Silylene and Germylene Additions to 1,3-Diynes: Bis(silacyclopropenes) versus Germaethenes Formation, a DFT Study

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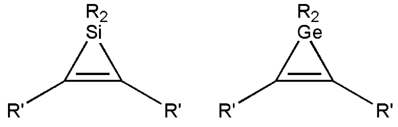
The addition of silylenes and germylenes to triple-bond systems has been investigated with density functional theory methods. The experimentally observed formation of bis(silacyclopropenes) upon reaction of silylenes with 1,3-diynes is explained in terms of their much higher thermodynamic stability compared to the alternative acetylene-linked bis(silaethenes). For the germanium counterparts, the energetic difference is calculated to be much smaller and is reversed for the addition to 1,3-diacetylene in the case of very bulky germylenes (Ge(2-*t*-Bu-Ph)$_2$). Silylenes add to triple bonds in a concerted reaction; no intermediate π complex nor transition state has been located, which is also true for most germylenes. Again, only for sterically demanding germylenes could these stationary points be found with a barrier between intermediate and TS of 1.7 kJ/mol. Generally, the additions of silylenes and germylenes to triple-bond systems take place in an electrophilic manner and appear to have the same mechanism.

Introduction

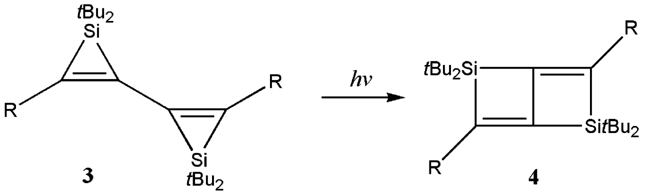
Silacyclopropenes (silirenes) **1**$^{1-10}$ and germacyclopropenes (germirenes) **2**$^{11-16}$ are well-known and well-characterized molecules that are mainly formed via cycloaddition reactions of sterically demanding silylenes R$_2$Si: or germylenes R$_2$Ge: with the triple bonds of acetylenes.

Chart 1



1 **2**

Chart 2



Conjugated di- and tetraynes react with di-*tert*-butylsilylene, which is generated photochemically from hexa-*tert*-butylcyclotrisilane,[17] also in a cycloaddition to the triple bond to give C−C-linked bis(silirenes) **3**[9] and quatersilirenes,[18] which, although thermally stable, rearrange to 2,5-disilabicyclohexadienes **4** under photochemical conditions.[9,18,19]

However, reaction of the diarylgermylene **5**, which is formed in solution from an appropriately substituted

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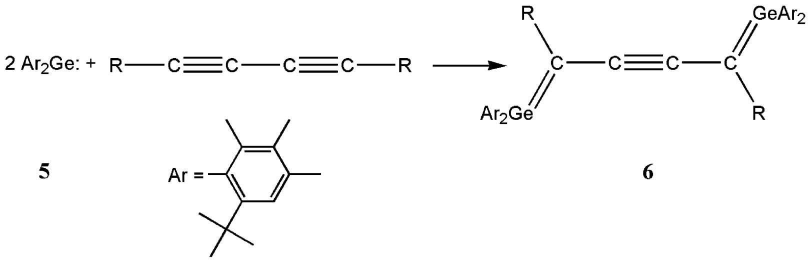
Chart 3



5 **6**

digermene,[20] with 1,3-diynes does not result in the expected bis(germirenes) but yields acetylene-linked bis(germaethenes) **6**, which contain conjugated Ge═C double bonds.[21,22]

There has been substantial theoretical interest in silylenes and germylenes, in particular in their electronic structures and their reactions. Several groups have investigated stable carbenes and related molecules including Arduengo carbenes and found a strong π-donor stabilization of the carbene (analogue) p_π orbital by the nitrogen lone pairs highly important.[23−27] Further studies deal with the singlet−triplet splitting in substituted carbene analogues, which exist exclusively as singlets.[28−30] Among the most important reactions theoretically studied are dimerization[31] and addition to systems with unsaturated bonds, in particular to ethylene.[32] Addition reactions are usually exothermic, more so for silylenes than for germylenes, which is attributed to the weaker Ge−C bonds in the cyclic products.[33] Also, the additions to double bonds proceed without activation barrier for silylenes and GeH_2.[34−36] Another difference between silylenes and germylenes is the existence of π complexes and subsequent transition states between the Ge analogues and the unsaturated bond systems.[37,38] The number of publications dealing with the addition of metallylenes to acetylene is more limited. Trends in reactivity are comparable, although additions to acetylenes are more exothermic and usually have lower activation barriers.[39,40]

Motivated by the experimentally observed different behavior of silylenes and germylenes and the lack of studies on the addition to (di)acetylenes we report in this paper a quantum chemical density functional theory study on the different addition behavior of dialkylsilylenes and diarylgermylenes to diynes. Substituent effects are investigated, and mechanistic details are discussed.

Computational Details

All structures were optimized with the hybrid functional B3LYP[41−43] and the 6-31G(d) basis set[44,45] employing the Gaussian 98 program package.[46] Frequency calculations of all obtained structures then gave zero-point vibrational energies and the number of imaginary frequencies.[47] The importance of diffuse functions[48,49] is taken into account;[50] energies were evaluated at the B3LYP/6-31+G(d) level of theory employing the above-mentioned geometries. Relative energies are determined using accordingly scaled zero-point vibrational energies.[51] CCSD(T)/6-311G(d) optimizations for several systems confirm the reliability of the DFT results, which are very close to these high-level calculations. The recently developed version of the 6-31G(d) basis set for third-row atoms[52] has been evaluated, but since it does not improve the reproduction of relevant systems, it has not been used herein.

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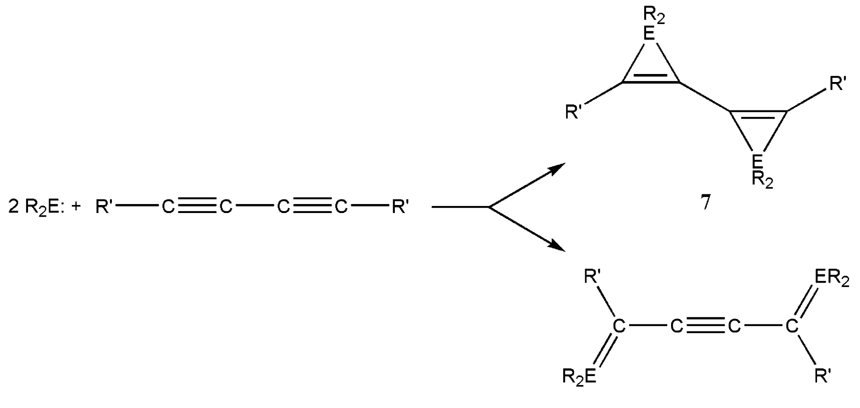
Chart 4



7

8

Natural population analysis (NPA) has been carried out with the NBO package[53,54] within Gaussian 98.

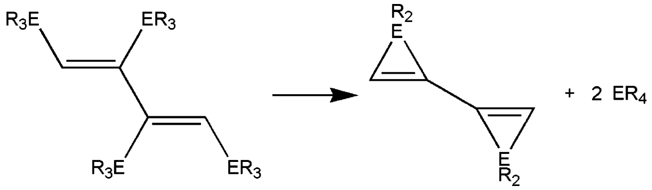
Results and Discussion

The above-mentioned experimental data suggest that the addition of metallylenes to conjugated triple bonds may proceed via different pathways, depending on the central atom of the carbene analogue. While silylenes add to diynes in the expected manner, i.e., formation of C−C-linked bis(silirenes) **7** (E = Si), the reaction with germylenes leads to the acetylene-linked bis(germaethenes) **8** (E = Ge). To investigate this behavior in more detail, we have performed calculations on the reaction shown in the generalized scheme below. Both products i.e., the structure **7** and the bis(silaethenes) and bis(germaethenes) **8** for both metallylenes have been optimized for a number of substituents R and R′. The carbene analogues have been calculated in their singlet states after verifying these as electronic ground states.

The first important finding is the fact that the additions are thermodynamically favorable. The reaction is significantly exothermic (250−400 kJ/mol) in all cases, not surprisingly considering the labile nature of the carbene analogue as reactant, but in contrast to the addition to acetylene, which is only slightly exothermic.[40] Furthermore, the preferred products are in most cases the C−C-linked bis(silirenes) and bis(germirenes). The former are thermodynamically clearly favored over the bis(silaethenes) by at least 30, usually 75−80 kJ/mol. In contrast, the energetic difference between the two germanium products is significantly smaller but still with a slight preference for bis(germirenes) (Tables 3 and 4). The different behavior can be explained mostly in terms of ring strain, which is significantly larger in the bis(germirenes) than in the bis(silirenes). Using the isodesmic reaction in Scheme 1, ring strain is calculated to be 100 kJ/mol lower in the cyclic Si compound.

Tables 1 and 2 contain selected geometrical data on the sterically least (R = R′ = H) and most (R = 2-*t*-Bu-Ph, R′ = Me) crowded representatives of **7** and **8**. Inspection of these data however reveals no additional information with respect to ring strain.

Scheme 1. Isodesmic Equation Used To Calculate the Ring Strain Differences in Bis(silirenes) (E = Si) and Bis(germirenes) (E = Ge)



Third, the influence of the substitution R′ at the diynes on the relative stabilities of the two possible products has been investigated. As shown in Table 3, terminal alkyl and aryl groups on 1,3-diynes have no significant influence, and the difference between **7** and **8** is in all cases around 80 (18) kJ/mol for E = Si (Ge) in favor of the product of type **7**. However, hydrogen atom substitution lowers this gap by 35 kJ/mol, so that the bis(germaethenes) **8** now become the preferred products. From a synthetical point of view, the use of diacetylene is not recommended, as it forms explosive mixtures with air. The observed preference of **8** compared to **7** can be explained in terms of steric hindrance. It can easily be seen that the substituents R and R′ are much closer in the bisethenes **8** than they are in **7**. Therefore a small group R′ will favor the open structure, whereas bulky substituents such as *t*-Bu significantly increase the preference of the dicyclic **7**. The only minor exception exists for the addition of SiH_2 to di-*tert*-butyldiacetylene: in **7**, the plane of the two three-membered rings is strongly twisted, destabilizing it.

In the following section, we have studied the dependency of the reaction of dimethyldiacetylene with different metallylenes. Table 4 contains data on the effect of different carbene analogues on the product stability. It can be seen that small- and medium-sized groups R do not significantly alter the energetic ordering of **7** and **8**. The bis(silirenes) are still the preferred products with an advantage of 80 kJ/mol. Again, the difference between bis(germirenes) and bis(germaethenes) is much smaller, the latter being less stable by 30 kJ/mol. Only the sterically demanding 2-*tert*-butylphenyl group as a model for the experimentally employed 2-*tert*-butyl-4,5,6-trimethylphenyl substituent shows a pronounced effect of lowering **8** relative to **7** by 40 kJ/mol, consequently rendering the bis(germaethene) the more stable structure. Inspection of these structures reveals steri-

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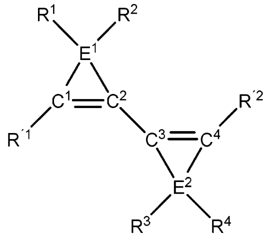
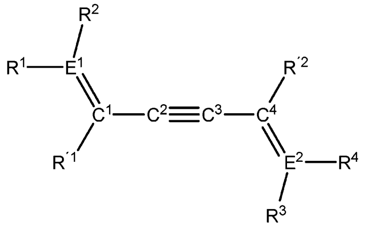
Table 1. Selected Structural Information for Two B3LYP/6-31G(d)-Optimized Bis(silirenes) and Bis(germirenes) 7



	E = Si R = H, R′ = H	E = Ge R = H, R′ = H	E = Si R = 2-*t*-Bu-Ph, R′ = Me	E = Ge R = 2-*t*-Bu-Ph, R′ = Me
		Bond Lengths (Å)		
R^1-E^1	1.485	1.539	1.918	1.973
E^1-C^1	1.824	1.912	1.827	1.914
E^1-C^2	1.838	1.925	1.851	1.937
C^1-C^2	1.342	1.335	1.352	1.345
C^2-C^3	1.443	1.430	1.453	1.434
		Bond Angles (deg)		
$R'^1-C^1-C^2$	135.2	135.3	139.0	136.5
$E^1-C^1-C^2$	69.1	70.2	69.4	70.5
$E^1-C^2-C^1$	67.9	69.1	67.5	68.6
$C^1-E^1-C^2$	43.0	40.7	43.1	40.9
$R^1-E^1-R^2$	111.1	114.7	110.2	110.9
$C^1-C^2-C^3$	137.6	138.5	138.2	140.0
		Dihedral Angles (deg)		
$E^1-C^2-C^3-E^2$	−179.4	179.9	179.5	152.1
$R^1-E^1-C^2-C^3$	76.6	78.6	81.9	99.5
$R^1-E^1-C^1-C^2$	104.7	103.7	115.6	121.5

Table 2. Selected Structural Information for Two B3LYP/6-31G(d)-Optimized Bis(silaethenes) and Bis(germaethenes) 8



	E = Si R=H, R′ = H	E = Ge R=H, R′ = H	E = Si R = 2-*t*-Bu-Ph, R′ = Me	E = Ge R = 2-*t*-Bu-Ph, R′ = Me
		Bond Lengths (Å)		
R^1-E^1	1.477	1.529	1.894	1.949
E^1-C^1	1.741	1.806	1.754	1.813
C^1-C^2	1.395	1.385	1.404	1.394
C^2-C^3	1.229	1.230	1.229	1.231
		Bond Angles (deg)		
$R^1-E^1-R^2$	117.0	117.1	125.8	129.4
$E^1-C^1-C^2$	126.8	125.5	120.9	118.9
$R'^1-C^1-C^2$	116.8	117.9	116.1	117.3
$C^1-C^2-C^3$	179.5	173.9	178.0	174.9
		Dihedral Angle (deg)		
E^1-$C^1-C^4-E^2$	180.0	−179.7	−179.8	179.8

cally crowded bis(silirenes) and bis(germirenes) due to the much shorter Si−Si and Ge−Ge distances (5.06 and 5.18 Å) compared to those in bis(silaethene) and bis(germaethene) (6.59 and 6.64 Å).

These findings are in agreement with the experiments, since all attempts with photochemically generated silylenes form the dicyclic bis(silirenes); no bis(silaethenes) have been observed.[9] Furthermore, the reaction of bis(2-*tert*-butyl-4,5,6-trimethylphenyl)germylene with alkyl- and aryl-1,3-diynes gives C−C-linked bis(germaethenes),[21,22] which is in accordance with our calculations, where only crowded germylenes lead to **8**.

An attempt has been made to combine the two sila- and germaethene-favoring factors in order to reduce the energy difference between the preferred bis(silirene) **7** and the bis(silaethene) **8**: the addition of the sterically demanding bis(2-*tert*-butylphenyl)silylene to the parent diacetylene (R′ = H). The smallest gap so far for the reaction of silylene and diacetylene is 27 kJ/mol (Table 3), so that the introduction of the 2-*t*-Bu-Ph group into the silylene should give an almost energy neutral situation. However, the resulting bis(2-*tert*-butylphenyl)silirene is still preferred by 13 kJ/mol over the corresponding bis(silaethene).

Table 3. Relative Energies (kJ/mol) of 7 and 8 for Different Groups R′ (B3LYP/6-31+G(d)//B3LYP/6-31G(d))

	R′ =													
	H		Me		Et		*n*-Bu		Ph		*t*-Bu		H^a	
ER_2	**7**	**8**	**7**	**8**	**7**	**8**	**7**	**8**	**7**	**8**	**7**	**8**	**7**	**8**
SiH_2	0	27.1	0	70.0	0	74.2	0	74.9	0	84.9	0	73.6	0	44.3
$SiMe_2$	0	36.9	0	83.2	0	76.2	0	75.6	0	93.7	0	113.0		
GeH_2	0	**−14.1**	0	20.0	0	14.7	0	5.1	0	20.9	0	24.9	0	**−26.3**
$GeMe_2$	0	**−17.4**	0	21.4	0	15.8	0	10.6	0	33.5	0	44.2		

^{a} CCSD(T)/6-311G(d)//CCSD(T)/6-311G(d).

Table 4. Relative Energies (kJ/mol) of 7 and 8 for Addition of Silylenes and Germylenes ER_2 to Dimethyldiacetylene (R′ = Me) (B3LYP/6-31+G(d)//B3LYP/6-31G(d))

	R =							
	H		Me		Ph		2-*t*-Bu-Ph	
ER_2	**7**	**8**	**7**	**8**	**7**	**8**	**7**	**8**
SiR_2	0	70.0	0	83.2	0	80.4	0	39.9
GeR_2	0	20.0	0	21.4	0	50.6	0	**−24.9**

The rearrangement of **3** to 2,5-disilabicyclohexadienes **4** under photolytical conditions can be explained in terms of thermodynamical stability.[9,18,19] The model compound 1,4-dimethyl-2,5-disilabicyclohexadiene (R = H, R′ = Me) is calculated to be more stable than the corresponding bis(silirene) **7** by 87 kJ/mol. This difference is even more pronounced in the case of the hypothetical germanium counterpart, which is stabilized by 136 kJ/mol compared to the bis(germirene).

Mechanism. From a mechanistic point of view, the addition of different carbene analogues to unsaturated bonds does not differ as much as one may expect when considering the experimental outcome of the reactions. It is know from both experimental[55−59] and theoretical studies[39,40] that silylenes bearing hydrogen atoms or alkyl groups add to ethylene and acetylene in a concerted mechanism with no activation barrier. This is consistent with our calculations: we find neither a transition state for the addition nor an intermediate π complex between the silylenes and the π bonds of 1,3-diynes. Taking into account the high exothermicities (ca. 400 kJ/mol) of the silylene additions, this result is in accordance with the Hammond postulate.

As mentioned above, the reactions of germylenes with diacetylenes are significantly less exothermic (ca. 250 kJ/mol). It is also known that germylenes are slightly less reactive than their silicon counterparts and can form π complexes with the double bond in ethylene more readily.[37,38] However, model complexes between acetylene and different germylenes GeR_2 are not found for R = H or Me. Only when the central germanium atom bears 2-*tert*-butylphenyl groups can a π complex be located (Figure 1), which is 0.3 kJ/mol lower in energy than the separate reactants. The most important distances are the two Ge−C bonds at 2.427 and 2.738 Å. Both contacts are about 0.3 Å longer than those in the system GeH_2−ethylene,[34] not surprising considering the sterically demanding groups on Ge, but 0.7 Å shorter than those reported for $Ge(CH_3)_2$−ethylene.[37] Bond angles are very similar.

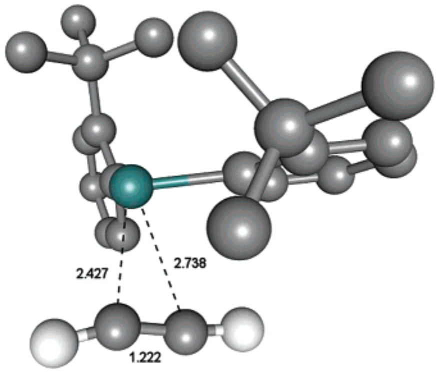


Figure 1. B3LYP/6-31G(d)-optimized π complex between bis(*tert*-butylphenyl)germylene (hydrogen atoms omitted) and acetylene, Ge−C and C−C distances in Å. The Ge−C−C angles are 91.1° and 62.4°; the C−Ge−C angle is 26.5°.

This is a significant difference between the (theoretical) addition to ethylene and acetylene. In the present study, bulky groups are needed for the formation of π adducts, indicating a very shallow minimum for this intermediate. Introducing constraints to the Ge−C−C angle of a potential complex, intermediate structures can be optimized for R = H and Me, but they collapse into the corresponding germirenes when removing the constraint. The same is true for intermediate π complexes between silylenes and acetylene, which can be located when restricting a Si−C−C angle but form silirenes upon free optimization.

The subsequent transition state connecting the intermediate with the germirene is shown in Figure 2. Its energy lies only 1.7 kJ/mol above the intermediate. This small activation barrier is consistent with a flat potential energy surface and the difficulties in locating π complexes and transition states for systems with sterically less demanding substituents. The two Ge−C contacts at 2.083 and 2.382 Å confirm the asynchronous nature of the addition. These values are very similar to those for $Ge(CH_3)_2$−ethylene and only about 0.1 Å longer than the bonds in the transition state of the small GeH_2−ethylene system. The larger Ge−C−C angle is close to 90°, compared to 76° in the latter system, further indicating an asynchronous pathway.

In principle, the above-mentioned complexes between silylenes/germylenes and multiple-bond systems can have different electronic structures. Since a singlet carbene (and its higher counterparts) can act inherently as both an electrophile and a nucleophile, two different orbital interactions are possible (Scheme 2): the interaction between the lone pair of the carbene (analogue)

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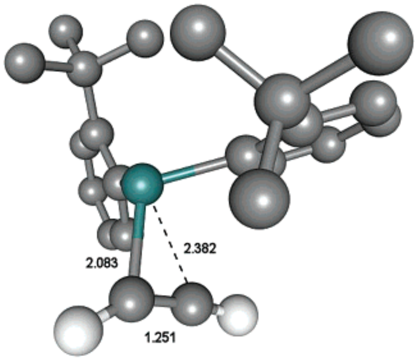
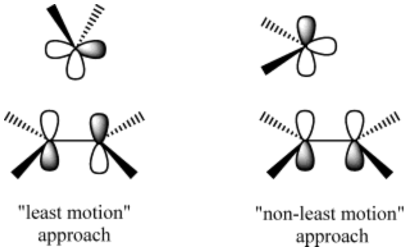


Figure 2. B3LYP/6-31G(d)-optimized transition state between bis(*tert*-butylphenyl)germylene (hydrogen atoms omitted) and acetylene, Ge−C and C−C distances in Å. The Ge−C−C angles are 87.5° and 60.9°; the C−Ge−C angle is 31.6°.

Scheme 2. Simplified Orbital Interaction Schemes for the Orbital Symmetry-Forbidden "Least Motion" (or σ-) and the Allowed "Non-Least Motion" (or π-) Approaches of a Carbene (analogue) to a π System



(HOMO) and an empty π* orbital (LUMO) of the ethylene or acetylene, which corresponds to the orbital symmetry "forbidden" "least motion" approach, and the interaction of a filled π orbital of the multiple-bond system (HOMO) and the vacant p orbital (LUMO) of the carbene (analogue). The latter can be described as a "non-least motion" approach. Both the geometries of the formed precursor and transition state complexes (Figures 1 and 2) and population analysis confirm this electrophilic behavior of the germylenes and the silylenes (in the constraint intermediates). The NPA analyses however show a net transfer of electron density from the carbene homologues to the acetylene in the intermediate structures, not surprising when taking into account the electropositive character of Si and Ge. This is even more pronounced in the transition state. For comparison, in the corresponding intermediate π complex between CH_2 and acetylene, the expected charge transfer from the carbene is observed.

Despite the nonexisting Si precursor complex, the addition appears to have the same mechanism in both cases, since the approach of the carbene analogues takes place in an electrophilic manner, thereby passing through an orientation relative to the triple bond similar to an intermediate π structure (as in Figure 1). It cannot be ruled out that the formation of the acetylene-linked bisgermaethenes from **7** takes place via facile ring-opening of the bis(germirenes): Table 1 shows slightly longer Ge−C bonds to the central carbon atoms than those to the terminal C atoms, indicating easier breaking of the former bonds. However, as demonstrated above, the potential energy surface is very shallow and does not allow a definite conclusion of the mechanism. The whole process has only a very small activation barrier (or none in the case of the silylenes), and therefore the relative thermodynamic stabilities are decisive for the formation of the product. In most substituent combinations R/R′, the bis(silirenes) and bis(germirenes) are preferred; however, hydrogen atoms on the 1,3-diynes and/or large groups on the germanium atom reverse the order of stability and lead to acetylene-linked bisgermaethenes.

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Supporting Information Available: Calculated energies and Cartesian coordinates of all optimized geometries are available free of charge via the Internet at http://pubs.acs.org.

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