Heteroorganic betaines
5.* A DFT study of the structure and reactivity of 6,6-dimethyl-6-silafulvene and silicon-containing organophosphorus betaine $^{-}C_5H_4SiMe_2CH_2PMe_3^{+}$

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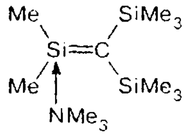
The structures of 6,6-dimethyl-6-silafulvene $C_5H_4SiMe_2$ (**3**), its donor-acceptor complex with ammonia, $C_5H_4SiMe_2 \cdot NH_3$, dimethylfulvene, a number of cyclopentadienylides, methylenetrimethylphosphorane (**6**), and silicon-containing organophosphorus betaine $^{-}C_5H_4SiMe_2CH_2PMe_3^{+}$ (**13**), the product of nucleophilic addition of **6** to **3**, were calculated using the density functional approach. For compound **13**, the potential energy minimum corresponds to the conformation with *gauche*-arrangement of the cyclopentadienyl anionic and trimethylphosphonium cationic centers and a C—Si—C—P dihedral angle of 30.5°, which is due to the Coulomb attraction between these centers. According to calculations, betaine **13** is rather stable toward decomposition into **3** and **6** (ΔH° = 42 kcal mol^{-1}, ΔG° = 30 kcal mol^{-1}). The main channel of thermal decomposition of compound **13** involves an intramolecular nucleophilic substitution, which proceeds with elimination of trimethylphosphine and results in 1,1-dimethyl-1-silaspiro[2.4]hepta-4,6-diene, which then undergoes a ready and irreversible isomerization into 6,6-dimethyl-6-silabicyclo[3.2.0]hepta-1,3-diene owing to the [1,5]-sigmatropic shift of the C—Si bond.

Key words: silaolefins, silafulvene, silicon-containing organophosphorus betaines, non-empirical quantum-chemical calculations, density functional theory.

The chemistry of compounds with multiple carbon-silicon bonds has been progressing rapidly in the last decades.[2,3] There are two major factors responsible for the kinetic instability of silaolefins, namely, the lower energy of the $3p_\pi$—$2p_\pi$-bonding in the Si=C fragment as compared to that of the $2p_\pi$—$2p_\pi$-bonding in the C=C olefin fragments and the high polarity of the $^{\delta+}$Si—C$^{\delta-}$ bond, which is due to the large difference between the electronegativities of carbon and silicon. The latter effect is even more pronounced for compounds with the Si=X (X = O, S, NR) double bonds. Because of this, the simplest silaolefins, silanones, and silanethiones can be detected and studied spectroscopically only in solid noble gas matrices at low temperatures.[4] In order to increase the kinetic stability of such compounds, bulky substituents are usually attached to both atoms of the Si=X dyad, thus producing steric hindrances.[2,3,5,6] Delocalization of the positive charge on the Si atom owing to the coordination of donor groups, as well as delocalization of the negative charge on the C atom or heteroatom X in the dyad, also have a stabilizing effect. In particular, this approach has been used for isolation of a complex between 1,1-bis(trimethylsilyl)-2-methyl-2-silaprop-1-ene, which is unstable under standard conditions, and trimethylamine (**1**).[7,8] The authors of the last-named two studies also succeeded in characterization of the structure of complex **1**. Silanethione (**2**), stabilized by the strong intramolecular N→Si coordination bond, has also been isolated and characterized.[9]



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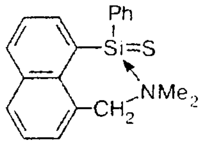

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Previously,[10] we have first hypothesized that delocalization of the negative charge on the carbon center in the $^{\delta+}$Si—C$^{\delta-}$ fragment must stabilize the structures of 6,6-dimethyl-6-silafulvene (**3**) and related compounds. This hypothesis was confirmed experimentally. It has been shown[11,12] that the gas-phase pyrolysis of silylcyclopentadienes does result in a highly reactive com-

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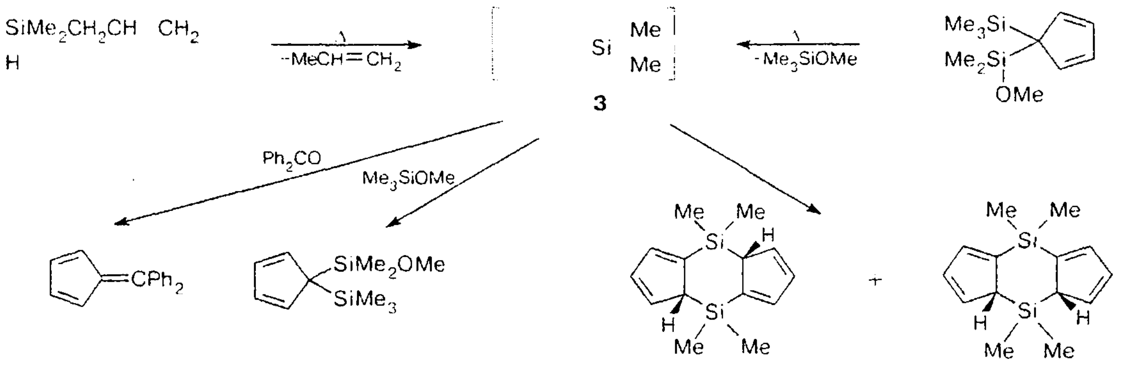
[*] For Part 4, see Ref. 1.

Published in *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 11, pp. 1850—1857, November, 2000.

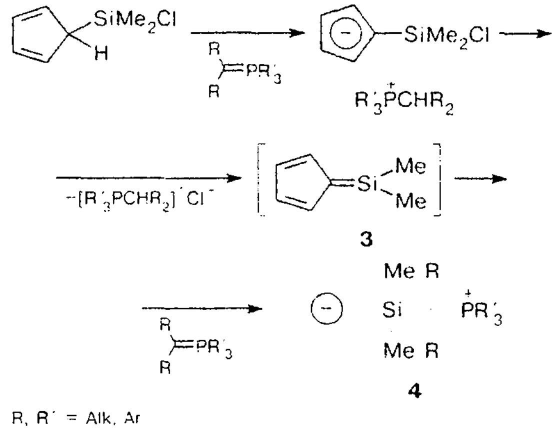
Scheme 1



pound **3**, which can either be trapped by benzophenone (or Me_3SiOMe) or undergo dimerization (Scheme 1).

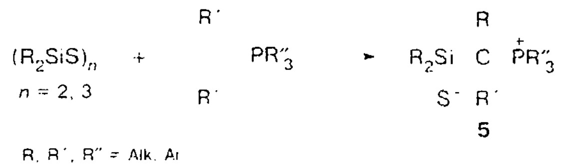
We succeeded in generating compound **3** and its dibenzo analogs in solutions in reactions of dialkylchlorosilylcyclopentadienes and dialkylchlorosilylfluorenes with phosphorus ylides (Scheme 2). The formation of silafulvenes and dibenzosilafulvenes was reliably confirmed both by carrying out the reactions in the presence of trapping agents and by spectroscopic methods.[13–17] Compound **3** can also be trapped by excess alkylidenephosphorane. The reactions result in silicon-containing organophosphorus betaines **4**, which were isolated as solids and characterized spectroscopically.

Scheme 2



Recently,[18–24] we have also synthesized a large group of silicon-containing organophosphorus betaines **5** with phosphonium cationic and thiolate anionic centers (Scheme 3) and carried out detailed studies of their structures and reactivities. Betaines **4** and **5** were found to possess some unusual properties. They can undergo various and rather complex chemical transformations. This, in principle, allows the use of these compounds in syntheses of organosilicon compounds with the silicon atoms in unusual oxidation states. Controlling the reactivity of betaines **4** and **5** requires knowledge of the factors responsible for their structure and properties. To this end, 6,6-dimethyl-6-silafulvene (**3**) and betaines **4** and **5** were studied theoretically in the framework of the density functional theory (DFT) approach. The aim of this work was to study compound **3** and one representative of betaines **4** (R = H, R′ = Me).

Scheme 3



Calculation Procedure

Currently, the DFT approach is finding increasing use in studies of complex molecular systems and mechanisms of chemical reactions. The results of DFT calculations are comparable in accuracy with those obtained by traditional *ab initio* methods with inclusion of correlation effects, but their computational cost is lower. In this work, all calculations were carried out using an original software.[25]

The exchange-correlation energy was calculated using the generalized gradient approximation and the Perdew—Burke—Ernzerhof (PBE) hybrid functional.[26] One-electron wave functions were expanded using extended basis sets of contracted Gaussian functions of size {311/1} for H, {611111/411/11} for C and N, and {611111111/5111111/11} for Si and P (figures in braces indicate the contraction patterns of the Gaussian functions for the s-, p-, and d-AOs, respectively). According to the algorithm proposed earlier,[25] the matrix elements of the Coulomb and exchange-correlation potentials were calculated using electron density expansion in an auxiliary basis set. In this work, the auxiliary basis set comprised uncontracted sets of atom-centered Gaussian functions of dimensions (5s1p) for H, (10s3p3d1f) for C and N, and (14s7p7d1f1g) for Si and P. Stationary points on the potential energy surfaces (PES) of the systems under study (Table 1) were located by analyzing the Hesse matrices. The second derivatives of energy with respect to coordinates were calculated analytically. Atomic charges were calculated using the Hirshfeld method. Previously, we used

Table 1. Total energies (*E*) of the structures under study and zero-point vibrational energy corrections (*ZPE*)

Structure	*E*	*ZPE*
	au	
3	−561.80977	0.14037
6	−500.04718	0.13364
7	−310.44136	0.14425
8	−670.45623	—
9	−653.54131	—
10	−618.35073	0.17855
13a	−1061.93313	0.27847
13b	−1061.91072	—
14	−601.08897	0.10957
PMe_3	−460.82468	0.10957
15	−1061.87690	0.27583
16	−601.08642	0.16808
17	−601.10326	0.16848

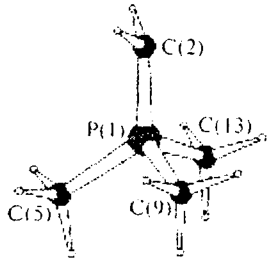


Fig. 1. Calculated molecular geometry of methylenetrimethylphosphorane (**6**).

this computational procedure and software in studies of the mechanisms of haptotropic rearrangements in transition-metal π-complexes[26] and alkane activation by cationic complexes of zirconium.[28] To check the adequacy of the approach employed, preliminary calculations of the structures of methylenetrimethylphosphorane (**6**) and a series of cyclopentadienylides were carried out.

Methylenetrimethylphosphorane (**6**) is the simplest phosphorus ylide. The structure of this compound (Fig. 1) has been the subject of several experimental and theoretical studies. According to the data of low-temperature X-ray diffraction study, the PMe_3 fragment has an asymmetric structure, while hydrogen atoms at the C(2) atom deviate from the plane passing through the C(2)=P bond. Pyramidal structure of the $P=CH_2$ fragment was also observed[29] for $CH_2=PPh_3$. However, these effects could be due to packing factors. The *sM*(*s*) curves obtained in the gas-phase electron diffraction study[30] of compound **6** were interpreted assuming a C_{3v} symmetry of the PMe_3 fragment and a planar PCH_2 unit. However, MP2/6-311G* calculations[29] of the equilibrium geometry of molecule **6** showed that the global potential energy minimum corresponds to the structure with C_s symmetry, the parameters of which are listed in Table 2. Re-analysis of the experimental *sM*(*s*) curves[30] under assumption of C_s symmetry has led to substantially improved fit of the experimental intensities relative to the old refinement. The new set of geometric parameters was found to be in excellent agreement both with the results of the MP2/6-311G* calculations[29] and with our results obtained from DFT calculations (see Table 2).

It is significant that both computational methods reproduce well such a distinctive feature of the molecular geometry as the nonplanar structure of the PC(2)H(3)H(4) unit with the "pyramidal" C(2) atom. The angle between the C(2)=P bond and the plane passing through the C(2), H(3), and H(4) atoms is 33.1°, which is in agreement with the values reported earlier[29] for CH_2PMe_3 (27.4°) and CH_2PPh_3 (26°). The energy of the transition state (TS) of inversion of the C(2) atom (with C_s symmetry) is 1.2 kcal mol^{-1}. This is also in good agreement with a value of 1.3 kcal mol^{-1} obtained from MP2/6-311G* calculations.[29]

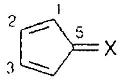
Yet another group of model compounds studied in this work comprised dimethylfulvene (**7**) and sulfur (**8**) and phosphorus (**9**) cyclopentadienylides. The calculated geometric parameters are listed in Table 3, which also includes experimental data given for comparison. As can be seen, the computational

Table 2. Molecular geometry parameters for methylenetrimethylphosphorane (**6**)

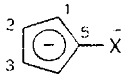
Parameter	Experiment		Calculations	
	ED[a]	X-ray analysis[b]	MP2/6-311G*	PBE/TZ2P[c]
Bond length/Å				
P(1)—C(2)	1.656(2)	1.678(2)	1.667	1.694
P(1)—C(5)	1.837(6)	1.791(2)	1.849	1.876
P(1)—C(9)	1.809(3)	1.808(1)	1.817	1.835
Bond angle/deg				
C(2)—P(1)—C(5)	122.4(7)	110.7(1)	123.9	124.2
C(2)—P(1)—C(9)	111.4(13)	115.69(6)	101.4	110.3
C(5)—P(1)—C(9)	101.0(20)	105.40(7)	101.7	101.62
C(9)—P(1)—C(13)	107.4(?)		100.5	107.46
P(1)—C(2)—H(3),	118.2(18)	111(2)	117	116.1
P(1)—C(2)—H(4)		[118(3)]		
H(3)—C(2)—H(4)	115.7(20)	118(3)	116.1	115.3
Dihedral angle/deg				
C(5)—P(1)—C(2)—H(3),	73.9(30)	180	72.2	72.5
C(5)—P(1)—C(2)—H(4)		40.9		

[a] The results of gas-phase electron diffraction study.[30]
[b] See Ref. 29.
[c] This work.

Table 3. Calculated and experimental (figures in parentheses) bond lengths in the cyclopentadienyl ring and the dipole moments (μ) of dimethylfulvene (**7**) and sulfur (**8**) and phosphorus (**9**) cyclopentadienylides



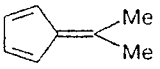
X = CMe_2 (**7**)



X = SMe_2 (**8**), PPh_3 (**9**)

X	Bond length/Å				μ/D	Reference
	C(1)—C(2), C(3)—C(4)	C(2)—C(3)	C(1)—C(4), C(1)—C(5)	C(5)—X		
CMe_2	1.364	1.465	1.468	1.366	1.94	
	(1.346)	(1.435)	(1.440)	(1.344)		32
SMe_2	1.394	1.432	1.434	1.711	6.1	
	(1.366)	(1.364)	(1.394)	(1.709)		33
PPh_3	1.394	1.425	1.437	1.845	7.11	
	(1.385)	(1.402)	(1.423)	(1.718)		34

method we employed reproduces fairly well the results of the X-ray study. The distinctive features of compounds **7—9** are equalization of the ring C—C bond lengths and an increase in the dipole moments with increasing degree of charge separation in the ylide.



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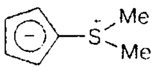

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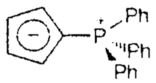
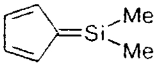


9

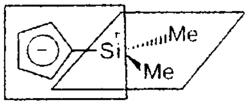
The results of our test calculations show that the method employed reproduces well the structures of fulvene **7** and ylides **8**, **9**. It should be noted that the large difference between the calculated and experimental P—C bond lengths in ylide **9** can be due to packing factors, which could not be taken into account. For other compounds, the calculated bond lengths differed from the experimental values by less than 0.04 Å, while the bond angles differed by at most 3°. This accuracy is typical of DFT calculations of the geometry of organic molecules.

Results and Discussion

Structure of 6,6-dimethyl-6-silafulvene (3). According to our DFT calculations with the PBE functional and TZ2P basis set, the global potential energy minimum on the PES of molecule **3** (Fig. 2) corresponds to planar structure **3a**. The energy of the "orthogonal" conformer **3b** is 27.4 kcal mol^{-1} higher, which makes it possible to assess the contribution of π-bonding to the formally double C(5)=Si bond in molecule **3**. According to theoretical estimates and thermodynamic data,[31] this energy in the silaolefin $CH_2=SiMe_2$ is 39±5 kcal mol^{-1}; our calculations give 39.0 kcal mol^{-1}.

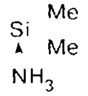


3a



3b

The geometric parameters, charge distributions, and the calculated dipole moments for both conformers of molecule **3** are listed in Table 4. The bond length distribution over the cyclopentadienyl ring of molecule **3** is close to that found for triphenylphosphonium cyclopentadienylide **9**. This is also in agreement with similarity in the chemical behavior of these compounds, in particular, with their ability to react with benzophenone "according to Wittig."[13] Molecule **3** exothermically adds an ammonia molecule to give the donor-acceptor complex **10** (see Fig. 2; $\Delta H^\circ = -13$ kcal mol^{-1}, $\Delta G^\circ = -5$ kcal mol^{-1}). The geometry of the complex differs appreciably from that of molecule **3** (see Table 4). The bond arrangement of the Si atom attains a configuration of a distorted tetrahedron. The C(5)—Si bond is somewhat lengthened, the dipole moment of complex **10** increases, and a tendency toward equalization of the ring C—C bond lengths is observed. According to calculations, the barrier to rotation about the Si—C(5) bond in complex **10** equals 6 kcal mol^{-1}, which indicates appreciable weakening of the $3p_\pi$—$2p_\pi$-bonding in the Si—C fragment. The results of calculations for complex **10** are in agreement with a number of experimental findings.



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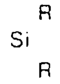

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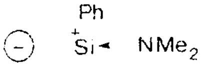

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For instance, we have previously found that the dibenzo derivatives with alkyl groups at the silicon atom

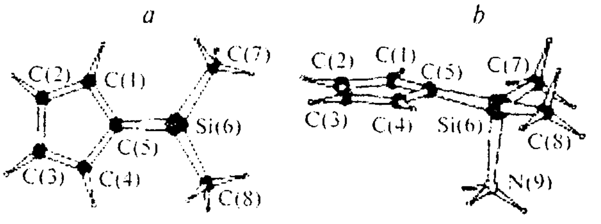
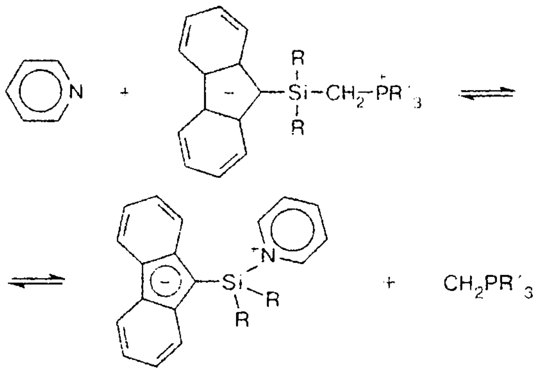


Fig. 2. Calculated molecular geometry of dimethylsilafulvene (**3**) (*a*) and its complex with ammonia (1 : 1) (**10**) (*b*).

(of type **11**) are highly reactive; on the other hand, compound **12**, which we have obtained and spectroscopically characterized earlier,[19] exhibits a sufficient kinetic stability owing to the formation of an intramolecular donor-acceptor bond. Most likely, it is the stabilization due to the formation of a donor-acceptor complex with pyridine that is responsible for the possibility for the equilibrium we found earlier to occur in pyridine solution[14b] (Scheme 4).

Scheme 4



The structure and properties of betaine 13. According to our DFT calculations with the PBE functional and TZ2P basis set, the gas-phase reaction between 6,6-dimethyl-6-silafulvene **3** and **6** proceeds barrierlessly with a strong exothermic effect ($\Delta H° = -42$ kcal mol^{-1}).

Table 4. Geometric parameters and atomic charges for 6,6-dimethyl-6-silafulvene (**3**) and its complex with ammonia (1 : 1) (**10**) obtained from DFT (PBE/TZ2P) calculations

Parameter	**3a**	**3b**	**10**
Bond length/Å			
C(5)—C(1), C(5)—C(4)	1.457	1.446	1.443
C(1)—C(2), C(4)—C(3)	1.376	1.395	1.395
C(2)—C(3)	1.453	1.421	1.426
C(5)—Si(6)	1.752	1.758	1.78
Si(6)—C(7), Si(6)—C(8)	1.883	1.871	1.887
Si(6)—N(9)	—	—	2.036
Bond angle/deg			
C(1)—C(5)—C(4)	106.8	107.5	106.8
Si(6)—C(5)—C(1)	126.6	126.3	125.0
Si(6)—C(5)—C(4)	126.6	126.2	125.4
C(5)—Si(6)—C(7)	121.9	125.0	119.8
C(5)—Si(6)—C(8)	121.9	123.6	119.9
C(7)—Si(6)—C(8)	116.3	111.4	112.5
Dihedral angle/deg			
C(1)—C(5)—C(4)—C(3)	0.0	0.0	1.2
C(1)—C(5)—Si(6)—C(7)	0.0	90.0	27.8
C(1)—C(5)—Si(6)—C(8)	180.0	−90.0	174.7
C(1)—C(5)—Si(6)—N(9)	—	—	−78.6
Atomic charge/au			
C(1)	−0.15	−0.19	−0.19
C(2)	−0.10	−0.12	−0.13
C(3)	[illegible]	−0.11	−0.11
C(4)	[illegible]	−0.11	−0.11
C(5)	−0.10	−0.12	−0.13
Si(6)	0.41	0.57	0.39
C(7)	−0.19	−0.19	−0.20
C(8)	−0.19	−0.19	−0.20
N(9)	—	—	−0.11
Dipole moment/D	4.35	7.20	8.73

The calculated structure of the simplest betaine (**13**) is shown in Fig. 3 and the geometric parameters are listed in Table 5. Some salient features of this structure should be pointed out. Among these is the accumulation of a rather large negative charge in the cyclopentadienyl ring, which leads to further equalization of the C—C bond

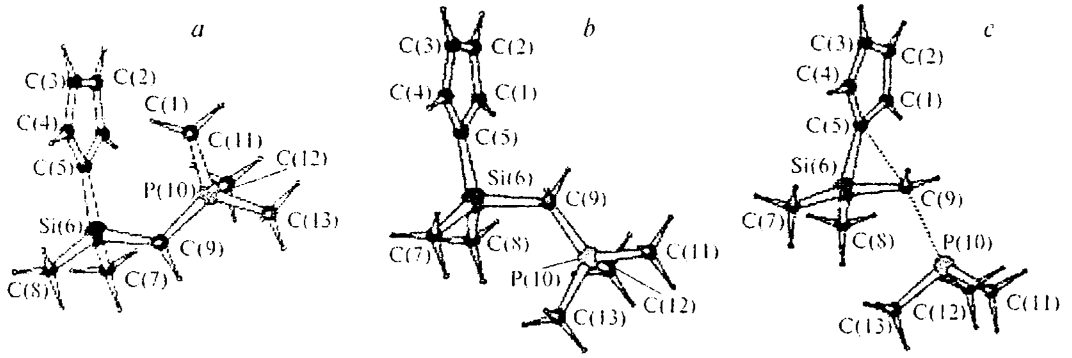


Fig. 3. Calculated molecular geometry of betaine **13** (*gauche*-conformer **13a** (*a*) and "rotated" conformer **13b** (*b*)) and geometry of transition state **15** (*c*).

Table 5. Geometric parameters of betaine **13a** and transition state **15** according to DFT (PBE/TZ2P) calculations

Parameter	**13a**	**15**
Bond length/Å		
C(5)—C(1), C(5)—C(4)	1.434	1.454
C(1)—C(2), C(4)—C(3)	1.406	1.388
C(2)—C(3)	1.421	1.456
C(5)—Si(6)	1.822	1.843
Si(6)—C(7), Si(6)—C(8)	1.899	1.893
Si(6)—C(9)	1.988	1.866
C(9)—P(10)	1.802	2.531
P(10)—C(11)	1.834	1.876
P(10)—C(12), P(10)—C(13)	1.813	1.854
Bond angle/deg		
C(1)—C(5)—C(4)	106.5	106.5
C(5)—Si(6)—C(9)	109.4	77.0
C(5)—Si(6)—C(7)	115.1	—
Si(6)—C(9)—P(10)	115.9	117.6
C(9)—P(10)—C(11)	112.9	—
C(9)—P(10)—C(12)	110.0	—
Dihedral angle/deg		
C(5)—Si(6)—C(9)—P(10)	30.5	185.0
Atomic charge/au		
C(1)	−0.18	—
C(2)	−0.21	—
C(3)	−0.12	—
C(4)	−0.12	—
C(5)	−0.21	—
Si(6)	0.35	—
C(7)	−0.14	—
C(8)	−0.14	—
C(9)	−0.19	—
P(10)	0.43	—
C(11)	−0.12	—
C(12)	−0.12	—
C(13)	−0.14	—
Dipole moment/D	10.45	—

lengths as compared to those in molecule **3** and to an increase in the dipole moment. The potential energy minimum corresponds to the *gauche*-conformer (**13a**) of the molecule with respect to the central C(9)—Si bond (the C(5)—Si—C(9)—P dihedral angle is 30.5°). The less sterically hindered conformation (**13b**) corresponds to a shallow local minimum on the PES (see Fig. 3), which lies 15 kcal mol^{-1} higher than the global minimum **13a** on the energy scale. Stabilization of the *gauche*-conformation **13a** is likely due to strong electrostatic attraction between the cationic and anionic centers.

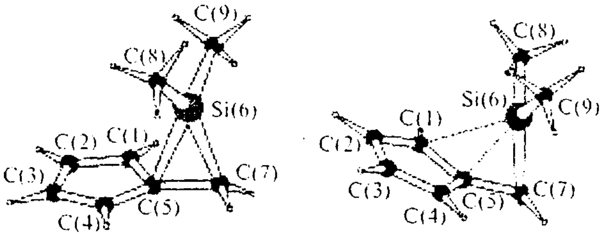
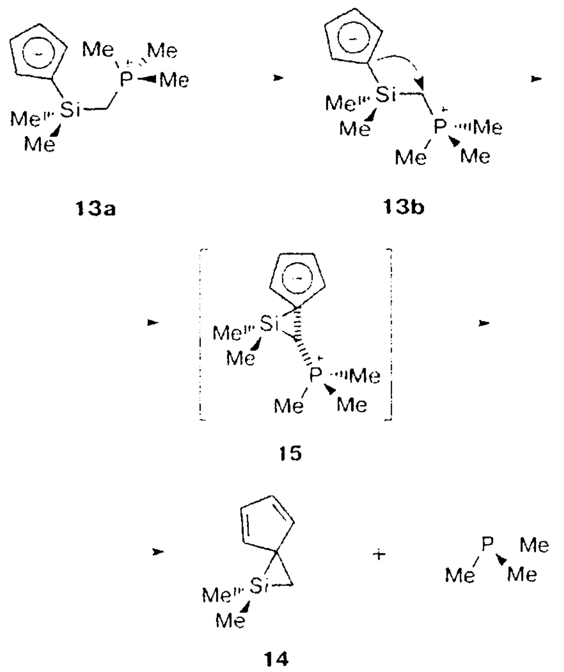


Fig. 4. Calculated molecular geometry of 1,1-dimethyl-1-silaspiro[2.4]hepta-4,6-diene (**14**) (*a*) and transition state **16** (*b*).

Thermal activation of molecule **13** involves an intramolecular nucleophilic substitution, which proceeds with elimination of trimethylphosphine (Scheme 5) and results in 1,1-dimethyl-1-silaspiro[2.4]hepta-4,6-diene (**14**).

Scheme 5



First, the interconversion **13a** → **13b** occurs. Transition state **15** is characterized by lengthened simple and shortened double bonds between the cyclopentadienyl ring atoms. The energy diagram of thermal decomposition of betaine **13a** is shown in Fig. 6. Analysis of the bond length ratio and energy parameters suggests that TS **15** is "closer" to the reaction products, *i.e.*, this is a "late" TS (see Table 5). Solvation will undoubtedly favor

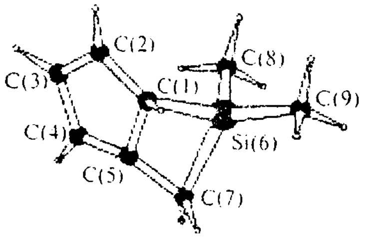


Fig. 5. Calculated molecular geometry of 6,6-dimethyl-6-silabicyclo[3.2.0]hepta-1,3-diene (**17**).

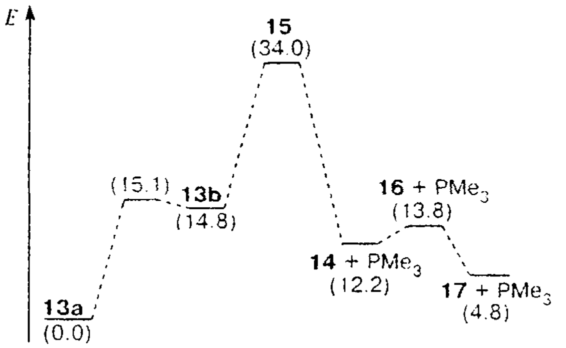


Fig. 6. The energy diagram of thermal decomposition of betaine **13a** (figures in parentheses are the relative energies given in kcal mol^{-1}).

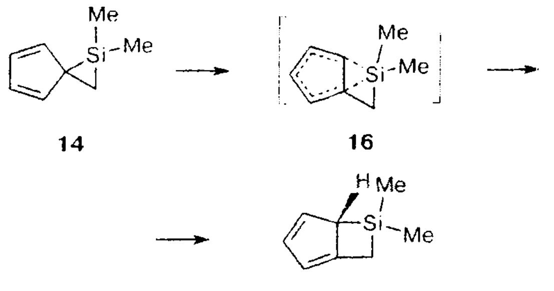
a decrease in the energy difference between conformers **13a** and **13b**. In this connection, the height of the activation barrier (34 kcal mol^{-1}) calculated for the gas phase should be regarded as the upper bound for this reaction in polar solvents.

It should be noted that compound **14** (see above) is not the end reaction product. A ready [1,5]-sigmatropic shift of the Si—C bond in **14** through TS **16** results in 6,6-dimethyl-6-silabicyclo[3.2.0]hepta-1,3-diene (**17**) (Scheme 6). This type of isomerization is typical of η^5-cyclopentadienyl derivatives of both non-transition and transition elements.[14b] Among characteristic features of TS **16** are the pentacoordination of the Si atom and rearrangement of double and single bonds in the cyclopentadienyl ring. The calculated activation energy is 1.6 kcal mol^{-1} ($\Delta H^{\neq}$ = −9 kcal mol^{-1}). The geometric parameters of structures **14**, **16**, and **17** are listed in Table 6.

Table 6. Geometric parameters of 1,1-dimethyl-1-silaspiro[2.4]hepta-4,6-diene (**14**), transition state **16**, and 6,6-dimethyl-6-silabicyclo[3.2.0]hepta-1,3-diene (**17**)

Parameter	**14**	**16**	**17**
Bond length/Å			
C(1)—C(2)	1.463	1.396	1.478
C(2)—C(3)	1.449	1.421	1.375
C(3)—C(4)	1.463	1.394	1.456
C(4)—C(5)	1.463	1.434	1.381
C(1)—C(5)	1.463	1.467	1.513
C(1)—Si(6)	—	2.511	1.972
C(5)—Si(6)	1.964	1.966	—
C(5)—C(7)	1.553	1.526	1.511
Si(6)—C(7)	1.853	1.862	1.918
Si(6)—C(8)	1.882	1.877	1.889
Si(6)—C(9)	1.882	1.886	1.892
Bond angle/deg			
C(1)—C(5)—C(4)	106.0	108.0	107.3
C(1)—C(5)—C(7)	125.8	124.6	111.2
C(4)—C(5)—C(7)	125.8	—	—
Si(6)—C(5)—C(7)	62.6	—	—
C(5)—Si(6)—C(7)	47.8	—	—
C(5)—Si(6)—C(8)	118.1	—	—
C(7)—Si(6)—C(8)	120.4	—	—
Si(6)—C(1)—C(5)	—	108.0	77.5
C(2)—C(1)—C(5)	—	106.6	108.4
C(5)—C(7)—Si(6)	—	71.4	79.4
C(1)—Si(6)—C(7)	—	72.8	79.8
C(1)—Si(6)—C(8)	—	—	114.0
C(1)—Si(6)—C(9)	—	—	112.9
Dihedral angle/deg			
C(1)—C(4)—C(5)—C(7)	17.0	—	—
C(1)—C(4)—C(5)—Si(6)	−55.1	—	—
C(7)—C(5)—Si(6)—C(8), C(7)—C(5)—Si(6)—C(9)	73.1	—	—
C(1)—Si(6)—C(5)—C(7)	—	82.1	40.7
C(2)—C(1)—C(5)—C(4)	—	1.0	—

Scheme 6



Summing up, mention may be made that the results of our theoretical study of compounds **3**, **6**, **10**, and **13** using the DFT approach with the PBE functional and TZ2P basis set are in good agreement with the known experimental data on their structures and reactivities. They confirm the hypothesis we proposed earlier[10] that delocalization of the negative charge on the carbon center in silaolefins increases their relative kinetic stability. According to calculations, there are two main decomposition channels of betaines **4** (and, in particular, compound **13**). They involve (a) homolysis of the central Si—C bond followed by formation of a silafulvene and phosphorane and (b) intramolecular nucleophilic substitution, which proceeds with elimination of a phosphine (see Scheme 5). Channel (b) is more energetically favorable for a gas phase and photochemically activated solutions, as was observed for betaines **5**.[22—24] However, the results of our calculations also suggest that in solvents of high polarity and in the presence of donor molecules the probability ratio of the different decomposition channels of betaines **4** can be changed in favor of channel (a). This allows *in situ* generation of silafulvenes in solution from betaines followed by introduction of these molecules into various chemical reactions. In this connection, the equilibria shown in Scheme 4 [14b] deserve detailed consideration. It is also believed that the thermal decomposition channels (a) and (b) should be common to compounds **4** and their carbon analogs generated from fulvenes and phosphoranes. This allows development of simple and easy procedures for the synthesis of spirocyclopentadienes from fulvenes and phosphoranes. We are going to check these assumptions experimentally in the immediate future.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 00-03-32889).

References

1. I. V. Borisova, N. N. Zemlyanskii, V. N. Khrustalev, Yu. A. Ustynyuk, and E. A. Chernyshev, *Izv. Akad Nauk, Ser. Khim.*, 2000, 1594 [*Russ. Chem. Bull., Int. Ed. Engl.*, 2000, **49**, 1583].
2. A. G. Brook and A. M. Brook, *Adv. Organomet. Chem.*, 1996, **39**, 71.
3. I. Hemme and U. Klingebiel, *Adv. Organomet. Chem.*, 1996, **39**, 159.
4. V. N. Knabashesku, K. N. Kudin, J. Tamas, S. E. Boganov, J. L. Margrave, and O. M. Nefedov, *J. Am. Chem. Soc.*, 1998, **120**, 5005.
5. M. Driess, *Adv. Organomet. Chem.*, 1996, **39**, 193.
6. R. Okazaki and R. West, *Adv. Organomet. Chem.*, 1996, **39**, 232.
7. N. Wiberg, G. Wagner, G. Reber, and G. Muller, *Organometallics*, 1987, **6**, 35.
8. N. Wiberg and H. Kopf, *J. Organomet. Chem.*, 1986, **315**, 9.
9. P. Arya, J. Boyer, F. Carre, R. Corriu, G. Lanneau, J. Lapassett, M. Perrot, and C. Prim, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1016.
10. Yu. A. Ustynyuk, P. I. Zakharov, A. A. Azizov, and G. A. Schembelov, *J. Organomet. Chem.*, 1975, **96**, 195.
11. Y. Nakadaira, H. Sakaba, and H. Sakurai, *Chem. Lett.*, 1980, 1071.
12. T. J. Barton, G. T. Burns, E. V. Arnold, and J. Clarly, *Tetrshedron Lett.*, 1981, **22**, 7.
13. N. N. Zemlyanskii, I. V. Beletskaya, V. K. Bel'skii, Yu. A. Ustynyuk, and I. P. Beletskaya, *Izv. Akad Nauk SSSR, Ser. Khim.*, 1983, 953 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1983, **32**, 863 (Engl. Transl.)].
14. I. P. Beletskaya and N. N. Zemlyansky, in *Adv. Organomet. Chem.*, Ed. O. A. Reutov, Mir, Moscow, 1984, a) p. 30; b) p. 88.
15. I. V. Borisova, N. N. Zemlyansky, V. K. Belsky, N. D. Kolosova, A. N. Sobolev, Yu. A. Ustynyuk, and I. P. Beletskaya, *J. Chem. Soc., Chem. Commun.*, 1982, 1090.
16. I. V. Borisova, N. N. Zemlyanskii, Yu. A. Ustynyuk, I. P. Beletskaya, and E. A. Chernyshev, *Metalloorg. Khim.*, 1992, **5**, 537 [*Organomet. Chem. USSR*, 1992, **5**, 262 (Engl. Transl.)].
17. I. V. Borisova, N. N. Zemlyanskii, Yu. N. Luzikov, Yu. A. Ustynyuk, V. K. Bel'skii, M. M. Shtern, and I. P. Beletskaya, *Dokl. Akad. Nauk SSSR*, 1983, **269**, 369 [*Dokl. Chem.*, 1983 (Engl. Transl.)].
18. I. V. Borisova, N. N. Zemlyanskii, A. K. Shestakova, and Yu. A. Ustynyuk, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 2140 [*Russ. Chem. Bull.*, 1993, **43**, 2137 (Engl. Transl.)].
19. I. V. Borisova, N. N. Zemlyanskii, Yu. A. Ustynyuk, V. N. Khrustalev, S. V. Lindeman, and Yu. T. Struchkov, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 339 [*Russ. Chem. Bull.*, 1994, **43**, 318 (Engl. Transl.)].
20. N. N. Zemlyanskii, I. V. Borisova, A. K. Shestakova, Yu. A. Ustynyuk, and E. A. Chernyshev, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 2246 [*Russ. Chem. Bull.*, 1994, **43**, 2116 (Engl. Transl.)].
21. I. V. Borisova, N. N. Zemlyansky, A. K. Shestakova, and Yu. A. Ustynyuk, *Mendeleev Commun.*, 1996, 90; 229.
22. I. V. Borisova, N. N. Zemlyanskii, A. K. Shestakova, Yu. A. Ustynyuk, and E. A. Chernyshev, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 922 [*Russ. Chem. Bull., Int. Ed. Engl.*, 2000, **49**, 920].
23. V. N. Khrustalev, N. N. Zemlyanskii, I. V. Borisova, Yu. A. Ustynyuk, and E. A. Chernyshev, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 931 [*Russ. Chem. Bull., Int. Ed. Engl.*, 2000, **49**, 929].
24. I. V. Borisova, N. N. Zemlyanskii, A. K. Shestakova, V. N. Khrustalev, Yu. A. Ustynyuk, and E. A. Chernyshev, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 935 [*Russ. Chem. Bull., Int. Ed. Engl.*, 2000, **49**, 933].
25. D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151.
26. J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
27. O. I. Trifonova, E. A. Ochertyanova, N. G. Akhmedov, V. A. Roznyatovsky, D. A. Laikov, N. A. Ustynyuk, and Yu. A. Ustynyuk, *Inorg. Chim. Acta*, 1998, 280; 328.
28. a) Yu. A. Ustynyuk, L. Yu. Ustynyuk, D. N. Laikov, and V. V. Lunin, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 2248 [*Russ. Chem. Bull.*, 1999, **48**, 2222 (Engl. Transl.)]; b) Yu. A. Ustynyuk, L. Yu. Ustynyuk, D. N. Laikov, and V. V. Lunin, *J. Organomet. Chem.*, 2000, **597**, 182.
29. N. W. Mitzel, D. H. Brown, S. Parsons, P. T. Brain, C. R. Pulham, and D. W. H. Rankin, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 1670.
30. H.-J. Bestmann and R. Zimmermann, *Methoden der Organischen Chemie (Houben-Weyl-Müller)*, 1982, **E1**.
31. M. Driess and H. Grutzmacher, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 828.
32. N. Norman and B. Post, *Acta Crystallogr.*, 1961, **14**, 503.
33. V. G. Andrianov and Yu. T. Struchkov, *Izv. Akad Nauk SSSR, Ser. Khim.*, 1977, 687 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1977, **26**, 687 (Engl. Transl.)].
34. H. L. Ammon, G. L. Wheeler, and P. H. Watts, Jr., *J. Am. Chem. Soc.*, 1973, **95**, 6158.

Received November 3, 1999;
in revised form July 20, 2000