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Computational study of reaction pathways in the course of interaction of deactivated silylenes with buta-1,3-diene

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ABSTRACT

The PESs of systems including deactivated silylenes (SiHHal, $SiHal_2$, Hal = F, Cl, and 2-silaimidazol-2-ylidene, $SiN_2H_2C_2H_2$) and buta-1,3-diene have been studied using G3(MP2)//B3LYP method. Two major reaction channels, (2 + 1) and (4 + 1) cycloaddition reactions, leading to 2-vinylsiliranes and silacyclopent-3-enes, respectively, as well as [1,3]-sigmatropic rearrangements between 2-vinylsiliranes and the corresponding silacyclopent-3-enes, have been considered in detail. Reactivity of silylenes toward buta-1,3-diene decreases in the following series: SiHHal > $SiHal_2$ > $SiN_2H_2C_2H_2$, which is reflected in increase of the reaction barriers for both cycloaddition reactions and in decrease of exothermicity of the formation of the corresponding products. The (4 + 1) cycloaddition is preferable for $SiHal_2$ and $SiN_2H_2C_2H_2$ and can compete with (2 + 1) cycloaddition for SiHHal. [1,3]-Sigmatropic rearrangement is important for isomerization of 2-vinylsiliranes to the corresponding silacyclopent-3-enes for all systems studied, except the $SiCl_2$ system.

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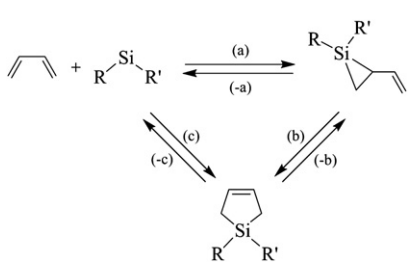
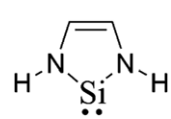
1. Introduction

Cycloaddition reactions play an important role in chemistry of silylenes [1–5]. The interaction of silylenes and 1,3-dienes is of especial significance because of wide use of this reaction for trapping transient silylenes. The general scheme of this interaction presently includes (2 + 1) cycloaddition reaction (a), [1,3]-sigmatropic rearrangement of the formed 2-vinylsiliranes (b), (4 + 1) cycloaddition reaction (c) and the corresponding reverse processes, (-a), (-b) and (-c):



The experimental data suggests that depending on the nature of silylene, 1,3-diene and reaction conditions either (2 + 1) cycloaddition [6] or (4 + 1) cycloaddition [7] can be carried out as the first stage, or both processes can proceed competitively [8].

In this work we extend recent theoretical studies of the 1,3-diene–SiR_2 systems (R = H [9], R = Me, Ph [10]) to deactivated silylenes, viz. SiHHal, $SiHal_2$ (Hal = F, Cl) and 2-silaimidazol-2-ylidene ($SiN_2H_2C_2H_2$),



which is a prototype of several stable silylenes. We have limited our consideration to the suprafacial processes, as it has been found in our previous detailed study of the C_4H_6–SiH_2 system [9], that the very processes represent the pathways of the lowest energies. To elucidate relative importance of the processes shown in the scheme above the potential energy surfaces (PESs) of the systems including these silylenes and buta-1,3-diene (C_4H_6) have been studied at the B3LYP/6-31G(*d*) level with subsequent evaluation of the energies of the stationary points using the G3(MP2)//B3LYP method. It has been shown that the less reactive silylenes are more prone to direct (4 + 1) cycloaddition, while more reactive undergo both (2 + 1) and (4 + 1) cycloadditions.

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2. Computational details

All calculations were performed with Gaussian 03 program package [11]. The potential energy surfaces were studied using B3LYP density functional [12,13] with the 6-31G(*d*) basis set. No symmetry constraints were applied during the optimization procedures. The character of the optimized stationary points (minimum or the first order saddle point) was controlled by calculating the eigenvalues of the hessian matrices. Cartesian coordinates, selected interatomic distances and energies for the B3LYP/6-31G(*d*) optimized structures are presented in the Supplementary material. To ascertain the topology of the potential energy surface mass-weighted intrinsic reaction coordinate (IRC) calculations [14,15] were carried out. The tight convergence criteria and the ultrafine grid were used for the geometry optimization and the reaction path following at the B3LYP/6-31G(*d*) level. The stability of the RB3LYP/6-31G(*d*) wave functions were checked. The RB3LYP/6-31G(*d*) wave functions are stable in all cases except **TS3-C** (for SiHF and SiHCl), for which an RHF to UHF instability was revealed (see Section 3.1). Thermodynamic functions at 298 K were calculated using the harmonic oscillator–rigid rotor approximation. The energies of the majority of stationary points found were reevaluated using the G3(MP2)//B3LYP method [16].

3. Results and discussion

3.1. C_4H_6–SiHHal (Hal = F, Cl) systems

According to the B3LYP/6-31G(*d*) calculations the interaction between SiHHal (Hal = F, Cl) and buta-1,3-diene (C_4H_6) starts with barrierless formation of complexes of two types, **C1** and **C2** (Fig. 1, Table 1). In both of them silylenes coordinate with one of double bonds of the diene, however the **C1** complexes are characterized by closer approach of C1 atom by Si atom, while Si atom is put closer to C2 atom in the complexes of **C2** type. The complexes of both types are represented by two stereoisomers with *cis* (**C**) and *trans* (**T**) orientation of vinyl group and Hal substituent relative to Si–C1–C2 plane, each of which has two conformers with s-*cis* (**c**) and s-*trans* (**t**) configuration of the butadiene moiety. The C1–C2 bonds in the complexes are elongated (up to ca. 1.41 Å for **C1** and ca. 1.39 Å for **C2**) in comparison to the C1–C2 bond of free buta-1,3-diene (1.34 Å). This indicates strong binding character of the interaction between the reagents. Indeed, exothermicity of the **C1** complex formation amounts to ca. 60 kJ/mol ($\Delta G \sim -15$ kJ/mol). The Si–C1 distances in complexes **C1** are ca. 0.15 Å shorter than the Si–C2 distances in complexes **C2**. The weaker interaction between silylene and butadiene moieties in the latter is reflected in decrease of their stability: the **C2** complexes are less stable than complexes **C1** by ca. 20 kJ/mol (Table 1). Effect of Hal substituent on the energy gain upon complexation is relatively small, Cl-for-F replacement results in some additional stabilization of all complexes by ca. 5 kJ/mol (Table 1). Interconversions of the complexes are hampered as the energies of the corresponding transition states are ca. −20 kJ/mol relative free silylene and *trans*-buta-1,3-diene.

The complexes **C1** and **C2** can readily transform via low-lying transition states **TS1** and **TS2** into 1-halo-2-vinylsiliranes **VS** (Fig. 1). Transition states **TS1** and **TS2** of this intramolecular (2 + 1) cycloaddition are characterized by shortening both Si–C1 and Si–C2 distances, with the longer distances in the complexes experiencing more reduction in the corresponding transition states (by ca. 0.15 Å for Si–C1 distances and by ca. 0.35 Å for Si–C2 distances in **C1**), by deviation of SiHHal moiety out of plane coplanar to the plane of the coordinated vinyl group, and by ca. 0.04 Å elongation of the C1–C2 bond compared to the complexes. Cl-for-F replacement has slight

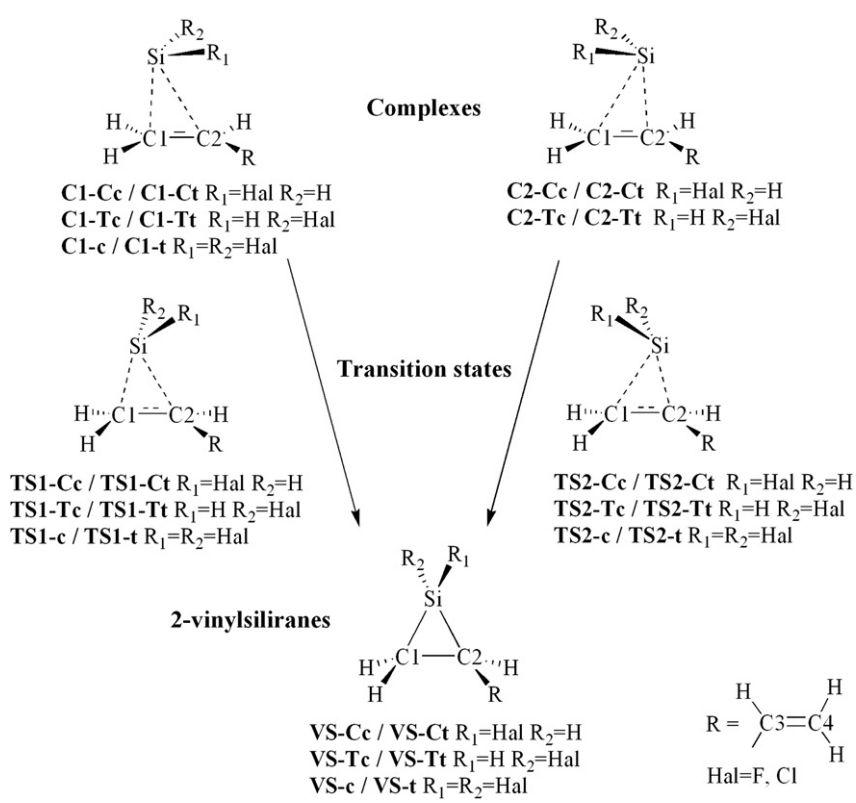


Fig. 1. Generic relationship between different structures involved in (2 + 1) cycloaddition reactions. Indexes **c** and **t** refer to s-*cis* and s-*trans* configuration of the C1–C2–C3–C4 chain. Indexes **C** and **T** refer to cis or trans orientation of Hal substituent and free vinyl group relative to the Si–C1–C2 plane.

Table 1
The total (E_0) and relative (ΔE_0) energies, and the Gibbs free energies[a] (ΔG) obtained at the G3(MP2)//B3LYP level for stationary points found on the PESs of the C_4H_6–SiHF and C_4H_6–SiHCl systems.

Species[b]	Hal = F			Hal = Cl		
	E_0, a.u	ΔE_0, kJ/mol	ΔG, kJ/mol	E_0, a.u	ΔE_0, kJ/mol	ΔG, kJ/mol
trans-C_4H_6 + SiHHal	−545.13526	0	0	−905.11808	0	0
C1-Cc	−545.15723	−58	−10	−905.14235	−64	−15
TS1-Cc	−545.15537	−53	−4	−905.14199	−63	−13
C1-Ct	−545.15779	−59	−12	−905.14271	−65	−18
TS1-Ct	−545.15486	−51	−3	−905.14180	−62	−13
C1-Tc	−545.15717	−58	−12	−905.14144	−61	−15
TS1-Tc	−545.15569	−54	−6	−905.14150	−61	−13
C1-Tt	−545.15640	−56	−9	−905.14160	−62	−15
TS1-Tt	−545.15375	−49	0	−905.14065	−59	−10
C2-Cc	−545.14742	−32	14	−905.13296	−39	7
TS2-Cc	−545.14776	−33	15	−905.13441	−43	6
C2-Ct	−545.14922	−37	9	−905.13411	−42	4
TS2-Ct	−545.14766	−33	16	−905.13427	−42	6
C2-Tc	−545.14988	−38	8	−905.13512	−45	2
TS2-Tc	−545.14994	−39	9	−905.13623	−48	1
C2-Tt	−545.14957	−38	8	−905.13476	−44	2
TS2-Tt	−545.14791	−33	15	−905.13453	−43	5
VS-Cc	−545.18208	−123	−75	−905.16501	−123	−75
VS-Ct	−545.18228	−123	−76	−905.16489	−123	−74
VS-Cg	−545.18069	−119	−72	−905.16280	−117	−69
VS-Tc	−545.18405	−128	−80	−905.16602	−126	−77
VS-Tt	−545.18257	−124	−76	−905.16477	−123	−74
VS-Tg	−545.18126	−121	−73	−905.16329	−119	−71
TS3-C[c]	−545.13649	−3	45	−905.12172	−10	39
TS3-T	−545.15794	−60	−9	−905.14040	−59	−7
TS4-C	−545.15178	−43	9	−905.12755	−25	27
TS4-T	−545.15718	−58	−5	−905.13654	−48	4
R1	−545.13260	7	48	−905.11617	5	47
R2	−545.13604	−2	38	−905.11531	7	48
SCP	−545.24284	−282	−232	−905.22287	−275	−225

[a] Calculated for $T = 298$ K and $p = 1$ atm.
[b] Designation of complexes **C1**, **C2**, transition states **TS1**–**TS4**, and 2-vinylsiliranes **VS** includes indication of *cis* (**C**) or *trans* orientation (**T**) of Hal substituent and free vinyl group relative to the Si–C1–C2 plane. Designation of complexes **C1**, **C2**, transition states **TS1**, **TS2**, and 2-vinylsiliranes **VS** also includes indication of conformation of the diene moiety: **c** for s-*cis*, **t** for s-*trans*, g for gauche configuration of the C1–C2–C3–C4 chain.
[c] An RHF to UHF instability of the RB3LYP/6-31G(*d*) wave function has been observed for **TS3-C** in both systems.

effect on geometries of the transition states and produce small impact on energetics of the rearrangement, decreasing the barrier heights from ca. 5 kJ/mol for Hal = F to ca. 2 kJ/mol in the case of Hal = Cl (Table 1).

1-Halo-2-vinylsiliranes **VS** retain the *cis* (**C**) or *trans* (**T**) configuration of Hal and vinyl substituents existing in the preceding complexes. The *trans* stereoisomers **VS-T** are somewhat more stable than the *cis* stereoisomers **VS-C**, and each of them has three stable conformations with approximate *cis* (**c**), *trans* (**t**) and *gauche* (**g**) configuration of the C1–C2–C3–C4 chain. The Si–C1 and Si–C2 bond lengths in **VS** are of 1.83–1.85 Å and 1.86–1.88 Å, respectively. Rearrangement of **C1** to **VS** results in further energy gain of ca. 60 kJ/mol (ca. 120 kJ/mol relative to free SiHHal and C_4H_6). The Cl-for-F replacement has very small effect on the relative stability of **VS** (Table 1). According to our previous data [9] unsubstituted vinylsilirane is ca. 40 kJ/mol more stable. Therefore, introduction of one halogen atom leads to considerable decrease of exothermicity of formation of **VS**.

Thus, formation of (2 + 1) cycloadducts in the case of interaction monohalogenated silylenes SiHHal with C_4H_6 proceeds in two stages. This contrasts to barrierless formation of analogous vinylsiliranes upon interaction of dienes with SiH_2 [9] and SiR_2, R = Me, Ph [10]. The difference in behavior of these silylenes can be understood in terms of general reaction scheme for interaction of silylenes with other unsaturated organic species [17]. This scheme divides the whole process into electrophilic and nucleophilic stages. The first stage of interaction is electrophilic attack of a silylene on the π-system, which can result in barrierless formation of a pre-reaction complex. The second stage is nucleophilic attack delivering the final product. When embarrassments for the nucleophilic attack are slack the barrier of this stage decreases up to its complete disappearance, and the addition proceeds in one stage. Obviously, as opposed to H, Me and Ph substituents, halogen substituents create remarkable embarrassments for the nucleophilic stage due to their high electronegativity, and thus determining passing of the addition in two stages.

Another likely pathway of further transformations of the initial complexes of SiHHal with C_4H_6 is intramolecular (4 + 1) cycloaddition with formation of 1-halosilacyclopent-3-enes **SCP**. Clearly, s-*trans* conformers of complexes **C1** and **C2** cannot participate in this process because dihedral angle of the C_4H_6 fragment is too far from that of **SCP**. Moreover no pathway leading to **SCP** has been found even for s-*cis* conformers of complexes **C2**. Hence tight interaction of silylene moiety with C2 atom precludes intramolecular (4 + 1) cycloaddition. Complexes **C1** (in their s-*cis* conformations) rearrange into **SCP** via **TS3** (Fig. 2). A surprising peculiarity of the (4 + 1) cycloaddition reaction in the C_4H_6–SiHHal systems consists in critical dependence of the **TS3** barrier height on the relative configuration of Hal atom and non-coordinated vinyl group (Figs. 2 and 3). If the configuration is *cis*, the corresponding transition state, **TS3**–**C**, connecting **C1**–**Cc** with **SCP**, is high lying (54 kJ/mol above complexes **C1**–**Cc** for both Hal = F and Cl). The Si–C1 and Si–C2 distances in **TS3-C** are elongated by ca. 0.07 Å and 0.27 Å in comparison with those in **C1**–**Cc**. The counterpart **TS3**–**T** connecting **C1**–**Tc** with **SCP** is very close in its structure to the initial complexes (Fig. 2) and the corresponding activation barrier

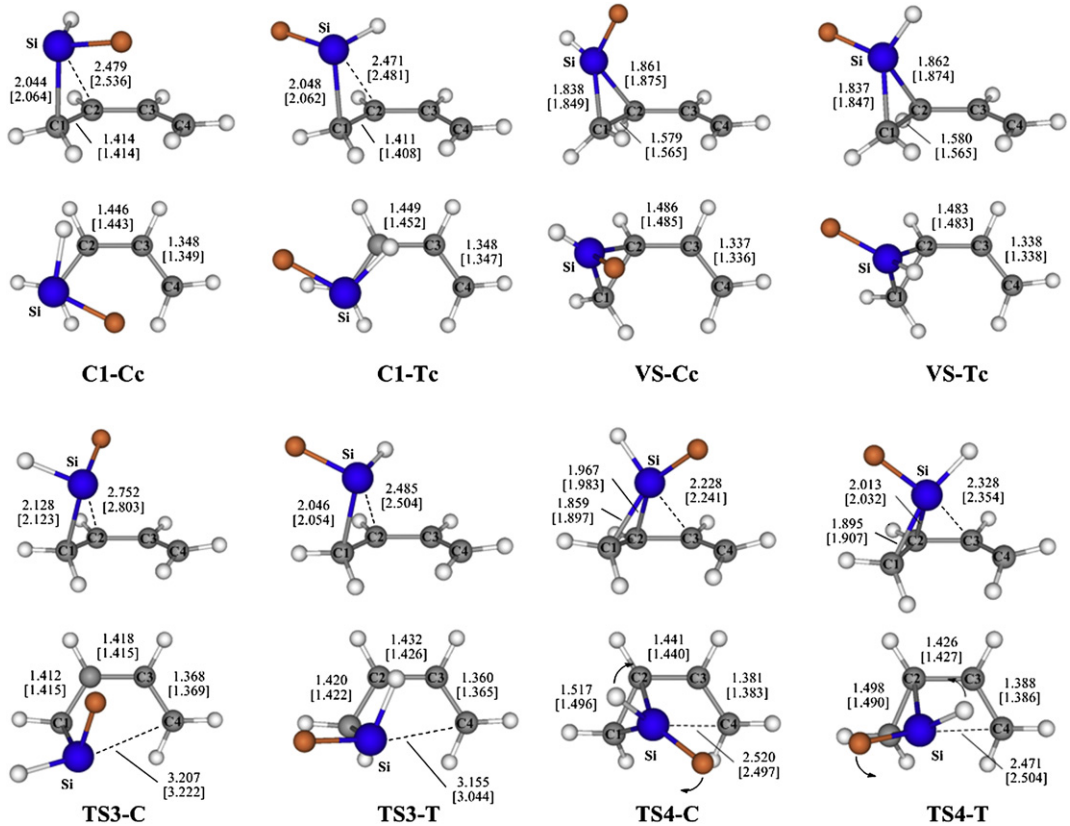


Fig. 2. Geometric structures corresponding to selected stationary points found in the B3LYP/6-31G(*d*) calculations of the C_4H_6–SiHHal systems. Two views are presented and interatomic distances are given in angstroms for Hal = F and Cl (in brackets). For **TS4-C** and **TS4-T** the direction of rotation of SiHHal groups in course of the formation of silacyclopent-3-ene are shown by curved arrows.

amounts to 3 kJ/mol for SiHCl system, while for SiHF system it falls down below the complex energy level by 2 kJ/mol at the G3(MP2)//B3LYP level ($\Delta E = +2$ kJ/mol at the B3LYP/6-31G(*d*) level), implying barrierless rearrangement. Taking into account quite low barriers **TS1**–**Tc** (Table 1) separating complexes **C1**–**Tc** from vinylsiliranes **VS** in both the systems one can conclude that both (2 + 1) and (4 + 1) cycloadditions are favored in this case and independent formation of both vinylsiliranes **VS** and silacyclopent-3-enes **SCP** is expected from **C1**–**Tc**. Thus, in the whole two channels are open for interaction of SiHHal with C_4H_6.

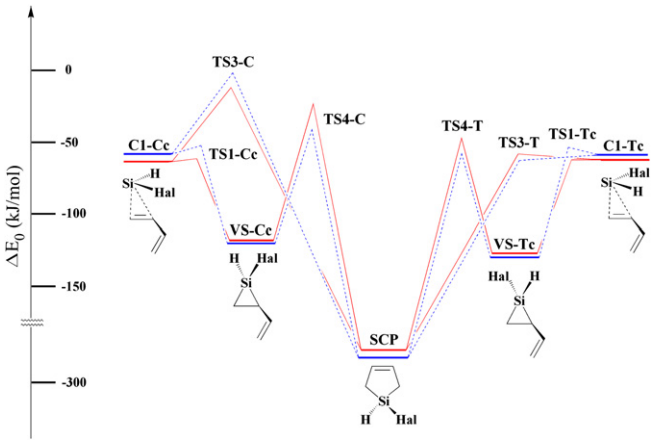


Fig. 3. Schematic potential energy surfaces of the C_4H_6–SiHF (dashed lines) and C_4H_6–SiHCl (continuous lines) systems according to the calculations at the G3(MP2)//B3LYP level.

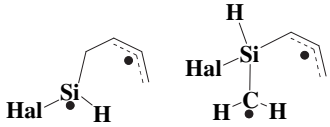
The RHF to UHF instability of the RB3LYP/6-31G(*d*) wave functions has been disclosed for high energy transition states **TS3**–**C** in both systems. Using the UB3LYP/6-31G(*d*) method transition states **TS3**–**C-oss** ($<S^2> = 0.691$ for SiHF and $<S^2> = 0.620$ for SiHCl) have been found, which structures and energies are close to those of **TS3**–**C** (see Supplementary material). Due to flatness of PESs around **TS3**–**C-oss** IRC calculations were stopped in vicinity of these transition states, but subsequent minimum search at the UB3LYP/6-31G(*d*) level led to the same minima as RB3LYP/6-31G(*d*) IRC calculations for **TS3**–**C**. Search for analogs of **TS3**–**T** and **TS4** in both systems on the UB3LYP/6-31G(*d*) PESs results in finding the same stationary points ($<S^2> = 0$ for all of them) as have been found on the RB3LYP/6-31G(*d*) PESs.

Formation of **SCP** is thermodynamically very favorable process, it gives ca. 220 kJ/mol starting from complexes and ca. 280 kJ/mol starting from free silylenes and buta-1,3-diene. The Cl-for-F replacement slightly decreases the exothermicity of formation of **SCP** from SiHHal and C_4H_6 by 7 kJ/mol (Table 1). It is interesting to note that **SCP** formation from SiH_2 and C_4H_6 is more exothermic and equal to 297 kJ/mol at the G3(MP2)//B3LYP level [9].

1-Halo-2-vinylsiliranes can rearrange to 1-halosilacyclopent-3-enes **SCP** via **TS4** corresponding to [1,3]-sigmatropic rearrangement. The rearrangement requires *s-cis* conformation of **VS**. Structures of transition states **TS4** resemble those of the corresponding **VS** (Fig. 2), although Si–C1 and Si–C2 bonds are somewhat elongated (1.86–1.91 Å and 1.97–2.03 Å, respectively) and Si–C3 and Si–C4 distances become remarkably shorter (2.23–2.35 Å and 2.47–2.52 Å, respectively). The energies of **TS4** like those of **TS3** are sensitive to the relative orientation of Hal and vinyl groups, although difference in this case is not so large. For SiHF system **TS4**–**C** lies higher than **TS4**–**T** by 14 kJ/mol, whereas

for SiHCl system **TS4**–**C** is higher by 24 kJ/mol. Therefore, *cis* stereoisomers are much less prone to this rearrangement too (Table 1). The Cl-for-F replacement destabilizes both transition states of [1,3]-sigmatropic rearrangement by 19 and 9 kJ/mol for **TS4**–**C** and **TS4**–**T**, respectively.

Being formed, 1-halo-2-vinylsiliranes can isomerize to 1-halosilacyclopent-3-enes by [1,3]-sigmatropic rearrangements or by dissociation to the complexes and following (4 + 1) cycloaddition (Fig. 3). From energetic consideration both pathways are equally accessible for 1-fluoro-2-vinylsilirane **VS**–**Tc** (Fig. 3), as well as for 1-chloro-2-vinylsiliranes **VS**–**Cc**, taking into account that interconversion of different complexes requires overcoming transition states with energies of ca. −20 kJ/mol. [1,3]-Sigmatropic rearrangement is more preferable for 1-fluoro-2-vinylsilirane **VS**–**Cc** and less preferable for 1-chloro-2-vinylsilirane **VS**–**Tc** (Fig. 3). It is noteworthy also that both homolitic Si–C and C–C bond cleavages leading to triplet diradicals **R1** and **R2**,.



R1 **R2**

are less favorable than retro (2 + 1) cycloaddition and [1,3]-sigmatropic rearrangement for 1-halo-2-vinylsiliranes (Fig. 3, Table 1), although rather non-operative **TS3-C** is very close in energy to **R2** in the C_4H_6–SiHF systems.

An analogy can be drawn out between the pathways of isomerization of 1-halo-2-vinylsiliranes and prototype 2-vinylsilirane studied by us earlier [9]. Two pathways of low-energy leading from 2-vinylsilirane to silacyclopent-3-ene have been found. Both of them correspond to suprafacial [1,3]-sigmatropic rearrangement and proceed via transition states denoted in the original paper [9] as TS2 and TS3 and referred here as **RKF**–**TS2** and **RKF**–**TS3**. The structures of **RKF**–**TS2** and **RKF**–**TS3** resemble those of **TS3** and **TS4**, respectively. Additionally, the lowest energy transition state **RKF**–**TS2** possesses slightly dissociative character, consisting in weakening of binding between silylene and buta-1,3-diene moieties [9]. This reinforces an analogy between the latter and **TS3**. Thus, the pathway from **VS** to **SCP** via **TS1**, **C1** and **TS3** degenerates into [1,3]-sigmatropic rearrangement via **RKF**–**TS2** for unsubstituted 2-vinylsilirane due to barrierless nature of (2 + 1) cycloaddition reaction in the C_4H_6–SiH_2 system. Like **TS4**, **RKF**–**TS3** is closer in its structure to 2-vinylsilirane. However it belongs to suprafacial process with inversion of configuration of migrating silylene group (so called *si* rearrangement [18]) as do transition states **TS4**–**T**, but not transition states **TS4**–**C** (Fig. 2), which lie on the way of *sr* processes (suprafacial rearrangements with retention of configuration), and therefore **RKF**–**TS3** is analog of **TS4**–**T** only. No obvious analog of **TS4**–**C** has been revealed on the PES of the C_4H_6–SiH_2 system [9], although existence of two different suprafacial channels (*si* and *sr* type) for degenerate [1,3]-sigmatropic rearrangement of allylsilane has been reported by Takahashi and Kira [19]. It is also important to note here, that symmetry-allowed *si* rearrangement pathways for the C_4H_6–SiHHal systems via **TS4**–**T** are energetically more favorable than symmetry-forbidden *sr* rearrangement via **TS4**–**C** (Table 1).

3.2. C_4H_6–$SiHal_2$ (Hal = F, Cl) systems

The chemistry of dihalosilylenes, $SiHal_2$, was a subject of numerous studies. The main results in this field are summarized in a series of reviews [20–25]. It has been shown that 1,1-dihalosilacyclopent-3-enes are typical products in the reactions of SiF_2 and $SiCl_2$ with acyclic 1,3-dienes. Despite significant deactivation effect of two halogen atoms, which will be discussed below, the reaction of $SiHal_2$ with 1,3-dienes retains its major importance as a reliable proof for formation of these intermediates in reaction mixture. One of the latest examples of this is provided by Goldberg et al. [26].

In contrast to the C_4H_6–SiHHal systems, only complexes of **C1** type, in which the Si–C1 distances are shorter than the Si–C2 distances, have been found at the B3LYP/6-31G(*d*) level for the C_4H_6–$SiHal_2$ (Hal = F, Cl) systems (Fig. 1, Table 2). These complexes are formed in course of barrierless addition of $SiHal_2$ to buta-1,3-diene. According to the B3LYP/6-31G(*d*) calculations the complexes are presented by series of conformers differing by C1–C2–C3–C4 dihedral angle and orientation of $SiHal_2$ group. By their energies and geometries the conformers in each system can be divided into two groups, one of the groups includes conformers, butadiene moiety of which has approximately s-*cis* configuration, and the

Table 2
The total (E_0) and relative (ΔE_0) energies, and the Gibbs free energies[a] (ΔG) obtained at the G3(MP2)//B3LYP level for the stationary points found on the PESs of the C_4H_6–SiF_2, C_4H_6–$SiCl_2$, and C_4H_6–$SiN_2H_2C_2H_2$ systems.

Species[b]	SiF_2 system			$SiCl_2$ system			$SiN_2H_2C_2H_2$ system		
	E_0, a.u	ΔE_0, kJ/mol	ΔG, kJ/mol	E_0, a.u	ΔE_0, kJ/mol	ΔG, kJ/mol	E_0, a.u	ΔE_0, kJ/mol	ΔG, kJ/mol
trans-C_4H_6 + silylene	−644.40455	0	0	−1364.35573	0	0	−632.65102	0	0
C1-c	−644.40483	−1	38	−1364.35981	−11	33	–	–	–
TS1-c	−644.37703	72	121	−1364.34942	17	66	−632.61486	95	145
C1-t	−644.40997	−14	24	−1364.36436	−23	19	–	–	–
TS1-t	−644.37614	75	123	−1364.35012	15	65	−632.60631	117	166
TS2-c	−644.37019	90	139	−1364.34280	34	83	−632.59933	136	186
TS2-t	−644.36813	96	143	−1364.34116	38	87	−632.59735	141	191
VS-c	−644.42349	−50	−1	−1364.38302	−72	−22	−632.64908	5	53
VS-t	−644.42359	−50	−2	−1364.38277	−71	−22	−632.64692	11	57
VS-g	−644.42279	−48	1	−1364.38117	−67	−18	−632.64665	11	58
TS3	−644.39687	20	69	−1364.35540	1	51	−632.63088	53	102
TS4	−644.39136	35	88	−1364.34578	26	79	−632.62924	57	109
R1	−644.37720	72	113	−1364.33754	48	90	−632.60460	122	165
R2	−644.38708	46	88	−1364.33915	44	86	−632.59822	139	182
SCP	−644.49301	−232	−182	−1364.44653	−238	−187	−632.70759	−149	−101

[a] Calculated for $T = 298$ K and $p = 1$ atm.
[b] Designation of complexes **C1**, transition states **TS1**, **TS2**, and 2-vinylsiliranes **VS** includes indication of conformation of the diene moiety: **c** for s-*cis*, **t** for s-*trans*, **g** for gauche configuration of the C1–C2–C3–C4 chain.

other contains conformers with nearly s-*trans* configuration of this moiety. Energies of the conformers constituting each group lie within several kJ/mol. Because the complication of the PESs, consisting in existence of multiple conformers, has no effect on further transformation occurring in the C_4H_6–$SiHal_2$ systems, it is not considered here in detail. Energies of s-*cis* and s-*trans* conformers most resembling the corresponding complexes in the C_4H_6–SiHHal systems are presented in Table 2 for each of the C_4H_6–$SiHal_2$ systems. The s-*trans* conformers are more stable than s-*cis* conformers by 12–14 kJ/mol. These values are in fact equal to the energy difference between s-*cis* and s-*trans* conformers of the buta-1,3-diene itself ($\Delta E_0 = 12$ kJ/mol at the G3(MP2)//B3LYP level).

The obvious reason of close difference in energies of s-*cis* and s-*trans* conformers of **C1** and buta-1,3-diene consists in weakness of interaction between the reactants in the complexes. Indeed, energy gain from **C1** formation lies between 1 and 23 kJ/mol for $SiHal_2$ (Table 2) that is by 40–60 kJ/mol less than in the case of SiHHal

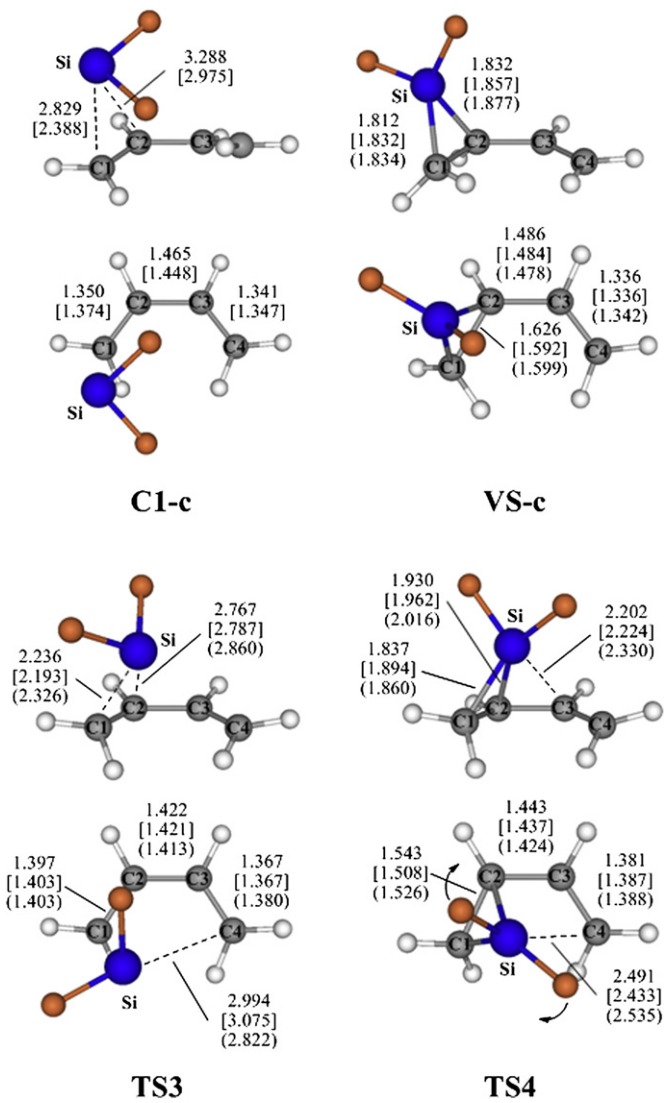


Fig. 4. Geometric structures corresponding to selected stationary points found in the B3LYP/6-31G(d) calculations of the C_4H_6–$SiHal_2$ and C_4H_6–$SiN_2H_2C_2H_2$ systems. Two views are presented and interatomic distances are given in angstroms for Hal = F and Cl (in brackets), and for $SiN_2H_2C_2H_2$ (in parentheses). For **TS4** the direction of rotation of SiR_2 groups in course of the formation of silacyclopent-3-ene are shown by curved arrows.

(Table 1). Weakness of binding between the silylenes and diene moieties in **C1** is clearly reflected in long Si–C1 and Si–C2 distances, which amount to 2.8 and 3.3 Å for complexes of SiF_2, and are reduced to 2.4 and 3.0 Å for complexes of $SiCl_2$ (Fig. 4), which are somewhat more strong (Table 2). As it is evidenced by values of relative Gibbs free energy (Table 2), the formation of complexes **C1** is thermodynamically unfavorable at normal conditions, and they should easily decompose to the starting silylene and buta-1,3-diene. Similar weak complex of SiF_2 with ethylene has been reported by Sakai, $\Delta E + ZPE$ value for it is equal to −13 kJ/mol relative to free reagents at the MP4/6-31G(*d*,*p*)//MP2/6-31G(*d*,*p*) level [27].

Transition states of both **TS1** and **TS2** types have been found on the B3LYP/6-31G(*d*) PESs of the C_4H_6–$SiHal_2$ systems. Both of them connect complexes **C1** with the corresponding vinylsiliranes **VS** (Fig. 1). As in the case of C_4H_6–SiHHal systems, **TS2** determines higher barrier than **TS1**. In the case of SiF_2 **TS1** lies in energy above the initial reagents by ca. 70 kJ/mol (Table 2). An analogy can be seen here again with the addition of SiF_2 to ethylene, where even higher barrier ($\Delta E + ZPE = 94$ kJ/mol) has been found at the MP4/6-31G(*d*,*p*)//MP2/6-31G(*d*,*p*) level [27]. $SiCl_2$ is less reluctant to (2 + 1) addition, the barrier determined by **TS1** in this case is much lower and amounts to ca. 15 kJ/mol relative $SiCl_2$ and *trans*-C_4H_6 (Table 2). Despite high energy contents, structures of **TS1** and **TS2** of the $SiHal_2$ systems are similar to those of SiHHal systems (Supplementary material).

The products of (2 + 1) cycloaddition, 1,1-dihalo-2-vinylsiliranes, have three stable conformations like 1-halo-2-vinylsiliranes (Table 2). Formation of 1,1-dihalo-2-vinylsilirane is exothermic with energy gain of ca. 50 kJ/mol in the case of SiF_2 and ca. 70 kJ/mol for $SiCl_2$. Enthalpy and entropy factors are practically compensated by each other upon the SiF_2 addition, making the whole reaction thermoneutral in terms of Gibbs free energy ($\Delta G = -2$ kJ/mol), whereas $SiCl_2$ addition shows negative ΔG (−22 kJ/mol) at normal conditions (Table 2). Thus, formation of **VS** from $SiCl_2$ and buta-1,3-diene requires overcoming much smaller reaction barrier and is more exothermic, than the analogous reaction of SiF_2. This observation conforms with previous study of (2 + 1) cycloaddition of SiF_2 and $SiCl_2$ to ethylene at the MP4/6-311G(*d*,*p*)//MP2/6-31G(*d*) level by Gordon and Nelson [28], where activation barriers of 77 and 19 kJ/mol were found for SiF_2 and $SiCl_2$, respectively, and $\Delta E + ZPE$ values are of −59 and −85 kJ/mol for the corresponding siliranes.

Another transformation which can be undergone by complexes **C1** is intramolecular (4 + 1) cycloaddition via corresponding **TS3** (Figs. 4 and 5). In the case of SiF_2 the **TS3** energy is 20 kJ/mol and for $SiCl_2$ it is 1 kJ/mol only (Table 2), both values are much lower than the corresponding **TS1** energies. Thus, (2 + 1) cycloaddition cannot compete with (4 + 1) cycloaddition in the case of C_4H_6–$SiHal_2$ systems (Fig. 5). It is interesting to note, that this conclusion coincides with an earlier prediction based on extended Hückel modeling [29] about preference of (4 + 1) cycloaddition over (2 + 1) cycloaddition for interaction of buta-1,3-diene with $SiCl_2$ (and also with $GeCl_2$).

The final products of (4 + 1) cycloaddition, the corresponding silacyclopent-3-enes **SCP**, are thermodynamically very favorable, their formation leads to decrease of energy contents in the systems by 232–238 kJ/mol (Table 2), although it is less than exothermicity of formation of silacyclopent-3-enes from SiHHal and buta-1,3-diene amounting to 275–282 kJ/mol (Table 1). The formation of 1,1-dichlorosilacyclopent-3-ene is found to be slightly more exothermic by 6 kJ/mol than that of its fluorine analog. This effect of Hal substituents is opposite to the situation in the C_4H_6–SiHHal systems, where formation of 1-fluorosilacyclopent-3-ene is more exothermic than formation of 1-chlorosilacyclopent-3-ene by approximately the same value.

1,1-Dihalo-2-vinylsilaranes **VS** are also connected with 1,1-dihalosilacyclopent-3-enes **SCP** by [1,3]-sigmatropic rearrangement via **TS4** (Figs. 4 and 5). Only **TS4** corresponding to *sr* type rearrangement have been revealed in the C_4H_6–$SiHal_2$ systems. Transition states **TS4** of both $SiHal_2$ systems lie substantially higher in energy than **TS3** (Table 2). Therefore decomposition of 1,1-dihalosilacyclopent-3-enes should result in extrusion of $SiHal_2$ with formation of buta-1,3-diene in retro (4 + 1) cycloaddition process rather than in production of the corresponding vinylsiliranes in [1,3]-sigmatropic rearrangement.

3.3. The C_4H_6–$SiN_2H_2C_2H_2$ system

For long time silylenes were known as transient reactive intermediates only. The first stable silylene, 1,3-di-tert-butyl-2-silaimidazol-2-ylidene ($SiN_2^tBu_2C_2H_2$), was synthesized by Denk et al. [30]. Since then several other stable silylenes have been prepared and their reactivity has been studied [31]. It has been shown that these species are strongly deactivated [4]. 2-Silaimidazol-2-ylidene fragment is retained in many stable silylenes [31]. Therefore interaction of parent 2-silaimidazol-2-ylidene, $SiN_2H_2C_2H_2$, with buta-1,3-diene has been explored to elucidate what are the effects of further deactivation on mechanisms of interaction of these species with 1,3-dienes.

According to the G3(MP2)//B3LYP calculations, PES of the C_4H_6–$SiN_2H_2C_2H_2$ system (Fig. 5) greatly differs from PESs of C_4H_6–$SiHal_2$ systems. No complexes like **C1** or **C2** have been found at the B3LYP/6-31G(*d*) level. The (2 + 1) cycloaddition is thermodynamically unfavorable, as 2-vinylsilirane in this system lies above the initial free reagents by 5 kJ/mol ($\Delta G = 53$ kJ/mol at normal conditions) at the G3(MP2)//B3LYP level, and transition states **TS1** and **TS2**, leading to **VS** directly from $SiN_2H_2C_2H_2$ and buta-1,3-diene, determine barriers of 95 kJ/mol or higher (Table 2). Therefore the (2 + 1) cycloaddition process is very unlikely reaction for such silylenes.

Barrier produced by **TS3** for (4 + 1) cycloaddition of $SiN_2H_2C_2H_2$ to buta-1,3-diene is also increased as compared to the corresponding barriers obtained for $SiHal_2$ systems, it amounts to 53 kJ/mol (Table 2). As it has been found for the other systems

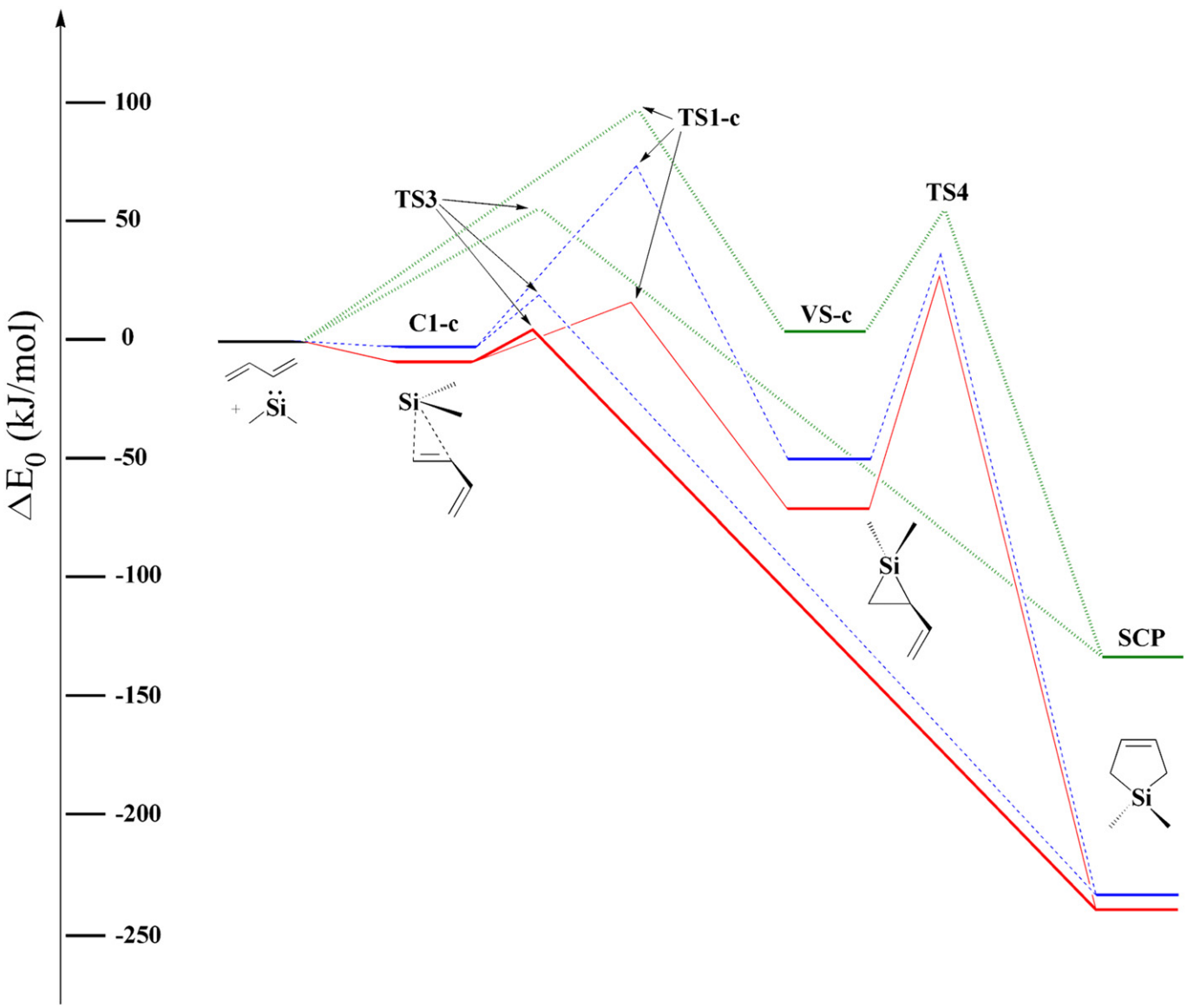


Fig. 5. Schematic potential energy surfaces of the C_4H_6–SiF_2 (dashed lines), C_4H_6–$SiCl_2$ (continuous lines), and C_4H_6–$SiN_2H_2C_2H_2$ (hashed lines) systems according to the calculations at the G3(MP2)//B3LYP level.

considered above, transition state **TS3** in this system (Fig. 4) demonstrates asynchronous formation of the Si–C1 and Si–C4 bonds. However Si–C1 and Si–C4 distances (2.326 and 2.822 Å, respectively) in it are closer to each other than in transition states **TS3** of the SiHHal (Fig. 2) and $SiHal_2$ (Fig. 4) systems and hence this **TS3** is more symmetric. In the whole, comparison of structures of transition states **TS3** (with exception of **TS3–C** for the SiHHal systems) allows conclude that they become more symmetric with increase of the barrier determined by them and thereby with decrease of reactivity of silylenes.

Formation of the corresponding silacyclopent-3-ene **SCP** from $SiN_2H_2C_2H_2$ is less exothermic by ca. 85 kJ/mol than formation of 1,1-dihalosilacyclopent-3-enes, nevertheless the entire process is still thermodynamically favored and has $\Delta G = -101$ kJ/mol at normal conditions (Table 2). Introduction of steric hindrance by substitution of the hydrogen at the nitrogen atoms of $SiN_2H_2C_2H_2$ by Me or ^{t}Bu groups has been found to produce only moderate effect on the energetics of the (4 + 1) cycloaddition at the B3LYP/6-31G(*d*) level (see Supplementary material). In both cases the activation barriers increase ($\Delta\Delta E_0 = 2$ and 12 kJ/mol for Me and ^{t}Bu, respectively) and exothermicity of the formation of corresponding silacyclopent-3-enes decreases ($\Delta\Delta E_0 = 7$ and 11 kJ/mol for Me and ^{t}Bu, respectively). Earlier similar (4 + 1) cycloaddition reactions of 2-silaimidazol-2-ylidenes $SiN_2R_2C_2H_2$ to diazadienes RN=CHCH=NR (R = H, Me, ^{t}Bu) were studied at the B3LYP/SDD(pol) level [32]. For all substituents the cycloadditions were predicted to be exothermic processes (−242 kJ/mol for R = H, −205 kJ/mol for R = Me, and −171 kJ/mol for R = ^{t}Bu) undergoing with the following activation barriers: 30 kJ/mol (R = H), 44 kJ/mol (R = Me), and 97 kJ/mol (R = ^{t}Bu).

Reactions of stable 1,3-di-tert-butyl-2-silaimidazol-2-ylidene with 1,3-dienes and diazadienes have been observed in experiments [7]. It is important, that addition of $SiN_2^tBu_2C_2H_2$ to E,E-1,4-diphenylbutadiene has been reported to give the corresponding silacyclopent-3-ene with *cis*-orientation of phenyl groups selectively. This is in accord with disrotatory rotation of the methylene groups during (4 + 1) cycloaddition of $SiN_2R_2C_2H_2$ to buta-1,3-diene via **TS3**.

Transition state **TS4** of [1,3]-sigmatropic rearrangement between the 2-vinylsilirane **VS** and silacyclopent-3-ene **SCP** lies in energy slightly above **TS3** ($\Delta\Delta E_0 = 4$ kJ/mol), but this reaction channel is switched off because of the high barrier for the formation of endothermic **VS** discussed above. Just as it is in the C_4H_6–$SiHal_2$ systems **TS4** in this system belongs to *sr* sigmatropic process.

4. Conclusions

The PESs of the systems including deactivated silylenes (SiHHal, $SiHal_2$ Hal = F, Cl, and 2-silaimidazol-2-ylidene, $SiN_2H_2C_2H_2$) and buta-1,3-diene have been explored, and (2 + 1) and (4 + 1) cycloaddition reactions between the reagents leading to the corresponding 2-vinylsiliranes and silacyclopent-3-enes, as well as [1,3]-sigmatropic rearrangement between **VS** and **SCP** have been studied using the G3(MP2)//B3LYP method.

Interaction of both SiHHal and $SiHal_2$ with buta-1,3-diene starts with barrierless formation of complexes. It contrasts with the analogous SiH_2 [9] and SiR_2, R = Me, Ph [10] systems studied earlier. The exothermicity of this process strongly decreases from SiHHal to $SiHal_2$, and is only slightly dependent on the type of Hal atom (F or Cl). At normal conditions formation of the complexes is thermodynamically favorable only for SiHHal. For 2-silaimidazol-2-ylidene, $SiN_2H_2C_2H_2$, which is a prototype of several stable silylenes, no such complex has been found at the B3LYP/6-31G(*d*) level. Clearly, this trend in ability of the silylenes in complex formation is reverse to the inclination of their substituents to donate electron density to the silylene *p* orbital. Further transformations in the SiHHal and $SiHal_2$ systems proceed from these complexes.

The barrier of further intramolecular (4 + 1) cycloaddition increases in the series SiHCl ∼ SiHF < $SiCl_2$ < SiF_2 < $SiN_2H_2C_2H_2$, as the barrier of (2 + 1) cycloaddition does. However the latter increases in this series more strongly, resulting in that (2 + 1) cycloaddition cannot compete with (4 + 1) cycloaddition in the case of $SiHal_2$ and $SiN_2H_2C_2H_2$, while for SiHHal both processes are possible and both can have barriers of merely several kJ/mol upon suitable approaches of buta-1,3-diene by silylene.

Exothermicity of formation of both **VS** and **SCP** also follows approximately the same order, it decreases from SiHHal to $SiHal_2$ and then to $SiN_2H_2C_2H_2$. The (2 + 1) cycloaddition is slightly more favorable for $SiCl_2$ as compared to SiF_2. Formation of **VS** for both SiHHal systems is approximately isoenergetic, as that of **SCP** for both SiHHal systems and for both $SiHal_2$ systems. Formation of **SCP** is thermodynamically favored at normal conditions for all of the systems, while that of **VS** is favorable at normal conditions for SiHHal and $SiCl_2$ only (see ΔG values in Tables 1 and 2). Formation of **VS** in the case of SiF_2 can be only marginally profitable, whereas formation of **VS** from $SiN_2H_2C_2H_2$ is endothermic.

Thus, reactivity of silylenes toward buta-1,3-diene decreases in the following series: SiH_2 [9] > SiHHal > $SiHal_2$ > $SiN_2H_2C_2H_2$, which is reflected in increase of reaction barriers for both (2 + 1) and (4 + 1) cycloaddition reactions and in decrease of exothermicity of the formation of the corresponding products **VS** and **SCP**.

[1,3]-Sigmatropic rearrangement of **VS** into **SCP** requires overcoming barriers from 52 kJ/mol in the C_4H_6–$SiN_2H_2C_2H_2$ system to 98 kJ/mol in the C_4H_6–$SiCl_2$ system, which are comparable with or lower than the barrier of [1,3]-sigmatropic rearrangement in the C_4H_6–SiH_2 system (97 kJ/mol) [9]. The barrier heights do not show any simple trend depending on the substituent type at Si atom. Transformation of **VS** into **SCP** by [1,3]-sigmatropic rearrangement is preferable than that by retro (2 + 1) cycloaddition followed by (4 + 1) cycloaddition in the C_4H_6–SiF_2 and C_4H_6–$SiN_2H_2C_2H_2$ systems. In the C_4H_6–SiHHal systems preference of either pathway depends on the type of the **VS** stereoisomer. The pathway including retro (2 + 1) cycloaddition followed by (4 + 1) cycloaddition is easier in the C_4H_6–$SiCl_2$ system. However, as it is mentioned above, formation of **VS** is expected upon interaction of SiHHal with buta-1,3-diene only and for both of these systems [1,3]-sigmatropic rearrangement can play its role in formation of **SCP**.

Decomposition of **SCP** can proceed both by [1,3]-sigmatropic rearrangement and by retro (4 + 1) cycloaddition reaction in the SiHF system and, probably, in the SiHCl and $SiN_2H_2C_2H_2$ systems. For the $SiHal_2$ systems retro (4 + 1) cycloaddition reaction is remarkably more favorable.

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Appendix. Supplementary material

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.jorganchem.2010.06.023.

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