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# Isomerization and decomposition of germiranes: a density functional study*

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The formation and decomposition pathways of germiranes (germacyclopropanes), *i.e.*, products of reactions of the $GeH_2$ and $GeMe_2$ germylenes with ethylene, tetramethylethylene, buta-1,2,3-triene, and tetramethylbuta-1,2,3-triene, were studied using the density functional approach (PBE/TZ2P approximation). The thermodynamic stabilities of the structures under consideration were evaluated by calculating the Gibbs free energies under normal conditions ($\Delta G°_{298}$). Addition of germylenes to the C=C bond can proceed as a single-step process without a barrier or involve the formation of a π-complex (the barrier to this process is lower than the sum of the energies of isolated reactants). Stability of the germiranes formed is determined by their stability to retrodecomposition into the initial germylene and olefin and to the three-membered ring opening followed by simultaneous 1,2-migration of the substituent at the Ge atom and formation of the secondary germylene. Alkyl substituents can efficiently block the opening of the three-membered ring and transformation of the cyclic structure into the secondary germylene, simultaneously decreasing the germirane stability to retrodecomposition. Decomposition into germylene and olefin under normal conditions is thermally favorable for hexamethylgermirane ($\Delta G°_{298}$ = –5.7 kcal mol$^{-1}$), being thermally forbidden for the other germiranes studied in this work ($\Delta G°_{298} > 0$). The activation energy ($E_a$) for the germirane ring opening depends on the substituents at the germanium atom, namely, $E_a \le 10$ kcal mol$^{-1}$ for unsubstituted germiranes and $E_a > 30$ kcal mol$^{-1}$ for methyl-substituted germiranes. Taking the experimentally isolated germirane as an example, it was shown how the introduction of substituents and modification of the carbon skeleton make it possible to stabilize the germacyclopropane system.

**Key words:** germylene, olefins, germirane (germacyclopropane), cycloaddition, quantum-chemical calculations, PBE density functional.

Attempts to obtain stable cyclopropane analogs in which one carbon atom is replaced by the atom of a heavier element of the same subgroup (E = Si, Ge, Sn) appeared to be successful only for silicon derivatives (E = Si).[1] Considerable efforts made to obtain germacyclopropanes (germiranes) succeeded after several years of research[2] and only in two cases.[3] Corresponding tin derivatives (stanniranes) have not been detected so far. Nevertheless, participation of germiranes, as intermediates in the reactions between germylenes and alkenes, was repeatedly postulated[2] in order to explain the character of reaction products. By analogy with the silicon compounds the addition of germylenes to the C=C bond is considered to be the most promising synthetic route to germiranes. Indeed, the known stable (under normal conditions) germiranes were obtained[3] by adding a stable germylene $Ge[C(SiMe_3)_2H]_2$ to the double bonds of the 2,5-dimethylhexa-2,3,4-triene and *N*-phenylmaleimide molecules. Preliminary data on the preparation of the third stable germacyclopropane, namely, a [6,5]-bridging adduct of germylene and fullerene are also available.[4] Failures in the earlier studies on the synthesis of stable germiranes were usually explained[2] by lower reactivity of germylenes compared to silylenes or by lability of the germirane ring. At present, the addition of the simplest germylenes $GeH_2$ [5,6] and $GeMe_2$ [7] to the C=C double bond has been studied in considerable detail. Gas-phase kinetic studies[5—7] showed that the activation barrier to cycloaddition of germylenes to the C=C bond is nearly zero; however, germiranes cannot be identified among reaction products and moreover isolated. Even more, most of final reaction products can not be identified. In both stable germiranes[3] the germacyclopropane fragment is a part of a rigid and rather strained framework; therefore, it is hard to understand why all previous attempts to isolate less strained three-membered rings in the interaction of germylenes with simple olefins failed.

Quantum-chemical calculations of the potential energy surface (PES) allow one to obtain quantitatie data on

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* Dedicated to Academician A. L. Buchachenko on the occasion of his 70th birthday.

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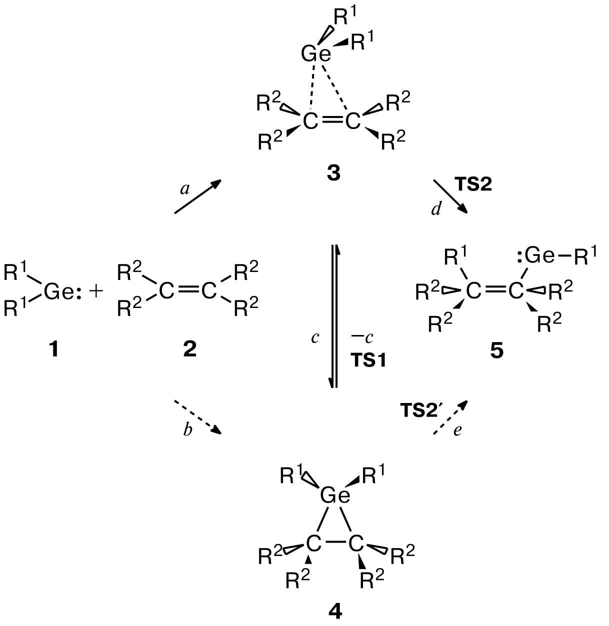
the activation energies and thermodynamic characteristics of various elementary stages of the formation and opening of cyclic structures and to establish factors responsible for stabilization or destabilization of small rings. Earlier,[6,8,9] the PESs of the cycloaddition reactions of germylenes to ethylene were studied using the *ab initio* (MP2, QCISD) and density functional (B3LYP) quantum-chemical calculations with small or medium-size basis sets. It was shown[8,9] that cycloaddition involves the formation of intermediate **3** (π-complex), which undergoes isomerization into germirane **4** (Scheme 1, reactions *a* and *c*), and that the barrier to the process (transition state **TS1**) is very low. The effect of substituents in the germylene molecule on the mechanism of this stage was investigated. Pathways of further transformations of the germirane ring were not considered in those studies.[8,9]

Scheme 1



A more detailed investigation[6] of the PES of the $GeH_2+C_2H_4$ system revealed not only structures **1**—**4** but also five minima with energies lower than the sum of the reactant energies and eight transition states connecting these minima. Except for vinylgermane $CH_2=CHGeH_3$, all the minima located correspond to highly reactive germanium compounds, namely, germylenes, germaethenes (germenes), germirane, and the π-complex. Germirane **4** and π-complex **3** are separated by a very low barrier ($E_a$ < 2 kcal mol$^{-1}$), being almost indistinguishable in regard to possibility of transformation into other structures. All other structures, except ethylgermylene **5**, are separated from germirane **4** by very high barriers and do not affect its stability under normal conditions. Ethylgermylene **5** is separated from the π-complex (germirane) by a low activation barrier **TS2** and has a lower energy than germirane **4**. The resulting barrier to the rearrangement of germirane **4** into ethylgermylene **5** involving formation of π-complex **3** (see Scheme 1, R = H; reactions −*c* and *d*) is less than 9 kcal mol$^{-1}$, being the reason for instability of the simplest germirane,[6] while a high reactivity of species **5** provides an explanation for difficulties in the identification of the final products. The critical ring-opening pathway in molecule **4** was established,[6] but the effect of substituents at the Ge and C atoms on the stability of the germirane could not be evaluated based on the small data set.

Cycloaddition reactions of germylenes having electron-acceptor substituents with ethylene is characterized by a high activation barrier, being thermodynamically unfavorable.[8,9] Clearly, in order to form a stable germirane ring, it is desired to have only electron-donor substituents at the germanium atom. In this work we studied the formation and isomerization of germiranes in the reactions of germylenes $GeH_2$ and $GeMe_2$ with ethylene, tetramethylethylene (TME), buta-1,2,3-triene (BT), and tetramethylbuta-1,2,3-triene (TMBT) using the PBE density functional[10] method. In studying the isomerization of germiranes we considered only the energetically most plausible (critical) ring-opening pathway established earlier[6] for the $GeH_2$+ethylene system. The thermodynamic stability of structures was assessed by calculating changes in the Gibbs free energy under normal conditions ($\Delta G°_{298}$). Taking products of the reactions of germylenes with ethylene and TME as examples, we studied the effect of substituents on the stability of the simple germiranes similar to the stable siliranes obtained earlier and established the reasons for different stability of the silicon and germanium heterocycles. In studying the interaction of germylenes with BT and TMBT we considered the systems that are most structurally similar to the experimentally isolated[3] stable germirane and checked the correctness of our conclusions about the reasons for stability/instability of germiranes. Using quantum-chemical calculations, we established the factors responsible for stability of saturated three-membered rings containing a germanium atom and formulated the principles of design of such systems.

## Calculation Procedure

Density functional quantum-chemical calculations were carried out by the PBE method[10] on PCs equipped with Pentium-IV® CPUs using the PRIRODA program[11] and, in some cases* (see below), by the B3LYP/6-31G(d) method using the GAUSSIAN-98 program.[12]

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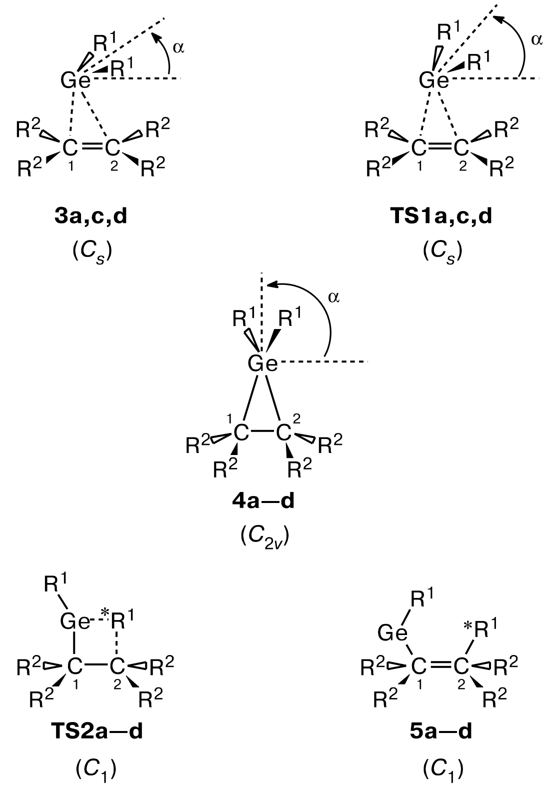
PBE calculations included full geometry optimization and vibrational frequency calculations. We employed a triple-zeta quality TZ2P basis set with two sets of polarization functions, namely, (5s2p) [3s2p] for H, (11s6p2d) [6s3p2d] for Cm and (18s14p9d) [13s10p5d] for Ge (figures in parentheses denote the uncontracted basis set, while figures in brackets denote the contracted basis set). The PRIRODA program employs the electron density expansion over an auxiliary uncontracted basis set,[13] *viz.*, (5s2p) for H, (10s3p3d1f) for C, and (18s3p3d1f1g) for Ge. The character of the stationary points located was controlled by calculating the eigenvalues of the Hessian. Correspondence between a particular transition state and a given reaction was checked by calculating the intrinsic reaction coordinate. The final energy values included the zero-point vibrational energy correction, ZPE. Thermodynamic functions were calculated using the "harmonic oscillator—rigid rotator" model.

## Results and Discussion

### *Reactions of germylenes with ethylene and tetramethylethylene*

Minima corresponding to π-complexes **3**, germiranes **4**, and secondary germylenes **5**, as well as the saddle points corresponding to the transition states **TS1** and **TS2** were located on the PESs of all the systems under consideration, except for the $GeMe_2$+ethylene system. The structures corresponding to the stationary points located are shown in Fig. 1 and Table 1 lists the key geometric parameters. The energies of the stationary points are given in Table 2. The PBE/TZ2P calculated structures corresponding to the stationary points **3a—5a**, **TS1a**, and **TS2a** in the simplest system $GeH_2+C_2H_4$ are in good agreement with the results of the earlier quantum-chemical calculations[6,8] (see Table 2). The formation of germirane **4a** involves two stages, namely, *a* and *–c*; ring opening in **4a** involves the stages *c* and *d* (see Scheme 1).

We failed to locate stationary points corresponding to the π-complex **3** and transition state **TS1** on the PES of the $GeMe_2$+ethylene system. According to PBE calculations, as $GeMe_2$ and ethylene approach each other, the energy monotonically decreases, except for a small region at Ge—C distances of the order of 2.3—2.5 Å, which is typical of π-complexes in similar (related) systems. Thus, the addition of $GeMe_2$ to ethylene should involve a single stage and proceed barrierlessly. This contradicts the conclusions drawn in a B3LYP/6-31G* study[8] which revealed that π-complex **3** and the corresponding transition state **TS1** differ in energy by ~2 kcal mol$^{-1}$ only. Our attempts to reproduce the results reported in study[8] failed. Namely, the B3LYP/6-31G* calculations using the GAUSSIAN-98 program showed that the structures reported[8] do not correspond to stationary points; geometry optimization starting from these structures always led to the minimum corresponding to germirane **4b**. From this we can conclude that both versions of the DFT calculations predict that the addition of $GeMe_2$ to ethylene should occur barrierlessly and involve a single step (see Scheme 1, route *b*). This is consistent with the results of gas-phase kinetic studies,[14] according to which this reaction belongs to the fastest reactions involving $GeMe_2$.



R$^1$ = R$^2$ = H (**a**), Me (**d**); R$^1$ = Me, R$^2$ = H (**b**); R$^1$ = H, R$^2$ = Me (**c**)

**Fig. 1.** Structures corresponding to the energy minima **3—5** and transition states **TS1** and **TS2** obtained from PBE/TZ2P calculations. The migrating group is asterisked. The symmetry group of the skeleton is given in parentheses.

The PESs of the $GeH_2$+TME and $GeMe_2$+TME systems are characterized by the same sets of stationary points as the PES of the $GeH_2$+ethylene system. π-Complexes **3a** and **3c** have similar structures (both with $C_s$ symmetry) in which the germylene and olefin fragments lie in nearly parallel planes. While on the subject of symmetry of the systems with methyl substituents, starting from this point we discuss the symmetry of the carbon skeleton rather than the symmetry of the entire molecule, which depends on the methyl group conformations. The angle α between the olefin and germylene planes in **3a** and **3c** is 13° (see Table 1). In π-complex **3d** ($GeMe_2$+TME system), the angle α increases to 30°, which is probably due to steric interactions. The Ge atoms in the π-complexes are appreciably displaced to one of the atoms involved in the C=C bond (see Fig. 1, C(1) atom in structures **3a,c,d**). Complexation causes insignificant changes in the reactant ge-

**Table 1.** Selected geometric parameters[a] of the stationary points on the PESs of the reactions of $GeH_2$ and $GeMe_2$ with ethylene and TME[b]

| System | Structure | $d$/Å | | | | | Angle/deg | |
|---|---|---|---|---|---|---|---|---|
| | | C(1)—C(2) | Ge—C(1) | Ge—C(2) | Ge—$R^1$ | C(2)—$R^1$ | $R^1$—C—C—Ge | α |
| $GeH_2$+$C_2H_4$ | **3a** | 1.40 (1.39) | 2.13 (2.17) | 2.38 (2.44) | — | — | — | 13.0 |
| | **TS1a** | 1.46 (1.45) | 2.01 (2.00) | 2.14 (2.16) | — | — | — | 38.2 |
| | **4a** | 1.53 (1.53) | 1.97 (1.95) | 1.97 | 1.55 | — | — | 90.0 |
| | **TS2a** | 1.42 (1.42) | 2.14 (2.13) | — | 1.65 (1.58) | 1.73 (1.70) | 13 | — |
| | **5a** | 1.53 (1.53) | 2.01 (2.00) | — | 3.25 | 1.10 | 55 | — |
| $GeMe_2$+$C_2H_4$[c] | **4b** | 1.55 (1.53) | 1.96 (1.94) | 1.96 (1.94) | 1.97 | — | — | 90.0 |
| | **TS2b** | 1.45 | 2.07 | — | 2.34 | 2.06 | 13 | — |
| | **5b** | 1.53 | 2.03 | — | 2.66 | 1.53 | 70 | — |
| $GeH_2$+TME | **3c** | 1.41 | 2.21 | 2.51 | — | — | — | 12.6 |
| | **TS1c** | 1.55 | 1.99 | 1.98 | — | — | — | 34.1 |
| | **4c** | 1.56 | 1.99 | 1.99 | 1.54 | — | — | 90.0 |
| | **TS2c** | 1.46 | 2.15 | — | 1.66 | 1.64 | 6 | — |
| | **5** | 1.56 | 2.06 | — | 2.94 | 1.11 | 68 | — |
| $GeMe_2$+TME | **3d** | 1.41 | 2.26 | 2.63 | — | — | — | 30.2 |
| | **TS1d** | 1.48 | 2.05 | 2.21 | — | — | — | 44.4 |
| | **4d** | 1.58 | 1.99 | 1.99 | 1.97 | — | — | 90.0 |
| | **TS2d** | 1.50 | 2.07 | — | 2.34 | 2.05 | 8 | — |
| | **5d** | 1.58 | 2.08 | — | 3.04 | 1.54 | 38 | — |

[a] The results of B3LYP calculations[6,8] are given in parentheses.

[b] The atomic numbering scheme is given in Fig. 1.

[c] No stationary points for π-complex **3** and **TS1** were located.

**Table 2.** The total[a] ($E_0$) and relative[b] energies ($\Delta E_0$) and the Gibbs free energies[c] ($\Delta G°$) of the structures corresponding to the stationary points on the PES of the reactions of $GeH_2$ and $GeMe_2$ with olefins, obtained from PBE/TZ2P calculations

| System[d] | π-Complex **3** | Transition state **TS1** | Germirane **4** | Transition state **TS2** | Germylene **5** |
|---|---|---|---|---|---|
| | | | $-E_0$/a.u. | | |
| $GeH_2$+$C_2H_4$ | 2156.34983 | 2156.34733 | 2156.35226 | 2156.34370 | 2156.35729 |
| $GeMe_2$+$C_2H_4$ | —[e] | —[e] | 2234.85992 | 2234.80982 | 2234.85618 |
| $GeH_2$+TME | 2313.33035 | 2313.323 | 2313.32662 | 2313.32049 | 2313.32578 |
| $GeMe_2$+TME | 2391.82894 | 2391.82446 | 2391.83172 | 2391.77926 | 2391.81925 |
| | | | $\Delta E_0$/kcal mol$^{-1}$ | | |
| $GeH_2$+$C_2H_4$ | −21.8 (−20.1)[f]<br>[−15.3][g] | −20.3 (−18.0)[f]<br>[−14.7][g] | −23.4 (−23.4)[f]<br>[−20.9][g] | −18 (−14.5)[f]<br>[−9.2][g] | −26.5 (−29.2)[f]<br>[−23.9][g] |
| $GeMe_2$+$C_2H_4$ | —[e] | —[e] | −20.1 | 11.3 | −17.8 |
| $GeH_2$+TME | −16.6 | −12.4 | −14.2 | −10.4 | −13.7 |
| $GeMe_2$+TME | −7.7 | −4.8 | −9.4 | 23.5 | −1.6 |
| | | | $\Delta G°$/kcal mol$^{-1}$ | | |
| $GeH_2$+$C_2H_4$ | −11.6 | — | −12.7 | — | −16.8 |
| $GeMe_2$+$C_2H_4$ | —[e] | — | −8.4 | — | −6.4 |
| $GeH_2$+TME | −3.3 | — | −0.4 | — | −0.6 |
| $GeMe_2$+TME | 7.6 | — | 5.7 | — | 14.2 |

*Note*. The numbering of structures is shown in Fig. 1.

[a] $E_0 = E + ZPE$.

[b] Relative to isolated germylene and olefin.

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

[d] The $E_0$ energies of reactants are as follows: −2077.86233 ($GeH_2$), −2156.37514 ($GeMe_2$), −78.45271 (ethylene), and −235.44160 (tetramethylethylene) a.u.

[e] No stationary point was located.

[f] Obtained from B3LYP/6-31G(d) calculations.[6]

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

ometries. Two parameters, namely, the distance between the germylene and olefin fragments and the angle $\alpha$, experience the most pronounced effect of substituents. Introduction of Me substituents causes the energy gain for the formation of $\pi$-complexes to decrease from 21.8 kcal $mol^{-1}$ for **3a** to 7.7 kcal $mol^{-1}$ for **3d**. However, the reason for instability of the $\pi$-complexes consists in very low (<4.2 kcal $mol^{-1}$) activation barriers **TS1a** and **TS1c,d** corresponding to isomerization of the complexes into germiranes **4** (see Table 2) rather than low complexation energies. The $GeMe_2+C_2H_4$ system is characterized by the absence of this barrier.

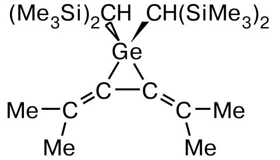
The structures of the transition states **TS1a** and **TS1c,d** are similar to those of the corresponding $\pi$-complexes **3a** and **3c,d**; however, the germylene fragments in **TS1a,c,d** are rotated by a larger angle relative to the double bond plane (the angles $\alpha$ vary from 34° to 44°, see Table 1). In the calculated structures of germiranes **4a—d**, the skeleton symmetry is $C_{2v}$; the symmetry of the entire molecule can be lower due to different angles of rotation of the Me groups. In spite of a rather high strain in the germirane ring, the calculated Ge—C bond lengths in **4a—d** (1.96—1.99 Å) are similar to the conventional Ge—C bond length calculated for, *e.g.*, $GeMe_2$ (1.99 Å, B3LYP; 2.01 Å, PBE), or to the most plausible value of this bond length (1.95—2.00 Å) determined using a large body of experimental structural data.[15] A feature of the transition states **TS2a—d** is that the C and Ge atoms and the central atom of the migrating substituent lie in nearly the same plane. It should be noted that the C(1)—C(2) bonds in the transition states of the opening ring germiranes are much shorter than in the reactants **4a—d** or in the reaction products **5a—d**. This feature of the transition states **TS2a—d** facilitates migration of the $^*R^1$ group.

The PBE/TZ2P calculated relative energies of the stationary points **3a—5a**, **TS1a**, and **TS2a** in the $GeH_2+C_2H_4$ system (see Table 2) are in good agreement with the results of the earlier quantum-chemical calculations.[6] Taking this system as an example, one can see that the PBE/TZ2P method employed in this work provides the structures and energies that are consistent with the results of the B3LYP/6-31G(d) or more rigorous G2//QCISD calculations.[6]

Now we will consider the effect of substituents on the energies of formation and decomposition of germirane **4**. No stationary points corresponding to the $\pi$-complex **3b** and transition state **TS1b** were located upon introduction of Me groups into germylene (see Table 2). The reaction of dimethylgermylene with olefin proceeds without a barrier and results in germirane. At first glance this must indicate an increase in stability of the three-membered ring **4b**. Actually, the reverse occurs. Cycloaddition of $GeMe_2$ to ethylene and TME to give germiranes **4b** and **4d**, respectively, is thermodynamically less favorable than the formation of molecules **4a** and **4c** in similar reactions involving $GeH_2$ (see Table 2). This is due to a higher diatomic state stabilization energy of $GeMe_2$ (30.1 kcal $mol^{-1}$) compared to that of $GeH_2$ (28.4 kcal $mol^{-1}$).[16] The presence of Me groups at the Ge atoms in molecules **4b** and **4d** leads to high activation barriers **TS2b** and **TS2d** to the opening of the three-membered rings and formation of secondary germylenes **5b** and **5d**. This can be explained by the 1,2-shift of the Me group (ring opening in **4b** and **4d**) rather than proton migration (germiranes **4a** and **4c**). Methyl groups in the TME molecule cause a slight increase in the barrier to isomerization of the $\pi$-complex into germirane; however, by and large the thermodynamics of addition is less favorable that for ethylene. Methyl groups at C atoms have almost no effect on the height of the activation barrier (**TS2**) to the three-membered ring opening (see Table 2). Noteworthy is that the Gibbs free energy under normal conditions, $\Delta G°_{298}$, of the formation of germiranes **4c** (**4d**) from $GeH_2$ ($GeMe_2$) and TME is positive, *i.e.*, the equilibrium is shifted toward the initial reactants. The same also holds for the secondary germylenes **5c** and **5d**. Thus, the alkyl groups at the Ge atom efficiently block the opening of the three-membered ring in **4** and the transformaton of this compound into the secondary germylene **5**. Simultaneously, this dramatically decreases the thermodynamic stability of **4** to retrodecomposition. The last-mentioned reaction should be very fast due to low barrier **TS1** (~5 kcal $mol^{-1}$). Thus, the germiranes stable under normal conditions can not be obtained by cycloaddition of germylenes to simple olefins.

## *Germylene reactions with substituted buta-1,2,3-trienes*

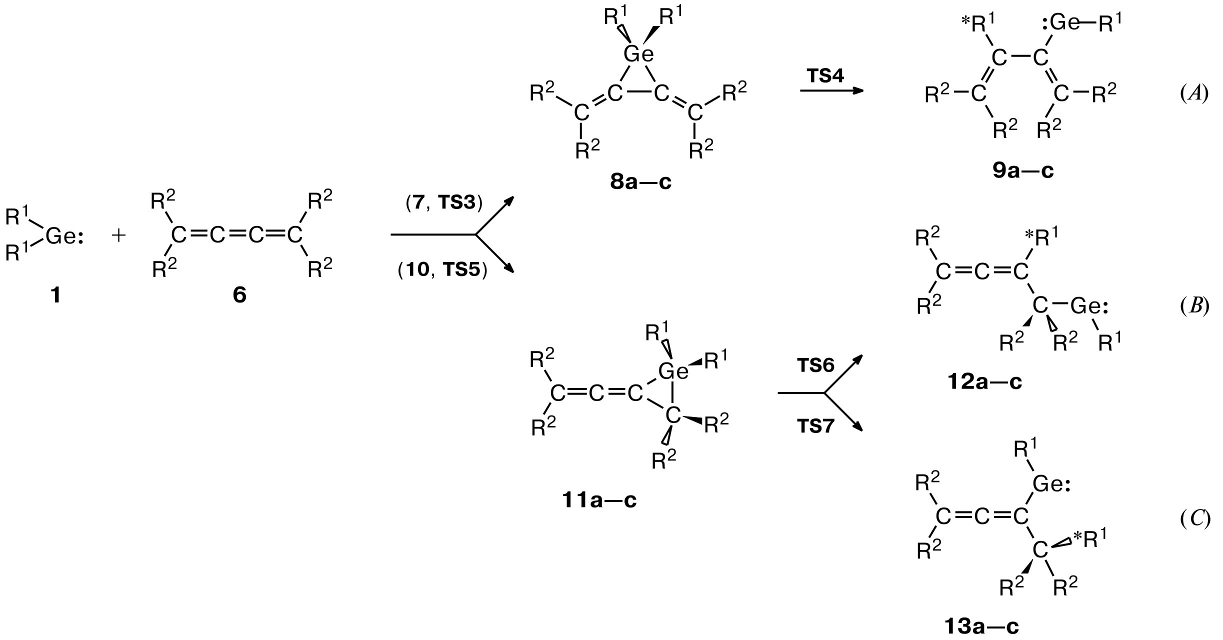
The first germirane stable under normal conditions is a three-membered ring with two methylene fragments. It was obtained[3] by cycloaddition of germylene $Ge[C(SiMe_3)_2H]_2$ to the central C=C bond of the TMBT molecule.



No product of alternative cycloaddition of germylene to a terminal C=C bond was revealed. We calculated the PESs of the formation and decomposition reactions of the model germiranes **8** and **11** (Scheme 2; $R^1$ = H, $R^2$ = H, Me and $R^1 = R^2$ = Me). In order to simplify the scheme, the $\pi$-complexes **7** and **10** and the corresponding transition states **TS3** and **TS5** are not shown.

The cycloaddition of germylene to the central C=C bond of molecule **6** resulting in germirane **8** followed by the opening of the germirane ring with the formation of the secondary germylene **9** (see Scheme 2, route *A*) can be

**Scheme 2**



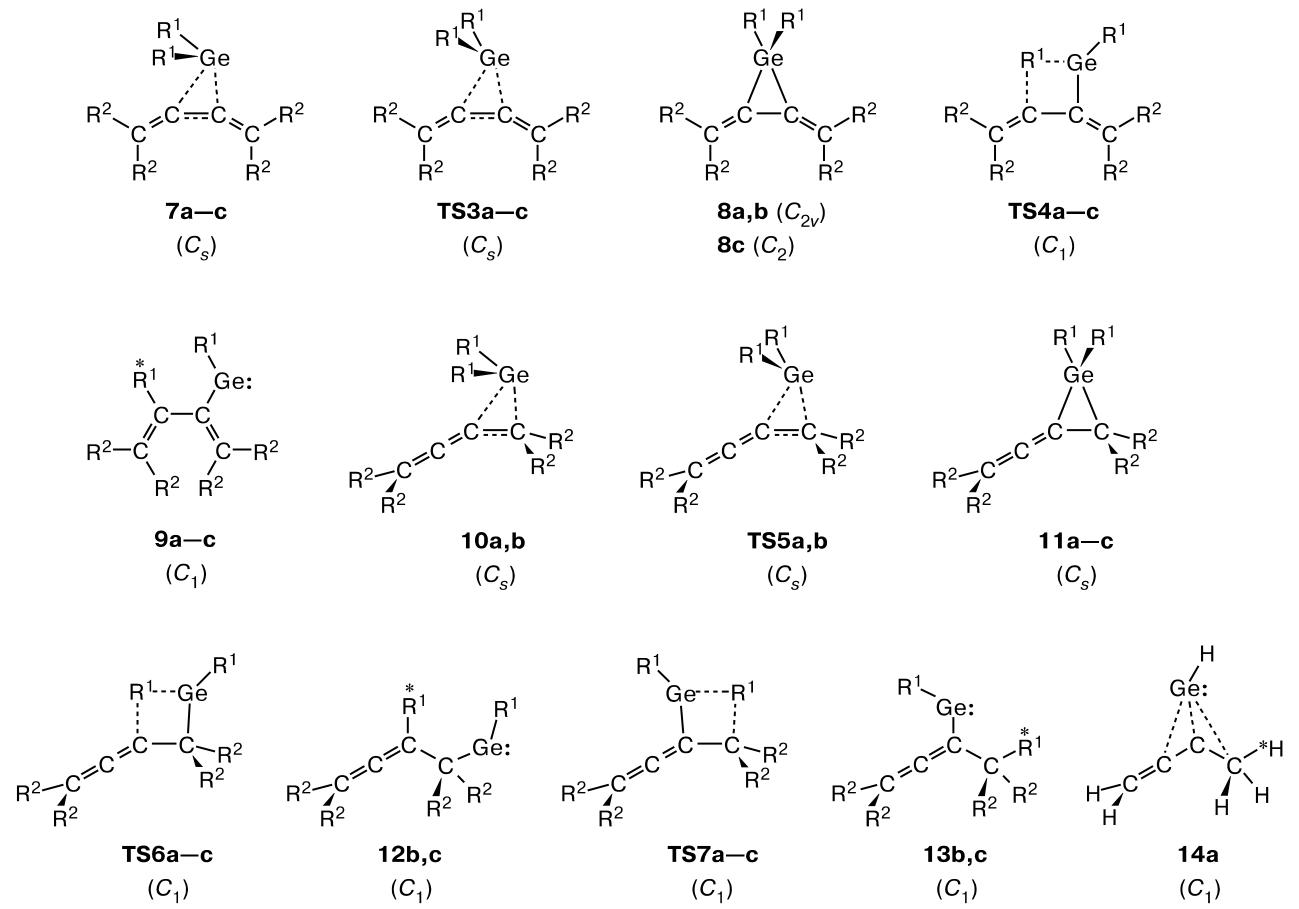
$R^1 = R^2 = H$ (**a**), Me (**c**); $R^1 = Me$, $R^2 = H$ (**b**)

treated as a reaction of germylene with symmetrically substituted olefin (both substituents are methylene groups). Route *A* is characterized by the same set of stationary points as the reactions between germylenes and symmetrically substituted ethylenes (see above, system **1**+**2**). Yet another route involving cycloaddition of germylene to a terminal bond of molecule **6** can be considered as a reaction of germylene with non-symmetrically substituted C=C bond (one substituent, $=C=CR_2$ group). In this case, two possible sets of nonequivalent π-complexes **10** and corresponding transition states **TS5** with different orientations of the Ge—R bonds in the germylene molecule and the $=C=CR_2$ substituent can lead to the same germirane **11**. Asymmetry also manifests itself in the ring opening in molecule **11**, being the reason for the formation of two different secondary germylenes **12** and **13** following routes *B* and *C*, respectively (see Scheme 2). Both nonequivalent orientations of the germylene were considered in studying routes *B* and *C* on the PESs. We studied the PESs of all the **1**+**6** systems and located minima corresponding to the germiranes **8** and **11**, the modified germylenes **9**, **12**, and **13** (except for **12a**, see below) and the saddle points corresponding to the transition states **TS4**, **TS6**, and **TS7** (Fig. 2). The stationary points corresponding to the π-complexes **7** and transition states **TS3** of the reactions of cycloaddition to the central C=C bond of buta-1,2,3-triene **6** (see Scheme 2, route *A*) were located only for two systems ($R^1 = R^2 = H$ and $R^1 = Me$, $R^2 = H$). The absence of corresponding stationary points on the PES of the third system ($R^1 = R^2 = Me$) means that the cycloaddition of dimethylgermylene to the central bond of the TMBT molecule is a single-step process, which proceeds without a barrier similarly to the reaction with ethylene.

Cycloaddition of germylenes to the terminal C=C bonds of molecule **6** (see Scheme 2, routes *B* and *C*) proceeds barrierlessly if the Ge—R bonds in the germylene molecule are oriented away from the $=C=CR_2$ substituent. Otherwise, the reactions involve π-complexes **10a,b** and transition states **TS5a,b** (see Fig. 2).

Structures **7**—**13** corresponding to minima on the PES and the structures of the transition states **TS3**—**TS7** of the reactions of germylenes with BT and TMBT have much in common with the corresponding structures that are formed in the reactions of germylenes with ethylene and TME (see Fig. 1). Here we will consider only the characteristic distinctions between the parameters of the structures corresponding to the stationary points of the **1**+**2** and **1**+**6** systems in the vicinity of the reaction centers. The C—C bonds in symmetrical 2,3-dimethylenegermiranes **8a**—**c** are 0.06—0.12 Å shorter than in the nonsymmetrical isomeric 2-vinylidenegermiranes **11a**—**c** or in the simple germiranes **4a**—**d**. This is likely due to conjugation of the double bonds, which are not aligned. As a consequence, germiranes **8a**—**c** have a somewhat lower symmetry ($C_2$) compared to the germiranes **4a**—**d** considered above ($C_{2v}$). One can expect that conjugation will cause an additional stabilization of structures **8a**—**c**.

Our study of the $GeH_2$+BT system revealed no stationary point corresponding to the secondary germylene **12a**.



$R^1 = R^2 = H$ (**a**), Me (**c**); $R^1$ = Me, $R^2$ = H (**b**)

**Fig. 2.** Structures **7**—**13** corresponding to the energy minima and transition states **TS3**—**TS7** obtained from PBE/TZ2P calculations. The migrating group is asterisked.

Energy minimization for **12a** led to intramolecular π-complex **14a** with the central double bond (see Fig. 2).

The number and character of substituents in germirane **8c** makes this compound the best approximation to the experimentally obtained stable bis(alkylidene)germirane.[3] The calculated geometric parameters of species **8c** are in good agreement with the X-ray analysis data (Table 3).

Addition of germylenes to the central C=C bonds of the BT and TMBT molecules is energetically much more favorable than their addition to ethylene and TME (Table 4). The addition to a terminal C=C bond may appear to be both more and less favorable; however, in all cases cycloaddition is thermodynamically favorable ($\Delta G°_{298} < 0$). The activation barriers **TS3** and **TS5** are at most 2 kcal mol$^{-1}$; they were not located at all for the $GeMe_2$+TMBT system. According to the calculations (see Table 4), the activation barriers to the ring opening in germiranes **8** and **11** and formation of the secondary germylenes **9**, **12**, and **13** (*via* **TS4**, **TS6**, and **TS7**, respectively) lie between 9.6 kcal mol$^{-1}$ for the unsubstituted system ($R^1$, $R^2$ = H) and 38.2 kcal mol$^{-1}$ for the fully substituted system **8c** ($R^1$, $R^2$ = Me). The last-mentioned system is most structurally similar to the real system[3] ($R^1 = SiHMe_2$, $R^2$ = Me) and, according to calculations, it is this system that exhibits the highest stability to isomerization into the secondary germylene **9c**. Taking into account that in a real system the ring opening in germirane requires a 1,2-migration of the $SiHMe_2$ group, which is bulkier than the Me group, one can expect that the activation barrier will be even higher. Isomeric non-symmetrical germirane **11c** ($R^1$, $R^2$ = Me) is characterized by nearly the same stability to ring opening as its symmetrical isomer **8c**; however, the former was not detected in the experiments. A possible explanation is provided by the results of the free energy calculations, according to which $\Delta G°_{298}$ (**11c**) = –3.1 kcal mol$^{-1}$ and the reaction resulting in **11c** should be reversible. At the same time the addition to the central C=C bond is characterized by a $\Delta G°_{298}$ gain of 9.8 kcal mol$^{-1}$ (see Table 4), *i.e.*, the reaction is irreversible under normal conditions. Thus, in the equilibrium the reaction will result in symmetrical germirane **8c**

**Table 3.** Selected geometric parameters (bond lengths (*d*) and angles (τ and α)) of the structures corresponding to the stationary points on the PESs of the reactions of $GeR_2$ with buta-1,2,3-trienes BT and TMBT[a]

| System | Structure | *d*/Å | | | | | τ/deg | α/deg |
|---|---|---|---|---|---|---|---|---|
| | | C(1)—C(2) | Ge—C(1) | Ge—C(2) | Ge—$R^1$ | C(2)—$R^1$ | $R^1$—C—C—Ge | |
| $GeH_2$+BT | **7a** | 1.34 | 2.07 | 2.36 | — | — | — | 14.6 |
| | **TS3a** | 1.36 | 2.03 | 2.24 | — | — | — | 23.8 |
| | **8a** | 1.45 | 1.96 | 1.96 | 1.54 | — | — | 90.0 |
| | **TS4a** | 1.36 | 2.07 | — | 1.62 | 1.86 | 18 | — |
| | **9a** | 1.47 | 2.00 | — | 3.26 | 1.09 | −39 | — |
| | **10a** | 1.39 | 2.10 | 2.42 | — | — | — | 16.4 |
| | **TS5a** | 1.43 | 2.01 | 2.15 | — | — | — | 36.2 |
| | **11a** | 1.51 | 1.98 | 1.95 | 1.53 | — | — | 90.0 |
| | **TS6a** | 1.41 | 2.11 | — | 1.65 | 1.69 | 20 | — |
| | **TS7a** | 1.41 | — | 2.10 | 1.63 | 1.84 | 16 | — |
| | **13a** | 1.52 | — | 2.00 | 3.37 | 1.10 | 59 | — |
| $GeMe_2$+BT | **7b** | 1.34 | 2.09 | 2.47 | — | — | — | 29.2 |
| | **TS3b** | 1.34 | 2.07 | 2.41 | — | — | — | 29.1 |
| | **8b** | 1.46 | 1.96 | 1.96 | 1.97 | — | — | 90.0 |
| | **TS4b** | 1.38 | 2.02 | — | 2.17 | 3.14 | −14 | — |
| | **9b** | 1.48 | 2.02 | — | 3.75 | 1.51 | 72 | — |
| | **10b** | 1.40 | 2.09 | 2.43 | — | — | — | 30.4 |
| | **TS5b** | 1.42 | 2.03 | 2.20 | — | — | — | 39.1 |
| | **11b** | 1.52 | 1.95 | 1.98 | 1.94 | — | — | 90.0 |
| | **TS6b** | 1.43 | 2.02 | — | 2.28 | 2.17 | 14 | — |
| | **12b** | 1.50 | 2.05 | — | 3.76 | 1.51 | 79 | — |
| | **TS7b** | 1.44 | — | 2.04 | 2.33 | 2.12 | 23 | — |
| | **13b** | 1.52 | — | 2.01 | 3.88 | 1.54 | 83 | — |
| $GeMe_2$+TMBT | **8c**[b] | 1.45 | 1.96 | 1.96 | 1.97 | — | — | 90.0 |
| | | (1.46) | (1.95) | (1.96) | (1.95) | | | |
| | **TS4c** | 1.38 | 2.05 | — | 2.28 | 2.15 | 40 | — |
| | **9c** | 1.49 | 2.01 | — | 3.75 | 1.51 | 85 | — |
| | **10c** | 1.39 | 2.15 | 2.47 | — | — | — | 28.4 |
| | **TS5c** | 1.43 | 2.06 | 2.18 | — | — | — | 38.6 |
| | **11c** | 1.53 | 2.00 | 1.95 | 1.97 | — | — | 90.0 |
| | **TS6c** | 1.45 | 2.03 | — | 2.24 | 2.18 | 4 | — |
| | **12c** | 1.54 | 2.02 | — | 3.43 | 1.54 | 60 | — |
| | **TS7c** | 1.45 | — | 2.03 | 2.29 | 2.17 | 3 | — |
| | **13c** | 1.54 | — | 2.02 | 3.41 | 1.54 | 59 | — |

[a] The numbering of structures is shown in Fig. 2.

[b] X-Ray analysis data for the stable germirane[3] are given in parentheses.

as exclusive product, which is in excellent agreement with the experiment.[3]

Traditionally, stability of small rings is treated in terms of steric strain, which is usually estimated by comparing the energies of the small rings with the energies of certain "ideal" structures that are considered unstrained (*e.g.*, acyclic isomers formed from cyclic structures as a result of pre-selected isodesmic reactions). Steric strain thus determined is still widely used[17] as a characteristic of the stability of small rings. This concept implies that different rings are opened by the same mechanism and that the activation energy, $E_a$, of the limiting stage correlates with the heat of reaction, Δ*H*. The existence of several ring-opening pathways characterized by their own Δ*H* and $E_a$ values casts some doubt on the substantiation of pure thermodynamic criteria for stability evaluation.

The addition of germylene and dimethylgermylene to the C=C double bonds of substituted ethylene and buta-1,2,3-triene either occurs as a single-step process without a barrier or involves the formation of a π-complex (here, the activation barrier is lower than the sum of the reactant energies). A very low barrier to the rearrangement of the π-complex into germirane means that it has no effect on the reaction kinetics and moreover on the reaction products. The overall stability of germiranes is governed by their stabilities to two processes, namely, the retro-decomposition into the initial germylene and olefin and

**Table 4.** The total[a] ($E_0$) and relative[b] energies ($\Delta E_0$) and the Gibbs free energies[c] ($\Delta G°$) of structures corresponding to the stationary points on the PESs of the reactions of $GeH_2$ and $GeMe_2$ with BT and TMBT (obtained from PBE/TZ2P calculations)

| System[d] | Reaction pathway | π-Complexes (**7** or **10**) | Transition states (**TS3** or **TS5**) | Germiranes (**8** or **11**) | Transition states (**TS4**, **TS6**, **TS7**) | Secondary germylene (**9**, **12**, **13**) |
|---|---|---|---|---|---|---|
| | | | $-E_0$/a.u (0 K) | | | |
| $GeH_2$+BT | *A* | 2232.41257 | 2232.41251 | 2232.42406 | 2232.40868 | 2232.44928 |
| | *B* | 2232.42022[e] | 2232.41748[e] | 2232.42435 | 2232.41155 | 2232.46284[f] |
| | *C* | 2232.42022[e] | 2232.41748[e] | 2232.42435 | 2232.40767 | 2232.44671 |
| $GeMe_2$+BT | *A* | 2310.91381 | 2310.91366 | 2310.93465 | 2310.88103 | 2310.95284 |
| | *B* | 2310.92511[e] | 2310.92368[e] | 2310.93520 | 2310.87948 | 2310.93803 |
| | *C* | 2310.92511[e] | 2310.92368[e] | 2310.93520 | 2310.88029 | 2310.94508 |
| $GeMe_2$+TMBT | *A* | —[g] | —[g] | 2467.93103 | 2467.87011 | 2467.94058 |
| | *B* | 2467.91304[e] | 2467.91009[e] | 2467.91949 | 2467.86528 | 2467.91703 |
| | *C* | 2467.91304[e] | 2467.91009[e] | 2467.91949 | 2467.87046 | 2467.92848 |
| | | | $\Delta E_0$/kcal mol$^{-1}$ (0 K) | | | |
| $GeH_2$+BT | *A* | −17.2 | −17.1 | −24.4 | −14.8 | −40.3 |
| | *B* | −22.0[e] | −20.3[e] | −24.6 | −16.6 | −48.8 |
| | *C* | −22.0[e] | −20.3[e] | −24.6 | −14.1 | −38.6 |
| $GeMe_2$+BT | *A* | −10.0 | −9.9 | −23 | 10.6 | −34.4 |
| | *B* | −17.0[e] | −16.2[e] | −23.4 | 11.6 | −25.2 |
| | *C* | −17.0[e] | −16.2[e] | −23.4 | 11.1 | −29.6 |
| $GeMe_2$+TMBT | *A* | —[g] | —[g] | −23 | 15.2 | −29 |
| | *B* | −11.7[e] | −9.9[e] | −15.8 | 18.3 | −14.2 |
| | *C* | −11.7[e] | −9.9[e] | −15.8 | 15.0 | −21.4 |
| | | | $\Delta G°$/kcal mol$^{-1}$ | | | |
| $GeH_2$+BT | *A* | −6.9 | | −13.8 | | −29.9 |
| | *B* | −11.6[e] | | −13.9 | | −37.4 |
| | *C* | −11.6[e] | | −13.9 | | −28.9 |
| $GeMe_2$+BT | *A* | 1.4 | | −10.2 | | −22.5 |
| | *B* | −5.1[e] | | −11.6 | | −13.7 |
| | *C* | −5.1[e] | | −11.6 | | −18.0 |
| $GeMe_2$+TMBT | *A* | —[g] | | −9.8 | | −16.3 |
| | *B* | 1.3[e] | | −3.1 | | −1.2 |
| | *C* | 1.3[e] | | −3.1 | | −8.6 |

*Note.* The numbering of structures is shown in Scheme 2 and Fig. 2.

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

[b] Relative to isolated reactants.

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

[d] The $E_0$ energies of buta-1,2,3-trienes are as follows: −154.52280 ($H_2CCCCH_2$) and −311.51923 ($Me_2CCCCMe_2$) a.u.

[e] Possible reaction pathway (see text).

[f] Intramolecular π-complex **14a** (see text).

[g] No stationary point was located.

the opening of the three-membered ring with simultaneous 1,2-migration of the substituent at the Ge atom to give the modified germylene. Alkyl groups at the Ge atom can efficiently block the opening of the three-membered ring and the formation of the secondary germylene; however, in this case the stability of the germirane to retro-decomposition decreases. Taking the experimentally isolated germirane as an example, it was shown how the introduction of substituents and modification of the carbon skeleton make it possible to stabilize the germacyclopropane system.

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