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Full Articles

Reactions of germylenes with alkynes: a quantum chemical study. Factors determining the stabilities of germacyclopropenes*

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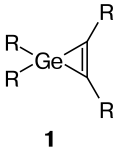
The addition of germylenes GeR_2 (R = H, Me) to alkynes (acetylene, dimethylacetylene, 4-thiacycloheptyne, 2,2,6,6-tetramethyl-4-thiacycloheptyne) and the pathways of thermal isomerization of reaction products, germacyclopropenes (germirenes) were studied by the density functional calculations with the PBE functional. Key factors determining the thermodynamic and kinetic stability of germacyclopropenes, including those related to further rearrangements of the title compounds were revealed.

Key words: germylenes, alkynes, cycloalkynes, small rings, germirenes, 4-thiacycloheptyne, cycloaddition, quantum chemical calculations, PBE density functional.

The addition of carbenes to the multiple carbon—carbon bonds is widely used for the synthesis of systems containing cyclopropane and cyclopropene fragments.[1] Evidently, the reactions of carbene analogs ER_2 (E = Si, Ge, Sn) with the multiple bonds can also be considered as the simplest general procedure[2—6] for the synthesis of three-membered rings containing the heteroatom E. The first attempts to synthesize sila- and germacyclopropenes in the reactions of silylenes and germylenes with acetylenes were made to test the hypothesis of aromatic stabilization of these molecules in the early 1960s.[7] However, they led to isolation of 1,4-disila(germa)cyclohexa-2,5-dienes, formal dimers of sila(germa)cyclopropenes, rather than the compounds in question. Silacyclopropenes were first synthesized fifteen years later.[2,3,5,8,9] Since then a large number of silacyclopropenes were synthesized.[3,5,6,8,9] Numerous attempts to synthesize germacyclopropenes **1** have failed for a long time.[4,7]



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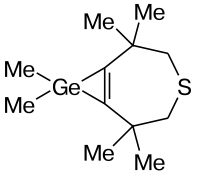

2

The first individual thermodynamically stable germacyclopropene (germirene) **2** was obtained in the crystal-

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* Dedicated to Academician O. M. Nefedov on the occasion of his 75th birthday.

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line state by the reaction of short-lived dimethylgermylene $GeMe_2$ generated from a 7-germanorbornadiene derivative with equimolar amount of 2,2,6,6-tetramethyl-4-thiacycloheptyne in the mid-1980s.[10] Its structure was unambiguously proved by X-ray diffraction analysis.[10] Attempts to synthesize other structural types of germirenes by the reactions of $GeMe_2$ with linear acetylenes were unsuccessful for long. Only recently[11,12] two germacyclopropenes were obtained by the cycloaddition of stable, sterically overcrowded germylenes to linear alkynes. The third germirene known to date, a formal cycloadduct of stable germylene and dehydrobenzene, has a bicyclic structure.[13]

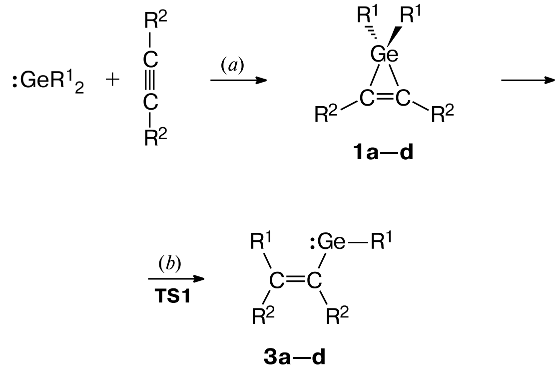
The only stannacyclopropene known so far was obtained by the reaction of stable stannylene with 2,2,6,6-tetramethyl-4-thiacycloheptyne[4,6] and also has a bicyclic structure.

Interest in strained heterocyclopropenes containing a silicon, germanium, or tin atom is due to several reasons. First of all, it is concerned with investigations of the electronic structure of these compounds including possible aromaticity as well as elucidation of factors affecting their thermodynamic and kinetic stability. For instance, the stability of germirene **2** is surprisingly high for a bicyclic structure. Indeed, its skeleton consists of two fused strained rings and thus has additional strain, and the germanium atom bears small methyl substituents. As mentioned above, all stable germirenes obtained later on[11,12,14,15] had bulky substituents R (R is bis(trimethylsilyl)methyl, 2,6-diisopropylphenyl (Dip), 2,4,6-triisopropylphenyl (Tip), and 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt)) at the germanium atom.

Quantum chemical calculations of the potential energy surface (PES) make it possible to obtain quantitative data on the activation energies and thermodynamic characteristics of various elementary stages of the formation and opening of cyclic structures and to establish factors responsible for stabilization (destabilization) of small rings. Theoretical investigations of the reactions of carbene analogs with the triple bond C≡C began with the Hartree—Fock calculations[16] of the reactions of ER_2 (E = C, Si, Ge, Sn; R = H, F) molecules with acetylene in a small basis set. It was shown[16] that cycloaddition of all EH_2 species except, probably, SnH_2 occurs barrierlessly and the exothermicity of the reaction abruptly decreases in the order C, Si, Ge, Sn. Reactions of difluoro-substituted EF_2 were shown to proceed with a noticeable activation barriers, being energetically less favorable than the addition of unsubstituted carbene analogs EH_2. Moreover, the cycloadditions reactions of GeF_2 and SnF_2 are endothermic. Only the cycloaddition reaction was investigated in that study,[16] whereas the possibility of further transformations of the three-membered ring was not considered.

Earlier, we reported an experimental and high-level quantum chemical study[17] of the reaction of the simplest germylene GeH_2 with acetylene and showed that the formation of germirene occurs without an activation barrier. This salient common feature of the 1,2-cycloaddition reactions of carbene analogs with electron-donating substituents to the multiple carbon—carbon bonds implies that heterocyclopropenes can be synthesized at low temperatures. In turn, this allows one to minimize the contributions of possible side processes including those leading to isomerization or decomposition of the target product. Our detailed study[17] of the PES of the simplest system $GeH_2 + C_2H_2$ showed that germirene **1a** formed in the first stage (*a*) can undergo a low-barrier rearrangement (*b*) into a lower-energy isomeric germylene **3a** (Scheme 1).

Scheme 1



	a	b	c	d
R^1	H	Me	H	Me
R^2	H	H	Me	Me

The secondary germylene **3a** is obviously as reactive as the initial GeH_2 and can enter in further chemical reactions. Exothermic reaction **1a** → **3a** is the main reason for instability of germirene **1a**. The addition of GeH_2 to the triple bond of acetylene occurs barrierlessly in one step unlike the reactions of germylenes with olefins which usually involve formation of a π-complex.[18—20]

Recently,[20] we reported a PBE [21] density functional study of the reactions of GeH_2 and $GeMe_2$ with olefins and buta-1,2,3-trienes and showed that the overall stability of the product, germacyclopropane (germirane), is determined by its stability to retrocycloaddition into initial reactants and to a rearrangement similar to rearrangement (*b*) in Scheme 1. Taking the stable germirane[10] as an example, we determined the effects of the olefin structure and the nature of the substituents at the Ge atom on the stability of the germacyclopropane system.

The aim of the present work was to elucidate the key factors which determine the stability of germacyclopropenes formed in the reactions of 1,2-cycloaddition of germylenes to linear and cyclic (4-thiacycloheptyne) alkynes. As mentioned above, the reaction of GeF_2 with acetylene is thermodynamically unfavorable.[16] Clearly, the formation of a stable germirene ring requires the presence of electron-donating substituents at the germanium atom. Therefore, we studied the reactions of germylene (GeH_2) and dimethylgermylene ($GeMe_2$) containing electron-donating methyl substituents with acetylene and dimethylacetylene (see Scheme 1). While considering the stability of monocyclic germirenes, we studied only the energetically most favorable (critical) ring opening pathway established earlier[17] for the system $GeH_2 + C_2H_2$. The thermodynamic stabilities of the equilibrium structures were assessed by calculating the changes in the Gibbs free energy, $\Delta G^0{}_{298}$, under normal conditions.

To find out factors determining the stabilities of the germirene fragment of the bicyclic structure, we studied the reactions of GeH_2 and $GeMe_2$ with 4-thiacycloheptyne and 2,2,6,6-tetramethyl-4-thiacycloheptyne. The results obtained provided an explanation for unusually high thermodynamic and kinetic stability of the first synthesized germirene **2**.

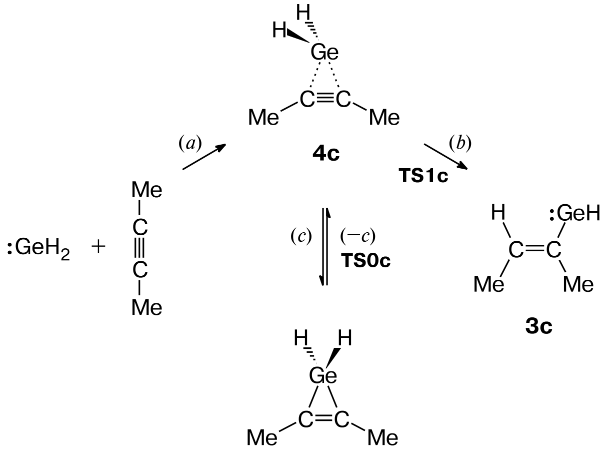
Calculation Procedure

Quantum chemical calculations with full geometry optimization were carried out with the PBE density functional[21] using the PRIRODA program[22,23] on personal computers equipped with Pentium® IV processors. The three-exponent basis set included two sets of polarization functions, namely, (5s2p) [3s2p] for H atoms, (11s6p2d) [6s3p2d] for C atoms, and (18s14p9d) [13s10p5d] for Ge atoms (figures in parentheses and in square brackets denote the initial and contracted basis set, respectively) and the electron density expansion over an auxiliary uncontracted basis set[22]: (5s2p) for H atoms, (10s3p3d1f) for C atoms, and (18s3p3d1f1g) for Ge atoms. The characters of the stationary points located were controlled by calculating the eigenvalues of the matrix of the second derivatives of energy. The final energies included zero-point energy corrections, ZPE. The thermodynamic functions were calculated using the "harmonic oscillator—rigid rotator" model.

Results and Discussion

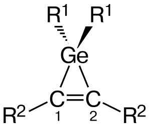
Reactions of germylenes with linear alkynes. Calculations of the PESs of all the systems under study found minima corresponding to germirenes **1a—d** and secondary germylenes **3a—d** and the saddle points corresponding to transition states **TS1a—d**. The set of the stationary points of the reactions resulting in germylenes **3a,b,d** is the same as that determined earlier[17] in the QCISD and B3LYP calculations of analogous transformations in the simplest system GeH_2 + acetylene. The addition of germylene (see Scheme 1) to the C≡C bond in these reactions proceeds as a single-stage barrierless process. The PES of the reaction leading to germylene **3c** is more complex. According to calculations, the cycloaddition in the system $GeH_2 + MeC{\equiv}CMe$ is preceded by the formation of very unstable π-complex **4c**, which undergoes rearrangement into germirene **1c** *via* a low-energy transition state **TS0** (Scheme 2).

Scheme 2



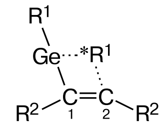
The isomerization of **1c** into **3c** proceds *via* the π-complex in two steps, namely, (*−c*) and (*b*) (see Scheme 2), the latter being the limiting step.

The PBE/TZ2P calculated structures corresponding to the stationary points located (minima and transition states of the reactions of formation of and ring opening of germirenes **1a—d**) are shown below (migrating group is marked by an asterisk; the symmetry group of the molecular skeleton is shown below the structure). Table 1 lists the key geometric parameters of these structures.



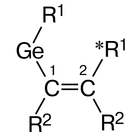
1a—d

C_{2v}



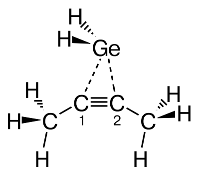
TS1a—d

C_1



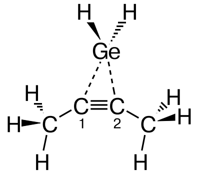
3a—d

C_s



4c

C_s



TS0c

C_s

From this point on the symmetry of the systems with methyl substituents is meant the symmetry of the carbon-germanium skeleton rather than the overall molecular symmetry that depends on the conformations of methyl hydrogens. The energies of the structures, which correspond to the stationary points are presented in Table 2.

Table 1. Selected interatomic distances[a] (d) in the structures corresponding to the stationary points on the PESs of the reactions of GeH_2 and $GeMe_2$ with acetylene and dimethylacetylene

System	Structure	d/Å				
		C(1)—C(2)	Ge—C(1)	Ge—C(2)	Ge—*R^1	C(2)—*R^1
GeH_2 + HC≡CH	**1a**	1.329	1.934	1.934	1.538	—
		(1.328)	(1.913)	(1.913)	(1.538)	
		[1.336]	[1.920]	[1.920]	[1.552]	
	TS1a	1.262	2.109	2.353	1.628	1.847
		(1.259)	(2.099)	(2.373)	(1.649)	(1.822)
		[1.268]	[2.098]	[2.370]	[1.674]	[1.784]
	3a	1.348	1.987	2.875	2.957	1.095
		(1.346)	(1.957)			
		[1.351]	[1.961]			
$GeMe_2$ + HC≡CH	**1b**	1.336	1.937	1.937	1.969	—
	TS1b	1.274	2.060	2.389	2.263	2.121
	3b	1.354	1.990	2.970	3.404	1.498
GeH_2 + MeC≡CMe	**1c**	1.334	1.940	1.940	1.543	—
	TS1c	1.271	2.107	2.354	1.639	1.756
	3c	1.362	1.983	2.795	2.758	1.098
	4c	1.256	2.117	2.332	—	—
	TS0c	1.268	2.058	2.232	—	—
$GeMe_2$ + MeC≡CMe	**1d**	1.341	1.942	1.942	1.976	—
	TS1d	1.287	2.038	2.420	2.270	2.111
	3d	1.370	2.008	2.913	3.196	1.511

[a] Figures in parentheses and square brackets denote the results of B3LYP/6-31G(d)[17] and QCISD/6-31G(d) calculations, respectively.

The ring opening in structures **1a—d** (see Scheme 1, stage *b*) occurs through similar transition states **TS1a—d** and results in the secondary germylenes **3a—d**. The PBE/TZ2P calculated geometric parameters of the structures corresponding to the stationary points **1a**, **3a**, and **TS1a** in the simplest system GeH_2 + C_2H_2 are in good agreement with the results of the previous quantum chemical calculations[17] (see Table 1).

The calculated structures of germirenes **1a—d** have the skeleton symmetry C_{2v}; the symmetry of the entire molecule can be lower owing to rotation of C—H bonds in methyl groups. The calculated Ge—C(sp^2) bond lengths in the three-membered rings of molecules **1a—d** lie in the range 1.934—1.942 Å, being appreciably smaller than the endocyclic Ge—C(sp^3) bond lengths in germacyclopropane or in its methyl-substituted derivatives (1.964—1.989 Å)[20] obtained by the same method. The shorter Ge—C(sp^2) bonds in germirenes **1a—d** indicate that they are stronger than corresponding Ge—C(sp^3) bonds in germiranes. This is also confirmed by comparison of the energies of germylene addition to acetylene and ethylene. Namely, PBE calculations showed that the exothermicity of GeH_2 addition to acetylene (28.3 kcal mol^{-1}, see Table 2) is 4.9 kcal mol^{-1} higher than the exothermicity of its addition to ethylene (23.4 kcal mol^{-1}).[20] At the same time it is clear that angular strain in germacyclopropene should be higher than in the germacyclopropane molecule. Therefore, we can assume that additional release of the energy of cycloaddition of germylenes to alkynes (compared to their addition to alkenes) is due to aromatic stabilization of germirene formed. Note that the energies of cycloaddition of singlet carbene to ethylene and acetylene obtained from our PBE calculations are −108.6 and −99.5 kcal mol^{-1}, respectively. Thus, as should be expected, the addition of carbene to acetylene resulting in non-aromatic cyclopropene is 9.1 kcal mol^{-1} less exothermic than the addition of carbene to ethylene.

The endocyclic bonds Ge—C(sp^2) are shorter than the exocyclic bonds Ge—C(sp^3) in germirenes **1b** and **1d** (1.969 and 1.976 Å, respectively) or the Ge—C(sp^3) bond in dimethylgermylene (2.015 Å).

In the transition states **TS1b** and **TS1d** the C* atom of the migrating Me group lies in almost the same plane with the carbon and germanium atoms of the ring being opened (angles C(2)—C(1)—Ge—*R^1 are 1.2° and 1.6°, respectively). At the same time in the transition states **TS1a** and **TS1c** the migrating H* atom is situated at a longer distance from the CCGe plane (angles C(2)—C(1)—Ge—H* are 14.8° and 12.0°, respectively). It should be noted that in all transition states **TS1a—d** the C(1)—C(2) bond is considerably (by 0.05—0.09 Å) shorter than in germirenes **1a—d** or in the corresponding rearrangement products **3a—d** (see Table 1). This feature of the transition states

Table 2. The total[a] (E_0/a.u.) and relative[b] energies (ΔE_0/kcal mol^{-1}) and the Gibbs free energies[c] (ΔG/kcal mol^{-1}) of the structures corresponding to the stationary points on the PESs of the reactions of substituted germylenes with alkynes obtained from PBE/TZ2P calculations

System[d]	Structure	E_0/a.u.	ΔE_0	ΔG
			kcal mol^{-1}	
GeH_2 + HC≡CH	**1a**	−2155.13326	−28.3 (−24.1)[e] [−23.7][f]	−18.9
	TS1a	−2155.11218	15.1 (−5.0)[e] [−4.4][f]	−5.9
	3a	−2155.15786	−43.7 (−38.8)[e] [−38.2][f]	−35.1
$GeMe_2$ + HC≡CH	**1b**	−2233.64353	−26.7	−16.3
	TS1b	−2233.59011	6.8	17.7
	3b	−2233.66385	−39.5	−29.6
GeH_2 + MeC≡CMe	**4c**	−2233.62840	−19.6	−9.4
	TS0c	−2233.62832	−19.5	—
	1c	−2233.63871	−26.0	−15.2
	TS1c	−2233.61980	−14.2	−3.3
	3c	−2233.65515	−36.4	−28.4
$GeMe_2$ + MeC≡CMe	**1d**	−2312.14609	−22.7	−10.6
	TS1d	−2312.09278	10.8	23.8
	3d	−2312.15454	−28.0	−15.2

[a] $E_0 = E$ + ZPE.

[b] All values are given relative to isolated germylene and alkyne.

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

[d] Energies of reactants, E_0, are as follows: −2077.86233 (GeH_2), −2156.37514 ($GeMe_2$), −77.22586 (HC≡CH), and −155.73487 a.u. (MeC≡CMe).

[e] Obtained from G2//B3LYP/6-31G(d) calculations.[17]

[f] Obtained from G2//QCISD/6-31G(d) calculations.[17]

should facilitate migration of the *R group. The introduction of Me substituents has a little effect on the geometric parameters of structures **1** and **3**. A direct comparison of the transition structures is impossible because in **TS1a** and **TS1c** we deal with migration of H atom, whereas in **TS1b** and **TS1d** the migrating methyl group is part of the reaction center rather than a substituent. A more correct comparison, namely, **TS1a** *vs.* **TS1c** and **TS1b** *vs.* **TS1d** also revealed small influence of substituents on the geometry of the reaction center.

A distinctive feature of the PES of the system GeH_2 + MeC≡CMe is the presence of additional stationary points corresponding to π-complex **4c** and transition state **TS0c** of its transformation into germirene **1c**. Both stationary points correspond to similar C_s structures in which the germylene and alkyne fragments are in nearly parallel planes. The Ge atoms in **4c** and **TS0c** are noticeably shifted to the C(2) atom. The geometric parameters of the reactants change insignificantly upon complexation. The Ge—C(1) and Ge—C(2) distances are the main characteristics that change on going from **4c** to **TS0c**. The barrier to germirene formation from **4c** is at most 0.5 kcal mol^{-1} (see Table 2); therefore, the formation of π-complex has no effect on the kinetics of the addition. However, a small energy difference between the π-complex and three-membered ring (ΔE_{comp} = 6.5 kcal mol^{-1}, see Table 2) should be pointed out. This means that germirene **1c** involved in the reactions with the activation barriers higher than ΔE_{comp} could have the electronic structure of either germacyclopropene and the π-complex (see Scheme 2). Clearly, this also holds for other germirenes, even if no stationary points corresponding to the π-complex are present on the PES. This makes it possible to treat the reactivity of germacyclopropanes[20] and germacyclopropenes in a new manner.

Unlike retrocycloaddition, the rearrangement of germirenes **1** into secondary germylenes **3** is a thermodynamically and kinetically favorable process (low barriers, see Table 2). This seems to be the reason for high lability of the simplest germacyclopropenes.

The results of the PBE and G2 calculations of the reaction **1a** → **3a** (see Table 2) show that the PBE method underestimates the energy of isolated reactants $GeH_2 + C_2H_2$ relative to **1a**, **3a**, and **TS1a** by 6 kcal mol^{-1} on the average. A similar drawback was reported earlier[17] for another version of the density functional approach, B3LYP (the average energy difference was 7 kcal mol^{-1}). When considering only the germirene ring opening, the results of the PBE and G2 calculations are in much better agreement, namely, the energy difference between **1a** and **3a** is at most 1 kcal mol^{-1}. Data in Table 2 show that accumulation of Me groups causes the exothermicity of addition to linear alkynes to decrease, although less noticeably compared to germylene reactions with olefins.[20] It is important that tetramethylgermirene **1d** remains thermodynamically stable to retrocycloaddition into initial $GeMe_2$ and MeC≡CMe (Gibbs free energy of retrocycloaddition $\Delta G^0{}_{298}$ = 10.6 kcal mol^{-1}), whereas hexamethylgermirane is unstable ($\Delta G^0{}_{298}$ = −5.7 kcal mol^{-1}).[20] Applying a correction for possible overestimation of the exothermicity of cycloaddition by the PBE method (see above) does not change this conclusion. Replacement of hydrogen atoms at the Ge atom by Me groups causes a dramatic (by nearly 20 kcal mol^{-1}) increase in the activation barrier to germirene ring opening, whereas methyl substituents at carbon atoms have almost no effect on the barrier height. A similar situation was reported earlier[20] in the study of the opening of germiranes. This can be explained by the fact that the opening of the three-membered ring is a result of 1,2-shift of the substituent at the Ge atom and in the case of Me group the barrier is higher than in the case of a proton. Additionally, methyl substituents at carbon atoms decrease the exothermicity of the ring opening and the formation

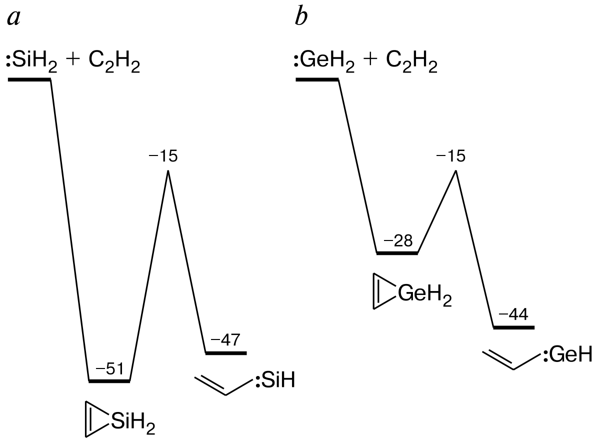


Fig. 1. Energy diagrams of systems $SiH_2 + C_2H_2$ and $GeH_2 + C_2H_2$ obtained from B3LYP/6-31G* (see Ref. 24) (*a*) and PBE/TZ2P calculations (*b*). The relative energies are given in kcal mol^{-1}.

of secondary germylene (see Table 2); however, even isomerization of permethylated **1d** into **4d** is thermodynamically favorable ($\Delta G^0{}_{298} = -4.6$ kcal mol^{-1}). Apparently, the larger the electron-donating substituents in germirene the higher its stability to rearrangement into the secondary germylene and the more probable the retrocycloaddition of the germirene. The synthesis of sterically overcrowded germirene and its thermal lability to retrocycloaddition[11] substantiate this conclusion.

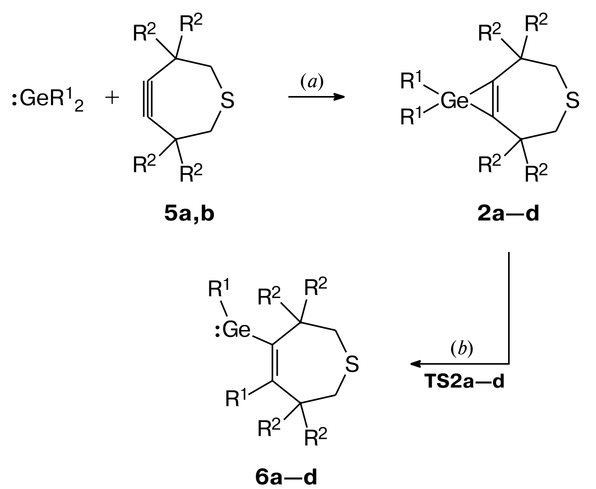
To understand the reasons for different stability of monocyclic sila- and germacyclopropenes, we will consider the energy diagrams of the simplest reactions of SiH_2 and GeH_2 with acetylene (Fig. 1).

The exothermicity of SiH_2 cycloaddition to acetylene is almost twice as high as that of the addition of GeH_2, but the main reason for the instability of germirene is the exothermicity of rearrangement of germirene **1a** into vinylgermylene **3a** as well as the low activation barrier to this process. In the case of silyrene the corresponding process is endothermic and the activation barrier is more than 20 kcal mol^{-1} higher than in the case of germirene. A similar picture is observed for the reactions of SiH_2 and GeH_2 with ethylene and subsequent opening of the opening sila- and germacyclopropanes.[25,26]

Reactions of germylenes with 4-thiacycloheptyne and 2,2,6,6-tetramethyl-4-thiacycloheptyne

To elucidate the reasons for high thermodynamic stability of the first synthesized germacyclopropene **2d**, we studied the reactions of GeH_2 and $GeMe_2$ with 4-thiacycloheptyne **5a** and its tetramethyl-substituted derivative **5b** (Scheme 3).

Scheme 3



5a,b **2a—d** **6a—d**

Taking into account the complex bicyclic structure of germacyclopropenes **2a—d**, we first carried out a detailed study of the factors determining the stability of compound **2a**, the simplest representative of this class of germirenes. Assessment of the stability of a chemical system requires a study of all possible pathways of its transformations and finding out the most probable decomposition channel. Clearly, the PES of system **2a** is much more complicated than that of the simplest germirene **1a** studied earlier[17] and permits a much larger number of reactions resulting in the opening of the three-membered ring. Therefore, we calculated the products of isomerization of compound **2a**, which are analogs of the structures formed upon the opening of the simplest monocyclic germirene[17] and could be produced from **2a** by minimum structural rearrangement involving, *e.g.*, transfer of a hydrogen atom and cleavage of one chemical bond C—Ge (Scheme 4). Additionally, we studied certain transformations characteristic of bicyclic systems only, namely, extension, contraction, and opening of the seven-membered ring. We considered only the "minor" changes in the molecular structure in the vicinity of the three-membered ring. The structures thus generated are presented in Scheme 4.

Table 3 lists the PBE/TZ2P calculated energies of the system GeH_2 + **5a**, molecule **2a**, and products of possible rearrangements of **2a** (see Scheme 4). It should be noted that cycloaddition of GeH_2 to cyclic alkyne **5a** is much more exothermic ($\Delta E_0 = -45.9$ kcal mol^{-1}) than its cycloaddition to acetylene ($\Delta E_0 = -28.3$ kcal mol^{-1}).

Among the investigated isomers of germirene **2a**, germylenes **6—9** have the lowest energies and the most stable structure with tetracoordinate germanium atom is germathiaoctyne **10** (see Table 3). These five molecules present a complete set of structures whose energies are lower than the energy of system **2a**. Low barriers to isomerization of **2a** into any structures **6—9** mean that germirene is unstable. The energies of structures **11—17** are much higher than that of **2a** and the formation of these species as possible source of germirene instability can be ruled out.

Scheme 4

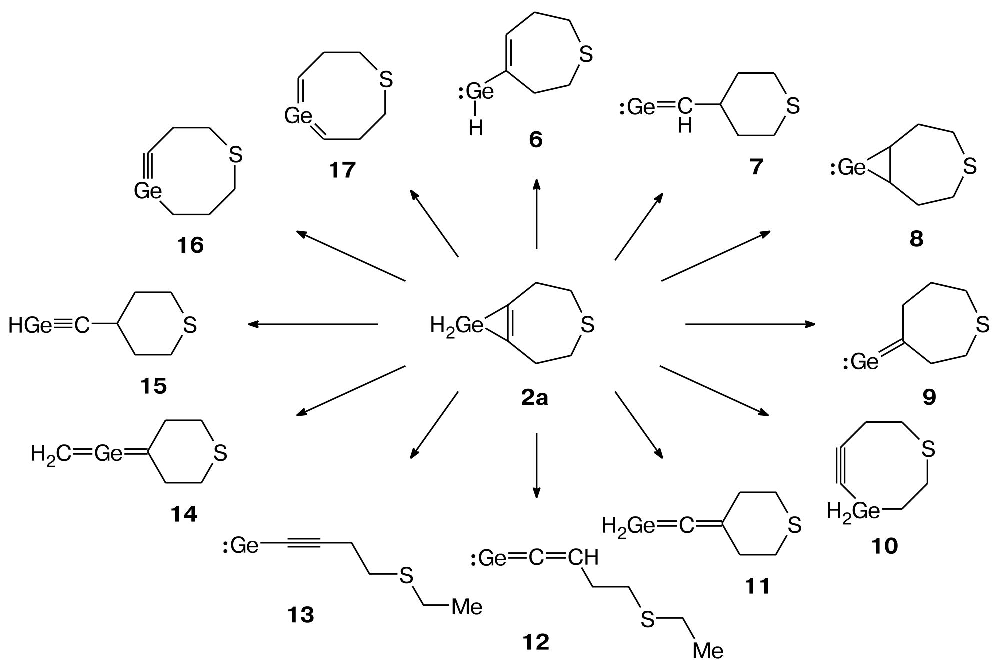
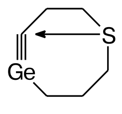


Table 3. The total (E_0/a.u.) and relative energies (ΔE_0/kcal mol^{-1}) of structures **2a**, **6**—**17**, and the system **5a** + GeH$_2$ obtained from the PBE/TZ2P calculations

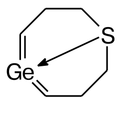
Structure	E_0	ΔE_0
5a + GeH$_2$	−2708.91781	0.0
2a	−2708.99094	−45.9
6	−2709.00298	−53.4
7	−2709.00395	−54.1
8	−2709.00720	−56.1
9	−2708.99446	−48.1
10	−2708.99140	−46.2
11	−2708.98056	−39.4
12	−2708.97674	−37.0
13	−2708.97387	−35.2
14	−2708.95575	−23.8
15	−2708.94998	−20.2
16	−2708.95637	−24.2
17	−2708.94662	−18.1

* $E_0 = E +$ ZPE.

According to calculations, the atom S forms an intramolecular coordination bond with the unsaturated carbon atom (in structure **16**) and germanium atom (**17**). However, even with allowance for this additional stabilization, structures **16** and **17** are the highest in energy among all isomers **6**—**17**. The set of possible candidate structures can be extended, but it seems to be hardly probable that it will include new isomers whose energies will be lower than that of germirene **2a**.



16



17

Let us consider the isomerization of **2a** into structures **6**—**9** in more detail. These species have analogs among the products of decomposition of the simplest germirene **1a**, which were studied in detail earlier.[17] Only vinylgermylene **3a** and ethynylgermane can be formed from **1a** in one step, whereas other germylenes are formed solely from **3a** (see Ref. 17).

Therefore, direct reactions **2a** → **8**, **2a** → **9**, and **2a** → **7** can be ruled out (the last-mentioned reaction is also hardly probable because it implies transfer of two protons and simultaneous rearrangement of the seven-membered ring into a six-membered one). By analogy with the prototype (isomerization of **1a** into ethynylgermane) one can assume a high barrier to reaction **2a** → **10**. Thus, the only low-barrier and energetically favorable isomerization reaction in question is reaction **2a** → **6**.

Therefore, it is this potential channel of decomposition of germirene **2a** that is the critical one, and the study of this teaction should clarify the nature of the factors determining the stability of the cycloadducts of the reactions shown in Scheme 3. Our further efforts were focussed on calculations of the activation barriers E_a and thermodynamic effects in the first (*a*) and second (*b*) stages of these reactions (see Scheme 3). On the PESs of the systems under study we located minima corresponding

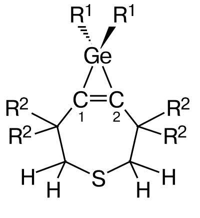
Table 4. Interatomic distances[a] (*d*) in the structures corresponding to the stationary points on the PESs of reactions **2a—d** → **6a—d**

System	Structure	*d*/Å				
		C(1)—C(2)	Ge—C(1)	Ge—C(2)	Ge—*R^1	C(2)—*R^1
GeH_2 + **5a**	**2a**	1.336	1.939	1.939	1.542	—
	TS2a	1.270	2.088	2.340	1.617	1.915
	6a	1.361	1.985	2.772	2.709	1.098
$GeMe_2$ + **5a**	**2b**	1.343	1.942	1.942	1.974	—
	TS2b	1.287	2.042	2.419	2.268	2.119
	6b	1.369	2.007	2.908	3.206	1.507
GeH_2 + **5b**	**2c**	1.334	1.943	1.943	1.542	—
	TS2c	1.269	2.096	2.354	1.625	1.880
	6c	1.363	2.001	2.777	2.686	1.099
$GeMe_2$ + **5b**	**2d**	1.341 (1.331)	1.946 (1.929)	1.946 (1.915)	1.975 (1.954)	—
	TS2d	1.294	2.036	2.455	2.267	2.100
	6d	1.356	2.035	2.846	2.826	1.526

[a] Figures in parentheses denote the experimental data.[27]

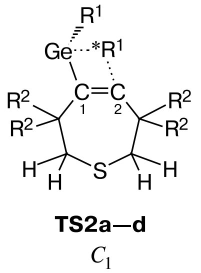
to germirenes **2a—d** and secondary germylenes **6a—d** and the saddle points corresponding to transition states **TS2a—d**. In all cases the cycloaddition proceeds in one step without activation barrier and involves no intermediate π-complex.

The PBE/TZ2P calculated structures corresponding to the energy minima and transition states of reactions **2a—d** → **6a—d** are shown below (the migrating group is marked by an asterisk; the symmetry group of the molecular skeleton is shown below the structure) and their geometric parameters and energies are listed in Tables 4 and 5, respectively.



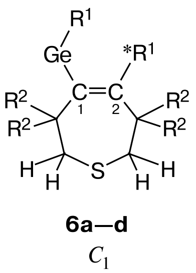
2a—d

C_s



TS2a—d

C_1



6a—d

C_1

The symmetry of the structures corresponding to the stationary points on the PESs of reactions **2a—d** → **6a—d** is lower than the symmetry of similar structures in the case of reactions **1a—d** → **3a—d**, because the C_s symmetry of 4-thiacycloheptyne molecules **5a** and **5b** is lower than the symmetry of the acetylene and dimethylacetylene molecules. The geometric parameters of the germirene fragments in molecules **2a—d** are almost the same as those of monocyclic germirenes **1a—d**. Mention may be made of a slight (0.007 Å) elongation of the C(1)—C(2) bonds in compounds **2a** and **2b**, which is probably due to minimization of strain in the seven-membered ring. The calculated geometric parameters of molecule **2d** are in good agreement with the experimental data obtained by X-ray

Table 5. The total[a] (E_0/a.u.) and relative[b] energies (ΔE_0/kcal mol^{-1}) and the Gibbs free energies[c] (ΔG/kcal mol^{-1}) of the structures corresponding to the stationary points on the PES of reactions of substituted germylenes with 7-thiacycloheptynes obtained from PBE/TZ2P calculations

System[d]	Structure	E_0/a.u.	ΔE_0	ΔG
			kcal mol^{-1}	
GeH_2 + **5a**	**2a**	−2708.99094	−45.9	−34.7
	TS2a	−2708.96789	−31.4	−20.4
	6a	−2709.00298	−53.4	−43.1
$GeMe_2$ + **5a**	**2b**	−2787.49989	−43.5	−31.0
	TS2b	−2787.44422	−8.6	4.6
	6b	−2787.50239	−45.1	−32.3
GeH_2 + **5b**	**2c**	−2865.96983	−44.6	−33.0
	TS2c	−2865.94893	−31.4	−20.1
	6c	−2865.97184	−45.8	−34.6
$GeMe_2$ + **5b**	**2d**	−2944.47845	−42.0	−29.1
	TS2d	−2944.41348	−1.2	12.9
	6d	−2944.46434	−33.1	−19.6

[a] $E_0 = E + \mathrm{ZPE}$.

[b] All values are given relative to isolated germylene and alkyne.

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

[d] The energies of reactants E_0 are −631.05548 (**5a**) and −788.03648 a.u. (**5b**).

analysis.[27] In particular, calculations reproduce the experimentally detected shortening of the endocyclic bonds Ge—C(sp^2) compared to the Ge—C(sp^3) bonds. Changes in the geometries of **TS2a—d** do follow the pattern established for reactions **1a—d** → **3a—d** (see above). The C(1)—C(2) bond in **TS2a—d** is 0.05—0.09 Å shorter than in reactants **2a—d** or products **6a—d**. Thus, the geometries of the germirene moieties in bicyclic systems **2a—d** are virtually the same as those of the germirene fragments in monocyclic molecules **1a—d**.

The data in Table 5 show that, thermodynamically, the cycloaddition to **5a,b** is much more favorable than the addition to acetylene (dimethylacetylene). A possible reason consists in removal of angular strain in the 4-thiacycloheptyne molecule (in the former case). It is natural to consider the hydrogenation energy difference between linear and cyclic alkynes as a measure of angular strain of the multiple bond. PBE calculations of the hydrogenation energies of acetylene and alkyne **5a** gave 44.2 and 52.8 kcal mol^{-1}, respectively, which allows the angular strain energy of the C≡C bond in molecule **5a** to be estimated at 8.6 kcal mol^{-1}. At the same time the cycloaddition energy difference between GeH_2 and acetylene (see Table 2) and **5a** (see Table 5) is about twice as large (17.6 kcal mol^{-1}). This means that removal of angular strain is accompanied by some additional effect that ensures stabilization of bicyclic structures **2a—d**. The nature of this effect is still to be clarified. Mention can also be made that in all cases the cycloaddition of GeH_2 is slightly more (by 1—3 kcal mol^{-1}) exothermic than the cycloaddition of $GeMe_2$ irrespective of the nature of the alkyne.

At first glance, changes in energy (see Table 5) upon ring opening in molecules **2a—d** obey the same rules as the changes in energy in analogous reactions of monocyclic germirenes. However, this process is thermodynamically much less favorable than in the case of compounds **1a—d**. The activation barriers to migration of H* atom are about 1 kcal mol^{-1} higher than the barriers to similar reactions **1a** → **3a** and **1c** → **3c**. The barriers to migration of methyl group are much higher than the barriers to migration of H atom. Calculations of ring opening in real system (germirene **2d**) give the maximum barrier height (40.8 kcal mol^{-1}). Besides, ring opening in this system and formation of secondary germylene appears to be thermodynamically unfavorable ($\Delta G^0{}_{298}$ = 9.5 kcal mol^{-1}). Therefore, reaction **2d** → **6d** is forbidden both kinetically (E_a = 40.8 kcal mol^{-1}) and thermodynamically ($\Delta G^0{}_{298}$ = 9.5 kcal mol^{-1}). Both these factors in combination with high exothermicity of the cycloaddition ($\Delta G^0{}_{298}$ = −29.1 kcal mol^{-1}), which is to a great extent due to removal of angular strain in the 4-thiacycloheptyne fragment of molecule **2d** result in unusually high thermodynamic stability of the first synthesised germirene. As mentioned above, aromaticity can also contribute to stabilization of germirenes. Analysis of the geometric parameters of the germirene molecules **1** and **2** revealed a bond length redistribution characteristic of the systems with electron delocalization, namely, a slight elongation of the multiple bonds C=C and a more pronounced shortening of the single bonds Ge—C(sp^2).

Thus, based on the results of quantum chemical studies we have shown that germylene and dimethylgermylene add to the triple bonds of alkynes without activation barrier. In most systems studied the primary reaction product is germacyclopropene (only in the reaction of germylene with dimethylacetylene the PES has a minimum corresponding to the π-complex whose energy is slightly different from that of the corresponding germirene). All germacyclopropenes studied are relatively stable to retrocycloaddition, but readily undergo rearrangements into secondary germylenes. This rearrangement is thermodynamically and kinetically (low barriers) favorable. It is this process that seems to be responsible for high lability of the simplest germacyclopropenes. Unlike carbene, the addition of germylenes to acetylenes is more exothermic than the addition to olefins, which indicates a possible aromatic stabilization of germirenes.

The interaction of germylene and dimethylgermylene with 4-thiacycloheptyne and its tetramethyl-substituted derivative is a one-step process resulting in corresponding germirenes similarly to the reactions with linear alkynes. A much higher exothermicity of cycloaddition is to a great extent due to removal of angular strain in the 4-thiacycloheptyne fragment. Among possible secondary transformations of bicyclic germirenes **2**, reaction **2** → **6** could play a key role. However, the rearrangement of real structure (reaction **2d** → **6d**) is forbidden both kinetically and thermodynamically.

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