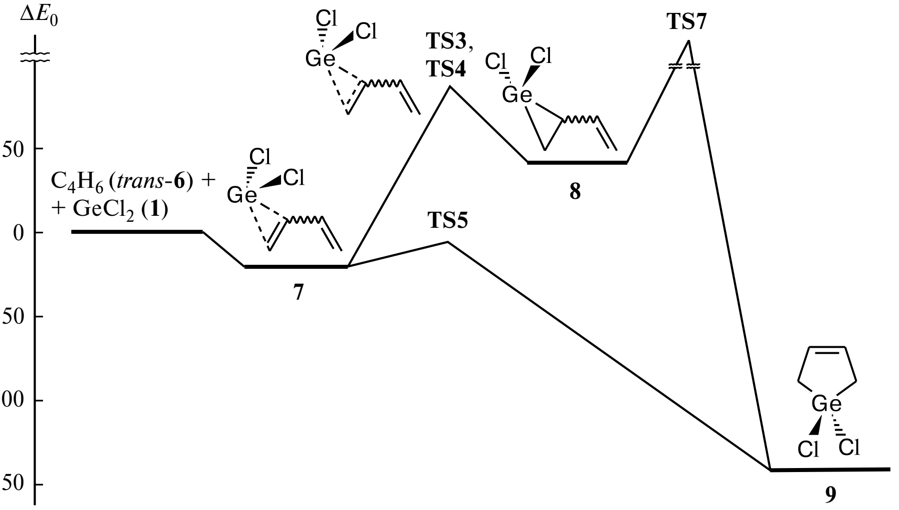


Fig. 2. Energy diagram of the system $GeCl_2 + C_4H_6$, obtained by the CBS-QB3 method. The relative energies are given in kJ mol^{-1}.

gate because the 1- and 1,4-substituted 1,3-dienes in the reactions with $GeCl_2 \cdot$ Diox are prone to copolymerization rather than [4+1] cycloaddition.[23] The stereochemistry of the reactions of germylenes with 1,3-dienes was studied taking $GeMe_2$ as an example (see Ref. 1). It was shown that the formation of 1,1-dimethylgermacyclopent-3-enes occurs stereospecifically and that the overall process corresponds to suprafacial [4+1] cycloaddition.

Although, as shown above, the formation of 2-vinylgermirane **8** in the reaction of $GeCl_2$ with butadiene is energetically unfavorable, in the case of more reactive germylenes GeR_2 (R = H, Me)[14—19] the [2+1] cycloaddition reaction occurs quite easily. Recently,[5] a theoretical study of the reactions of $GeMe_2$ with buta-1,3-diene (CCSD(T, FC)/cc-pVTZ//B3LYP/[6-31G(d,p) for the H and C atoms and 6-311G(d,p) for the Ge atom]) and of $GePh_2$ with isoprene (B3LYP/[6-31G(d,p) for the H and C atoms and 6-311G(d,p) for the Ge atom]) has been reported. The reaction of $GeMe_2$ begins with a barrierless formation of isomeric π-complexes, which readily transform to 1,1-dimethyl-2-vinylgermirane, whose formation is thermodynamically favorable ($\Delta G°_{298} < 0$). At the same time, only one high-lying transition state ($\Delta E + ZPE = 62$ kJ mol^{-1}) of subsequent [1,3] sigmatropic rearrangement of 1,1-dimethyl-2-vinylgermirane to 1,1-dimethylgermacyclopent-3-ene was located; it is structurally similar to **TS7**. Transformation of one of the π-complexes corresponding to the [4+1] cycloaddition reaction appeared to be a low-energy channel of formation of 1,1-dimethylgermacyclopent-3-ene. By and large, the system $GePh_2$ + isoprene resembles the system $GeMe_2$ + buta-1,3-diene, although the barriers to the [2+1] and [4+1] cycloaddition reactions in this system are somewhat higher and the exothermicity of both processes is lower.[5] The recently obtained kinetic data[6] also agree with the results of this theoretical consideration. Thus, for a wide range of germylenes the only pathway of formation of germacyclopent-3-enes is the [4+1] cycloaddition reaction.

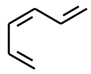
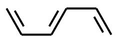
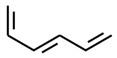
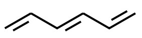
$GeCl_2$ reactions with hexa-1,3,5-trienes

Previously,[23,24] it has been shown that the reaction of complex $GeCl_2 \cdot$ Diox with hexa-1,3,5-triene (mixture of isomers) resulted in 1,1-dichlorogermacyclohepta-3,5-diene, a product of formal [6+1] cycloaddition of $GeCl_2$. In this Section, we will consider the PES of the reaction of $GeCl_2$ with both stereoisomers of hexa-1,3,5-triene, namely, hexa-1,3*Z*,5-triene (**10**) and hexa-1,3*E*,5-triene (**11**) (Table 5). Based on the results of the exploration of the systems $GeCl_2 + C_2H_4$ and $GeCl_2 + C_4H_6$ (see above), the formation and rearrangements of the corresponding 2-vinylgermiranes, as well as antarafacial channels of the [4+1] cycloaddition reaction will be left out of consideration because they are thermodynamically unfavorable *a priori* and kinetically inaccessible.

Similarly to the systems $GeCl_2 + C_2H_4$ and $GeCl_2 + C_4H_6$ considered above, the reactions of both compounds **10** and **11** with $GeCl_2$ begin with a barrierless formation of π-complexes. For instance, the reaction of *trans*,*trans*-**11** with $GeCl_2$ results in the corresponding complex stabilized relative to the starting reactants by 44 kJ mol^{-1} (CBS-QB3 calculations). We will not dwell on the issues concerning the complexes in the system $GeCl_2 + C_6H_8$. However, one should keep in mind that all processes considered below begin with π-complexes.

PBE/TZ2P calculations of the PES of the system $GeCl_2 + C_6H_8$ revealed eight transition states of the [4+1] cycloaddition reaction (Fig. 3, Tables 6 and 7). Four of them (**TS8** family) correspond to the cycloaddition of $GeCl_2$ to **10** while the other four transition states (**TS9** family) correspond to the reaction between **11** and $GeCl_2$. Within each family, transition states differ in the direction

Table 5. Total[a] (E_0/au) and relative energies (ΔE_0/kJ mol^{-1}), and the Gibbs free energies[b] (ΔG/kJ mol^{-1}) of the conformers of hexa-1,3*Z*(*E*),5-trienes C_6H_8

Structure		PBE/TZ2P			B3LYP/6-311G(2*d*,*d*,*p*)			CBS-QB3		
		$-E_0$	ΔE_0	ΔG	$-E_0$	ΔE_0	ΔG	$-E_0$	ΔE_0	ΔG
cis,*cis*-**10**		233.02846	0	0	233.32782	0	0	232.90412	0	0
cis,*trans*-**10**		233.03848	−26	−23	233.33702	−24	−24	232.91182	−20	−20
trans,*trans*-**10**		233.04502	−43	−40	233.34315	−40	−39	232.91661	−33	−31
cis,*cis*-**11**		233.03595	−20	−18	233.33470	−18	−20	232.90930	−14	−15
cis,*trans*-**11**		233.04227	−36	−33	233.34074	−34	−35	232.91444	−27	−28
trans,*trans*-**11**		233.04819	−52	−48	233.34645	−49	−47	232.91919	−40	−38

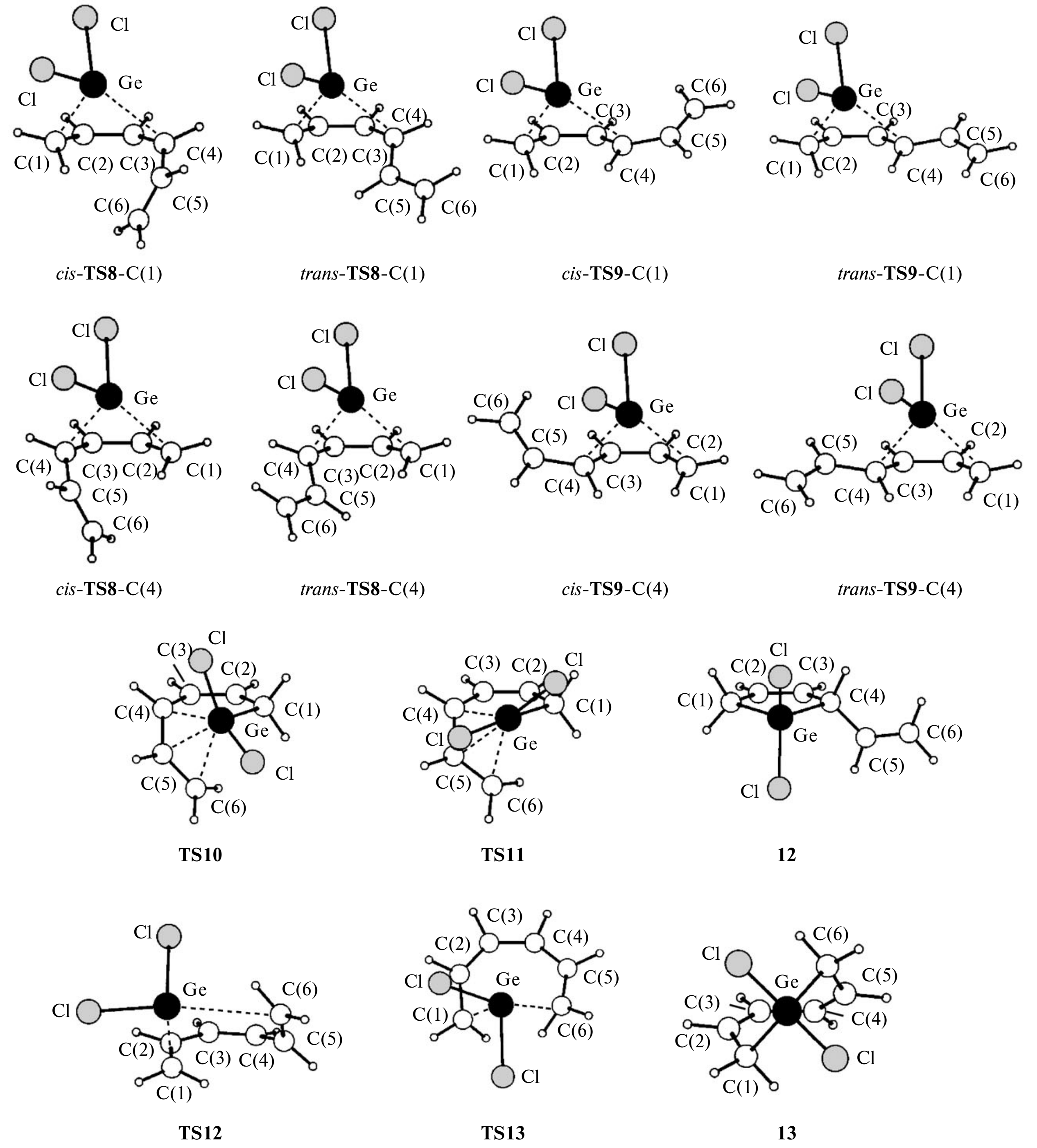
[a] $E_0 = E + ZPE$.
[b] For $T = 298$ K and $p = 1$ atm.

of attack of the $GeCl_2$ and orientaton of the free vinyl group. In accordance with this, their notations include the carbon atom being the major target and the orientation of the vinyl group. The order of the relative energies of the transition states **TS8** and **TS9** (see Table 6) resembles that of the relative energies of the conformers **10** and **11** in which the orientation of the hexatriene moiety is the most similar to the corresponding transition states. It should be noted that all pairs of transition states corresponding to the same conformer of **10** or **11**, *i.e.*, *cis*-**TS8**-C(1)/*cis*-**TS8**-C(4) (*cis*,*cis*-**10**), *trans*-**TS8**-C(1)/*trans*-**TS8**-C(4) (*cis*,*trans*-**10**), *cis*-**TS9**-C(1)/*cis*-**TS9**-C(4) (*cis*,*cis*-**11**), and *trans*-**TS9**-

Table 6. Total[a] (E_0/au) and relative[b] energies (ΔE_0/kJ mol^{-1}), and the Gibbs free energies[c] (ΔG/kJ mol^{-1}) of the structures corresponding to stationary points on the PES of the reaction of $GeCl_2$ with C_6H_8

Structure	PBE/TZ2P			B3LYP/6-311G(2*d*,*d*,*p*)			CBS-QB3		
	$-E_0$	ΔE_0	ΔG	$-E_0$	ΔE_0	ΔG	$-E_0$	ΔE_0	ΔG
1+*trans*,*trans*-**11**	3229.95168	0	0	3230.89728	0	0	3228.22397	0	0
1+*trans*,*trans*-**10**	3229.94851	8	8	3230.89398	9	8	3228.22139	7	6
cis-**TS8**-C(1)	3229.93742	37	91	3230.87146	68	118	3228.21739	17	68
trans-**TS8**-C(1)	3229.94040	30	83	3230.87357	62	112	3228.21890	13	63
cis-**TS8**-C(4)	3229.93502	44	97	3230.86901	74	124	3228.21673	19	69
trans-**TS8**-C(4)[d]	3229.93747	37	90	—	—	—	—	—	—
cis-**TS9**-C(1)	3229.94628	14	67	3230.87954	47	97	3228.22492	−2	47
trans-**TS9**-C(1)	3229.94958	6	60	3230.88248	39	90	3228.22793	−10	40
cis-**TS9**-C(4)[d]	3229.94138	27	79	—	—	—	—	—	—
trans-**TS9**-C(4)[d]	3229.94479	18	69	—	—	—	—	—	—
12	3229.97430	−59	−6	3230.91111	−36	15	3228.27209	−126	−75
TS10	3229.92509	70	130	3230.84982	125	181	3228.21480	24	81
TS11	3229.90727	117	176	3230.83167	172	228	3228.19289	82	138
TS12	3229.94417	20	73	3230.88187	40	91	3228.22164	6	56
TS13	3229.91262	103	158	3230.84116	147	200	3228.18212	110	162
13	3229.98910	−98	−41	3230.92541	−74	−18	3228.28369	−157	−101

[a] $E_0 = E +$ ZPE.
[b] Relative to isolated $GeCl_2$ (**1**) and the most stable conformer of hexa-1,3*E*,5-triene (*trans*,*trans*-**11**).
[c] For $T = 298$ K and $p = 1$ atm.
[d] Attempts to locate the corresponding transition states on the PES by the B3LYP/6-311G(2*d*,*d*,*p*) method have failed.



cis-**TS8**-C(1) *trans*-**TS8**-C(1) *cis*-**TS9**-C(1) *trans*-**TS9**-C(1)

cis-**TS8**-C(4) *trans*-**TS8**-C(4) *cis*-**TS9**-C(4) *trans*-**TS9**-C(4)

TS10 **TS11** **12**

TS12 **TS13** **13**

Fig. 3. Structures corresponding to the stationary points on the PES of the system $GeCl_2$ + C_6H_8.

C(1)/*trans*-**TS9**-C(4) (*cis*,*trans*-**11**) clearly demonstrate preference of the attack of $GeCl_2$ on the sterically more accessible terminal carbon atom. The difference between the Ge—C(1) and Ge—C(4) distances in **TS8** and **TS9** varies over a wide range from 0.18 Å (*trans*-**TS9**-C(4), PBE/TZ2P calculations) to 0.67 Å (*cis*-**TS8**-C(1), PBE/TZ2P calculations); however, this does not correlate with the relative energies of these transition states. It is important that the energies of all transition states **TS8** and **TS9** obtained from CBS-QB3 calculations are lower than those of free $GeCl_2$ and the corresponding conformer **10** or **11** and thus the [4+1] cycloaddition reaction of $GeCl_2$ to both isomers of hexa-1,3,5-triene should proceed quite easily.

Table 7. Interatomic distances[a] in the structures corresponding to stationary points on the PES of the reaction of $GeCl_2$ with C_6H_8[b]

Structure	*d*/Å						
	C(1)—C(2)	C(2)—C(3)	C(3)—C(4)	C(4)—C(5)	C(5)—C(6)	Ge—C(1)	Ge—C(4)
cis-**TS8**-C(1)	1.403 (1.409)	1.416 (1.402)	1.391 (1.396)	1.460 (1.464)	1.347 (1.339)	2.283 (2.260)	2.948 (2.797)
trans-**TS8**-C(1)	1.417 (1.420)	1.403 (1.393)	1.403 (1.406)	1.452 (1.457)	1.349 (1.340)	2.236 (2.229)	2.831(2.742)
cis-**TS8**-C(4)	1.376 (1.382)	1.421 (1.408)	1.407 (1.410)	1.480 (1.483)	1.343 (1.335)	2.805 (2.674)	2.384 (2.382)
trans-**TS8**-C(4)	1.388	1.411	1.414	1.473	1.344	2.678	2.380
cis-**TS9**-C(1)	1.419 (1.424)	1.401 (1.390)	1.398 (1.404)	1.454 (1.458)	1.348 (1.339)	2.211 (2.195)	2.811 (2.705)
trans-**TS9**-C(1)	1.423 (1.427)	1.397 (1.387)	1.405 (1.408)	1.449 (1.453)	1.348 (1.339)	2.195 (2.186)	2.730 (2.657)
cis-**TS9**-C(4)	1.381	1.415	1.404	1.470	1.344	2.708	2.427
trans-**TS9**-C(4)	1.385	1.413	1.405	1.459	1.345	2.646	2.463
TS10	1.497 (1.500)	1.349 (1.339)	1.470 (1.477)	1.436 (1.429)	1.407 (1.400)	1.973 (1.969)	2.294 (2.281), 2.166 (2.182),[c] 2.374 (2.372)[d]
TS11	1.483 (1.486)	1.343 (1.335)	1.476 (1.480)	1.434 (1.431)	1.403 (1.396)	2.033 (2.032)	2.305 (2.293), 2.293 (2.312),[c] 2.362 (2.385)[d]
12	1.507 (1.511)	1.347 (1.339)	1.516 (1.520)	1.495 (1.499)	1.339 (1.331)	1.973 (1.969)	2.002 (1.996)
TS12	1.378 (1.387)	1.441 (1.425)	1.365 (1.368)	1.457 (1.438)	1.347 (1.357)	2.372 (2.292)	3.466 (2.861)[d]
TS13	1.405 (1.416)	1.418 (1.401)	1.401 (1.403)	1.403 (1.398)	1.403 (1.397)	2.324 (2.250)	2.331 (2.423)[d]
13	1.490 (1.496)	1.356 (1.345)	1.459 (1.465)	1.356 (1.345)	1.490 (1.496)	1.985 (1.976)	—

[a] Calculated by the PBE/TZ2P and B3LYP/6-311G(2*d*,*d*,*p*) methods (in parentheses).

[b] The numbering of the atoms is shown in Fig. 3.

[c] Ge—C(5).

[d] Ge—C(6).

The [4+1] cycloaddition of $GeCl_2$ to both **10** and **11** results in 1,1-dichloro-2-vinylgermacyclopent-3-ene (**12**), whose formation is thermodynamically favorable, *viz.*, $\Delta E_0 = -126$ kJ mol^{-1} and $\Delta G^{\circ}{}_{298} = -75$ kJ mol^{-1} (relative to $GeCl_2$ and *trans*,*trans*-**11**). Unfortunately, compound **12** was not isotated[2] from the reaction of $GeCl_2 \cdot$Diox with a mixture of **10** and **11** owing to copolymerization of hexatriene with $GeCl_2$ (see Ref. 24) which competes with the [4+1] cycloaddition reaction. A comparison of the systems $GeCl_2 + C_4H_6$ and $GeCl_2 + C_6H_8$ shows that the formation of **9** is about 20 kJ mol^{-1} (CBS-QB3 calculations) more exothermic than that of **12**, which can be explained by a lower energy of conjugation in *trans*-**6** compared to *trans*,*trans*-**11**.

To explore the possibility of direct isomerization of 1,1-dichloro-2-vinylgermacyclopent-3-ene **12** to 1,1-dichlorogermacyclohepta-3,5-diene (**13**), the formal [6+1] cycloaddition product, we studied the corresponding [1,3] sigmatropic rearrangement; two transition states, **TS10** and **TS11** (see Fig. 3 and Table 7), of the suprafacial process were located. The rearrangement *via* **TS10** is accompanied by retention of the configuration of the migrating group, which corresponds to a process forbidden by the Woodward—Hoffmann rules. Contrary to this, the rearrangement *via* **TS11**, which is characterized by longer distances Ge—C(1), Ge—C(4), Ge—C(6), and, especially, Ge—C(5), follows an allowed pathway and is accompanied by inversion of bond configuration. Nevertheless, it is migraton with retention of the bond configuration at the germanium atom that is more favorable, namely, according to CBS-QB3 calculations, the energy of **TS10** is 58 kJ mol^{-1} lower than that of **TS11**. This agrees with theoretical data for the degenerate [1,3] sigmatropic rearangement of allylgermane[25] in which the symmetry-forbidden suprafacial process also appeared to be more favorable. However, it should be noted that the barrier determined by **TS10** is also rather high (150 kJ mol^{-1}) and a direct transformation of **12** to **13** is blocked (Fig. 4).

In addition, two transition states **TS12** and **TS13** (see Fig. 3 and Table 7) located on the PES of the system $GeCl_2 + C_6H_8$ correspond to concerted [6+1] cycloaddition of $GeCl_2$ to hexa-1,3Z,5-triene in its *cis*,*cis*-**10** conformation, which ensures the spatial proximity of the terminal carbon atoms C(1) and C(6). As for the [4+1] cycloaddition reaction in the system $GeCl_2 + C_4H_6$ (see above), the cyclization can proceed upon supra- and antarafacial approach of the reactants. In this respect, an important feature differing the reaction of $GeCl_2$ with hexa-1,3,5-triene from the reaction with buta-1,3-diene is that the antarafacial approach (**TS12**) corresponds to a much lower activation energy than suprafacial approach (**TS13**), *viz.*, $\Delta\Delta E_0$ = 104 kJ mol^{-1} (CBS-QB3). The hexatriene moiety in **TS12** to a great extent retains its starting geometry, and highly asymmetric binding of the

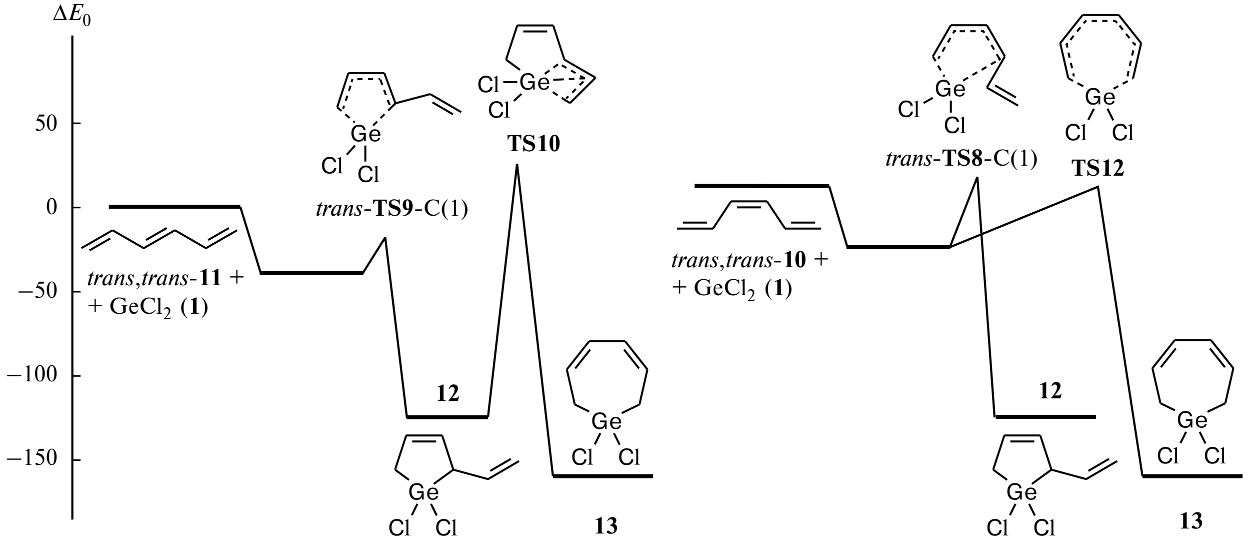


Fig. 4. Energy diagram of the system $GeCl_2 + C_6H_8$ obtained by the CBS-QB3 method. The relative energies are given in kJ mol^{-1}.

germanium atom to the terminal carbon atoms C(1) and C(6) (see Fig. 3 and Table 7) takes place. The antarafacial cyclization involves rotation of the $GeCl_2$ fragment about the Ge—C(1) bond accompanied by a gradual shortening of the Ge—C(1) and Ge—C(6) distances; simultaneously, the carbon—carbon bond lengths approach their values in **13**. It should be noted that the orientation of the hexatriene and germylene fragments in **TS12** resembles that in the end product **13**; this probably significantly facilitates the antarafacial cyclization. Structurally, **TS13** significantly differs from **TS12**, *viz.*, the Ge—C(1) and Ge—C(6) distances in **TS13** are much shorter, the bonding with the C(1) and C(6) atoms is more symmetric, and the carbon—carbon bonds in the hexatriene moiety are equilibrated (1.40—1.42 Å long).

Energetically, the [6+1] cycloaddition reaction of hexa-1,3Z,5-triene with $GeCl_2$ resulting in **13** is 30 kJ mol^{-1} (CBS-QB3) more favorable than the [4+1] cycloaddition reaction resulting in **12**. The energies of the transition states of the [4+1] cycloaddition reaction (**TS8** family) are 7—13 kJ mol^{-1} (CBS-QB3) higher than the energy of **TS12**, which indicates that [6+1] cycloaddition is kinetically more preferable. The energies of the transition states **TS12** (−1 kJ mol^{-1}) and *trans*-**TS8-C(1)** (7 kJ mol^{-1}) differ insignificantly from those of the starting *trans*,*trans*-**10** and $GeCl_2$ (see Table 6), which predetermines the possibility for both reactions to be fast.

Summing up, antarafacial [6+1] cycloaddition should be accompanied by a conrotatory motion of terminal methylene groups in the hexatriene fragment. Unfortunately, no data on the stereochemistry of the [6+1] cycloaddition reactions of carbene analogs are available at the moment.

Our study showed that the [2+1] cycloaddition reactions in the systems $GeCl_2 + C_2H_4$ and $GeCl_2 + C_4H_6$ are accompanied by overcoming rather high activation barriers and that the formation of end products, germiranes, is endothermic. At the same time, in the system $GeCl_2 + C_4H_6$ the suprafacial [4+1] cycloaddition reaction resulting in thermodynamically stable 1,1-dichlorogermacyclopent-3-ene can proceed with ease.

In the system $GeCl_2$ + hexa-1,3,5-triene, the [4+1] cycloaddition reactions can proceed with low activation barriers for both *Z*- and *E*-isomers. The attack of $GeCl_2$ on the sterically more accessible terminal carbon atom is more preferable. For hexa-1,3*Z*,5-triene, we found a reaction channel corresponding to concerted [6+1] cycloaddition, whose activation energy is lower than that of the [4+1] cycloaddition reaction. Unlike the [4+1] cycloaddition reaction, antarafacial approach of reactants is more preferable for the [6+1] cycloaddition reaction. It was shown that [1,3] sigmatropic rearrangement between 1,1-dichloro-2-vinylgermacyclopent-3-ene and a thermodynamically more stable 1,1-dichlorogermacyclohepta-3,5-diene (products of the [4+1] and [6+1] cycloaddition reactions, respectively) is hindered and that the lowest-energy transition state corresponds to a process that is forbidden by the Woodward—Hoffmann rules.

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