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Cyclotrimetallenes: Bridged and Distorted Structures

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The geometry and the energetic aspects of the stable isomers of trimetallenes (X_2YR_4: X, Y = Si, Ge) were investigated, and some exotic di- and monobridge structures were found. Many of the bridge structures were identified as stable intermediates or transition states during the two-step substituent migration reactions. The effect of bulky substituents on the stability and geometry of the monobridge structures was studied. The bulkier bridging substituents cause a larger deviation from the ideal bridge structure. SiH_3 and $Si(SiH_3)_3$ substituents confer a direct benefit on the bridge geometry, in spite of their bulkiness, via electronic effects. According to these results and considering the electronic effect of the $Si(SiC_nH_m)_3$-type substituents, there is hope to synthesize bridge silicon compounds with bulky substituents.

Introduction

In the last couple of years two important developments of the unsaturated silicon species occurred: the synthesis of cyclotrisilene and trisilaallene were reported in 1999[1] and in 2003.[2] The parent compounds of both structures correspond to two stable isomers of the same (Si_3R_4) potential surface.

Four stable allene derivatives, containing three heavy group 14 atoms, were reported: stannylene,[3] trisilaallene,[2] 1,3-digermasilaallene, and trigermaallene.[4] More recently some novel allenic anionic species consisting of two silicons and a gallium or indium atom were also isolated (1,3-disila-2-gallataallenic anion and 1,3-disila-2-indataallenic anion).[5] These compounds have some quite unusual features, such as the strongly bent allenic framework and pyramidal surrounding of the terminal heavy atoms. For example, the central silicon atom in trisilaallene, Si_β, cannot be described with a simple sp-hybrid state, because of the 136.49(6)° central bond angle.[6] A theoretical study showed that the stability of the synthesized trisilaallene is caused by electronic (electropositive, π-acceptor groups on the silicons) and kinetic effects.[7]

The synthesis of the first cyclotrimetallene, the thermally unstable and photosensitive cyclotrigermene derivative and its structural characterization with X-ray crystallography[8a,b] were reported by Sekiguchi et al. in 1995. More recently they also synthesized halogen-substituted cyclotrigermenes.[8c] They concluded that, depending on the electronegativity of the applied substituents, the geometry around the Ge=Ge bond changes from *cis*-bent to planar and then to *trans*-bent. A fascinating observation was the circumambulatory motion of the halogen over the three-membered-ring skeleton.

The structure of the air- and moisture-sensitive cyclotrisilene was determined by Kira and co-workers.[1a] The geometry around the Si=Si double bond was found to be *trans*-bent,[1b] while the only cyclotristannene synthesized so far has a planar environment around the Sn=Sn double bond.[3] One of the most important findings concerning the last step of the synthesis of the tin analogue was the discovery of the intermediately formed tristannaallene. However, it was thermally unstable and gradually rearranged to the isomeric cyclotristannane at room temperature.

The 1H-disilagermirene derivative and its photolysis product, the 3H-disilagermirene derivative, were also synthesized.[9] Interesting reactions of these compounds are the ring-expansion reactions.[10]

Synthesizing the aromatic cyclotrigermenylium ($R_3Ge_3^+$)[11] and cyclotrisilanylium ion ($R_3Si_3^+$)[12] was also feasible due to the substituent effects on the heavy ring atoms.

Studying the Si_3H_4 potential surface in detail, we found in our recent paper that the global minimum is neither cyclotrisilene nor trisilaallene but a strongly bent open-chain silylene.[13] Also, theoretical prediction suggests a stable three-membered ring with a divalent β heavy atom; however no experimental evidence is known about these two derivatives. Nonetheless, Wiberg suggested that the strongly bent stannylene structure consists of an active lone pair of electrons on the central Sn_β[3] (Scheme 1a). This assumption was supported by the ^{119}Sn and ^{29}Si NMR and the X-ray spectra ($\omega(Sn_\alpha - Sn_\beta - Sn_\gamma) = 156°$). Kira

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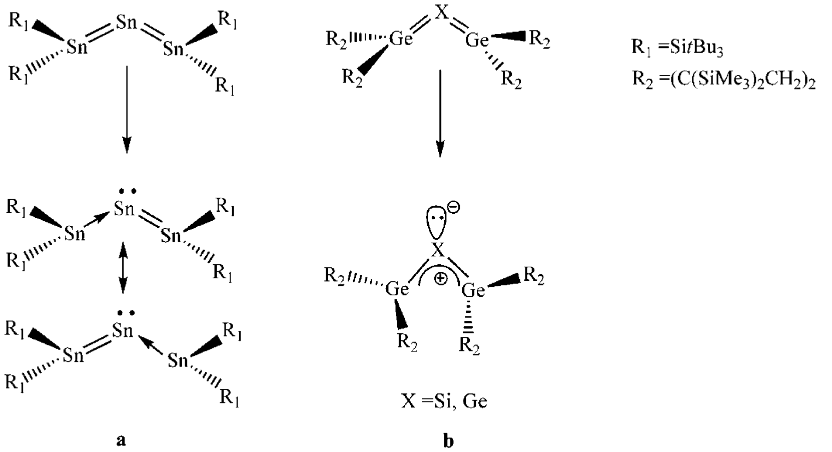
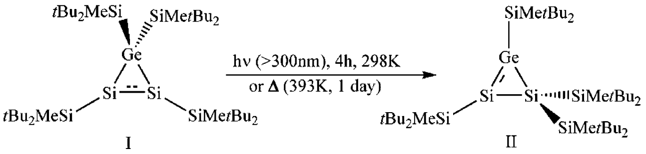
10.1021/om700267j CCC: $37.00

Scheme 1. Structure of Stannaallene (a) and a Trigermaallene and a 1,3-Digermasilaallene (b)



Scheme 2. Reaction Conditions of the α,*β*-Migration of a Di-*tert*-butyl-(methyl)silyl Group on the 1-Disilagermirene Ring



explained that the skeletons of trimetallenes are very flexible and able to deform from the most stable zwitterionic structure to the bent allenic structures to avoid steric strains between bulky alkyl substituents[4] (Scheme 1b).

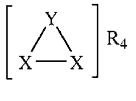
The stability of both cyclic and open-chain silylene structures can be enhanced by π-electron-donor substituents. Although the two different silylene isomers have a very similar geometry, a strict distinction can be made between them based on their geometrical and electronic properties and topological analysis.[13]

Studying the mechanism of α,β-migration reactions[14] of disilagermirenes (Scheme 2), siladigermirenes, cyclotrisilenes, and cyclotrigermenes, we found some low-energy bridge isomers containing three-membered-ring structures. The calculations suggest that the stability of these strange isomers is always comparable to the cyclotrisilene. The aim of this paper is to investigate the structure and stability of the mono- and dibridge isomers and their role in the isomerization reactions.

Hydrogen-bridged structures are well-known in the chemistry. The most well-known example is diborane,[15] but other dibridge structures were also found on the X_2H_6 PES (X = B, Al, Ga).[16] In 2003 Andrews et al. could detect the $H_2Al{-}\mu H_2{-}AlH_2$ dimer in a soft hydrogen matrix at 6.5 K.[17] A few months ago Bowen et al. proved the presence of Al_4H_6 in the cooling environment of a fast helium gas expansion.[18] The analysis of the X_2H_4 PES with group 13 elements[19] showed that in all the cases but boron the global minimum is found to be the dibridge structure.

One of the earlier papers in 1983 reports a nonplanar bridge structure in the singlet and a planar bridge structure in the triplet ground state in the system of Si_2H_2 based on ab initio quantum chemical calculations.[20] Since their discovery in 1991,[21] bridge structures containing group 14 elements became objects of intense research. The former calculations were revisited later with detailed discussion.[22] Further theoretical and experimental studies supported the existence of dibridge and monobridge isomers in the case of X_2H,[23] X_2H_2,[24] X_2H_4[25] (X = Si, Ge, Sn, Pb) and Si_2H_3[26] systems. In the beginning of the 1990s Trinquier discussed the bonding character of *trans*-bent doubly bonded and *trans*-bridge isomers in detail for X_2H_4 (X = Si, Ge, Sn, Pb).[25] More recently Frenking et al.[24] analyzed the bonding orbitals of the X_2H_2 (X = Si, Ge, Sn, Pb) systems and concluded that the stability of these structures is caused by the interactions between the SiH moieties in the electronic ground state.

Scheme 3. Different Structures Investigated in This Paper



A: X, Y = C
B: X, Y = Si
C: X = Si; Y = Ge
D: X = Ge; Y = Si
E: X, Y = Ge

In spite of the numerous publications about the mono-H-bridge and di-H-bridge structures, relatively few publications discuss bridge isomers of three-membered rings. One of them reported low-lying bridge isomers in the system of Si_3H_2 and $Si_3H_2^+$ and showed that the global minimum of the $Si_3H_2^-$ system is a mono-H-bridge structure.[27]

First in this paper we briefly discuss the geometry and the energetic aspects of the relevant structures. Next we study the transition structures and intermediates of the α,β-migration reactions, focusing on the importance and the role of the bridge structures. Finally we test the effect of substituents on the existence of bridge structures.

Results and Discussion

Geometry. Considering the possible stable isomers of trimetallenes listed in Scheme 3, one may encounter ring (**1**−**8**)

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Scheme 4. Possible Trimetallene Isomers (X, Y = Si, Ge; R = H, SiH_3)[3]

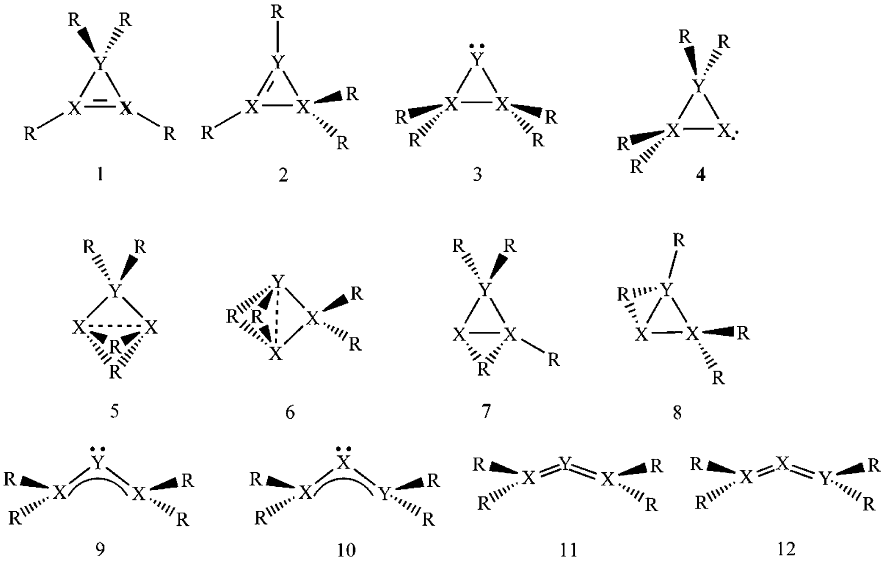

Table 1. Selected Calculated and *Experimental* Geometrical Data of Different X_2YR_4 (X, Y = Si, Ge) Isomers

skeleton	isomer	substituents	$r(X_\alpha-X_\beta)$ (Å)	$r(X_\alpha-X_\beta)$ (Å)	$r(X_\alpha-X_\beta)$ (Å)	$\omega(X_\alpha-X_\beta-X_\gamma)$ (deg)	ref
B	1	SiH_3	2.338	2.338	2.134	54.3	14
		Si^tBu_2Me	*2.364(3)*	*2.352(3)*	*2.138(2)*	*53.9(1)*	1b
C	1	SiH_3	2.407	2.407	2.133	52.6	14
		Si^tBu_2Me	*2.415(1)*	*2.420(1)*	*2.146(1)*	*52.71(3)*	10
D	1	SiH_3	2.421	2.421	2.284	56.3	14
		Si^tBu_2Me	*2.4168(10)*	*2.4165(10)*	*2.2429(6)*	*55.30(2)*	11
E	1	SiH_3	2.509	2.503	2.309	54.9	14
		Si^tBu_3	*2.522(4)*	*2.522(4)*	*2.239(4)*	*52.7(1)*	8a
B	11	SiH_3	2.200	2.200	4.017	131.9	
		$C(SiMe_3)_2CH_3$	*2.177(1)*	*2.188(1)*	*4.05411*	*136.49(6)*	2
D	11	SiH_3	2.275	2.275	3.968	121.4	
		$C(SiMe_3)_2CH_3$	*2.2694(8)*	*2.2694(8)*	*4.039(1)*	*125.71(7)*	4
E	11	SiH_3	2.390	2.390	3.563	96.4	
		$C(SiMe_3)_2CH_3$	*2.321(2)*	*2.330(2)*	*4.080(2)*	*122.61(6)*	4

and open-chain structures (**9**−**12**) (Scheme 4). There are some other possible isomers on the X_2YR_4 potential surface that are not discussed in this paper (for Si_3H_4 PES see ref 28).

Selected geometrical parameters compared with experimental data of different structures on the X_2YR_4 PES are tabulated in Table 1. (For detailed geometrical parameters, see the Supporting Information.)

The first two structures (**1** and **2**) are "classical" unsaturated rings (Scheme 4). The geometry around the X=X double bond in **1** and **2** was found to be planar (**A**, **B**, **C**) or *trans*-bent (**D**, **E**) (Figure 1). This observation meets the expectations since disilene, digermene, and distannene generally exhibit a *trans*-bent structure (see Figure 1).[29] The length of Si=Si, Si=Ge, and Ge=Ge double bonds with silyl substituents are 2.132 Å (exptl data: 2.138(2) Å),[1b] 2.191 Å,[30] and 2.309 Å (exptl data: 2.239(4) Å),[9] respectively. As expected, the double bonds are shorter than in the corresponding acyclic derivatives ($r_{(Si,Si)}$= 2.202(1) Å[31] and r(Ge,Ge) = 2.3568(6) Å).[32]

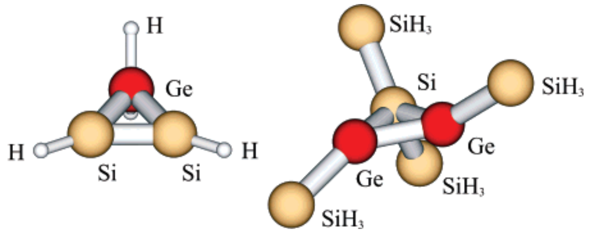

Figure 1. Example of a planar (Si_2GeH_4) and a *trans*-bent ($SiGe_2(SiH_3)_4$) structure

Rings containing a divalent atom fall into class **3** and **4**. The symmetry of this class is typically C_2, rarely C_{2v}. Representatives of classes **5** and **6** have remarkable dibridge structures. The dibridge is formed between the unsaturated atoms by their two ligands. One can imagine the three-membered dibridge ring as an adduct of a dibridge X_2H_2 and an XH_2 moiety. Topological analysis showed no formal bond between the pillar atoms, $X_\alpha-X_\gamma$ (Figure 2). The distance between the two pillar atoms bridged by a hydrogen is 2.576 Å, which is much longer than the usual Si−Si single bond (r(Si−Si) = 2.352 in Si_2H_6). In the dibridge isomers the topology of the original three-membered ring has been modified to a cage of the ring atoms and the two bridged

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(28) Kosa, M.; Karni, M.; Apeloig, Y. *J. Chem. Theor. Comput.* **2006**, *2*, 956.

(29) The geometry around the $X_\alpha=X_\gamma$ double bond (see Scheme 5) depends on the nature of the metal and the substituents; see refs 1b, 8a, and 10. The geometries around the Si=Si and Si=Ge double bonds were calculated to be *trans*-bent for **D** and **E**: the substituents move above and below the ring plane by 45° and 51°, respectively.

(30) (a) No available experimental data could be found for the length of the Si=Ge double bond; determination of the Si=Ge bond length in 2-disilagermirene failed because of the significant disorder in the positions of double-bonded Si and Ge atoms (ref 10). (b) Baines, K. M.; Cooke, J. A. *Organometallics* **1992**, *11*, 3487.

(31) The length of the Si=Si double bond in disilenes is between 2.2 and 2.25 Å depending on the substituents. See for example: Kira, M.; Iwamoto, T. *J. Org. Met. Chem.* **2000**, *611*, 236.

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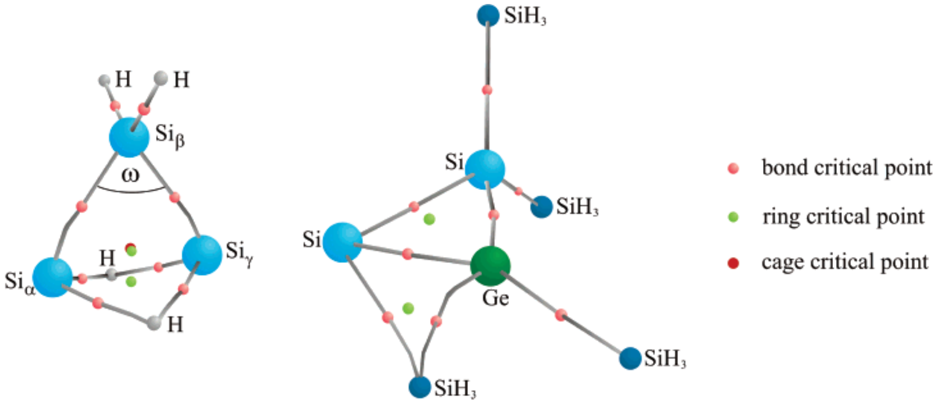

Figure 2. Topological analysis of the dibridge (left, Si_3H_4) and monobridge (right, $Si_2Ge(SiH_3)_4$) structures. Bond paths and critical points.

substituents. This exotic structure, however, becomes a first-order saddle point on the PES with silyl substituents.

The only difference between the two monobridge structures **7** and **8** is the position of the formally unsaturated bond: homonuclear in **7** and heteronuclear in **8**. In these structures the $X_\alpha{-}X_\beta$ bond is longer than the usual X−X (X = Si, Ge) single bond (Figure 2). We discuss the structure and detailed topological analysis in a later section.

Generally, the central angle $\omega(X_\alpha{-}X_\beta{-}X_\gamma)$ increases with the substitution of silicon atoms with germanium (**C**, **D**, **E**) and converges to 60°. We found that the heteronuclear double bonds are always surprisingly short: 2.191 and 2.230 Å in **C** and **D** with silyl substituents, respectively. Replacing the hydrogen substituents with silyl groups, the $X_\alpha{-}X_\beta$ and $X_\beta{-}X_\gamma$ bonds elongate, while the central $\omega(X_\alpha{-}X_\beta{-}X_\gamma)$ angle does not differ too much from $\omega(X_\alpha{-}X_\beta{-}X_\gamma)$ in the H-substituted derivatives.

With the exception of carbon derivatives, all the isomers with an open geometry (**9**−**12**)[33] are significantly bent around the central atom. True divalent isomers are the representatives of class **9** and **10**, while class **11** and **12** form allenic structures. The Laplace distributions show a clear lone pair around the central atom and a delocalized π-system of **9** and **10**.[34] No lone pairs can be found in class **11** and **12**. The central angle is also larger in structures **11** and **12** than in **9** and **10**, and their symmetry is C_2 (isomers in class **9** and **10** have C_s symmetry).

Energetic Considerations. The relative energies of isomers **1**−**12** were investigated (Table 2), and the relationship between these structures was determined. We found the well-known fact that the cyclopropyl derivatives (**A**) behave differently from the other rings containing heavy atoms. The energies of its isomers cover a wide range; both three-membered-ring isomers, cyclopropene and carbene structures, lie more than 25 kcal/mol higher than the most stable linear allene structure, while the mono- and dibridge isomers are assigned to first- and second-order saddle points, respectively.

The PES of the cyclotrisilene derivatives (**B**) is considerably flat. With hydrogen substituents the global minimum is the open-chain silylene, while the dibridged structure is the second most stable isomer. On the other hand, with silyl substitutents the cyclic structures become more preferable. As we substitute silicon atoms with germaniums (**C**, **D**, **E**), germylenes become more preferable, and the bridge structures are always assigned to global minima. In the series **C** the most stable isomer is the open structure **9** (R = H) or the cyclic structure **3** (R = SiH_3).

Table 2. Relative Energies (ΔE, kcal/mol) of the Investigated Isomers

	A R = H	**B** R = H	**C** R = H	**B** R = SiH_3	**C** R = SiH_3	**D** R = SiH_3	**E** R = SiH_3
1	25.7	2.9	20.1	0.0	13.5	9.5	11.2
2	25.7	2.9	13.1	0.0	10.3	1.5	11.2
3	70.8	5.4	1.4	0.0	0.0	13.1	3.5
4	70.8	5.4		0.0	11.8	1.2	3.5
5	123.1[b]	0.7	15.0	2.5	14.3	0.0	0.0
6	123.1[b]	0.7		2.5			0.0
7	84.6[a]	3.6	19.0	3.8	13.5	6.7	7.9
8	84.6[a]	3.6	15.6	3.8	16.1	9.2	7.9
9		0.0	0.0				
10		0.0	11.9				
11	0.0			10.8	15.6	17. 6	9.6
12	0.0			10.8	19.3	13.23	9.6

[a] First-order saddle point. [b] Second-order saddle point.

Open-chain isomers with C_s symmetry, **9** and **10**, are divalent compounds and mainly favorable with hydrogen substituents. Allenic open-chain species with C_2 symmetry, i.e., **11** and **12**, are stabilized by silyl groups. As one can see from Table 2, depending on the substituents, one of the isomers (**9** or **10**) or (**11** or **12**) can be found on the PES but never both of them.

Ring versus Open-Chain Structures. Structures **3** (and the asymmetric analogue **4**) and **9** (and the asymmetric analogue **10**) seem quite similar to each other at first glance. **3** and **4** are three-membered rings with a divalent atom in β-position, with fairly small $\omega(X_\alpha{-}X_\beta{-}X_\gamma)$ bond angles, C_2 (or C_{2v}) symmetry, stabilized by silyl substituents. **9** and **10** are also divalent compounds, but they are open-chain with C_s symmetry, mainly favorable with hydrogen substituents. Both the cyclic and acyclic types prefer germanium as a divalent atom. However, remarkable electronic differences can be found with further investigations. Topological and electronic properties clearly show a bond that closes the ring in **3** and **4**, while no such bond exists in **9** and **10**. One can easily distinguish between these isomers on the basis of bond angles and symmetry considerations, and the results can be proved with bond order, charge distribution, or molecular orbital analysis.

The investigation of the critical points obtained from the topological analysis of the electron density shows a ring critical point in **3** and **4**, which is missing in **9** and **10**. The Wiberg bond indices suggest three single bonds between the ring atoms in **3** and **4** ($n_{\mathrm{Wiberg}}(Si_\alpha{-}Si_\beta) = 0.96$, $n_{\mathrm{Wiberg}}(Si_\alpha{-}Si_\gamma) = 1.05$). In **9** and **10** an enhanced interaction between X_α and X_β ($n_{\mathrm{Wiberg}}(Si_\alpha{-}Si_\beta) = 1.34$, $n_{\mathrm{Wiberg}}(Si_\alpha{-}Si_\gamma) = 0.65$)[35] is observed. The Laplacian distributions of electron densities demonstrate the appearance of an in-plane electron pair on X_β in both **3**/**4** and

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(33) Although in Scheme 4 **9** and **11** (as well as **10** and **12**) are shown and discussed as "isomers" while **9** and **11** (as well as **10** and **12**) cannot both be located for any of the systems studied, they should not be called isomers. It is best to describe them as limiting electronic structures of the same isomer.

(34) Laplace distributions of **B9** and **B11** can be found in ref 13. A full series of figures are also given in the Supporting Information of ref 13.

Scheme 5

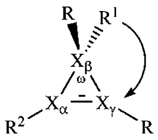


Table 3. Energy and Gibbs Free Energy Data in the Substituent Migration Reactions (in kcal/mol)

X_α	X_β	X_γ	R^c	stat. point	ΔE	ΔG
Si	Si	Si	SiH_3	reactant	0.0	0.0
Si	Si	Si	SiH_3	monobridge	3.8	5.5
Si	Si	Si	SiH_3	product	0.0	0.0
Si	Si	Ge	SiH_3	reactant	0.0	0.0
Si	Si	Ge	SiH_3	monobridge	0.5	4.6
Si	Si	Ge	SiH_3	product	−3.3	−3.4
Ge	Ge	Si	SiH_3	reactant	0.0	0.0
Ge	Ge	Si	SiH_3	monobridge	−0.3	1.6
Ge	Ge	Si	SiH_3	product	4.0	7.8
Ge	Ge	Ge	SiH_3	reactant	0.0	0.0
Ge	Ge	Ge	SiH_3	monobridge	−3.3	−3.1
Ge	Ge	Ge	SiH_3	product	0.0	0.0
Si	Si	Si	H	reactant	0.0	0.0
Si	Si	Si	H	monobridge	0.8	1.0
Si	Si	Si	H	product	0.0	0.0
Si	Si	Ge	H	reactant	0.0	0.0
Si	Si	Ge	H	monobridge	−4.6 −1.2[a] −3.5[b]	−4.2 −0.2[a]
Si	Si	Ge	H	product	−6.96 −6.9[a] −6.8[b]	−7.24 −6.6[a]

[a] MP2 results. [b] CCSD results. [c] $R = R^1 = R^2$.

9/10, proving that they are silylenes. In **9** and **10** there is a delocalized π-system perpendicular to the plane containing the three heavy atoms.

Isomerization Mechanism from 1-Disilagermirene to 2-Disilagermirene. In our previous paper we studied the mechanism of silyl group migration for different ring compounds (see Scheme 5). The reactions follow a two-step mechanism via a stable intermediate with the exception of cyclopropene, which isomerizes in one step. The energies of reactant, intermediate, and product are comparable for all of the investigated cyclometallenes (Table 3). As the number of Ge atoms increases, the intermediate gets more and more stable. In some cases the intermediate is more stable than the reactant or the product.

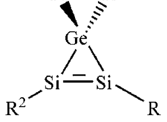
The rearrangement starts with the shift of the silyl group (R^1) from the saturated ring atom (X_β) to an unsaturated one. In the transition state the migrating R^1 group is situated above the ring, almost halfway between its original and final position (see Scheme 5). At the same time R^2 curves strongly behind the ring plane, forming a pronounced pyramidal structure at X_α. In this manner the transition state is an asymmetric monobridge structure. Reaching the intermediate, the migrating group (R^1) acquires a position near that of the product, while R^2 bends further toward X_β and forms a new three-membered ring with X_α and X_β. The resulting stable intermediate has a new monobridge structure of type **8**. It is interesting to note that both the transition state (T1) and the intermediate (I) have monobridge structures of a different type. In the second step of the reaction, the bridging group turns back to the original position via a combined motion and rotation. The transition from the monobridge structure to the *trans*-bent product is very similar to the scheme described in the case of X_2H_2 (X = Si, Ge, Sn, and Pb).[36]

Table 4. Relative Energies of the Reactants, Intermediates, and Products (in kcal/mol)[a]

	13	14	15	16	17	18	19	20	21
reactant	0.0	0.0	0.0	0.0	0.0; 0.0[c]	0.0	0.0	0.0	0.0
intermediate	5.9	5.6	6.5		−3.2; 0.5[c]	3.5	7.2	5.0	11.0
product	3.6	4.6	6.5	8.9	−3.1; −3.3[c]	3.7	4.6	3.7	2.2
ΔE^b	2.3	1.0	−0.1		−0.2; 3.8[c]	−0.1	2.6	1.3	8.7

[a] All values were obtained at the B3LYP/6-31g* level. [b] ΔE is the energy difference between the intermediate (I) and the product. [c] B3LYP/cc-pVTZ level.

Scheme 6



13; R^2=$SiMe_3$, R^1, R=$SiMe_3$
14; R^2=$SiMe_3$, R^1, R=$SiMe_2t$Bu
15; R^2=$SiMe_2t$$Bu_3$, R^1, R=$SiMe_3$
16; R^2=$SiMe_2t$$Bu_3$, R^1, R=$SiMe_2t$Bu
17; R^2=SiH_3, R^1, R=SiH_3
18; R^2=SiH_3, R^1, R=$SiMe_3$
19; R^2=SiH_3, R^1, R=$SiMe_2t$Bu
20; R^2=$Si(SiH_3)_3$, R^1, R=$SiMe_3$
21; R^2=$Si(SiH_3)_3$, R^1, R=$SiMe_2t$Bu

At the beginning of the reaction the double bond ($X_\alpha-X_\gamma$) is slightly elongated. The bond length reaches the maximum either in the first transition state or in the intermediate. For these structures the $X_\alpha-X_\gamma$ bond is longer than the usual X−X (X = Si, Ge) single bond. Nevertheless, the rings remain closed during the reaction, which is indicated by the presence of a ring critical point. However, if the ring contains at least one germanium atom, there is no $X_\beta-X_\gamma$ bond in the first transition structure and the rings are open. The motion of the migrating group is characterized by the $r(X_\gamma R_1)$ and $r(X_\beta R_1)$ distances, while $r(X_\alpha R_2)$ describes the formation of the bridge structure. It can be concluded that the migrating group almost reached its final position even in the intermediate.

Effect of Bulky Substituents. Comparable stability of the monobridge intermediate and the final product during the substituent migration reaction poses the question of why a bridged intermediate has never been observed. Although the bulkier groups kinetically stabilize the reactive center and seem to be essentially helpful during the actual synthesis, it seems that their presence hinders the formation of bridge structures. To answer this question, we compared the geometry and relative stability of the intermediate and the product with different bulky substituents (Scheme 6, Table 4).

One can easily track the steric effect of growing substituents to the geometry of the bridge structures (Figure 3, Scheme 6). The bulkier bridging substituent (R^1) induces a larger deviation from the ideal bridge structure. On the other hand, substituents that are not forming the bridge orientation directly (R) strengthen the trend, although with a smaller efficiency.

Using SiH_3 and $Si(SiH_3)_3$ substituents (Figure 4), the trend seems to fail, as the bigger groups cause smaller distortions in geometry (comparing **13**−**20** or **14**−**21**). A possible explanation is the electronic effect of the substituents. If the bridging group (R^1) is SiH_3 or $Si(SiH_3)_3$, there are energetically also well distinguishable intermediates having a monobridge orientation. Thus with these substituents, one can predict a two-step mechanism with an intermediate during the isomerization process. Increasing the size of the other substituents (R) has a negligible effect on the geometry.

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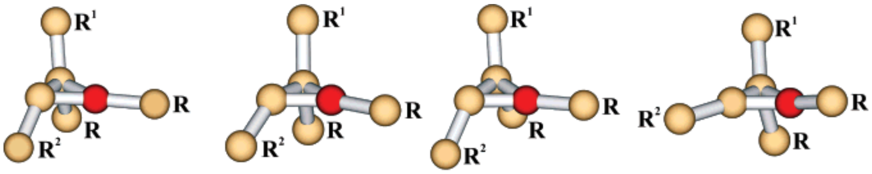
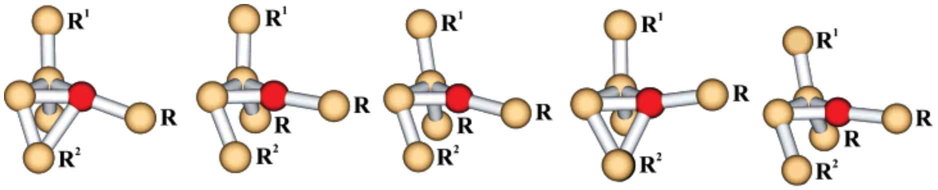
(35) Wiberg indices for comparison: Si−Si in Si_2H_6: 0.9807 Å, Si=Si in Si_2H_4: 1.9134 Å.

(36) Nagase, S.; Kobayashi, K.; Takagi, N. *J. Org. Chem.* **2000**, *611*, 264.



13 **14** **15** **16**

Figure 3. Change of the geometry of intermediates with increasing size of substituents. For simplicity, only the position of the ring atoms and the connected silicons are shown.



17 **18** **19** **20** **21**

Figure 4. Intermediate geometry of compounds containing SiH_3 and $Si(SiH_3)_3$ groups with increasing size of substituents. For simplicity, only the position of the ring atoms and the connected silicons are shown.

The distortion caused by the bulky substituents can be so large that one cannot even distinguish between intermediate and product. That can be proved comparing the relative energies of intermediates (I) and products (P) (ΔE), which are approaching each other progressively from **13** to **16**. In the case of **15** ΔE is less than 0.1 kcal/mol, and for **16**, which has been synthesized, calculations predict just one structure and a one-step mechanism of the isomerization reaction.

In the photochemical isomerization of cyclotrisilene, which was reported by Kira, one of the substituents is $Si(SitBu_2Me)_3$; that is, assuming the above-discussed mechanism, the group migration can occur via a monobridged intermediate. (For a detailed discussion of the mechanism of isomerization of cyclotrisilene see ref 15.) According to these results and considering the electronic effect of the $Si(SiC_nH_m)_3$-type substituents, there is hope to synthesize bridged silicon compounds despite the substituent bulkiness.

Bridged or Distorted Structure. Our calculations suggest the existence of the intermediate in many cases. However, studying these compounds, one may ask whether a structure has a bridged or only a distorted geometry. The easiest way to define the bridge structure is based on the topological analysis of the electron density; the existence of a ring critical point between the two pillar and the bridge atoms proves the proper structure. In the absence of a ring critical point it is only a distorted geometry.

Topological analysis of the bridged isomers of **B**, **C**, **D**, and **E** demonstrates the bond between the two pillar atoms. The bridging ligand can be bonded to both pillar atoms (Figure 2) or to only one of them (Figure 5). It depends on the actual ring atoms. Nevertheless, the existence of the ring critical point in all cases indicates that the $X_\alpha X_\beta X_\gamma$ rings are not opened in these isomers. Yet, we found that only the disilagermirene ring with silyl substituents has real bridge geometry (Figure 2 (right)).

Conclusion

Novel ring (**1**−**8**) and open-chain structures (**9**−**12**) (see Scheme 4) have been found on the X_2YR_4 (X, Y = Si, Ge) PESs.

On the one hand, open-chain silylenes with hydrogen substituents belong to global minima; the dibridge structures are also favorable. On the other hand, the cyclic structures become more preferable with silyl substituents. As we substitute silicon atoms with germanium, germilenes become more preferable. The structures where the bridge is between two germanium atoms are always assigned to global minima.

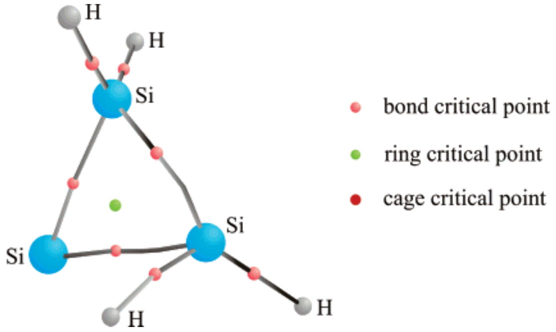


Figure 5. Topological analysis of a strongly distorted but not bridge structure.

All of the substituent migrations (with the exception of cyclopropene) proceed in a two-step mechanism via a stable intermediate. Both the first transition state (T1) and the intermediate (I) suggest monobridge structures of different type.

The bulkier the bridging substituents applied (R^1), the larger the deviation from ideal bridge structure. This trend fails using SiH_3 and $Si(SiH_3)_3$ substituents (Figure 4) due to different electronic effects of the SiH_3.

A remarkable observation can be made for monobridge (**7**) structures: ring critical points always appear in monobridge structures. In the absence of the ring critical point, intermediates have only distorted geometry without a monobridge.

It has also been found that only the disilagermirene ring with silyl substituents has real bridge geometry.

Computational Details

Geometry optimizations and frequency analysis were performed with the hybrid B3LYP functional[37] and the correlation-consistent, polarized cc-pVTZ basis set to obtain accurate energetic and geometric data on the investigated molecules. The reliability of the B3LYP/cc-pVTZ level of theory has already been validated in earlier studies for Si_3H_4 and Si_2GeH_4.[14] MP2 and CCSD methods were used with the 6-311++g** basis set for the migration reaction of Si_2GeH_4 to check the reliability of the selected level of theory.

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(37) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

Each geometry is fully optimized, as verified by the frequency analysis, and the energies are corrected for zero-point vibrational energy (ZPE). The existence of only one imaginary frequency was checked for the transition states. IRC calculations were performed for all the reaction paths at the B3LYP/cc-pVDZ level to confirm the reaction coordinates from transition states to stable products. All quantum chemical calculations were performed with the Gaussian 03 program suite.[38] Atomic populations were obtained using the natural population analysis (NPA),[39] in order to compute atomic charges. Topology of the electron density was analyzed using the AIM2000 program.[40]

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Supporting Information Available: Selected geometric data of stationary points along the investigated substituent migration reactions; standard orientation of all investigated molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700267J

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(38) *Gaussian 03*, Revision C.02, see Supporting Information.

(39) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. *NBO 5.0*; Theoretical Chemistry Institute, University of Wisconsin: Madison, 2001.

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