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# Effects of substituents and n-donors on the energies of Si←N, Si←O, and Si=C bonds in hypervalent silenes*

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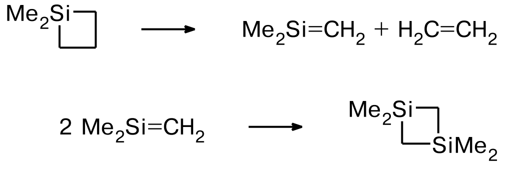
The effect of the nature of substituents at sp$^2$-hybridized silicon atom in the $R_2Si=CH_2$ (R = $SiH_3$, H, Me, OH, Cl, F) molecules on the structure and energy characteristics of complexes of these molecules with ammonia, trimethylamine, and tetrahydrofuran was studied by the *ab initio* (MP4/6-311G(d)//MP2/6-31G(d)+ZPE) method. As the electronegativity, $\chi$, of the substituent R increases, the coordination bond energies, $D$(Si←N(O)), increase from 4.7 to 25.9 kcal mol$^{-1}$ for the complexes of $R_2Si=CH_2$ with $NH_3$, from 10.6 to 37.1 kcal mol$^{-1}$ for the complexes with $Me_3N$, and from 5.0 to 22.2 kcal mol$^{-1}$ for the complexes with THF. The n-donor ability changes as follows: THF $\le$ $NH_3$ < $Me_3N$. The calculated barrier to hindered internal rotation about the silicon—carbon double bond was used as a measure of the Si=C $\pi$-bond energy. As $\chi$ increases, the rotational barriers decrease from 18.9 to 5.2 kcal mol$^{-1}$ for the complexes with $NH_3$ and from 16.9 to 5.7 kcal mol$^{-1}$ for the complexes with $Me_3N$. The lowering of rotational barriers occurs in parallel to the decrease in $D_\pi$(Si=C) we have established earlier for free silenes. On the average, the $D_\pi$(Si=C) energy decreases by ~25 kcal mol$^{-1}$ for $NH_3 \cdot R_2Si=CH_2$ and $Me_3N \cdot R_2Si=CH_2$. The $D$(Si←N) values for the $R_2Si=CH_2 \cdot 2Me_3N$ complexes are 11.4 (R = H) and 24.3 kcal mol$^{-1}$ (R = F). sp$^2$-Hybridized silicon atom can form transannular coordination bonds in 1,1-bis[*N*-(dimethylamino)acetimidato]silene (**6**). The open form (**I**) of molecule **6** is 35.1 and 43.5 kcal mol$^{-1}$ less stable than the cyclic (**II**, one transannular Si←N bond) and bicyclic (**III**, two transannular Si←N bonds) forms of this molecule, respectively. The $D$(Si←N) energy for structure **III** was estimated at 21.8 kcal mol$^{-1}$.

**Key words:** silenes; hypervalent silenes; complexes of silenes with ammonia, trimethylamine, and tetrahydrofuran; tetracoordinate silenes, pentacoordinate silenes, n-donors (ammonia, trimethylamine, tetrahydrofuran); energies of intermolecular coordination bonds, energies of intramolecular transannular coordination bonds, rotational barriers, *ab initio* quantum-chemical calculations.

Compounds with silicon—carbon double bonds (silenes) are known since 1967 when it was established[1] that [2+2] cycloreversion of 1,1-dimethyl-1-silacyclobutane in the gas phase involves an intermediate formation of 1,1-dimethylsilene. Owing to its high reactivity, the latter undergoes a fast "head-to-tail" dimerization into 1,3-disila-1,1,3,3-tetramethylcyclobutane.



The dimerization proceeds barrierlessly; therefore, the lifetime of free dimethylsilene molecules is only determined by the rate of mutual collisions of molecules, which depends on the vapor pressure.[2]

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In the liquid phase, silenes can be stabilized by framing the Si=C bond with bulky substituents[3] or by complexation with n-donors, *e.g.*, tertiary amines or tetrahydrofuran (THF).[4] The latter procedure employs the ability of the $sp^2$-hybridized Si atom to form coordination bonds with electron donors. High strength of such bonds was first demonstrated in theoretical studies of the structure and energy characteristics of 5-aza-2,8-dioxa-5-methyl-1-methylene-1-silacyclooctane[5] and 1,1-bis[*N*-(dimethylamino)acetimidato]silene.[6] At the same time interrelations between the nature of substituent at the silicon atom and the strength of the coordination bond and the energy of the Si=C π-bond in the complexes of silenes with hypervalent bonds have not been studied so far.

In this work we report on an *ab initio* quantum-chemical study of the effect of the nature of substituents and n-donors on the structure and energies of hypervalent bonds Si←N and Si←O and on the energies of the Si=C π-bonds in the complexes of silenes $R_2Si=CH_2$ (R = $SiH_3$, H, Me, OH, Cl, F) with ammonia, trimethylamine ($Me_3N$), and THF. The height of the barrier to hindered internal rotation about the Si=C double bond was used as a measure of the energy of the π-component of this bond. The reasons for the choice of the n-donors employed in this work were as follows. Tetrahydrofuran was used in the experimental study.[4] The structure and properties of $Me_3N$ provide the best approximation to those of dimethylethylamine, which was used in the study cited.[4] Ammonia was chosen for comparative evaluation of the effect of the Me groups on the donor ability of amines. Substituents at the silicon atoms were chosen in order to cover the full range of changes in the Pauling electronegativities $\chi$.[7]

| R | $SiH_3$ | H | Me | Cl | OH | F |
|---|---|---|---|---|---|---|
| $\chi$ | 1.9 | 2.2 | 2.55 | 3.16 | 3.44 | 3.98 |

## Calculation Procedure

Full geometry optimization of the molecules of silenes $R_2Si=CH_2$ (R = $SiH_3$, H, Me, OH, Cl, F), n-donors ($NH_3$, $Me_3N$, and THF), and complexes of the silenes with n-donors was carried out with inclusion of electron correlation at the second-order Møller—Plesset (MP2) level of perturbation theory[8,9] using the 6-31G(d) basis set. This method was also employed for calculating the zero-point energy corrections (ZPE) in the harmonic approximation. The weight of hydrogen atom was taken to be 1.088 (see Ref. 10). This allowed the difference between the calculated and experimental vibrational frequencies, $\Delta\nu = \nu_{theor} - \nu_{exp}$, to be essentially "linearized" and thus the same scaling factor of 0.96 to be used for the whole frequency region. The final values of the total energies of all molecules, which were then used in calculations of the enthalpies of reactions, were obtained with inclusion of electron correlation at the fourth-order Møller—Plesset (MP4) level of perturbation theory for the molecules optimized by the MP2/6-31G(d) method. The MP4 calculations were carried out with the 6-311G(d) basis set[11] for the second-row elements and hydrogen and with the (12s,9p)/[6s,5p](d) McLean—Chandler basis set for the third-row elements.[12] Thus, all calculations were carried out at the MP4/6-311G(d)//MP2/6-31G(d)+ZPE level, which allowed us to determine the enthalpies of the reactions of the silenes mentioned above with the same accuracy as that achieved using the standard heats of formation.[13] All calculations were performed using the GAMESS program[14] (PC GAMESS version). The total energies $E_{total}$, ZPE corrections, and the $E_0$ values ($E_0 = E_{total(MP4/6\text{-}311G(d))}$ + ZPE) for silenes **1** and their complexes **2**—**4** with $NH_3$, $Me_3N$, and THF, respectively, are listed in Table 1.

Strictly speaking, the coordination bond energy, $D$(Si←N(O)), equals the difference between the enthalpy of complexation, $\Delta H_1$, and the sum of the relaxation energies of the silene and base structures in the complex. The latter quantity can not be calculated with the same accuracy as the $\Delta H_1$ values; therefore, in this work we conditionally set the $D$(Si←N(O)) energy equal to the enthalpy of complexation $\Delta H_1$ taken with the opposite sign because complexation is energetically favorable; *i.e.*,

$$D(\mathrm{Si{\leftarrow}N(O)}) \equiv -\Delta H_1 = -(E_0{}^1 - E_0{}^2 - E_0{}^3), \qquad (1)$$

where $E_0{}^1$, $E_0{}^2$, and $E_0{}^3$ are the energies of the complex, free silene, and n-donor, respectively.

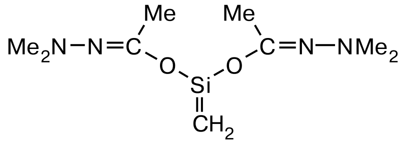
The rotational barriers were calculated for the complexes of the silenes with ammonia and $Me_3N$ as the differences between the $E_0$ energies of the equilibrium states of the complexes and of the complexes optimized with the $CH_2$ group rotated by 90° about the Si=C bond (Table 2). This conformation of the complex corresponds to the transition state (TS) of internal rotation and is characterized by one negative eigenvalue of the Hessian.

The ability of the Si($sp^2$) atom to pentacoordination was studied taking complexes of the silenes with two $Me_3N$ molecules, $2Me_3N \cdot R_2Si=CH_2$ (**5**), as examples. The enthalpies of formation of these complexes were calculated using the following equation

$$\Delta H_{compl} = E_0(2Me_3N \cdot R_2Si=CH_2) - E_0(R_2Si=CH_2) - 2E_0(Me_3N). \qquad (2)$$

The $\Delta H_{compl}$ values and the $\Delta H_{compl}$(**5**) – $\Delta H_{compl}$(**3**) differences, which characterize the increase in enthalpy due to the formation of the second coordination bond, are listed in Table 3.

The ability of the Si($sp^2$) atom to form transannular coordination bonds in the molecule of 1,1-bis[*N*-(dimethylamino)acetimidato]silene **6** was studied at the MP4/6-311G(d)//MP2/6-31G(d)+ZPE level. This made it possible to compare the structures and energies of the complexes of simple silenes and those of compound **6** capable of forming an intramolecular hypervalent bond using the same computational method. Geometry optimization of molecule **6** led to two structures, a mono-chelate structure (**II**) with one coordination bond



**6**

**Table 1.** Calculated energy characteristics of silenes $R_2Si{=}CH_2$ and their complexes with $NH_3$, $Me_3N$, and THF

| Compound | R | $-E_{\text{total}}$ | ZPE | $-E_{\text{total}}$ | $-E_0$ |
|---|---|---|---|---|---|
| | | MP2/6-31G(d) | | MP4/6-311G(d) | |
| | | | $R_2Si{=}CH_2$ | | |
| **1a** | $SiH_3$ | 909.58243 | 0.07204 | 909.73161 | 909.65958 |
| **1b** | H | 329.25119 | 0.03798 | 329.32240 | 329.28442 |
| **1c** | Me | 407.60795 | 0.09522 | 407.74063 | 407.64541 |
| **1d** | Cl | 1247.41114 | 0.02696 | 1247.56776 | 1247.54080 |
| **1e** | OH | 479.41460 | 0.04946 | 479.56343 | 479.51398 |
| **1f** | F | 527.42679 | 0.02899 | 527.61345 | 527.58446 |
| | | | $H_3N \cdot R_2Si{=}CH_2$ | | |
| **2a** | $SiH_3$ | 965.94690 | 0.10719 | 966.13889 | 966.03170 |
| **2b** | H | 385.61884 | 0.07524 | 385.73272 | 385.65748 |
| **2c** | Me | 463.97418 | 0.12854 | 464.15106 | 464.02252 |
| **2d** | Cl | 1303.79979 | 0.06426 | 1303.99864 | 1303.93438 |
| **2e** | OH | 535.81395 | 0.08830 | 536.00599 | 535.91769 |
| **2f** | F | 583.82607 | 0.06649 | 584.05688 | 583.99039 |
| $NH_3$ | — | 56.35421 | 0.03268 | 56.39734 | 56.36466 |
| | | | $Me_3N \cdot R_2Si{=}CH_2$ | | |
| **3a** | $SiH_3$ | 1083.42655 | 0.18921 | 1083.69529 | 1083.50607 |
| **3b** | H | 503.10203 | 0.15663 | 503.29376 | 503.13713 |
| **3c** | Me | 581.45465 | 0.21181 | 581.70841 | 581.49660 |
| **3d** | Cl | 1421.28348 | 0.14513 | 1421.55809 | 1421.41296 |
| **3e** | OH | 653.29924 | 0.16936 | 653.56840 | 653.39904 |
| **3f** | F | 701.31451 | 0.14761 | 701.62080 | 701.47319 |
| $Me_3N$ | — | 173.26930 | 0.12042 | 173.95001 | 173.82959 |
| | | | $THF \cdot R_2Si{=}CH_2$ | | |
| **4a** | $SiH_3$ | 1141.26386 | 0.18498 | 1141.56073 | 1141.37575 |
| **4b** | H | 560.93325 | 0.15265 | 561.15144 | 560.99879 |
| **4c** | Me | 639.29099 | 0.20758 | 639.57152 | 639.36395 |
| **4d** | Cl | 1479.10946 | 0.14088 | 1479.41252 | 1479.27164 |
| **4e** | OH | 711.12122 | 0.16505 | 711.41692 | 711.25187 |
| **4f** | F | 759.13688 | 0.14315 | 759.47114 | 759.32799 |
| THF | — | 231.67020 | 0.11176 | 231.81990 | 231.70815 |

*Note.* $E_{\text{total}}$/Hartree is the total energy, ZPE/Hartree is the zero-point vibrational energy, and $E_0$/Hartree is the equilibrium-state energy of the molecule.

Si←N and a bischelate structure (**III**) with two coordination bonds Si←N (see below).

## Results and Discussion

***Structures of complexes of silenes with one ligand molecule.*** The structures of the complexes of silenes with one donor molecule are shown in Fig. 1. The Si←N and Si←O coordination bond lengths and the Si=C bond lengths are listed in Table 4.

### *Complexes with ammonia*

In the complexes of the silenes with ammonia (**2**, see Fig. 1, *a*), except for the complex $H_3N \cdot (SiH_3)_2Si{=}CH_2$ (**2a**), the N atom is coordinated to the Si(sp$^2$) atom and the *r*(Si←N) distances approach 2.2 Å (see Table 4). These Si←N bonds are longer than the covalent bond Si—N in the $(H_2N)_2Si{=}CH_2$ molecule (1.718 Å),[13] being much shorter than the sum of the van der Waals radii of N and Si atoms (~3.5 Å);[15] therefore, in these complexes of silenes we deal with typical coordination bonds. In the complex $H_3N \cdot (SiH_3)_2Si{=}CH_2$, the N atom lies in the bisectrix of the Si—Si—Si angle symmetrically with respect to two sp$^3$-hybridized silicon atoms of silyl groups within the plane passing through all silicon atoms (see Fig. 1, *d*). Comparison of the *r*(Si(sp$^3$)←N) and *r*(Si(sp$^2$)←N) values (3.289 and 3.610 Å, respectively) shows that in this complex ammonia forms the coordination bonds with the silyl substituents rather than the Si(sp$^2$) atom.

### *Complexes with trimethylamine*

In the complexes of the silenes with $Me_3N$ (**3**, see Fig. 1, *b*) the nitrogen atom is coordinated to the

**Table 2.** Calculated energy characteristics ($E'_{total}$, ZPE′, $E'_0$/Hartree) of the complexes of silenes $R_2Si=CH_2$ with $NH_3$ and $Me_3N$ with the 90° angle of rotation of the $CH_2$ group about the Si=C bond[a]

| Compound | $-E'_{total}$ | ZPE′ | $-E'_{total}$ | $-E'_0$ |
|---|---|---|---|---|
| | MP2/6-31G(d) | | MP4/6-311G(d) | |
| | | $H_3N \cdot R_2Si=CH_2$ | | |
| **2a** | 965.91263 | 0.10653 | 966.10818 | 966.00165 |
| **2b** | 385.58965 | 0.07456 | 385.70832 | 385.63377 |
| **2c** | 463.95182 | 0.12913 | 464.13083 | 464.00170 |
| **2d** | 1303.78825 | 0.06363 | 1303.98715 | 1303.92352 |
| **2e** | 535.80181 | 0.08727 | 535.99437 | 535.90711 |
| **2f** | 583.81758 | 0.06590 | 584.04800 | 583.98211 |
| | | $Me_3N \cdot R_2Si=CH_2$ | | |
| **3a** | 1083.39423 | 0.18800 | 1083.66717 | 1083.47918 |
| **3b** | 503.07368 | 0.15629 | 503.26885 | 503.11256 |
| **3c** | 581.43234 | 0.21142 | 581.68796 | 581.47653 |
| **3d** | 1421.27282 | 0.14559 | 1421.54868 | 1421.40309 |
| **3e** | 653.28868 | 0.16986 | 653.55781 | 653.38795 |
| **3f** | 701.30472 | 0.14755 | 701.61174 | 701.46419 |

$sp^2$-hybridized Si atom. The Si$\leftarrow$N coordination bond lengths vary from 1.991 to 2.243 Å (see Table 4).

### *Complexes with tetrahydrofuran*

In complexes **4** (see Fig. 1, *c*) the five-membered ring of the THF molecule adopts a half-chair conformation. The oxygen atom of THF is coordinated to the Si($sp^2$) atom, except the complex $THF \cdot (SiH_3)_2Si=CH_2$ (**4a**, see Fig. 1, *e*). The Si$\leftarrow$O coordination bond lengths vary from 1.94 to 2.26 Å, which is much longer than the Si—O covalent bond length (1.665 Å) in free $(HO)_2Si=CH_2$ molecule but shorter than the sum of the van der Waals radii of O and Si atoms (~3.4 Å).[15] In the complex $THF \cdot (SiH_3)_2Si=CH_2$ the oxygen atom is situated above one Si—Si bond in such a fashion that the atoms of the Si($sp^2$)—O—Si($sp^3$) fragment occupy vertices of an almost equlateral triangle in which both Si$\leftarrow$O distances are

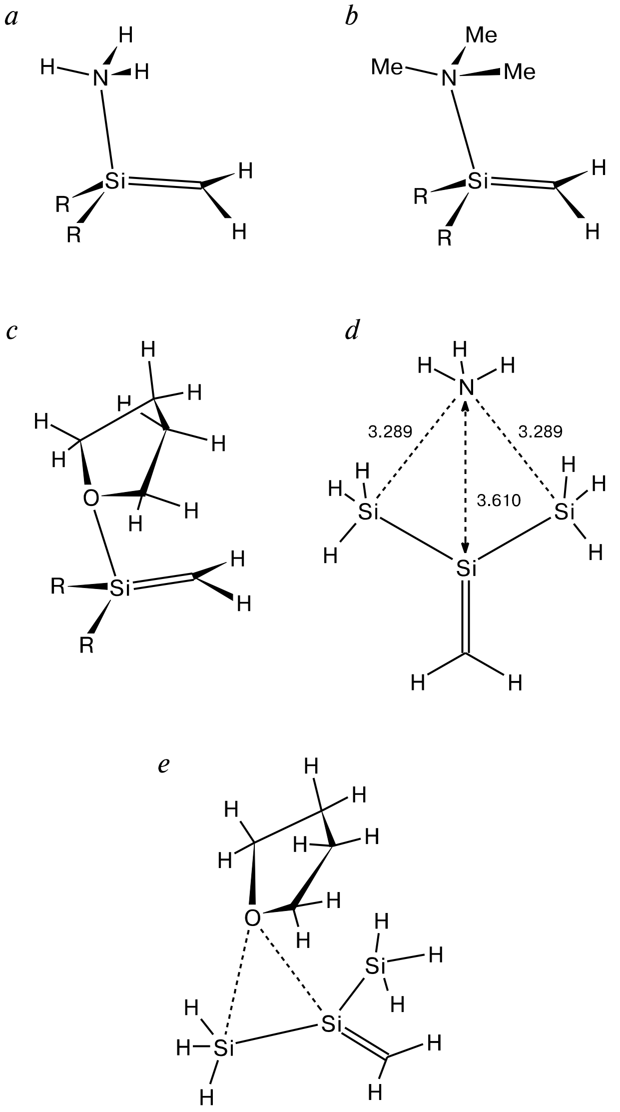


**Fig. 1.** Structures of the complexes of silenes with ammonia, trimethylamine, and tetrahydrofuran: $H_3N \cdot R_2Si=CH_2$ (**2**) (*a*), $Me_3N \cdot R_2Si=CH_2$ (**3**) (*b*), $THF \cdot R_2Si=CH_2$ (**4**) (*c*), $H_3N \cdot (SiH_3)_2Si=CH_2$ (**2a**) (*d*), $THF \cdot (SiH_3)_2Si=CH_2$ (**4a**) (*e*).

**Table 3.** Energy characteristics of complexes $2Me_3N \cdot R_2Si=CH_2$, used in calculations of the enthalpy of complexation ($\Delta H_{compl}$/kcal $mol^{-1}$)[a]

| Compound | R | $-E_{total}$ | ZPE | $-E_{total}$ | $-E_0$ | $\Delta H_{compl}$ | $\Delta\Delta H^b$ |
|---|---|---|---|---|---|---|---|
| | | MP2/6-31G(d) | | MP4/6-311G(d) | | | |
| **5a** | $SiH_3$ | 1257.26438 | 0.30664 | 1257.65478 | 1257.34815 | 18.4 | 7.8 |
| **5b** | H | 676.93966 | 0.27383 | 677.25375 | 676.97991 | 22.8 | 8.3 |
| **5c** | Me | 755.29278 | 0.35901 | 755.66876 | 755.30975 | 3.2 | −10.3 |
| **5d** | Cl | 1595.11955 | 0.29106 | 1595.51767 | 1595.22661 | 16.7 | −10.0 |
| **5e** | OH | 827.14932 | 0.28707 | 827.53875 | 827.25168 | 49.3 | 14.5 |
| **5f** | F | 875.16074 | 0.26509 | 875.58601 | 875.32092 | 48.5 | 11.4 |

[a] For notations $E_{total}$, ZPE, and $E_0$, see Note to Table 1.

[b] $\Delta\Delta H$/kcal $mol^{-1}$ = $\Delta H_{compl}(2Me_3N \cdot R_2Si=CH_2) - \Delta H_{compl}(Me_3N \cdot R_2Si=CH_2)$.

**Table 4.** Si←N(O) and Si=C bond lengths (Å) in the complexes of silenes **2—4** and the Si=C bond lengths (Å) in silenes **1** optimized at the MP2/6-31G(d) level of theory

| R | $r$(Si←N) | | $r$(Si←O) | $r$(Si=C) | | | |
|---|---|---|---|---|---|---|---|
| | **2** | **3** | **4** | **1**[a] | **2** | **3** | **4** |
| $SiH_3$ | 3.610[b]<br>3.289[c] | 2.056 | 2.934[f]<br>3.081[g] | 1.738 | 1.740 | 1.739 | 1.736 |
| H | 2.290 | 2.156 | 2.264 | 1.718 | 1.739 | 1.721 | 1.718 |
| Me | 2.222[d] | 2.243 | 2.388 | 1.716 | 1.720[d] | 1.724 | 1.718 |
| Cl | 2.184 | 2.056 | 1.986 | 1.698 | 1.709 | 1.708 | 1.699 |
| OH | 2.225[e] | 1.991 | 2.022 | 1.693 | 1.720[e] | 1.716 | 1.708 |
| F | 2.243 | 1.998 | 1.956 | 1.685 | 1.724 | 1.703 | 1.695 |

[a] The $r$(Si=C) values for free silenes were taken from Ref. 13.
[b] The distance between the nitrogen and $Si(sp^2)$ atoms.
[c] The distance between the nitrogen and $Si(sp^3)$ atoms.
[d] The $r$(Si←N) and $r$(Si=C) distances are 2.227 and 1.720 Å, respectively (see Ref. 5).
[e] $r$(Si←N) 1.990 Å and $r$(Si=C) 1.711 Å in the complex of dimethoxysilene with ammonia.[5]
[f] $r(O \rightarrow Si(sp^2))$.
[g] $r(O \rightarrow Si(sp^3))$ and $r$(Si=C) 1.724 Å in the crystalline complex $Me_2Si=C(SiMe_2Ph)_2 \cdot NEtMe_2$ (see Ref. 4c).

**Table 5.** Coordination bond energies $D$(Si←N(O)) in complexes **2—4**, barriers to rotation in the complexes of silenes **2** and **3**, and the energies of π-bonds, $D_\pi$(Si=C), in free silenes **1** obtained from MP4/6-311G(d)//MP2/6-31G(d)+ZPE calculations

| R | $D$(Si←N) | | $D$(Si←O) | $D_\pi$(Si=C)[a] | Rotational barrier | |
|---|---|---|---|---|---|---|
| | **2** | **3** | **4** | **1** | **2** | **3** |
| | kcal mol$^{-1}$ | | | | | |
| $SiH_3$ | 4.7 | 10.6 | 5.0 | 41.7 | 18.9 | 16.9 |
| H | 5.3 | 14.5 | 3.9 | 39.6 | 14.9 | 15.4 |
| Me | 7.8[b] | 13.6 | 6.5 | 38.7 | 13.1 | 12.6 |
| Cl | 18.2 | 26.7 | 14.2 | 32.0 | 6.8 | 6.2 |
| OH | 24.5[c] | 34.8 | 18.7 | 33.4 | 6.6 | 7.0 |
| F | 25.9 | 37.1 | 22.2 | 28.9 | 5.2 | 5.7 |

[a] Data taken from Ref. 13.
[b] 7.5 kcal mol$^{-1}$ (see Ref. 5).
[c] The energy of transannular donor-acceptor bond Si←N is 18.0 kcal mol$^{-1}$ in 1-methylene-5-methyl-5-aza-2,8-dioxa-1-silacyclooctane and 19.7 kcal mol$^{-1}$ in the complex of dimethoxysilene with ammonia.[5]

shorter than the sum of the van der Waals radii of the O and Si atoms, namely, $r(O \rightarrow Si(sp^2))$ = 2.934 Å and $r(O \rightarrow Si(sp^3))$ = 3.081 Å (see Fig. 1, *e*, Table 4).

In the complexes of $H_2Si=CH_2$ and $Me_2Si=CH_2$ with THF the ligand and the $Si=CH_2$ fragment lie on the same side relative to the Si←O coordination bond. The complexes $THF \cdot R_2Si=CH_2$ (R = OH, Cl, F) adopt such a conformation that one R—Si bond is projected on the bisectrix of the C—O—C angle in the THF molecule. The Si=C double bonds in the complexes with THF are longer than in free silenes. The exception are the complexes of the unsubstituted silene and disilylsilene with THF, where the Si=C distances remain almost unchanged. For all the complexes, except $THF \cdot (SiH_3)_2Si=CH_2$, the calculated $r$(Si=C) distances are shorter than 1.724 Å,[4c] as was determined by X-ray analysis for a crystalline complex $THF \cdot Me_2Si=C(SiMe_2Ph)_2 \cdot NEtMe_2$.

***Coordination bond energies.*** A comparison of the energies of the coordination bonds between the silenes and donor molecules (Table 5) shows that the $D$(Si←N) values obtained for the $H_3N \cdot Me_2Si=CH_2$ complex from the MP2/6-31G(d) [5] and MP4/6-311G(d)//MP2/6-31G(d) calculations are in good agreement with each other. This also holds for the $D$(Si←N) energies of the $H_3N \cdot (MeO)_2Si=CH_2$ and $H_3N \cdot (HO)_2Si=CH_2$ complexes calculated by the MP2/6-31G(d) [5] and MP4/6-311G(d)//MP2/6-31G(d) methods, respectively.

Compared to ammonia and THF, $Me_3N$ forms stronger complexes with silenes. This characterizes $Me_3N$ as the strongest among the electron donors studied in this work (see Table 5). In order to study how the inductive properties of substituents affect the Si←N(O) coordination bond energies, the $D$(Si←N(O)) values were plotted *vs*. χ (Fig. 2). Here, complex **2a** is excluded because ammonia is coordinated to the $Si(sp^3)$ atom.

As the electronegativity of the substituent at the silicon atom increases, the coordination bond energy also increases (see Fig. 2). The $D$(Si←N) energy correlates with the coordination bond length in the complexes of silenes with $Me_3N$; namely, the shorter the $r$(Si←N) distance, the stronger the Si←N bond (Fig. 3).

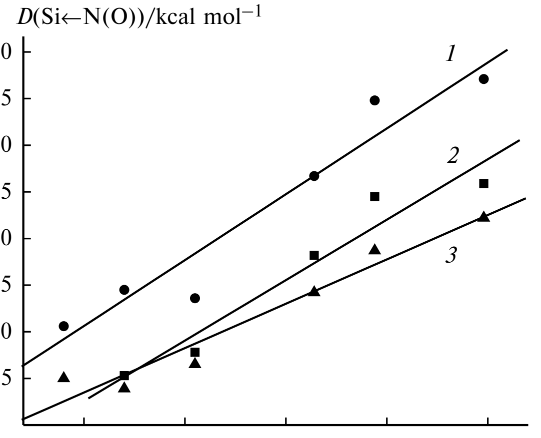


**Fig. 2.** Plot of coordination bond energies $D$(Si←N(O)) *vs*. electronegativity (χ) of the substituent at the silicon atom in the complexes $Me_3N \cdot R_2Si=CH_2$ (**3a—f**) ($R$ = 0.967) (*1*), $H_3N \cdot R_2Si=CH_2$ (**2b—f**) ($R$ = 0.970) (*2*), $THF \cdot R_2Si=CH_2$ (**4a—f**) ($R$ = 0.974) (*3*).

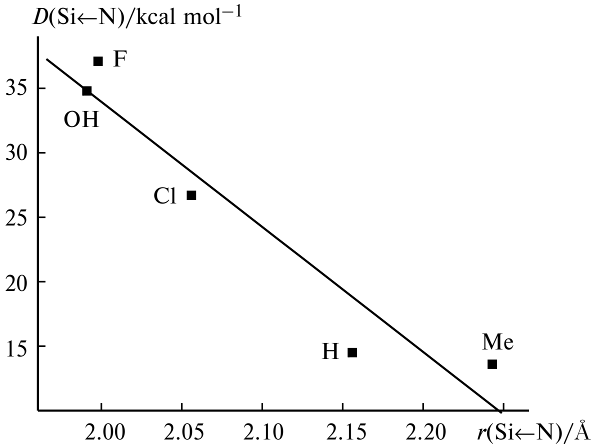


**Fig. 3.** Plot of coordination bond energies $D(Si{\leftarrow}N)$ *vs.* bond length $r(Si{\leftarrow}N)$ in complexes $Me_3N\cdot R_2Si=CH_2$ (**3b—f**) ($R = 0.97$)).

Similar dependences were also established for other complexes (see Tables 4 and 5). Thus, the higher the negative inductive effect of the substituent at the $Si(sp^2)$ atom, the shorter the coordination bond and the stronger the complex of the silene with the n-donor.

***Structures of complexes of silenes with the $CH_2$ group rotated by 90° about the Si=C bond.*** All such complexes belong to the same structural type (Fig. 4), being different only in geometric parameters (see Table 6). Rotation of the methylene group in the complexes by 90° about the Si=C bond leads to singlet biradical structures corresponding to the TS of internal rotation and characterized by a single negative eigenvalue of the Hessian. In these structures the π-overlap between the $2p_z$-AO of carbon and $3p_z$-AO of silicon is minimum; therefore, no π-bond formation is suggested.[14,16] This manifests itself in a marked elongation of the Si—C distance (Table 6), as in the case of the structure of the TS of internal rotation in free silene, calculated by the *ab initio* UHF/6-31G* method; here, the Si—C distance increased from 1.694 Å (in $H_2Si=CH_2$) to 1.863 Å (in $H_2{}^\bullet Si—C^\bullet H_2$).[16] Elongation of the Si—C bond in the complexes is accompanied by a marked shortening of Si←N bonds in the structures in which the angle τ is less than 90°, namely, they are shorter than 2 Å (see Table 6), which indicates strengthening of the coordination bond. Thus, violation of the π-overlap enhances the acceptor ability of the silicon atom.

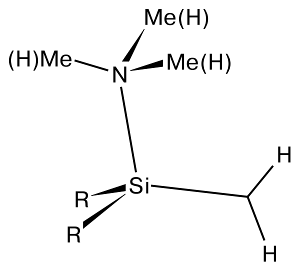


**Fig. 4.** General view of the structures of the complexes with the $CH_2$ group rotated by 90° about the Si=C bond.

**Table 6.** Si←N and Si=C bond lengths in the complexes **2** and **3** with the 90° angle of rotation of the $CH_2$ group about the Si=C bond optimized at the MP2/6-31G(d) level of theory

| R | r(Si←N)/Å | | r(Si=C)/Å | | |
|---|---|---|---|---|---|
| | **2** | **3** | **1**[a] | **2** | **3** |
| $SiH_3$ | 1.973 | 1.990 | 1.738 | 1.740 | 1.742 |
| H | 1.969 | 1.966 | 1.718 | 1.728 | 1.731 |
| Me | 1.976 | 1.995 | 1.716 | 1.735 | 1.739 |
| Cl | 1.948 | 1.915 | 1.698 | 1.706 | 1.699 |
| OH | 1.966 | 1.996 | 1.693 | 1.719 | 1.723 |
| F | 1.944 | 1.941 | 1.685 | 1.700 | 1.703 |

[a] The r(Si=C) value in free silenes.[13]

***Rotational barriers and decrease in the energy of π-component of the Si=C bond, $D_\pi$(Si=C), in complexes of silenes with ammonia and $Me_3N$.*** The π-component of the Si=C double bond is formed owing to lateral overlap of two unpaired p-electrons in the $R_2Si^\bullet—^\bullet CH_2$ biradical. This overlap is efficient due to planar configuration of the $R_2Si—C$ and $Si—CH_2$ fragments and parallel spin orientations of the unpaired 3p(Si)- and 2p(C)-electrons. Weak involvement of the unpaired 3p-electron of the $R_2Si^\bullet—^\bullet CH_2$ biradical in the overlap with the $^\bullet CH_2$ group is due to the fact that the $R_2Si^\bullet$ radical in the ground state has a pyramidal configuration and should adopt a planar configuration in order to provide efficient overlap with the $^\bullet CH_2$ radical.[17] This requires some energy expenditure (the higher the electronegativity of the substituent R, the higher the energy expenditure). As a result the π-bond Si=C, although being formed in the classical planar configuration, has a lower energy compared to the π-bond C=C.[18]

The rotational barriers can serve as a measure of the π-component of the double bond energy.[16,19] It was shown earlier[17] that the rotational barriers calculated for a broad range of silenes obey a law we have found for the $D_\pi$(Si=C) energies, namely, the higher the electronegativity of the substituent at the silicon atom, the lower the $D_\pi$(Si=C) value.[13] The rotational barriers calculated in this work for the complexes of silenes with n-donors show a similar dependence on χ (Fig. 5).

As can be seen, both plots, the $D_\pi$(Si=C) values and the barrier heights, are nearly parallel, with the slopes of –6.2 for the former and –6.8 for the latter. Comparison of the $D_\pi$(Si=C) values for free silenes with the barrier heights in the complexes shows that involvement of the $Si(sp^2)$ atom in the coordination bond Si←N results in a decrease in $D_\pi$(Si=C) values in the complexes of silenes.

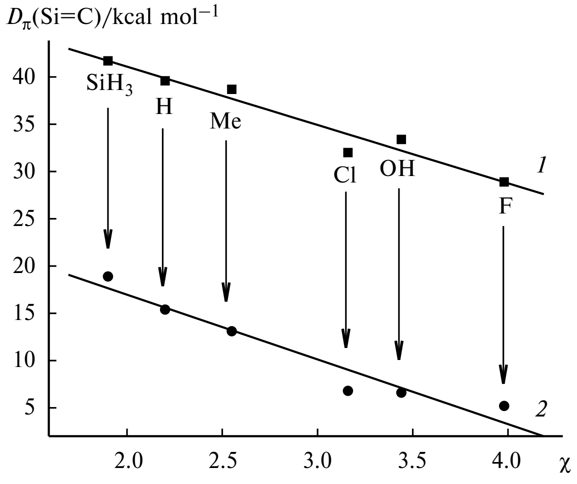
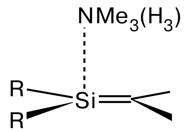
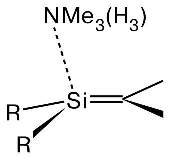


**Fig. 5.** Plot of the π-component of the energy of the Si=C bond ($D_\pi$(Si=C), $R$ = 0.98) (*1*) and barriers to rotation about the Si=C bond ($R$ = 0.97) (*2*) *vs.* electronegativity (χ) of the substituent at the silicon atom in the complexes $H_3N \cdot R_2Si=CH_2$ (**2a—f**).

The reason is pyramidalization of the silicon atom, which leads to a decrease in the efficiency of the lateral overlap between the $R_2Si$ and $CH_2$ fragments and, hence, to the lowering of the π-component of the energy of the Si=C bond.





The average energy loss, $\Delta E_{av}$, of the π-component of the double bond Si=C for the complexes of the silenes with ammonia and $Me_3N$ is 24.8±1.4 and 25.0±1.5 kcal mol$^{-1}$, respectively.

***Structures of complexes of silenes with two $Me_3N$ molecules.*** Structure optimization of the complexes $2Me_3N \cdot R_2Si=CH_2$ (**5**) carried out in order to check the ability of the Si(sp$^2$) atom to form two hypervalent bonds led to unexpected results. We found that only two complexes, **5b** and **5f** (R = H, F; both with $C_{2v}$ symmetry), have two coordination bonds Si←N, *i.e.*, pentacoordinate silicon atoms. In the structures of these two complexes (Fig. 6, *b*, *f*) the silicon atoms are at the centers of distorted trigonal bipyramids with vertices occupied by nitrogen atoms. The Si←N (2.315 and 2.191 Å) and Si=C (1.733 and 1.720 Å) bonds are longer than in the monocoordinated silenes, *viz*., 2.156 and 1.998 Å and 1.721 and 1.703 Å (see Table 4), respectively.

Now consider the key geometric parameters of the complexes $2Me_3N \cdot R_2Si=CH_2$ (**5**) having one coordination bond Si←N involving the sp$^2$-hybridized Si atom (see Fig. 6).

In the complex $2Me_3N \cdot (SiH_3)_2Si=CH_2$ (**5a**) the second coordination bond is formed between the nitrogen atom of the second $Me_3N$ molecule and the Si(sp$^3$) atom of a silyl substituent (see Fig. 6, *a*). The *r*(N—Si(sp$^2$)) distance (3.690 Å) is longer than the sum of the van der Waals radii. The addition of the second $Me_3N$ molecule has no effect on *r*(Si=C).

Complex $2Me_3N \cdot Me_2Si=CH_2$ (**5c**) (see Fig. 6, *c*) has a $C_s$ symmetry. Here, the distance between the Si atom and the N atom of the second $Me_3N$ molecule exceeds the sum of the van der Waals radii. The complex seems to be stabilized by four weak hydrogen bonds between hydrogen atoms of two Me groups and the nitrogen atom of the $Me_3N$ group and hydrogen atoms of the NMe group with the negatively charged methylene carbon. The Si←N coordination bond and the Si=C bonds are longer than in the monocoordinated silene (*cf.* Table 4).

The complex $2Me_3N \cdot (HO)_2Si=CH_2$ (**5e**) has an asymmetrical structure. It seems likely that the second coordination bond Si←N is not formed in this case, because the distance between the Si atom and the N atom of the second $Me_3N$ molecule exceeds the sum of the corresponding van der Waals radii. The complex is stabilized by two hydrogen bonds, namely, a strong bond between the N atom of the second $Me_3N$ molecule and the silene OH group (*r*(OH...N) = 1.790 Å, O—H...N = 175.2°) and a weak bond between an H atom of the NMe group and the methylene carbon ($r(CH...C_{CH_2})$ = 2.925 Å, the angle $C—H...C_{CH_2}$ = 141.0°) (see Fig. 6, *e*).

Complex $2Me_3N \cdot Cl_2Si=CH_2$ (**5d**) has a $C_s$ symmetry. The coordination bond lengths are 2.090 and 3.054 Å long (see Fig. 6, *d*), the shorter Si←N bond being apparently stronger than the other bond. Two Me groups form weak hydrogen bonds with negatively charged methylene carbon. The second $Me_3N$ molecule is arranged above the $Si=CH_2$ plane in such a fashion that the second coordination bond and both hydrogen bonds have almost equal lengths.

In the four complexes under study the Si=C bonds are longer than in the corresponding complexes of monocoordinated silenes irrespective of the type of the interactions involved to hold the second $Me_3N$ molecule.

***Coordination bond energies in complexes $2Me_3N \cdot H_2Si=CH_2$ and $2Me_3N \cdot F_2Si=CH_2$.*** The $\Delta H_{compl}$ values calculated for these complexes using Eq. (2) are −22.8 and −48.5 kcal mol$^{-1}$, respectively, being 8.3 and 11.4 kcal mol$^{-1}$ lower than in the complexes of these silenes with one $Me_3N$ ligand. According to structural data, both the Si←N coordination bonds in the complexes $2Me_3N \cdot H_2Si=CH_2$ and $2Me_3N \cdot F_2Si=CH_2$ are almost equivalent; therefore, we evaluated the *D*(Si←N) values as the halved enthalpies of complexation, *viz*., 11.4 for the former and 24.3 kcal mol$^{-1}$ for the latter complex. This is respectively 3.1 and 12.8 kcal mol$^{-1}$

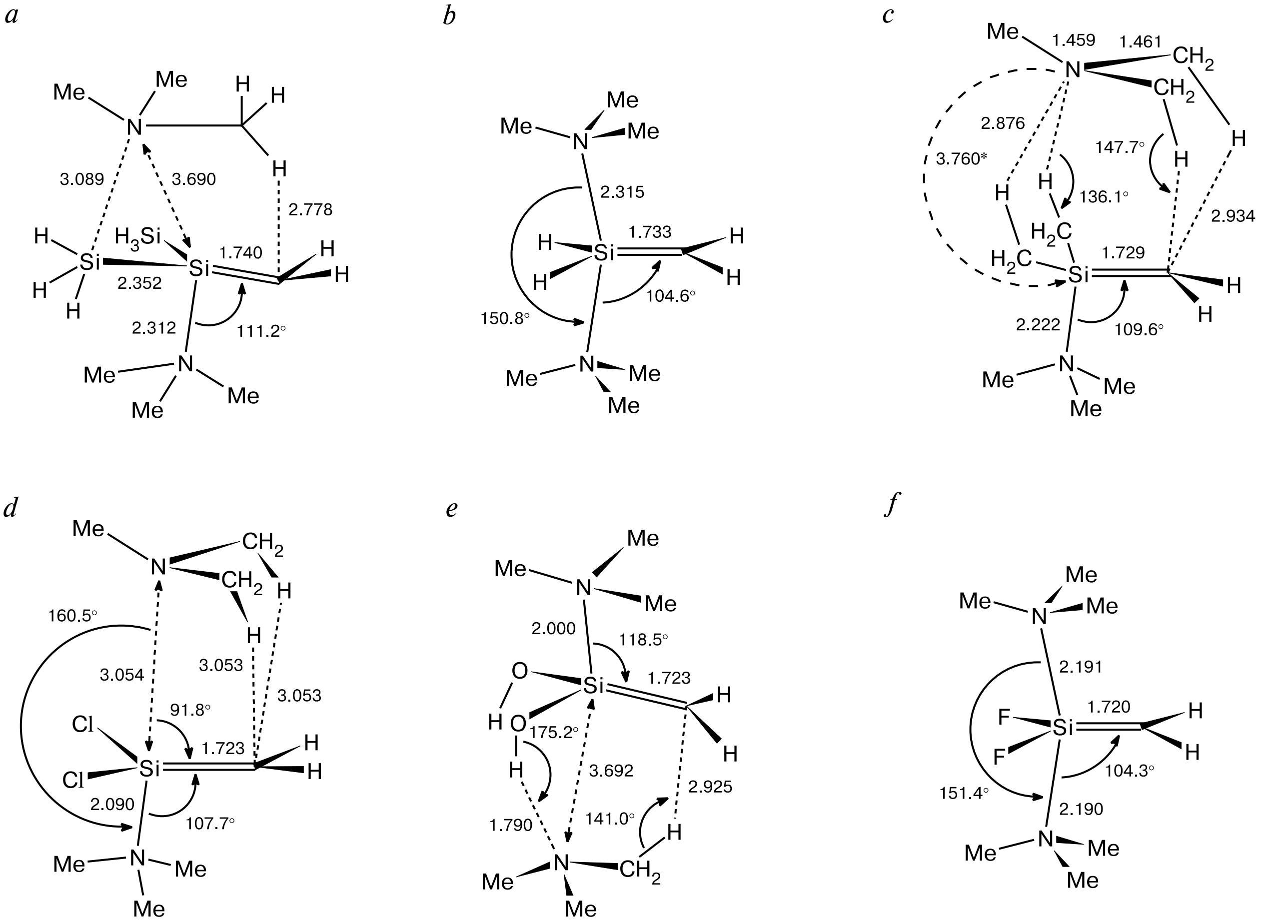


**Fig. 6.** Structures of complexes $2Me_3N\cdot(SiH_3)_2Si{=}CH_2$ (**5a**) (*a*), $2Me_3N\cdot H_2Si{=}CH_2$ (**5b**) (*b*), $2Me_3N\cdot Me_2Si{=}CH_2$ (**5c**) (*c*), $2Me_3N\cdot Cl_2Si{=}CH_2$ (**5d**) (*d*), $2Me_3N\cdot(HO)_2Si{=}CH_2$ (**5e**) (*e*), and $2Me_3N\cdot F_2Si{=}CH_2$ (**5f**) (*f*). The bond lengths are given in Å.
* The $r$(Si←N) distance.

lower than the $D$(Si←N) values for the complexes of the same silenes with one $Me_3N$ molecule (see Table 5).

Other silenes either do not form the second coordination bond with the nitrogen atom of the $Me_3N$ group, being stabilized by hydrogen bonds, or the second (longer) Si←N bonds in them are much weaker than the first coordination bond (the case of the $2Me_3N\cdot Cl_2Si{=}CH_2$ complex). In this connection it is difficult to attribute the change in the energy of complexation to a particular type of interactions.

Thus, the $sp^2$-hybridized silicon atom can form two equivalent hypervalent bonds $Si(sp^2)$←N only in the complexes of $H_2Si{=}CH_2$ and $F_2Si{=}CH_2$ with two $Me_3N$ molecules.

***Structures of 1,1-bis[N-(dimethylamino)acetimidato]silene (6) and its mono- (II) and biscoordinated (III) isomers. Energies of transannular coordination bonds in structures II and III.*** Two transannular coordination bonds $N(sp^3)$—$Si(sp^2)$ can be formed in molecule **6**.[6]

Structure **I** of molecule **6** calculated in this work contains an almost planar fragment $O_2Si{=}CH_2$ (Fig. 7, *a*). The $r$(Si=C) distance (1.694 Å) is similar to the Si=C bond length in the $(HO)_2Si{=}CH_2$ molecule (1.693 Å). Similar Si=C bond length values for molecule **6** and dihydroxysilene (both molecules have the same nearest environment of the silicon atom) indicate that replacement of hydrogen atom in the latter molecule by the $C(Me){=}NNMe_2$ fragment in the open form of molecule **6** has a little effect on $r$(Si=C).

In structure **II** (see Fig. 7, *b*), the Si←N transannular coordination bond (1.959 Å) is shorter than in the $Me_3N\cdot(HO)_2Si{=}CH_2$ complex with the same environment of the silicon atom, while the Si=C bond (1.706 Å) is longer than in structure **I**. The mid-plane of the five-membered ring is nearly perpendicular to the plane of the $Si{=}CH_2$ group. Tetracoordinate silicon atom is at the center of a distorted tetrahedron (see the Newman projection in Fig. 7, *b*). The Si←N transannular bond closes a five-membered ring in which all distances are much longer than in structure **I**, the Si—O bond being particularly lengthened (by more than 0.1 Å).

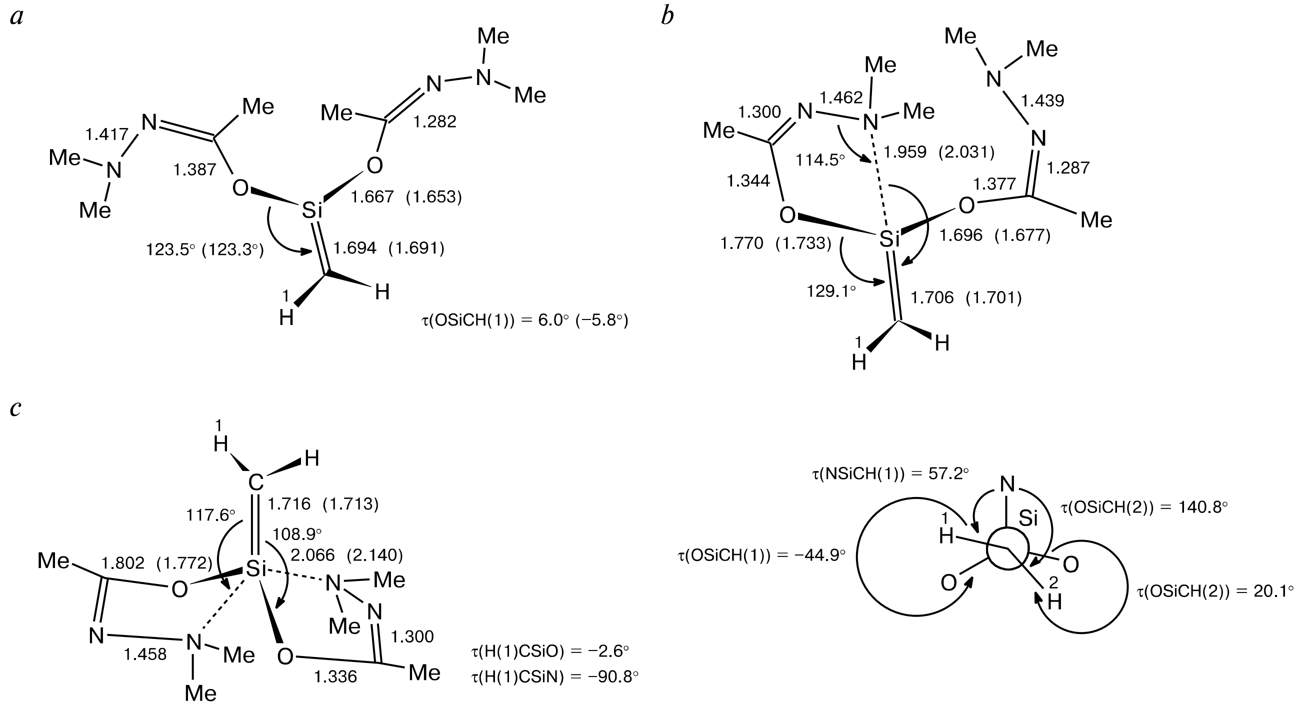


**Fig. 7.** *a*. The open form (**I**) of 1,1-bis[*N*-(dimethylamino)acetimidato]silene (**6**). From this point on the optimized parameters obtained from density functional B3LYP/6-31(d) calculations[6] are given in parentheses. *b*. Structure **II** of monocoordinated silene **6**. *c*. Structure **III** of biscoordinated silene **6**.

A comparison of the bond lengths in structures **I—III** calculated using different methods (see Fig. 7) shows that the coordination bond length, *r*(Si←N), predicted by the *ab initio* method is less than the *r*(Si←N) value obtained from DFT calculations[6] (see Fig. 7, *b*). *Vice versa*, the *ab initio* calculated Si=C and Si—O covalent bond lengths exceed the corresponding bond lengths obtained using the DFT approach.[6] The results of both calculations are consistent with each other and predict elongation of covalent bonds after formation of the cyclic chelate structure with the Si←N coordination bond.

In structure **III** having two coordination bonds Si←N (2.066 Å) the silicon atom is at the center of a tetragonal pyramid with the carbon atom at the vertex and two O atoms and two N atoms in the basal plane (see Fig. 7, *c*). This type of coordination is not characteristic of the compounds of pentacoordinate Si($sp^3$) atom; however, DFT calculations[6] led to the same shape of the molecule; therefore, the results obtained seem to be reliable. Structure **III** has a $C_2$ symmetry, *viz*., the twofold axis is aligned with the Si=C bond, the $O_2Si=CH_2$ fragment being nearly planar and perpendicular to the $N_2Si=CH_2$ fragment. The Si←N bonds are longer than in the monocoordinated structure **II**. The Si—O bonds (1.802 Å) are lengthened to the greatest extent and approach the Si←O coordination bond length (1.946 Å) in the THF•$(HO)_2Si=CH_2$ complex.

Transition from structure **I** to **II** is accompanied by a decrease in the total energy of 35.1 (26.8)[6] kcal mol$^{-1}$ (Table 7), while the energy gain on going from structure **I**

**Table 7.** Energy characteristics of 1,1-bis[*N*-(dimethylamino)acetimidato]silene (**6**) used in calculations of the coordination bond energies (*D*(Si←N)/kcal mol$^{-1}$)[a]

| Structure | $-E_{total}$ | ZPE | $-E_{total}$ | $-E_0$ | $\Delta E_0$ | *D*(Si←N) |
|---|---|---|---|---|---|---|
| | MP2/6-31G(d) | | MP4/6-311G(d) | | | |
| **I** | 1011.05618 | 0.28509 | 1011.50963 | 1011.22454 | 0 | — |
| **II** | 1011.11828 | 0.28779 | 1011.56834 | 1011.28055 | −35.1[b] | 35.1 |
| **III** | 1011.13725 | 0.28902 | 1011.58284 | 1011.29382 | −43.5[c] | 21.8 |

[a] For notations $E_{total}$, ZPE, and $E_0$, see Note to Table 1.

[b] $\Delta E_0$/kcal mol$^{-1}$ = *E*(**II**) − *E*(**I**).

[c] $\Delta E_0$/kcal mol$^{-1}$ = *E*(**III**) − *E*(**I**).

to **III** is 43.5 (31.4)[6] kcal $mol^{-1}$ (from this point on the energies obtained from DFT calculations are given in parentheses). Thus, we estimated the *D*(Si←N) value for structure **II** at 35.1 (26.8)[6] kcal $mol^{-1}$. Because both Si←N bonds in structure **III** are equivalent, the *D*(Si←N) energy is half the energy of coordination, *i.e.*, 21.8 (15.7)[6] kcal $mol^{-1}$. This is in reasonable correspondence with the energy of formation of intramolecular transannular bond in 5-aza-2,8-dioxa-5-methyl-1-methylene-1-silacyclooctane (19.7 kcal $mol^{-f1}$).[5] The formation of bischelate form **III** is accompanied by a decrease in *D*(Si←N) by 8.3 (11.4)[6] kcal $mol^{-1}$ compared to *D*(Si←N) of **II**. This is consistent with elongation of the Si←N bonds in structure **III** compared to structure **II** and can be explained by intramolecular electron density redistribution following the formation of the bischelate form **III**.

The *D*(Si←N) values for the $Me_3N \cdot (HO)_2Si{=}CH_2$ complex (34.8 kcal $mol^{-1}$) and structure **II** (35.1 kcal $mol^{-1}$) are in good agreement. This suggests that the energy characteristics of coordination are primarily determined by the nature of the atoms in the nearest environment of the Si($sp^2$) atom, namely, in both cases these are two O atoms, one N atom, and the $=CH_2$ group. Therefore, we can assume that the $D_\pi$(Si=C) value for **I** is similar to 33 kcal $mol^{-1}$, as for dihydroxysilene, while the rotational barrier for **II** seems to be at most 7.0 kcal $mol^{-1}$, as for the $Me_3N \cdot (HO)_2Si{=}CH_2$ complex (see Table 5).

Unfortunately, it is impossible to compare the *D*(Si←N) values for structure **III** and complex $2Me_3N \cdot (HO)_2Si{=}CH_2$, because the second Si←N coordination bond is not formed in the latter. However, owing to the fact that the *D*(Si←N) values for $Me_3N \cdot F_2Si{=}CH_2$ and for structure **II** are similar (37.1 and 35.1 kcal $mol^{-1}$, respectively), we can compare the changes in the *D*(Si←N) energies on going from structure **II** to **III** and from the complex $Me_3N \cdot F_2Si{=}CH_2$ to $2Me_3N \cdot F_2Si{=}CH_2$ (see Tables 3 and 7). The *D*(Si←N) energy decreases by 8.3 kcal $mol^{-1}$ in the former and by 11.4 kcal $mol^{-1}$ in the latter case. Thus, there is general consensus in trends of the changes in the coordination bond energies on going from mono- to bis-coordination in conventional and cyclic complexes of silenes.

Comparison of the energy characteristics calculated by different methods shows that the DFT method underestimates the *D*(Si←N) energies for structures **II** and **III** compared to the *ab initio* technique. At the same time the change in the *D*(Si←N) values on going from structure **II** to **III** predicted by the *ab initio* method (−8.3 kcal $mol^{-1}$) is smaller than that obtained from DFT calculations (−11.1 kcal $mol^{-1}$).

Thus, the results obtained in this work and in previous calculations[5,6] show that the $sp^2$-hybridized silicon atom in simple and complex silenes can form hypervalent compounds with two strong coordination bonds, which favor stabilization of the compounds with the silicon—carbon double bonds.

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