

# Classical planar doubly bonded Si-substituted silenes—a boundary system between olefins and heavier Group 14 analogs

## Geometric and electronic structures, rotational barriers about the Si=C double bond, and comparison with the analogs and isoelectronic phosphenes, further evidence against C-ylides of silicon

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### Abstract

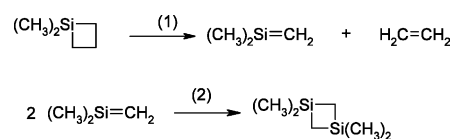
An ab initio study of a number of isostructural ethenes, silenes, and germenes at the MP4/6-311G(d)//MP2/6-31G(d)+ZPE level of theory showed that R<sub>2</sub>Si=CH<sub>2</sub> silenes are the last classical planar doubly bonded system because unlike the heavier Group 14 analogs electronegative substituents do not disturb a planar geometry, shorten and weaken the Si=C double bond. The calculations of the potential energy profiles and the rotational barriers of isoelectronic silene and phosphene as well as phosphorane are in favor of silenes to be more like phosphenes rather than phosphoranes. The rotational barriers decrease as more electronegative substituents are attached to the Group 14 atom. For ethenes, silenes, and germenes the maximal effect is observed for fluorine substitution. Fluorine does not affect the rotational barrier in phosphenes. A thermochemical approach based on the strain energies and 2+2 cycloreversion enthalpies was used to estimate the difference between the E=C (E = C, Si, Ge, P) σ- and π-bond energies in elementalkenes. The Bader analysis of the electron density distribution results in a covalent and highly polar double bonds whose polarity decreases in the order: silenes > phosphenes > germenes.

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### 1. Introduction

Until the mid-1960s the compounds containing a doubly bonded silicon were considered to be nonexistent [1]. The first compound containing the silicon–carbon double bond (dimethylsilene, Me<sub>2</sub>Si=CH<sub>2</sub>) is known from the work by Gusel'nikov and Flowers [2] who discovered that the gas phase pyrolysis of 1,1-dimethyl-1-silacyclobutane occurs as a clean 2+2 cycloreversion—transient dimethylsilene 2+2 cycloaddition sequence.



Since then a variety of silenes were described among which those bearing sterically non-hindered substituents appeared to be transient intermediates [3]. What is a silicon–carbon double bond and why small silenes being immediate analogs of olefins (only one sp<sup>2</sup> carbon atom is replaced by silicon!) are kinetically unstable [4], whereas olefins themselves are stable substances? What is their instability due to? Obviously, the answer is behind the nature of silicon, and the planar R<sub>2</sub>Si=CH<sub>2</sub> silenes are just the systems destined to disclose it. Like the carbon–carbon double bond in alkenes is formed by

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the  $2p_{\pi}-2p_{\pi}$  bonding between the  $sp^2$ -hybridized carbon atoms, the silicon–carbon double bond in silenes,  $R_2Si=CH_2$ , is formed by the  $3p_{\pi}-2p_{\pi}$  bonding between the  $sp^2$ -hybridized atoms of silicon and carbon. Such bonding results in a non-disturbed planar doubly bonded system with the  $\pi$ -bond, which energy does not exceed two-thirds of that in olefins. Naturally, the chemistry of silenes is mostly similar to that of alkenes. Indeed, silenes are readily involved in a great body of reactions typical for alkenes, such as addition, cycloaddition, polymerization, etc. [3]. However, their rates are so much greater than those for alkenes that most of the reactions occur spontaneously when silenes are generated as intermediates. Two factors are considered to be the driving forces of the outstanding reactivity of silenes: (1) the high polarity of the silicon–carbon double bond and (2) the lower Si=C  $\pi$ -bond energy. In the absence of traps silenes dimerize spontaneously (cyclodimerization is a zero activation energy process). Some of silenes bearing the appropriate substituents at the double-bonded silicon atom (H,  $SiMe_3$ ,  $CH_2CH_2CH_2$ , *o*-tolyl, etc.) may rearrange to produce silylenes, silacycles, but their intramolecular rearrangements mostly require thermal or photochemical activation. To achieve the kinetic stabilization of silenes one should either (1) create the appropriate conditions preventing them from cyclodimerization (generation in a flow system at a very low pressure, matrix isolation) or (2) attach bulky groups to the double-bonded atoms (crowded silenes) [3m]. Thermodynamic stabilization may be achieved by the coordination of a donor (Lewis base) on the silicon center or by the complexation with a transition metal [3k].

Recently, we published that the substituents affect the Si=C bond length and  $\pi$ -bond energy of the silicon–carbon double bond in opposite fashions in silenes,  $R_2Si=CH_2$  (R = H,  $CH_3$ ,  $SiH_3$ ,  $CH_3O$ ,  $NH_2$ , Cl, F) [5]. It was formulated as follows: the higher the substituents electronegativity, the shorter the Si=C distance, the weaker the  $\pi$ -bond. The weakening Si=C  $\pi$ -bond energy in the silenes series ( $SiH_3$ ) $_2Si=CH_2$  (42.0 kcal mol<sup>-1</sup>),  $H_2Si=CH_2$  (40.4 kcal mol<sup>-1</sup>), and  $F_2Si=CH_2$  (30.7 kcal mol<sup>-1</sup>) was rationalized in terms of their more strained geometry resulting from the energetic cost for planarizing  $R_2SiC$  moiety. The effect mentioned above may be considered to be rather curious because (1) any shortening of the distance is normally associated with the bond strengthening, and (2) an ICR study [6] produced an opposite trend in changing of the energy of the  $\pi$ -bond on going from  $(CH_3)_2Si=CH_2$  ( $39 \pm 5$  kcal mol<sup>-1</sup>) to  $F_2Si=CH_2$  ( $50 \pm 5$  kcal mol<sup>-1</sup>). Besides, we observed in the series of 1,1,3,3-tetrasubstituted 1,3-disilacyclobutanes the increase in the strain energy and 2+2 cycloreversion enthalpy as substituents electronegativity grows: the higher the electronegativity, the greater the strain energy and the enthalpy. In particular, on going

from silyls to fluorines the strain energy rises. The endothermicity of the 2+2 cycloreversion of 1,1,3,3-tetrasubstituted 1,3-disilacyclobutanes also increases by 41.5 kcal mol<sup>-1</sup>, cf. 72.7 kcal mol<sup>-1</sup> (R =  $SiH_3$ ) and 114.2 kcal mol<sup>-1</sup> (R = F) [5]. The latter effects were deduced from the strain energies and the reaction enthalpies (so-called thermochemical approach) obtained from the ab initio computations at the MP4/6-311(d)//MP2/6-31G(d) level of theory.

In this paper, we extend the study of the substituent effect in the wider range of  $R^1R^2Si=CH_2$  silenes by measuring the Si=C  $\pi$ -bond energies as the rotational barriers about the Si=C double bond. We also report here the geometric and electronic structures of Si-substituted silenes paying attention to their similarities to (and discrepancies between) the selected carbon and germanium analogs as well as to the isoelectronic phosphenes. In particular, we aimed at finding whether silenes are the last planar Group 14 hetero- $\pi$ -systems, followed by heavier analogs having a trans-bent geometry. By comparing silenes and their analogs,  $X=CH_2$  (X =  $R_2E$ , E = C, Ge), and isoelectronic phosphene,  $RP=C$ , we were mainly interested in tracing the changing of their structural and energetic parameters depending on the nature of E and R. At last, we present a further evidence resulting from our study of the rotational barriers and the potential energy profiles of the internal rotation about the Si=C bond in silene [7] and  $P^+-C^-$  bond in phosphorane [8] against the statement to “consider silaolefines as C-ylides of silicon” [9].

## 2. Computational methods

### 2.1. Full geometry optimization

Full geometry optimization of silenes (Table 1) as well as the selected alkenes, germenes, and phosphenes (Table 5) was performed using the standard 6-31G(d) basis set at MP2 level of theory [10]. Zero-point vibrational energies (ZPE) were determined at MP2/6-31G(d) level of theory. Hydrogen atomic mass of 1.088 [11] linearizing the difference  $\Delta v = v_{\text{calc}} - v_{\text{exp}}$  and the scale factor of 0.96 were used when calculating ZPE. Final energies were calculated using the fourth-order perturbation theory MP4 for the MP2/6-31G(d) geometries. These single-point MP4 calculations were carried out employing an extended basis denoted 6-311G(d). This basis consists of the 6-311G(d) basis for the elements of the second period and hydrogen, and the McLean–Chandler (12s, 9p)/(6s, 5p)(d) basis for the third period elements [12]. The full notation for the basis used is MP4/6-311G(d)//MP2/6-31G(d). All MP2 and MP4 calculations were performed using GAMESS suite [13] except the MP4 calculations for the germanium

Table 1

Geometric parameters for silenes,  $R^1R^2Si=CH_2$ , described by Fig. 1 (E = Si, bond lengths in (Å) and bond angles in (°))

$R^1$	$R^2$	$r_1$	$r_2$	$r$	$r_3$	$r_4$	$\alpha$	$\beta_1$	$\beta_2$	$\gamma$	$\varepsilon_1$	$\varepsilon_2$	$\tau_1$ ( $\tau_2$ )
H <sup>a</sup>	H	1.482	1.482	1.718	1.085	1.085	115.1	122.4	122.4	116.1	121.9	121.9	0
CH <sub>3</sub> <sup>b</sup>	H	1.878	1.487	1.716	1.086	1.086	115.0	124.5	120.5	115.9	122.5	121.6	0
SiH <sub>3</sub> <sup>c</sup>	H	2.333	1.489	1.728	1.086	1.087	119.2	121.6	119.2	115.9	121.8	122.3	0
OH <sup>d</sup>	H	1.667	1.476	1.703	1.084	1.086	106.9	127.8	125.3	116.3	125.0	118.7	0
NH <sub>2</sub>	H	1.718	1.482	1.706	1.085	1.086	109.1	127.2	123.7	116.3	124.4	119.2	2.0 (4.2)
Cl	H	2.045	1.477	1.706	1.084	1.087	111.1	123.4	125.6	117.2	123.5	119.4	0
F <sup>e</sup>	H	1.619	1.477	1.698	1.084	1.087	109.2	124.2	126.5	117.2	124.2	118.7	0
SiH <sub>3</sub>	CH <sub>3</sub>	2.025	1.610	1.726	1.083	1.083	108.4	126.3	125.3	118.5	120.3	121.1	0
OH	CH <sub>3</sub>	2.335	1.888	1.706	1.086	1.087	118.5	119.8	121.7	115.7	121.6	122.7	0
MeO	CH <sub>3</sub>	1.674	1.874	1.707	1.084	1.085	113.1	121.6	125.3	116.8	122.9	120.1	0.7 (5.8)
Cl	CH <sub>3</sub>	2.056	1.868	1.706	1.084	1.086	111.2	121.1	127.7	122.9	120.1	116.9	0
F	CH <sub>3</sub>	1.725	1.873	1.699	1.085	1.085	109.8	125.0	125.1	116.1	123.8	120.0	3.2 (5.6)
SiH <sub>3</sub>	F	1.619	1.888	1.706	1.087	1.088	118.6	119.8	121.7	115.7	121.6	122.7	0.0
Cl	F	1.624	1.863	1.699	1.084	1.085	109.6	121.9	128.4	116.9	123.4	119.7	0

The following geometric parameters (basis 3-21G) were published [21].

<sup>a</sup>  $r_1 = 1.474$ ,  $r = 1.718$ ,  $\beta_1 = 122.2$ ,  $r_3 = 1.074$ ,  $\varepsilon_1 = 122.6$ .

<sup>b</sup>  $r_1 = 1.907$ ,  $r = 1.716$ ,  $\beta_1 = 124.5$ ,  $r_3 = 1.086$ ,  $\varepsilon_1 = 122.5$ .

<sup>c</sup>  $r_1 = 2.333$ ,  $r = 1.725$ ,  $\beta_1 = 122.2$ ,  $r_3 = 1.075$ ,  $\varepsilon_1 = 122.3$ .

<sup>d</sup>  $r_1 = 1.659$ ,  $r = 1.705$ ,  $\beta_1 = 126.5$ ,  $r_3 = 1.074$ ,  $\varepsilon_1 = 123.4$ .

<sup>e</sup>  $r_1 = 1.628$ ,  $r = 1.698$ ,  $\beta_1 = 127.7$ ,  $r_3 = 1.074$ ,  $\varepsilon_1 = 120.4$ .

compounds which were performed using GAUSSIAN 98 package [14].

## 2.2. Calculation of the rotational barriers

$\pi$ -bond energy,  $D_\pi(E=C)$ , in simple molecules, such as ethylene and silene, can be calculated as a rotational barrier about the E=C bond. The latter is the difference between the energy of the ground state of the doubly bonded molecules and the energy of their “perpendicular” conformation which being the transition state on the rotational path is of a singlet biradical nature [15].

$$\Delta E_r = E_{\text{total}}(\varphi = 90^\circ) - E_{\text{total}}(\varphi = 0^\circ) \quad (1)$$

A reasonable estimation of the barriers can be achieved by using multiconfigurational self-consistent approaches (MCSCF) [16]. However, the calculation of the rotational minima and the rotational transition states at the same level of theory is problematic because MCSCF approach requires an application of the complete valent active spaces of different sizes for various molecules which are to be compared. Benassi et al. developed a method for the calculation of the rotational barriers of ethylenes [17] based on the interpolation of the energy of the perpendicular conformation using a Fourier truncated function analytically extended from the HF molecular energies calculated for the frozen conformations twisted up to 60°. The method suggests that the  $\pi$ -bond character is progressively lost when the molecules are twisted from their planar conformations about the double bond. The energy of the perpendicular conformation was found by extrapolating the potential energy profile for the internal

rotation about the double bond described by a Fourier-type series Eq. (2).

$$V(\varphi) = \frac{1}{2}[V_2(1 - \cos 2\varphi) - V_4(1 - \cos 4\varphi)] \quad (2)$$

Here  $V_2$  is the barrier height and  $V_4$  a parameter showing the deviation of  $V(\varphi)$  from a pure cosine dependence. We extended this approach to determine the rotational barriers about the E=C (X = Si, C, Ge, P) bonds in silenes, their analogs, and phosphenes. The parameters  $V_2$  and  $V_4$  were obtained through a  $V(\varphi)$  non-linear regression of the total molecular energies, calculated at the MP4/6-311G(d)//MP2/6-31G(d) level, plotted for the conformations obtained by simultaneously freezing the rotational angle  $\varphi$  (at 0°, 10°, 20°, 30°, 40°, 50°, and 60°), preserving the  $R_1R_2SiC$  and  $H_2CSi$  fragments planar, and relaxing all the other geometrical parameters [18]. The calculation of  $V_2$  for ethylene produced the value 64.2 kcal mol<sup>-1</sup> which is in a good agreement with the previously estimated value of  $D_\pi(C=C)$  being equal to 65 kcal mol<sup>-1</sup> [16].

The calculation of the potential energy function (PEF) for the parent ethylene, silene, germene, and phosphene was carried out as follows. The values of  $E(\varphi)$  were calculated as it was described previously, whereas the energies  $E(70^\circ)$  and  $E(80^\circ)$  were obtained from a non-linear extrapolation of the potential function (Eq. (1)) using  $V_2$  and  $V_4$  values. For the estimation of  $E(90^\circ)$   $V_2$  values were used. The estimation of PEF for phosphorane was performed by calculating the total molecular energies at the MP4/6-311G(d)//MP2/6-31G(d) level for the conformations obtained by freezing the rotational angle  $\varphi$  from 0° to 360° with 5° steps applying the flexible rotor approximation. The station-

ary points of phosphorane's PEF were determined by using the MP4/6-311G(d)//MP2/6-31G(d)+ZPE level of theory.

### 2.3. Energies of singlet–triplet splitting for carbenoid species

A calculation of the inequality (Eq. (3)) was performed to check the substituents' effect on the planarity of silenes and their Group 14 analogs from the viewpoint of Carter–Goddard–Malrieu–Trinquier (CGMT) model [19].

$$\sum \Delta E_{S \rightarrow T} < \frac{1}{2} D_{\sigma+\pi}(E=C) \quad (3)$$

Here  $E = R_2C$ ,  $R_2Si$ ,  $R_2Ge$ , and  $\sum \Delta E_{S \rightarrow T}$  is the sum of singlet–triplet splitting of the carbenoids from which the double bond is formed. The geometries of  $R_2C$ ·,  $R_2Si$ ·, and  $R_2Ge$ · in the singlet and triplet states were optimized and their vibrational frequencies were calculated in the harmonic approximation employing the B3LYP/6-31+G(d,p) method of the density functional theory using GAUSSIAN package [14].

### 2.4. Topological analysis of electron density

The topological analysis of the electron density, based on the Bader's "Atoms in Molecules" theory [20], was performed using the B3LYP/6-31+G(d,p) method of the density functional theory in GAUSSIAN package [14].

## 3. Results and discussion

### 3.1. Silenes

#### 3.1.1. Geometries

The structures of disubstituted silenes,  $R_2Si=CH_2$ , optimized at the MP2/6-31G(d) level were published earlier (Fig. 1) [5]. The following trend in changing of the Si=C bond distance may be observed: in  $R_2Si=CH_2$  silenes it shortens by 0.053 Å (3.05%) on going from 1,1-disilylethene to 1,1-difluoroethene. Geometries of silenes bearing miscellaneous substituents are given in Table 1.

Like  $R_2Si=CH_2$  most of  $R^1R^2Si=CH_2$  silenes possess fully planar geometries (the sum of the angles of

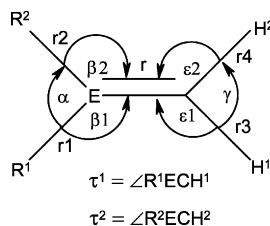


Fig. 1. Schematic for the optimized geometries of silenes, their analogs, and phosphenes.

$R^1R^2SiC$  and  $H_2CSi$  fragments is equal to  $360 \pm 0.1^\circ$ ). Silenes  $NH_2(H)Si=CH_2$  and  $CH_3(F)Si=CH_2$  are exclusions. Their out of plane angles of  $CH_2$  moiety are  $2.3^\circ$  and  $2.8^\circ$ , respectively (Table 1). As it was expected electronegative substituents at silicon shorten the Si=C bond in  $R^1R^2Si=CH_2$ , e.g. on going from  $SiH_3(H)Si=CH_2$  to  $F(H)Si=CH_2$  the silicon carbon double bond is getting shorter by 0.03 Å.

The planar geometries of a number of calculated gem-substituted silenes are in agreement with the CGMT model requiring for the planar doubly bonded molecules the inequality (Eq. (3)) to be valid for  $E = Si$  [19], i.e.  $0.5D_{\sigma+\pi}(Si=C) - \sum \Delta E_{S \rightarrow T} > 0$ . The terms of the equation, i.e. the energies of the singlet–triplet splitting of the carbenoid species and the total Si=C bond energies [5], are listed in Table 2 [22].

The plot of the difference  $0.5D_{\sigma+\pi}(Si=C) - \sum \Delta E_{S \rightarrow T}$  vs. Pauling electronegativity of substituents produces a good linear relationship (Fig. 2). It is seen that the difference remains positive indicating the planar geometry of  $R_2Si=CH_2$  silenes bearing various substituents.

The difference between the half-sums of  $\sigma+\pi$  Si=C bond energies and the singlet–triplet splitting becomes smaller as more electronegative substituents are attached to silicon. It falls from 67.1 ( $(SiH_3)_2Si=CH_2$ ) kcal mol<sup>-1</sup> to 4.0 ( $F_2Si=CH_2$ ) kcal mol<sup>-1</sup>, i.e. even for difluorosilene the inequality (Eq. (3)) is still valid [33]. Therefore, CGMT calculations predict the planar geometry for the whole family of  $R_2Si=CH_2$  silenes which is in a perfect agreement with the geometries calculated at the MP2/6-31G(d) level (see Table 1). In this sense, silenes are a "classical" planar doubly bonded system [3p].

#### 3.1.2. Electronic structure of silenes and a nature of Si=C double bond

According to Alrichs' and Heinzmann's [15] ab initio calculations using the double  $\zeta$  quality basis set, a covalent and high-polar  $Si^{+\delta}=C^{-\delta}$  double bond was predicted. Another claim based on the valence bond theory says that the  $\pi$ -bond in the second and the third row molecules is neither covalent nor ionic but originates in the covalent–ionic mixing resulting in a charge shift bonding [34]. Also, there is a suggestion "to consider silaolefins as C-ylides of silicon" (see Section 3.3) [9]. The effect of substituents at silicon on the polarity of the Si=C double bond was examined by Apeloig and Karni [21]. Having compared the total and  $\pi$ -charges (the 6-31G\*/3-21G level of theory) in mono-substituted silenes they concluded that "the charge polarization mainly occurs in the  $\sigma$ -framework".

To compare the effect of substituents on the nature of the Si=C and C=C double bonds in silenes and ethylenes, we calculated at the MP4/6-311G(d)//MP2/6-31G(d) level of theory (Table 3) [35] the Mulliken and Bader total charges on Si and C atoms,  $Q_{Si}$  and  $Q_C$ , as

Table 2

Energies of singlet–triplet splitting of the carbenoid species,  $\Sigma\Delta E_{S\rightarrow T}$ , and the total E=C bond energies,  $D_{\sigma+\pi}(E=C)$ , in  $R_2E=CH_2$  (E=Si, Ge) (in kcal mol<sup>-1</sup>)

Cabenoid	$\Delta E_{S\rightarrow T}$	X in X=CH <sub>2</sub>	$\Sigma\Delta E_{S\rightarrow T}$	$0.5D_{\sigma+\pi}-\Sigma\Delta E_{S\rightarrow T}$	$D_{\sigma+\pi}(E=C)$	$0.5D_{\sigma+\pi}$
SiH <sub>2</sub>	20.2 <sup>a</sup>	H <sub>2</sub> Si	7.8 <sup>b</sup>	56	127.5 <sup>c</sup>	63.8
Si(CH <sub>3</sub> ) <sub>2</sub>	26.4	(CH <sub>3</sub> ) <sub>2</sub> Si	14.0	50.2	128.4 <sup>c</sup>	64.2
Si(SiH <sub>3</sub> ) <sub>2</sub>	8.7	(H <sub>3</sub> Si) <sub>2</sub> Si	-3.7	67.1	126.8 <sup>c</sup>	63.4
Si(OCH <sub>3</sub> ) <sub>2</sub>	65.2	(CH <sub>3</sub> O) <sub>2</sub> Si	51.9	13.2	130.2 <sup>c</sup>	65.1
Si(NH <sub>2</sub> ) <sub>2</sub>	56.1	(H <sub>2</sub> N) <sub>2</sub> Si	43.7	21.1	129.5 <sup>c</sup>	64.8
SiCl <sub>2</sub>	52.8	Cl <sub>2</sub> Si	40.4	24.5	129.7 <sup>c</sup>	64.9
SiF <sub>2</sub>	74.0 <sup>d</sup>	F <sub>2</sub> Si	61.6 <sup>e</sup>	4	131.2 <sup>c</sup>	65.6
CH <sub>2</sub>	-12.4 <sup>f</sup>	H <sub>2</sub> C	-24.8 <sup>g</sup>	100.8	152 <sup>h</sup>	76
CF <sub>2</sub>	52.2	F <sub>2</sub> C	39.8	36.9	153.3 <sup>h</sup>	76.7
GeH <sub>2</sub>	27.6 <sup>i</sup>	H <sub>2</sub> Ge	15.2 <sup>j</sup>	46.3	123.0 <sup>h</sup>	61.5
GeF <sub>2</sub>	71.2 <sup>k</sup>	F <sub>2</sub> Ge	58.8 <sup>l</sup>	-4.3	109.0 <sup>h</sup>	54.5

<sup>a</sup> 17.7 [23], 17.7 [24], 16.7 [25], 19.0 [26].

<sup>b</sup> 9.0 [27].

<sup>c</sup>  $D_{\sigma+\pi}(Si=C)$  was taken as the sum of  $D(Si-C)$  in  $R_2MeSi-CH_3$  and  $D_{\pi}(Si=C)$  [5]; for  $H_2Si=CH_2$ : 118.6 [28],  $131 \pm 5$  [29].

<sup>d</sup> 73.5 [30].

<sup>e</sup> 63.0 [27].

<sup>f</sup> -15.5 [23], -12.7 [27], -14.1 [27].

<sup>g</sup> -20.0 [27].

<sup>h</sup> Values obtained from the difference,  $D_{\sigma}(E=C)-D_{\pi}(E=C)$ , and rotational barriers around E=C bonds (see Section 3.2.3).

<sup>i</sup> 22.5 [31], 22.9 [23].

<sup>j</sup> 12.5 [27].

<sup>k</sup> 74.0 [32].

<sup>l</sup> 64.0 [27].

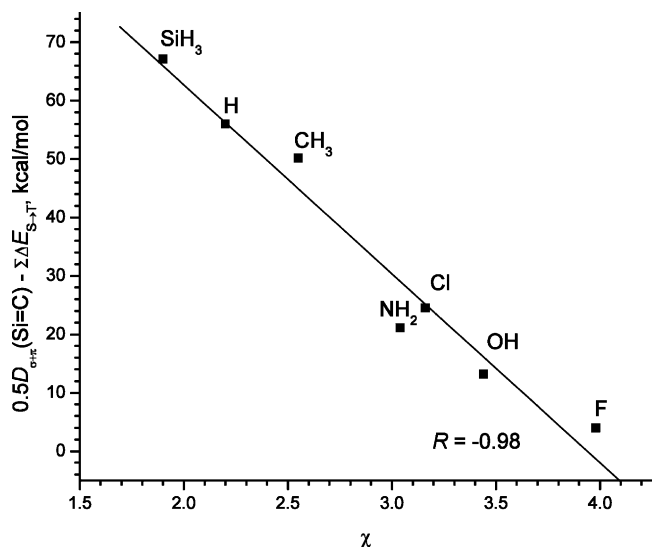


Fig. 2. Plot of  $0.5D_{\sigma+\pi}(Si=C)-\Sigma\Delta E_{S\rightarrow T}$  vs. electronegivity.

well as the following Bader's [20] topological indices: the position of the bond critical point,  $d_c$ , given by its distance to C atom in  $R_2X=CH_2$  (X = C and Si), the electron charge density at the bond critical point,  $\rho$ , the Laplacian of the charge density,  $\nabla^2\rho$ , the bond ellipticity,  $\varepsilon$ , and the energy of the electrostatic interaction between the doubly bonded atoms,  $E_{el.-static}$ .

Bader's indices together with the isodensity contour maps of  $\pi$ -HOMO are used below to distinguish between the homonuclear covalent and the hetero-

nuclear polar double bonding in olefins and silenes. According to Bader, the rank of the bond's critical point is one of the main characteristics of the type of bonding. Both olefins and silenes have the same rank of the critical point (3, -1) inherent to the covalent bond. The rank shows that the electronic charge density is accumulated between the nuclei that are linked [20b].

The isodensity contour map of  $\pi$ -HOMO in Fig. 3 demonstrates a symmetrical distribution of the  $\pi$ -electron density between the both  $sp^2$ -hybridized carbon atoms in ethylene. In contrast, the  $\pi$ -electron density in silene is mainly concentrated on the carbon atom [36]. The cloud of electron density is highly asymmetric and elongates towards the silicon.

The ellipticity,  $\varepsilon$ , being a measure of skewness of the electron charge density distribution in the doubly bonded molecules is sensitive to the variation of substituents' electronegativity.

In ethylene,  $\varepsilon$  is equal to 0.359 (Table 3). In disilylethene it falls to 0.261, whereas in difluoroethene it rises up to 0.562. Due to their asymmetrical charge distribution,  $\varepsilon$  in silenes is higher (0.424–0.843) and grows linearly as substituents' electronegativity increases (Fig. 4). The higher the electronegativity, the higher is  $\varepsilon$ .

The position of the bond's critical point is also indicative of an asymmetry in the electron charge distribution. In ethylene with a symmetrical electron distribution,  $d_c$  is located in the middle of the C=C bond. In disubstituted ethylenes,  $d_c$  is shifted to a more

Table 3  
Bader data on silenes, their analogs, and isoelectronic phosphenes, X=CH<sub>2</sub>

X	$r(\text{E}=\text{C})$	$d_c^a$	$\rho$	$\nabla^2\rho$	$\varepsilon$	$Q_x$	$Q_C$	$E_{\text{el.-static}}$
H <sub>2</sub> Si	1.718 <sup>b</sup>	1.033	0.141	0.555	0.523	+2.374	-1.236	-1.208
SiCH <sub>4</sub> (60°)	1.736	0.929	0.139	0.499	0.467	+2.377	-1.252	-1.202
Me <sub>2</sub> Si	1.716 <sup>b</sup>	1.027	0.142	0.554	0.570	+2.586	-1.307	-1.337
(H <sub>3</sub> Si) <sub>2</sub> Si	1.738 <sup>b</sup>	1.049	0.136	0.527	0.424	+0.844	-1.179	-0.679
(HO) <sub>2</sub> Si	1.698 <sup>b</sup>	1.012	0.148	0.550	0.768	+2.827	-1.377	-1.498
(H <sub>2</sub> N) <sub>2</sub> Si	1.703 <sup>b</sup>	1.049	0.146	0.542	0.660	+2.856	-1.420	-1.540
Cl <sub>2</sub> Si	1.698 <sup>b</sup>	1.016	0.147	0.546	0.701	+2.538	-1.311	-1.319
F <sub>2</sub> Si	1.685 <sup>b</sup>	1.004	0.150	0.548	0.843	+2.848	-1.381	-1.506
H <sub>2</sub> Ge	1.784	0.929	0.158	0.224	0.292	+1.220	-0.773	-0.334
F <sub>2</sub> Ge	1.774	0.9	0.159	0.138	0.342	+1.866	-0.768	-0.408
(H <sub>3</sub> Si) <sub>2</sub> Ge	1.799	1.457	0.154	0.226	0.253	+0.405	-0.749	-0.189
H <sub>2</sub> C	1.336	0.668	0.335	-0.977	0.359	-0.116	-0.116	0.067
(H <sub>3</sub> Si) <sub>2</sub> C	1.353	0.689	0.322	-0.884	0.261	-1.431	-0.117	0.070
F <sub>2</sub> C	1.325	0.544	0.335	-0.979	0.562	+0.929	+0.035	0.091
HP	1.677	1.031	0.183	0.387	0.395	+1.279	-0.988	-0.821
FP	1.657	1.018	0.196	0.400	0.602	+1.657	-1.094	-1.044
H <sub>3</sub> SiP <sup>c</sup>	1.685	1.035	0.180	0.372	0.325	-	-	-

<sup>a</sup> Distance from the critical point to C atom of the CH<sub>2</sub> group.

<sup>b</sup> Distances taken from Ref. [5].

<sup>c</sup> The atomic surface sheet was not determined due to the iterative divergence.

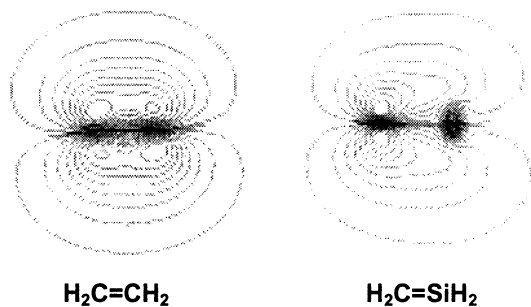


Fig. 3. Highest occupied molecular orbitals (isodensity lines are located with the interval 0.02 e).

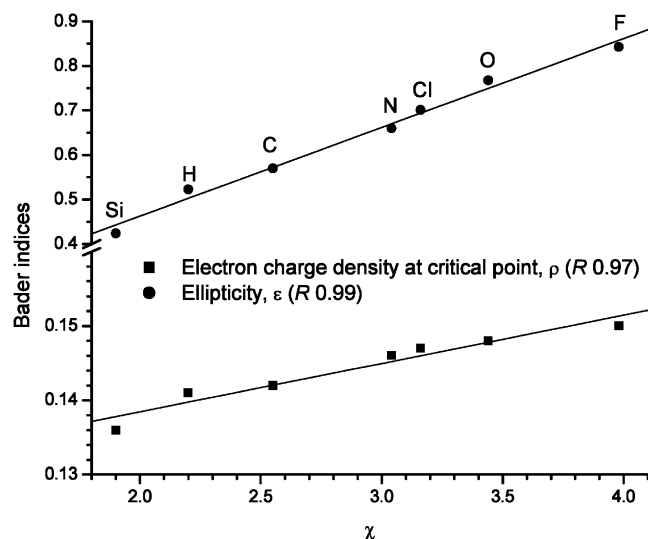


Fig. 4. Plots of electron charge density at the critical point and ellipticity of the Si=C bond vs. Pauling electronegativity.

electronegative moiety of the molecule. Thus, in disilylene, it is closer to the more negative carbon atom bearing silyl substituents (-1.431 e against -0.117 e for CH<sub>2</sub> group). In difluoroethylene,  $d_c$  is closer to the methylene group (0.035 e against 0.929 e in F<sub>2</sub>C group). In contrast, the bond's critical point in silenes is always closer to a positively charged doubly bonded atom, i.e. silicon (Table 3). As more electronegative substituents are attached to silicon, its position shifts to a C atom (Fig. 5) making more asymmetrical the electron charge distribution [37]. It results in the accumulation of the electron density by carbon making the positive charge on Si and the negative charge on C

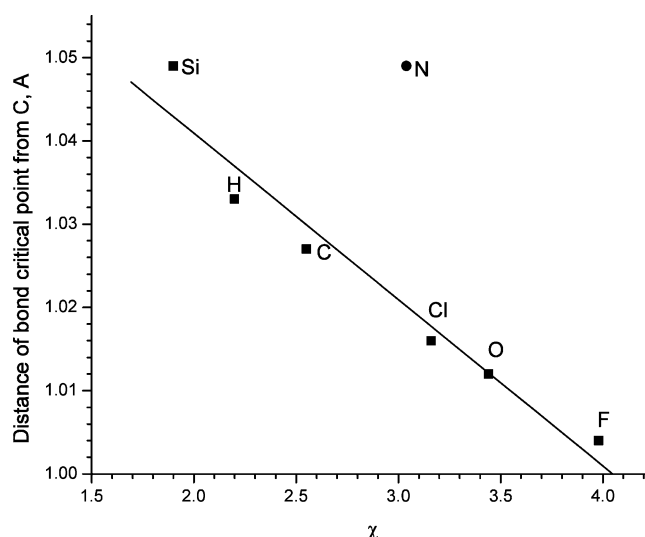


Fig. 5. Plot of the distance from the Si=C bond's critical point to C atom vs. Pauling electronegativity ( $R = 0.97$ ).

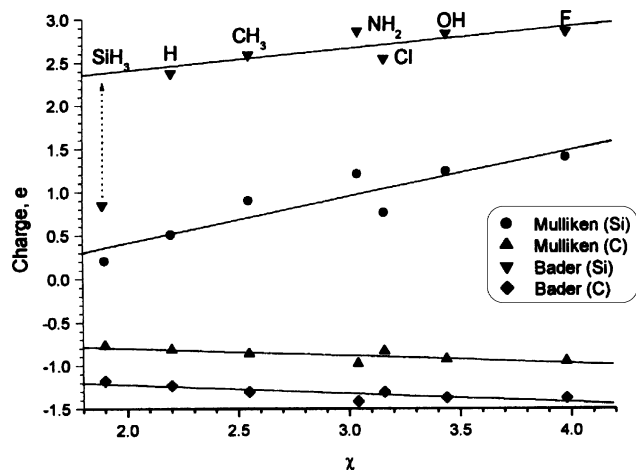


Fig. 6. Plot of Mulliken and Bader charges on Si and C atoms in disubstituted silenes vs. Pauling electronegativity.

increased. Overall, the Bader's charges are greater by absolute value than Mulliken's (Fig. 6) [38].

The increase in the accumulation of the negative charge at C also leads to the growth of the electron density at the bond's critical point. On going from the less to more electronegative substituents in silenes  $\rho$  grows from 0.136 to 0.150 e and linearly depends on electronegativity (Fig. 4). The low  $\rho$  values that are about a half lower than those for the pure covalent bonds in ethylenes (0.322–0.338 e) indicate a high polarity of the Si=C bond. Similarly, the positive sign of the Laplacian of the electron charge density is also indicative of a strong polar character of the Si=C bonds (olefins are characterized by the negative values of  $\nabla^2\rho$ ). In turn, the growth of charge separation in silenes (Table 3) is followed by the increase in the electrostatic contribution to the bond energy,  $E_{\text{el.-static}}$ .

We suggested that the increase in the electron density at the critical point is correlated to the change in the Si=C bond energy. Indeed, the plot of  $D_{\sigma+\pi}(\text{Si}=\text{C})$  for seven silenes  $\text{R}_2\text{Si}=\text{CH}_2$  (Table 2) vs.  $\rho$  (Table 3) turned to be a linear relationship (Fig. 7).

### 3.1.3. Rotational barriers about the Si=C bond

The main feature of the rotational barriers is that being rotated up to  $90^\circ$  about the double bond the molecule transforms into a biradical transition state, the  $\pi$ -bond of which is broken while the  $\sigma$ -bond remains intact. Of course, the other changes in the geometry can be associated with the rotation. These are the lengthening of the Si–C bond, the changing in the R–Si and C–H distances, the pyramidalization of the  $\text{R}_2\text{SiC}$  node, etc.

As it was pointed out in Section 2.2, the interpolation method [17] used in this work for the estimation of the rotational barriers requires the total molecular energies calculation for several conformations with the rotational angle up to  $60^\circ$ . Being rotated up to  $60^\circ$  the Si=C bond

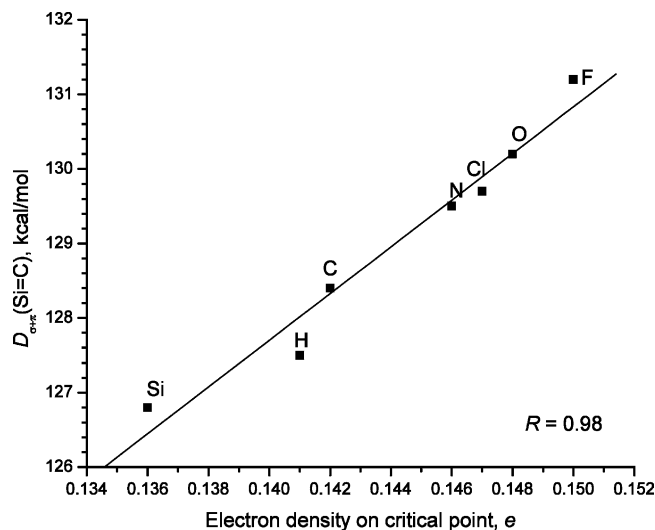


Fig. 7. Plot of  $D_{\sigma+\pi}(\text{Si}=\text{C})$  of  $\text{R}_2\text{Si}=\text{CH}_2$  vs. Bader charges at critical points ( $R = 0.969$ ).

elongates by 0.018, 0.01, and 0.023 Å in the parent, dimethyl-, and disilylsilenes, respectively. In particular, the Si=C bond distance in silene is equal to 1.736 Å (Table 3). The elongation for the other silenes is negligible (0.002–0.004 Å). Dihydroxy and difluorosilenes are rather an exception. Their Si=C bond distance shortens by 0.007 and 0.004 Å, respectively. The Si–R distances also increase by 0.0006–0.007 Å, respectively, except dihydroxy-, diamino-, and difluorosilene for which it shortens by 0.007, 0.01, and 0.004 Å, respectively. The obtained rotational barriers are given in Table 4 [39].

The relationship between the rotational barriers and the Si=C distances is shown in Fig. 8.

It is seen that having a reasonably good correlation coefficient the plot is similar to the previously published [5] dependence of  $D_{\pi}(\text{Si}=\text{C})$  vs.  $r(\text{Si}=\text{C})$  for seven 1,1-disubstituted silenes. The dispersion of the points is mainly caused by the redistribution of the electron density during the mutual rotation of the both planar  $\text{R}^1\text{R}^2\text{SiC}$  and  $\text{H}_2\text{CSi}$  fragments. In particular, in hydroxy-, methoxy-, and amino-substituted silenes the electron density is shifted to the oxygen and the nitrogen atom, respectively, forming the partial double bond between Si and O, and Si and N. Silyls make the rotational barriers rather underestimated. Nevertheless, our results show that the rotational barriers tend to decrease as more electronegative substituents are attached to silicon. For instance, in the series  $\text{Me}_2\text{Si}=\text{CH}_2$ ,  $\text{MeFSi}=\text{CH}_2$ , and  $\text{F}_2\text{Si}=\text{CH}_2$  the values of the barriers decrease, cf. 36.5, 31.2, and 26.3 kcal mol $^{-1}$ , respectively. This trend sharply contrasts with that published by Allison and McMahon [6]. Thus, the theory makes a challenge to the experiment.

In supporting information we listed the values of the Mulliken  $\pi$ -population in silenes studied which also

Table 4  
Rotational barriers about the Si=C double bond in  $R^1R^2Si=CH_2$  (in kcal mol<sup>-1</sup>)

$R^1$	$R^2$	Rotational barrier	$R^1$	$R^1$	Rotational barrier
H	H	40.0 <sup>a</sup>	Cl	CH <sub>3</sub>	33.8
CH <sub>3</sub>	H	38.7	F	CH <sub>3</sub>	31.2
SiH <sub>3</sub>	H	38.5	CH <sub>3</sub>	CH <sub>3</sub>	36.5
OH	H	27.7	SiH <sub>3</sub>	SiH <sub>3</sub>	38.0
NH <sub>2</sub>	H	25.5	OH	OH	26.3
Cl	H	34.6	NH <sub>2</sub>	NH <sub>2</sub>	19.5
F	H	32.0	Cl	Cl	31.1
SiH <sub>3</sub>	CH <sub>3</sub>	36.1	F	F	26.3 <sup>a</sup>
OH	CH <sub>3</sub>	31.3	SiH <sub>3</sub>	F	31.7
MeOH	CH <sub>3</sub>	29.5	Cl	F	28.4

<sup>a</sup> Our values of the rotational barriers calculated as the difference between the total energies of the planar and “perpendicular” structures [15] of the parent silene and difluorosilene are 39.3 and 26.1, respectively.

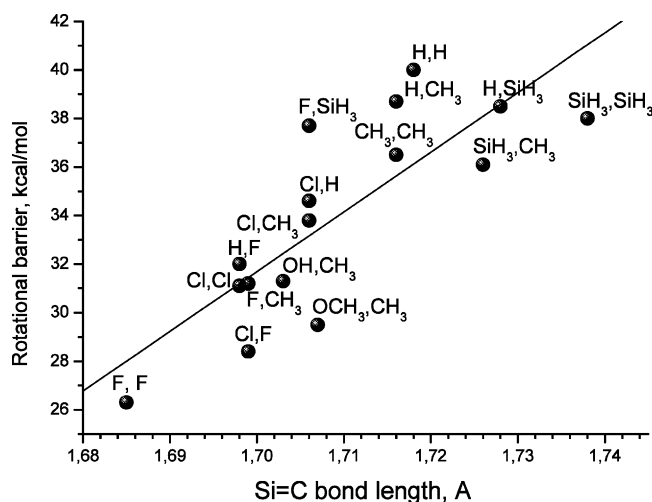


Fig. 8. Rotational barriers about the Si=C double bond vs. Si=C bond distance ( $R = 0.8$ ).

similarly depend on the substituents' electronegativity. This observation stimulated us to seek a correlation between the rotational barriers and the Mulliken  $\pi$ -population. Such dependence is shown in Fig. 9. It is seen that the lower the  $\pi$ -electron density on silene's HOMOs, the lower is the rotational barrier about the Si=C double bond.

### 3.2. Silene analogs and isoelectronic phosphenes

#### 3.2.1. Geometric and electronic structure

The geometries of silene analogs, i.e. olefins and germenes, as well as the isoelectronic phosphenes are given in Table 5 for comparison with silenes (Table 1) [40].

Unlike its Si-substituted and parent analogs, difluorogermene possesses a non-planar trans-bent geometry. CGMT analysis of the planar  $R_2E=CH_2$  series ( $E = C, Si$ ) results in the positive sign of the difference  $0.5D_{\sigma+\pi}(E=C) - \Sigma\Delta E_{S\rightarrow T}$  (Table 2), whereas of trans-bent difluorogermene in the negative one.

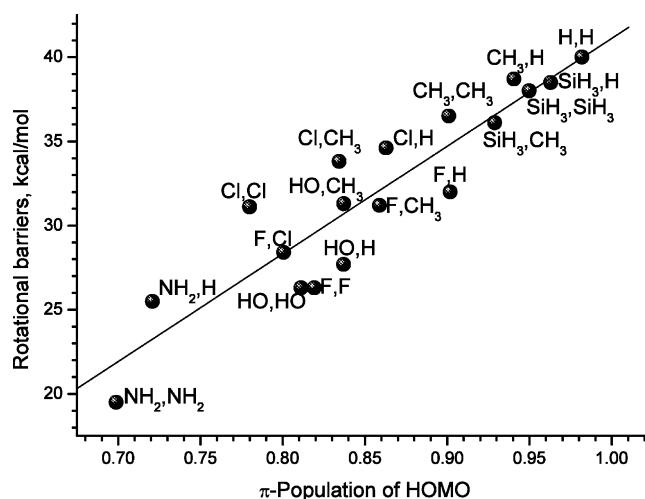


Fig. 9. Plot of rotational barriers of silenes vs. their  $\pi$ -population of HOMO ( $R = 0.917$ ).

For the all calculated doubly bonded compounds the similar trend in changing of the E=C bond distance is observed on going from silyl- to fluorine-substituted derivatives. For instance, in olefins the C=C bond shortens by 0.028 Å (2.07%). In germenes and phosphenes the Ge=C and P=C double bonds shortening is almost similar and amounts to 0.029 (1.61%) and 0.028 (1.67%) Å, respectively. Interestingly, the same trend in silenes is much more pronounced (see Section 3.1.1). Thus, on going from less to more electronegative substituents the double bond shortening is a generic feature of the  $X=CH_2$  compounds (where  $X = R^1R^2C, R^1R^2Si, R^1R^2Ge, RP$ ). Besides, upon increasing the electronegativity of the substituents, the angle  $\alpha$  (Table 5) decreases monotonically in olefins and germenes. A similar trend in  $\alpha$  (Table 1) was previously observed in silenes [5].

The isodensity contour diagrams of germene [48] and phosphene are looking similar to that of silene (Fig. 3) [13] and reveal a high asymmetry in the electron charge distribution in these molecules. All the Bader topologi-



Table 5  
Geometric parameters for silene analogs and phosphenes described by Fig. 1 (bond lengths in (Å) and bond angles in (°))

X	$r_1$	$r_2$	$d$	$r_3$	$r_4$	$\alpha$	$\beta_1$	$\beta_2$	$\gamma$	$\varepsilon_1$	$\varepsilon_2$	$\tau_1$ ( $\tau_2$ )
(H <sub>3</sub> Si) <sub>2</sub> C	1.879	1.879	1.353	1.090	1.090	122.3	118.8	118.8	115.0	122.5	122.5	0
H <sub>2</sub> C	1.085	1.085	1.336 <sup>a</sup>	1.085	1.085	116.6	121.7	121.7	116.6	121.7	121.7	0
F <sub>2</sub> C	1.331	1.331	1.325 <sup>b</sup>	1.079	1.079	109.9	125.0	125.0	120.0	120.0	120.0	0
(H <sub>3</sub> Si) <sub>2</sub> Ge	2.374	2.374	1.803	1.087	1.087	121.5	119.2	119.3	116.5	121.8	121.8	0
H <sub>2</sub> Ge	1.540	1.540	1.784 <sup>c</sup>	1.085	1.085	114.9	122.5	122.5	117.3	121.3	121.3	0
F <sub>2</sub> Ge	1.743	1.743	1.774	1.085	1.085	103.2	126.6	126.6	118.3	116.6	116.6	28.8 <sup>d</sup>
H <sub>3</sub> SiP	2.264	–	1.685	1.088	1.089	–	98.5	–	115.4	125.7	118.9	0
HP	1.421	–	1.677 <sup>e</sup>	1.086	1.087	–	97.2	–	116.0	124.8	119.2	0
FP	1.626	–	1.657	1.086	1.087	–	103.5	–	117.8	124.4	117.8	0
H <sub>3</sub> P <sup>+</sup> –CH <sub>2</sub> <sup>–</sup>	1.405	1.440	1.676 <sup>f</sup>	1.084	1.084	–	111.4	111.4	116.6	116.7	116.7	33.2

<sup>a</sup> 1.337 Å [41].

<sup>b</sup> 1.314 ± 0.006 Å [42], 1.340 Å [43], 1.315 Å [44], 1.323 Å [45].

<sup>c</sup> 1.770 Å [23].

<sup>d</sup> The out of plane angles in F<sub>2</sub>GeC and H<sub>2</sub>CGe nodes are equal to 16.4° and 29.1°, respectively.

<sup>e</sup> 1.62–1.71 Å with 1.67 Å being a typical value [46].

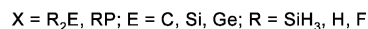
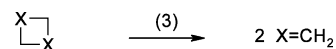
<sup>f</sup>  $r(\text{C–P})$ : 1.630–1.70 Å [47].

cal indices of Group 14 silene analogs and phosphenes are indicative of a strong polarity of the covalent X=C bonds (Table 3). The polarity is decreased in the following order: silenes > phosphenes > germenes. Like in silenes both the positive charge on X and the negative charge on C is accumulated on going from silyl- via hydrogen to fluorine-substituted E atom [49]. Accordingly, the electrostatic interaction between the doubly bonded atoms,  $E_{\text{el.-static}}$ , increases simultaneously with the growth of the charge separation. The positive sign of Laplacian,  $\nabla^2\rho$  (Table 3), for germenes and phosphenes also indicates the polarity of the E=C bonds. All the studied molecules containing the E=C bond have the common rank of the critical point (3, –1). Like in silenes the position of the critical points on the E=C bonds in germenes and phosphenes is always shifted closer to the heteroatom which is manifested by the values of  $d_c$  that are greater than the half of the E=C distance (Table 3). On going from the disilyl- to difluoro-substituted compounds the critical point gets slightly shifted to the more negatively charged carbon atom. Therefore, the distance from the critical point to the C atom of the CH<sub>2</sub> group,  $d_c$ , shrinks. For the all Group 14 silene analogs and phosphenes the ellipticity grows as the more electronegative substituents are attached to the E atom. The charge density at the critical point, which is maximal in olefins, seeks to decrease in the series: phosphenes > germenes > silenes. Thus, the trend in the charge density to grow as more electronegative substituents appear is a common property of the doubly bonded systems.

### 3.2.2. $\sigma$ - and $\pi$ -bond energy differences

Recently [5], we applied an ab initio thermochemical approach to the 2+2 cycloreversion reaction of 1,3-disilacyclobutanes (reaction (3), E = Si) to calculate the

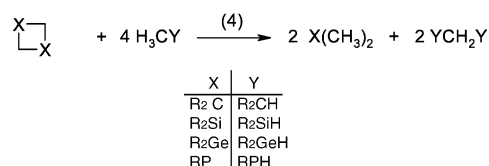
bond energies in silenes. With the same intention this approach was extended over the 2+2 cycloreversions of the other Group 14 1,3-dielementacyclobutanes:



The difference between the bond energies,  $D(\text{E–C})$  and  $D_\pi(\text{E=C})$ , was measured as the half-sum of the four-membered ring strain energy and the reaction enthalpy (Eq. (4)).

$$D(\text{E–C}) - D_\pi(\text{E=C}) = 0.5(E_s + \Delta H) \quad (4)$$

The merit of this equation is that both the strain energy and the 2+2 cycloreversion enthalpy are obtained directly from the computational experiments. The strain energies were calculated as the enthalpies of the homodesmic reactions (4).



To minimize the contribution of the correlation error in reactions (4) the strained ring systems were compared to the related unstrained counterparts so that the number of the chemical fragments is conserved. Earlier we calculated the strain energies of a number of tetrasubstituted 1,3-disilacyclobutanes using Y = SiH<sub>3</sub> and obtained the following strain energies (in kcal mol<sup>–1</sup>) [5]: 14.9 (R = SiH<sub>3</sub>) [50], 19.3 (R = H), and 27.0 (R = F). Although this reaction is fairly good for the parent rings, it does not work well for the substituents which can strongly affect the E–C bond

in the case of variously substituted rings. Now we used  $Y = R_2EH$  to minimize the correlation error. Particularly, it leads to the following strain energies in the above 1,3-disilacyclobutane series (in kcal mol<sup>-1</sup>): 17.9 (R = SiH<sub>3</sub>), 19.3 (R = H), and 26.8 (R = F). The calculated strain energies, 2+2 cycloreversion enthalpies, and differences between  $\sigma$ - and  $\pi$ -bond energies are given in Table 6.

The geometries of the four-membered rings (Fig. 10) given in Table 7 were studied to trace how the substitution at silicon atom by fluorines and silyls affects the structure of 1,1,3,3-tetrasubstituted cyclobutanes and 1,3-dielementacyclobutanes and how the latter affects the strain energies.

The following trends characterizing the substituent effect on the geometry of the Group 14 1,3-dielementacyclobutanes when compared to the non-planar parent molecules (flap angles,  $\tau$ , are equal to 30.8°, 21.4°, and 31.8° in cyclobutane, 1,3-disilacyclobutane, and 1,3-digermacyclobutane, respectively) were observed. Silyl flattens the four-membered rings making the flap angles 0.3°, 6.1°, and 0.5° and lengthens the E–C distances by 0.023 (3.5%) Å, 0.016 (0.8%) Å, and 0.012 (0.6%) Å, respectively. Despite the flattening, the strain energies are not increased but fall by 1.7, 1.4, and 1.6 kcal mol<sup>-1</sup>, respectively. Fluorine also flattens the four-membered rings in 1,3-disila- and 1,3-digermacyclobutanes making the E–C bonds shorter by 0.026 (1.4%) Å and 0.029 (1.5%) Å, respectively. In the case of fluorine substitution, the strain energies are increased by 7.5 and 11.8 kcal mol<sup>-1</sup>, respectively. Since both silyl and fluorine substitutions result in practically planar 1,3-

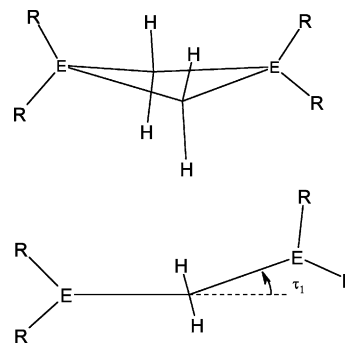


Fig. 10. Schematic for the optimized geometries of 1,1,3,3-tetrasubstituted cyclobutanes and 1,3-dielementacyclobutanes.

disila- and 1,3-digermacyclobutanes, the strain energies become lower upon silyl substitution due to the ring expansion ( $r_{Si...Si} = 2.664$  Å and  $r_{Ge...Ge} = 2.768$  Å) and higher upon fluorine substitution due to the ring contraction ( $r_{Si...Si} = 2.579$  Å and  $r_{Ge...Ge} = 2.675$  Å).

In the case of cyclobutanes fluorine flattens the ring but does not make the four-membered ring planar ( $\tau = 22.4^\circ$ ); it shortens the C–C bond by 0.023 (3.5%) Å. Although in the cyclobutane series the C–C bond lengths are changed to the greater extent than Si–C and Ge–C bonds in the Group 14 1,3-dielementacyclobutanes, the substituents affect the strain energy of the cyclobutane ring to a smaller extent. Indeed, silyl makes the strain energy lower by only 1.7 kcal mol<sup>-1</sup>, whereas fluorine makes it greater by 3.8 kcal mol<sup>-1</sup>.

Similarly to the Group 14 1,3-dielementacyclobutanes, the P–C bonds in 1,3-diphosphetanes become shorter when fluorine and longer when silyl is attached

Table 6

Strain energies of 1,1,3,3-tetrasubstituted cyclobutanes, 1,3-dielementacyclobutanes, *cyclo*-1,3-(X–CH<sub>2</sub>)<sub>2</sub>, 2+2 cycloreversion enthalpies,  $\sigma$ - and  $\pi$ -bond energy difference, and the rotational barriers of the double-bonded molecules, X=CH<sub>2</sub> (in kcal mol<sup>-1</sup>)

X	$E_s$	$\Delta E_s$	$\Delta H$	$\Delta\Delta H$	X=CH <sub>2</sub>	
					$D_\sigma(E=C) - D_\pi(E=C)$	Rotational barrier about E=C
(H <sub>3</sub> Si) <sub>2</sub> C	24.5	–1.7	13.5	–5.8	19.0	49.7
H <sub>2</sub> C	26.2	0	19.3	0	22.8	64.2 <sup>a</sup>
F <sub>2</sub> C	30.0	3.8	33.5	14.2	31.8	59.7
(H <sub>3</sub> Si) <sub>2</sub> Si	17.9	–1.4	74.1	–4.2	46.0	38.0
H <sub>2</sub> Si	19.3	0	78.3	0	48.8	40.0 <sup>b</sup>
F <sub>2</sub> Si	26.8	7.5	112.5	34.2	69.6	26.3
(H <sub>3</sub> Si) <sub>2</sub> Ge	15.3	–1.6	65.7	–3.5	40.5	34.7
H <sub>2</sub> Ge	16.9	0	69.2	0	43.0	40.0 <sup>c</sup>
F <sub>2</sub> Ge	28.7	11.8	104.8	35.6	66.7	21.1
<i>cis</i> -H <sub>3</sub> SiP	14.7	–0.2	33.9	3.2	24.3	36.8
<i>cis</i> -HP	14.9	0	30.7	0	22.8	46.1
<i>cis</i> -FP	12.0	–2.9	32.1	1.4	22.1	46.0
<i>trans</i> -H <sub>3</sub> SiP	13.9	–0.7	34.7	1.1	24.3	36.8
<i>trans</i> -HP	12.8	0	32.8	0	22.8	46.1 <sup>d</sup>
<i>trans</i> -FP	10.8	+1.2	33.4	–0.6	22.1	46.0

<sup>a</sup> 65.0 [16], 66.0 [51].

<sup>b</sup> 35.6 [16], 37.0 [16], 36.0 [51], 39.5 [52].

<sup>c</sup> 32.3 [53], 31.0 [51].

<sup>d</sup> 48.0 [54], 49.4 [28], 43.1 [16], 45.0 [16], 44.3 [52].

Table 7

Geometric parameters for 1,1,3,3-tetrasubstituted cyclobutanes and 1,3-dielementacyclobutanes, *cyclo*-1,3-(X-CH<sub>2</sub>)<sub>2</sub>, described by Fig. 10 (bond lengths in (Å) and bond angles in (°))

X	E–C	E···E	R–E	∠CEC	∠ECE	∠REC	∠RER	τ <sub>1</sub> <sup>a</sup>	τ <sub>2</sub>
(H <sub>3</sub> Si) <sub>2</sub> C	1.568	2.212	1.890	90.2	89.2	113.7	110.5	0.3	0.3
H <sub>2</sub> C	1.545	2.145	1.100	90.0	86.7	114.8	107.1	30.8	30.8
F <sub>2</sub> C	1.532	2.096	1.362	91.4	86.3	116.6	107.6	22.4	22.4
(H <sub>3</sub> Si) <sub>2</sub> Si	1.923	2.664	2.351	92.2	87.7	112.2	112.7	6.1	6.1
H <sub>2</sub> Si	1.907	2.632	1.494	90.7	87.3	111.8	108.9	21.4	21.4
F <sub>2</sub> Si	1.881	2.579	1.615	93.4	86.6	114.0	107.3	0.0	0.0
(H <sub>3</sub> Si) <sub>2</sub> Ge	1.992	2.768	2.384	92.0	88.0	111.9	115.3	0.5	0.5
H <sub>2</sub> Ge	1.980	2.709	1.543	89.7	88.8	112.0	109.7	31.8	31.8
F <sub>2</sub> Ge	1.951	2.675	1.748	93.4	86.6	115.0	103.8	0.0	0.0
<i>cis</i> -H <sub>3</sub> SiP	1.887	2.669	2.256	84.6	90.0	101.8	–	35.6	35.6
<i>cis</i> -HP	1.880	2.671	1.419	83.5	90.5	100.9	–	37.7	37.7
<i>cis</i> -FP	1.861	2.685	1.634	81.9	92.4	102.3	–	37.6	37.6
<i>trans</i> -H <sub>3</sub> SiP	1.885, 1.891	2.749	2.253	85.7	93.4	99.3, 100.7	–	15.2	16.3 <sup>b</sup>
<i>trans</i> -HP	1.883, 1.869	2.698	1.422	82.4	91.9	95.4, 102.2	–	33.2	35.9
<i>trans</i> -FP	1.858, 1.863	2.678	1.637	81.7	92.1	97.3, 102.8	–	36.1	39.5

<sup>a</sup> Flap angle.

<sup>b</sup> τ<sub>1</sub> ≠ τ<sub>2</sub> due to the asymmetry of *trans*-1,3-diphosphetanes.

to phosphorus (Fig. 10). The flap angles in 1,3-diphosphetanes are ca. 35° except *trans*-1,3-disilyl-1,3-diphosphacyclobutane which has the smaller value of τ (15.2°). Therefore, the main difference between 1,3-diphosphetanes and the Group 14 1,3-dielementacyclobutanes is that neither fluorine nor silyl substituents make the 1,3-diphosphetane ring flatter. That is probably why there are only negligible changes in the strain energies.

The substitution also affects the 2+2 cycloreversion enthalpies, Δ*H*<sub>3</sub>, of 1,1,3,3-tetrasubstituted cyclobutanes and the Group 14 1,3-dielementacyclobutanes [55]. Thus, silyl lowers Δ*H*<sub>3</sub> by 5.8, 4.2, and 3.5 kcal mol<sup>-1</sup>, whereas fluorine increases Δ*H*<sub>3</sub> by 14.2, 34.2, and 35.6 kcal mol<sup>-1</sup>, respectively. While both effects are inherent to the Group 14 1,3-dielementacyclobutanes, for *cis*- and *trans*-1,3-diphosphetanes they are negligible.

In silenes and their Group 14 analogs, the substituents affect the differences between the E=C σ- and π-bond energies, *D*<sub>σ</sub>(E=C)–*D*<sub>π</sub>(E=C), calculated from Eq. (4) (Table 6) [56]. The differences are about twice as greater for silenes, germenes, and phosphenes as for olefins themselves. Evidently, the latter is explained by the weaker X=C π-bonds in Group 14 analogs than those in olefins. Silyl lowers the difference, whereas fluorine mounts it in the Group 14 heavier analogs of olefins. Earlier, we concluded that the *D*<sub>σ</sub>(Si=C)–*D*<sub>π</sub>(Si=C) difference changes due to the strengthening σ-bond and the weakening π-bond on going from silyl to fluorine substituents at silicon [5]. The same effect is inherent to germenes and olefins. Neither silyl nor fluorine affects *D*<sub>σ</sub>(P=C)–*D*<sub>π</sub>(P=C) (Table 6).

### 3.2.3. Rotational barriers about the E=C bonds

High rotational barriers about the E=C bond in silene analogs and phosphenes (Table 6) are attributable to the doubly bonded molecules. For the parent compounds they correspond well to the literature data on the π-bond energies (see footnotes to Table 6). Like in 1,1-difluorosilene, the rotational barriers in 1,1-difluoro-substituted ethylene and germene are lower than those in the parent molecules. The effect grows on going from alkenes to silenes and germenes. In all the cases it is accompanied by the clear shortening of the E=C bond, which is the most pronounced for silenes (Tables 1 and 5). The rotational barriers for the silyl-substituted compounds are a fortiori underestimated. Therefore, they may not be used in the thermochemical calculations. Phosphenes are rather exclusionary. The prominent contraction of their P=C bond (Table 5) in the case of fluorine derivative does not affect the rotational barrier (Table 6) [57]. Therefore, the effect of π-bond weakening in silenes due to the pyramidalization of the geometry of tricoordinate silicon [5] is not characteristic of phosphenes where pyramidalization for dicoordinate phosphorus is undefined.

### 3.3. A comparison of silene with phosphorane

Earlier, Nefedov and coworkers [9] suggested “to consider silaolefins as C-ylides of silicon” based on the observation that “vibrational frequencies and force constants are practically the same for Si=C bond in Me<sub>2</sub>Si=CH<sub>2</sub> and P<sup>+</sup>–C<sup>-</sup> in Me<sub>3</sub>P<sup>+</sup>–CH<sub>2</sub><sup>-</sup>”. The definition that “an ylide is a hypervalent molecule in which a three-center bond is reduced to a two-center

bond using a single orbital from the hypervalent atom and formally transferring one electron from the main group atom to the ylide carbon" [58] seems to match to the structures of the silene N-donor complexes [59,60] rather than silenes themselves. Indeed, both phosphoranes and silene N-donor complexes are the compounds of hypervalent phosphorus and silicon, respectively. On the contrary, silenes are the compounds of the three-coordinate four-valent doubly bonded silicon and carbon atoms [15]. Therefore, there should be a certain resemblance between isoelectronic silenes and phosphenes rather than phosphoranes [61].

Further evidence in favor of the olefinic structure of silenes comes if the potential energy profiles as the functions of the internal rotation in silene, ethylene (Fig. 11), and phosphorane (Fig. 12) are compared. The curves in Fig. 11 have two minima ( $\varphi = 0^\circ$  and  $180^\circ$ ) and two maxima ( $\varphi = 90^\circ$  and  $270^\circ$ ) with the cycle multiplicity equaling to 2 [62]. Being the measures of the  $\pi$ -bond energies of the molecules, the rotational barriers (in kcal mol<sup>-1</sup>) of H<sub>2</sub>C=CH<sub>2</sub> (64.2) and H<sub>2</sub>Si=CH<sub>2</sub> (40.0) correspond to the hump in the figure.

Unlike for the discussed diagrams, the potential energy profile for phosphorane (Fig. 12) consists of three global (at  $\varphi = 0^\circ$ ,  $120^\circ$ , and  $240^\circ$ ) and three local minima (at  $\varphi = 60^\circ$ ,  $180^\circ$ , and  $300^\circ$ ) as well as six maxima (at  $\varphi = 50^\circ$ ,  $75^\circ$ ,  $170^\circ$ ,  $195^\circ$ ,  $290^\circ$ , and  $315^\circ$ ). The periodicity of the curve in phosphorane equals to 6 and the rotational barrier is extremely low (1.0 kcal mol<sup>-1</sup>). The latter value is in an excellent agreement with the values known from literature (0.96–1.2 kcal mol<sup>-1</sup>) [47,63]. This comparison indicates the analogous relationship between silene and ethylene [64] and the dramatic gap between silene and phosphorane. In fact, silenes are more like phosphenes than phosphoranes. Similar to silene, the potential energy profile for phosphene (Fig. 11) has the cycle multiplicity equal to 2 and the rotational barrier 46.1 kcal mol<sup>-1</sup>. In Fig. 13,

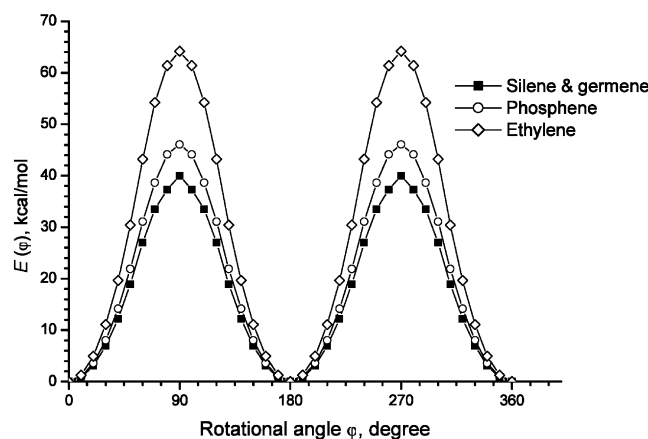


Fig. 11. Diagram of the potential energy profile as a function of internal rotation about E=C bonds.

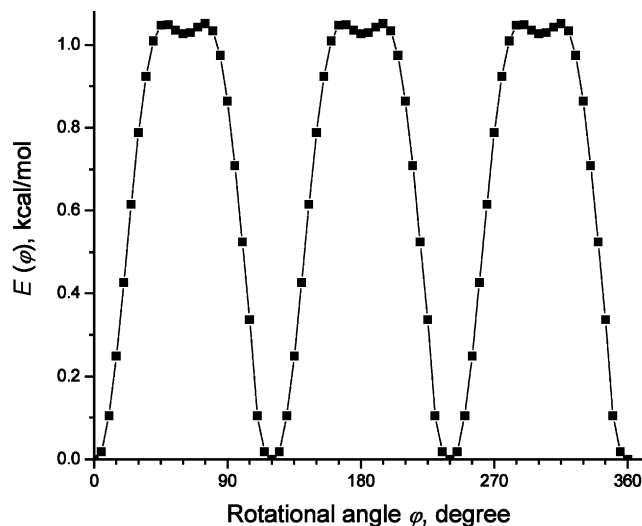


Fig. 12. Diagram of the potential energy profile as a function of internal rotation about P<sup>+</sup>-C<sup>-</sup> bond in phosphorane.

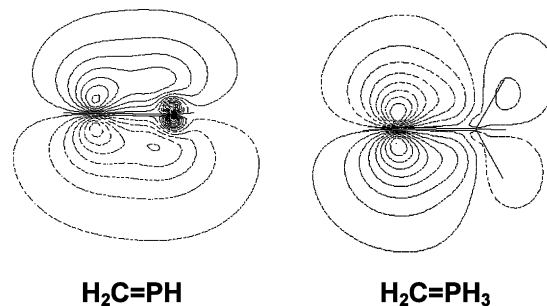


Fig. 13. Highest occupied molecular orbitals of phosphene and phosphorane (isoelectronic density lines are located with interval 0.02 e).

the contour maps of the electronic density on the  $\pi$ -HOMO of phosphene and phosphorane are shown.

It is seen that like silene (Fig. 3) phosphene has the  $\pi$ -orbital localized on the C atom and elongated towards the heteroatom, providing the  $3p_\pi-2p_\pi$  bonding between the P and C atoms. In contrast, in phosphorane HOMO corresponds to the lone pair of the carbon anion rather than to the  $\pi$ -bond between the P and C atoms [65]. The above comparison makes silene and phosphene the isoelectronic relatives being structural analogs of ethylene and methyleneimine, respectively. Therefore, the suggestion [9] that "structural and chemical properties of silaethylenes compared to ylides emphasized their clear similarity and allows to consider silaolefins as C-ylides of silicon" is not the case.

#### 4. Conclusion

An ab initio study of a number of R<sup>1</sup>R<sup>2</sup>Si=CH<sub>2</sub> silenes with different combinations of substituents (SiH<sub>3</sub>, H, CH<sub>3</sub>, NH<sub>2</sub>, Cl, OH, F) covering the wide

range of Pauling electronegativities (from 1.9 to 3.98) as well as their precursors in the reaction of 1,3-disilacyclobutanes' 2+2 cycloreversion was performed to estimate the substituent effect on (1) the rotational barriers about the Si=C double bond as the measure of  $D_{\pi}(\text{Si}=\text{C})$ , (2) the relationship between the sums of the singlet–triplet separations of the carbenoids  $\text{R}^1\text{R}^2\text{Si}$  and  $\text{CH}_2$  constituting the Si=C bond, and the half of the total energy of the Si=C double bond, (3) their electronic and geometric structures, and (4) the similarities of (discrepancies between) the selected silenes and their carbon and germanium analogs and isoelectronic phosphenes. An approach based on using the strain energies of 1,3-disilacyclobutanes and the enthalpies of their 2+2 cycloreversions as a measure of the differences between the Si=C  $\sigma$ - and  $\pi$ -bond energies,  $D(\text{Si}-\text{C})-D_{\pi}(\text{Si}=\text{C})$ , was extended to 1,1,3,3-tetrasubstituted cyclobutanes, 1,3-digermacyclobutanes, and 1,3-diphosphacyclobutanes.  $D_{\sigma}(\text{E}=\text{C})-D_{\pi}(\text{E}=\text{C})$  difference (where E = C, Si, Ge, P) considerably grows on going from silyl- to fluoro-substituted alkenes, silenes, and germenes (12.8, 26.5, and 26.2 kcal mol<sup>-1</sup>, respectively). Neither silyl nor fluoro substitution affects the  $D_{\sigma}(\text{P}=\text{C})-D_{\pi}(\text{P}=\text{C})$  difference. Substituents affect the 2+2 cycloreversion enthalpies and the strain energies of 1,1,3,3-tetrasubstituted cyclobutanes and 1,3-dielementacyclobutanes as follows: fluorines increase whereas silyls decrease both the 2+2 cycloreversion enthalpies and the strain energy regarding the parent molecules. The rotational barriers are lowered as more electronegative substituents are attached. For ethylenes, silenes, and germenes the effect is maximal upon fluorine substitution (in kcal mol<sup>-1</sup>), cf. 64.2 ( $\text{H}_2\text{C}=\text{CH}_2$ ) and 59.7 ( $\text{F}_2\text{C}=\text{CH}_2$ ), 40.0 ( $\text{H}_2\text{Si}=\text{CH}_2$ ) and 26.3 ( $\text{F}_2\text{Si}=\text{CH}_2$ ), and 40.0 ( $\text{H}_2\text{Ge}=\text{CH}_2$ ) and 21.1 ( $\text{F}_2\text{Ge}=\text{CH}_2$ ). Fluorine does not affect the rotational barrier about the double bond in phosphenes, cf. 46.1 kcal mol<sup>-1</sup> ( $\text{HP}=\text{CH}_2$ ) and 46.0 kcal mol<sup>-1</sup> ( $\text{FP}=\text{CH}_2$ ). The Bader analysis of the electron density distribution in silenes, phosphenes, and germenes results in a covalent and highly polar double bond with the polarity decreasing in the following order: silenes > phosphenes > germenes. The Bader charge density at the critical point of the E=C bonds in alkenes, silenes, germenes, and phosphenes follows the trend in the total  $\sigma+\pi$  E=C bond energy on going from the silyl- to fluoro-substituted molecules. The different periodicity of the potential energy profiles in the E=C hetero- $\pi$ -systems and the P=C bond in phosphorane as well as their rotational barriers (above 40.0 kcal mol<sup>-1</sup> and ca. 1.0 kcal mol<sup>-1</sup>, respectively) provides an evidence for the inconsistency of the earlier suggestion that silaolefines are C-ylides of silicon.

Finally, in this paper we emphasize that  $\text{R}_2\text{Si}=\text{CH}_2$  silenes are the last classical planar doubly bonded system in the series of the analogs of olefins. Unlike the heavier Group 14 analogs electronegative substitu-

ents do not disturb a planar geometry, shorten, and weaken the C=C and Si=C double bonds in olefins and  $\text{R}_2\text{Si}=\text{CH}_2$  silenes. This conclusion allows us to consider  $\text{R}_2\text{Si}=\text{CH}_2$  silenes as a boundary system between olefins and heavier Group 14 analogs.

**Supporting information includes** tables of total energies and zero-point energies of (1) carbenoids, (2) silenes, (3) ethenes, germenes, and phosphenes, (4) 1,3-dielementacyclobutanes, (5)  $\text{H}_3\text{CY}$ , (6)  $\text{YCH}_2\text{Y}$ , (7)  $\text{X}(\text{CH}_3)_2$ , (8) total energies of ethenes, silenes, germenes, and phosphenes calculated at the MP4/6-311G(d)//MP2/6-31G(d) level of theory for the determination of the rotational barriers, (9) energetic data for the diagram of the potential energy profile as a function of the internal rotation about X=C bonds, (10) energetic data for the diagram of the potential energy profile as a function of the internal rotation about P–C bond in phosphorane, and (11) Mulliken atomic charges and  $\pi$ -orbital population in silenes,  $\text{R}_2\text{Si}=\text{CH}_2$ . The Tables are available from authors.

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