Molecular Design of Bis-Chelate N-Donor-Stabilized Silaethenes: Theoretical Study of 1,1-Bis[*N*-(dimethylamino)acetimidato]silene

Valery F. Sidorkin,* Elena F. Belogolova, and Vadim A. Pestunovich

A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, Irkutsk 664033, Russia

Received December 12, 2003

RHF/6-31G* and B3LYP/6-31G* computations were performed on the silene $[Me_2NN{=}C(Me)O]_2Si{=}CH_2$ (**6**) and analyzed through the use of properties of atoms in molecules. Three stationary states of **6** belong to its non-chelate (**6a**) and two intramolecularly N-donor-stabilized forms, five-membered mono-chelate (**6b**) and previously unknown (for the silenes) bis-chelate (**6c**), with three-, four-, and five-coordinate doubly bonded silicon, respectively. On going from **6a** to **6b** and **6c**, initially planar silicon attains distorted tetrahedral and square pyramidal structures, whereas the Si═C double bond becomes more polar and changes its distance from 1.674 Å to 1.693 and 1.704 Å and from 1.691 Å to 1.701 and 1.713 Å at the RHF and B3LYP levels, respectively. The RHF and B3LYP N−Si distances in **6b** (1.988 and 2.031 Å) are shorter than in **6c** (2.187 and 2.140 Å). The N→Si bond in chelates **6b**,**c** is described as highly polar, but of sufficiently covalent character. The four-center six-electron (4c-6e) model is proposed for the silicon bonding in the $N_2Si{=}C$ moiety of **6c**. High energetic advantages of the chelate **6b** and **6c** forms over **6a** (26.8 and 31.4 kcal/mol at the B3LYP/6-31G* level including the ZPE correction and 32.4 and 36.3 kcal/mol at the RHF/6-31G* level, respectively) suggest that intramolecular N-donor stabilization may be sufficient to observe silene **6** under relatively mild conditions.

Introduction

The first strong evidence for the existence of silaalkenes[1] has initiated impressive progress in silene chemistry.[2] Owing to the extremely high reactivity of a silicon−carbon double bond, most silenes are transient compounds that can be observed in the condensed phase using only a matrix isolation technique at extra-low temperatures.[2] Kinetic stabilization of silenes through sterical protection of the Si═C bond by bulky substituents and/or intermolecular or intramolecular complexation of a highly electrophilic sp^2-hybridized silicon with an *n*-donor (D) affords their study under milder conditions and even isolation at ambient temperature.[2−5] The higher the sterical shielding of the silicon−carbon double bond or the energy of the complex formation, the lower the rate of the most widespread types of chemical transformations of silenes such as their cyclodimerization or oligomerization.

The molecular design of intramolecular complexes of silenes is of special interest because the chelate effect usually enhances the strength of a donor−acceptor (DA) bond. However, only a few intramolecularly donor-stabilized silenes are known now. These are silene-like dibenzosilafulvene **1**[5a,b] and 1,2,2-tris(trimethylsilyl)silenes **2**−**4** containing a “pincer”-type chelating ligand at a doubly bonded silicon.[5c−e] Structural information on intramolecularly donor-stabilized silenes is limited by the X-ray data on complexes **2**−**4**[5c−e] and by the results of an ab initio study of 1-methylene-5-methyl-5-aza-2,8-dioxa-1-silacyclooctane (**5**).[6]

To our best knowledge, none of the bis-chelate silenes containing pentacoordinate unsaturated silicon have been described in the current literature. Remarkably, even with substitution by a *tridentate* 2,6-bis(dimethylaminomethyl)phenyl ligand the silene silicon remains tetracoordinate and forms a DA bond only with one of the nitrogen atoms in **4**.[5e]

---

* Corresponding author. E-mail: svf@irioch.irk.ru.

[1] (a) Gusel’nikov, L. E.; Flowers, M. C. *J. Chem. Soc., Chem. Commun.* **1967**, 864. (b) Flowers, M. C.; Gusel’nikov, L. E. *J. Chem. Soc. (B)* **1968**, 419.

[2] Recent reviews on silenes: (a) West, R. *Polyhedron* **2002**, *21*, 467. (b) Müller, T.; Ziche, W.; Auner N. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, 1998; pp 857−1062. (c) Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem.* **1995**, *39*, 125. (d) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z.; Patai, S., Eds.; Wiley: New York, 1989; pp 1015−1142.

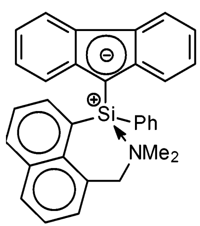
[3] Sterically crowded silenes: (a) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Kallury, R. K. M. R.; Poon, Y. C.; Chang Y.-M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1993**, *115*, 11598. (b) Wiberg, N.; Wagner, G.; Riede J.; Müller, G. *Organometallics* **1987**, *6*, 32. (c) Apeloig, Y.; Bendikov, M.; Yuzefovich, M.; Nakash, N.; Bravo-Zhivotovskii, D.; Bläser D.; Boese, R. *J. Am. Chem. Soc.* **1996**, *118*, 12228.

[4] Intermolecular silene complexes: (a) Wiberg N.; Köpf, H. *J. Organomet. Chem.* **1986**, *315*, 9. (b) Wiberg, N.; Wagner, G.; Reber, G.; Riede, J.; Müller, G. *Organometallics* **1987**, *6*, 35. (c) Wiberg, N.; Joo K.-S.; Polborn, K. *Chem. Ber.* **1993**, *126*, 67. (d) Auner, N.; Grobe, J.; Muller, T.; Rathmann, H. W. *Organometallics* **2000**, *19*, 3476.

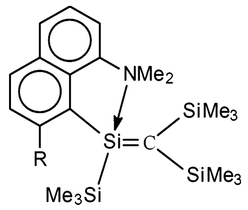
[5] Intramolecular silene complexes: (a) Zemljanskii, N. N.; Borisova, I. V.; Shestakova, A. K.; Ustynyuk, Yu. A.; Chernyshov, E. A. *Izv. Akad. Nauk, Ser. Khim.* **1998**, 469. (b) Zemljanskii, N. N.; Borisova, I. V.; Shestakova, A. K.; Ustynyuk, Yu. A.; Chernyshov, E. A. *Russ. Chem. Bull.* **1998**, *47*, 469. (c) Mickoleit, M.; Schmohl, K.; Kempe, R.; Oehme, H. *Angew. Chem.* **2000**, *112*, 1679. (d) Mickoleit, M.; Schmohl, K.; Kempe, R.; Oehme, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 1610. (e) Mickoleit, M.; Kempe, R.; Oehme, H. *Chem. Eur. J.* **2001**, *7*, 987. (f) Pötter, M.; Böumer, U.; Mickoleit, M.; Kempe, R.; Oehme, H. *J. Organomet. Chem.* **2001**, *621*, 261.

[6] Avakyan, V. G.; Gusel’nikov, L. E.; Pestunovich, V. A.; Bagaturyants, A. A.; Auner, N. *Organometallics* **1999**, *18*, 4692.

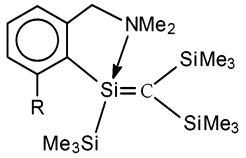
10.1021/om034364m CCC: $27.50



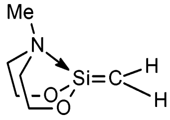
1



2



3 (R = H)
4 (R =CH$_2$NMe$_2$)

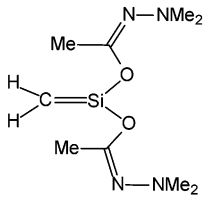


5

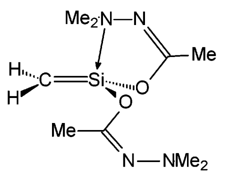
In this paper we report the results of an ab initio and DFT study of novel potentially donor-stabilized silaethene: 1,1-bis[*N*-(dimethylamino)acetimidato]silene, [Me$_2$NN=C(Me)O]$_2$Si=CH$_2$ (**6**). The choice of this target is not arbitrary. Compared to the 2-aminodiethoxy and pincer aminoaryl ligands used previously for intramolecular stabilization of silenes, the Me$_2$NN=C(R)O group has a stronger chelating capability. Precisely this trait affords the stronger intramolecular DA interaction N(sp^3)→Si(sp^3) in hypervalent [*N*-(dimethylamino)acylimidato]silanes than in other related (N−Si)chelate organosilicon compounds.[7] Moreover, bis-substitution by this group leads usually to bis-chelation of neutral or positively charged silicon.[7,8] Therefore, of the most probable structures of the molecule **6**, namely, non-chelate **6a**, mono-chelate **6b**, and bis-chelate **6c**, the latter two seem to be more advantageous. We felt it of interest to study **6a**−**c** computationally to give deeper insight into the nature of the DA interaction and structural trends in donor-stabilized silenes and to obtain the first information *on the structure of bis-chelate silenes*. Experimentally, silene **6** could be generated by the [2 + 2] cycloreversion of 1,1-bis[*N*-(dimethylamino)acetimidato]silacyclobutanes, [Me$_2$NN=C(Me)-O]$_2$Si(CH$_2$)$_3$, prepared recently.[9]

Computational Methods

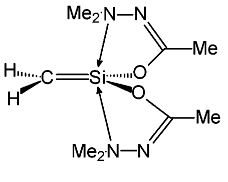
All computations on the **6a**−**c** species were performed with full optimization of geometry at the RHF/6-31G* level of theory[10] using the GAMESS[11] electron structure code and at the B3LYP/6-31G* level using the GAUSSIAN 98[12] package of programs. For the silicon atom in ab initio calculations we used the 6-31G basis set revised by the Gordon group[10f] and at the DFT level that given by Pople.[10g] The correspondence of optimized structures **6a**−**c** to the local minima on the potential energy surface was proved by positive eigen values of the related Hessians. The zero-point energy (ZPE) correction was evaluated at the B3LYP level. Estimations of differences of the enthalpies (ΔH_{298}) and free energies (ΔG_{298}) of bis- and mono-chelate forms were performed for standard conditions (298.15 K, 1 atm). The ΔH_{298}, ΔG_{298}, and ZPE values were not scaled.



6a



6b



6c

The medium effect on the RHF/6-31G* geometry of **6b**,**c** was studied in the framework of the self-consistent Onsager reaction field cavity model, SCRF,[13] and the polarized continuum model, PCM.[14] A quantum-chemical topological analysis was performed within Bader's "atoms in molecules" method[15] using the AIMPAC package of programs.[16]

Results and Discussion

Computations came up to expectations for the possibility of the existence of silene **6** in the mono-chelate

---

(7) Kost, D.; Kalikhman, I. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z.; Apeloig, Y., Eds.; Wiley: Chichester, 1998; pp 1339−1445. (b) Lukevics, E.; Pudova, O. A. *Chem. Heterocycl. Compd.* **1966**, *32*, 1381.

(8) (a) Kalikhman, I.; Krivonos, S.; Lameyer, L.; Stalke, D.; Kost, D. *Organometallics* **2001**, *20*, 1053. (b) Kingston, V.; Gostevskii, B.; Kalikhman, I.; Kost, D. *Chem. Commun.* **2001**, 1272. (c) Kost, D.; Kingston, V.; Gostevskii, B.; Ellern, A.; Stalke, D.; Walfort, B.; Kalikhman, I. *Organometallics* **2002**, *21*, 2293.

(9) Belogolova, E.; Gostevskii, B.; Pestunovich, V.; Sidorkin, V.; Avakyan, V.; Gusel'nikov, L.; Auner. N. In *The 12th International Symposium on Organosilicon Chemistry. Program, Abstracts, and List of Participants*, May 23−28, 1999, Sendai, Japan, p 172.

(10) For an introduction to the applied methods and basis set, see: (a) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986. (b) Foresman, J. B.; Frisch, Æ. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian Inc.: Pittsburgh, PA, 1996. (c) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, A1133. (d) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, 1989. (e) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (f) Gordon M. S. *Chem. Phys. Lett.* **1980**, *76*, 163. (g) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(11) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian Inc.: Pittsburgh, PA, 1998.

(13) (a) Kirkwood, J. G. *J. Chem. Phys.* **1934**, *2*, 351. (b) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486. (c) Szafan, M.; Karelson, M. M.; Katritzky, A. R.; Koput, J.; Zerner, M. C. *J. Comput. Chem.* **1993**, *14*, 371, and references therein.

(14) (a) Miertus S., Scrocco E., Tomasi J. *Chem. Phys.* **1981**, *55*, 117. (b) Tomasi J., Persico M. *Chem. Rev.* **1994**, *94*, 2027. (c) Cammi R., Tomasi J. *J. Comput. Chem.* **1995**, *16*, 1449.

(15) (a) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Clarendon Press: Oxford, 1990. (b) Bader, R. F. W.; Nguyen-Dang, T. T. *Adv. Quantum Chem.* **1981**, *14*, 63. (c) Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893.

(16) Biegler-König, F. W.; Bader, R. F. W.; Tang, T. H. *J. Comput. Chem.* **1982**, *3*, 317.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 6a−c (RHF/6-31G* and B3LYP/6-31G* calculations)

	6a		**6b**		**6c**	
	HF	DFT	HF	DFT	HF	DFT
Si(2)−C(1)	1.674	1.691	1.693	1.701	1.704	1.713
Si(2)−N(8)			1.988	2.031	2.187	2.140
Si(2)−N(16)					2.187	2.140
Si(2)−O(3)	1.628	1.653	1.710	1.733	1.715	1.772
Si(2)−O(11)	1.628	1.653	1.654	1.677	1.715	1.772
C(1)−Si(2)−O(3)	125.4	123.3	119.8	119.1	116.3	110.9
C(1)−Si(2)−O(11)	125.4	123.3	120.9	120.8	116.3	110.9
O(3)−Si(2)−O(11)	109.2	113.4	107.3	108.4	127.4	138.1
C(1)−Si(2)−N(8)			123.8	123.8	111.6	115.6
N(8)−Si(2)−N(16)					136.9	128.8
N(8)−Si(2)−O(3)			83.3	83.4	77.8	79.1
Si(2)−C(1)−H(4)	121.5	121.2	123.1	122.8	122.1	122.0
Si(2)−C(1)−H(12)	121.5	121.2	120.9	120.5	122.1	122.0
H(4)−C(1)−H(12)	117.0	117.6	115.9	116.3	115.8	116.0
H(4)−C(1)−Si(2)−O(3)	−1.3	−5.8	27.4	30.9	5.3	1.7
C(1)−Si(2)−O(3)−C(5)	99.1	120.4	−141.6	−139.4	83.1	89.8
C(1)−Si(2)−O(11)−C(13)	97.1	120.4	−51.0	−86.4	83.1	89.8
Si(2)−O(3)−C(5)−N(7)	172.8	178.5	13.9	12.2	24.5	22.3
Si(2)−O(11)−C(13)−N(15)	174.0	178.5	148.0	−166.7	24.5	22.3

6b and unusual bis-chelate **6c** forms. These made it possible to establish regular trends in the structural and energetic changes induced by chelation of silenes. In a qualitative sense, the corresponding RHF/6-31G* and B3LYP/6-31G* results are in close agreement, and a small quantitative difference in a particular description of a given structure is usual for these methods.

Geometries of 6a−c. Selected geometrical parameters of optimized structures **6a−c** are collected in Table 1, and the B3LYP/6-31G* molecular structures of these species are illustrated in Figure 1.

The geometry of the non-chelate form **6a** was found to be typical of usual silenes, without any additional bonding. The doubly bonded Si and C atoms are planar since the sums of their bond angles, $\sum_{Si}$ and $\sum_{C}$, are 360°. The double bond is slightly twisted (by 1.3° and 5.8° at the RHF/6-31G* and B3LYP/6-31G* levels, respectively). Two imidate groups take up symmetric positions about the SiO_2 plane. The RHF/6-31G* Si═C bond distance in **6a**, $d(\mathrm{Si{=}C}) = 1.674$ Å, is shorter than in 1,1-dimethylsilene (**7**) (1.696 Å)[6] and 1,1-dimethoxysilene (**8**) (1.680 Å)[6] recently studied by the same method. The reliability of these estimations is evident from a close agreement between the predicted value of $d(\mathrm{Si{=}C})$ in **7** and that determined by microwave spectroscopic methods (1.692 Å).[17] The decrease in the calculated $d(\mathrm{Si{=}C})$ values with increasing electronegativity of silicon substituents on going from **7** to **8** and **6a** is in agreement with structural trends known for silenes.[18,19] The majority of the B3LYP/6-31G* bond distances in **6a** (and in **6b**,**c** as well) are longer than those calculated by the RHF/6-31G* method.

For the mono-(N−Si)chelate form **6b**, the RHF/6-31G* computations demonstrate a very strong N→Si interaction between a nitrogen of one of the dimethylamino groups and a silicon atom. The N→Si distance (1.988 Å) was found to be shorter than that determined experimentally (X-ray) for 1,2,2-tris(trimethylsilyl)silene chelates **2−4** (2.004−2.069 Å)[5c−f] and calculated (RHF/6-31G*) for intramolecular complex **5** (2.126 Å).[6]

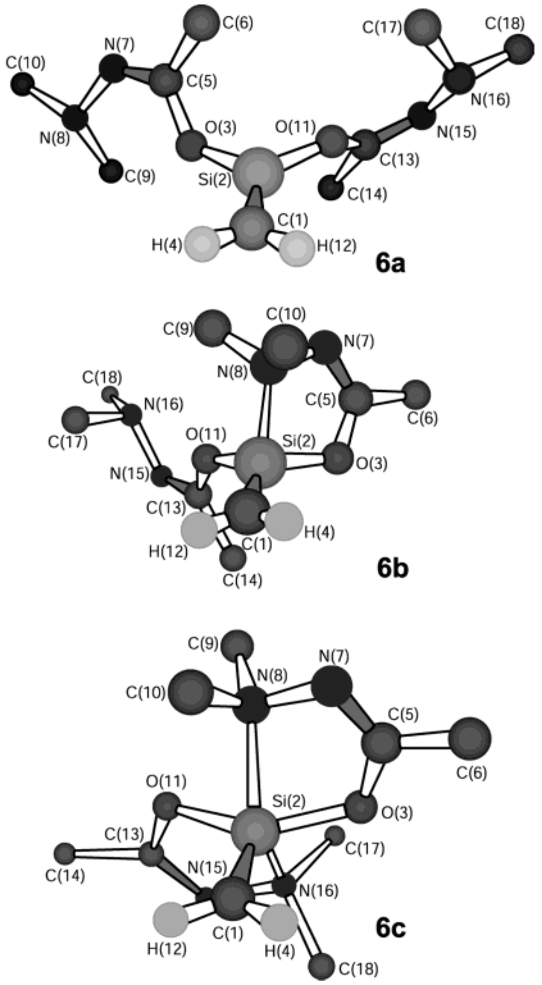


Figure 1. Molecular structures of **6a−c** calculated by the RHF/6-31G* method (most of the H atoms omitted for clarity).

The formation of the intramolecular Si←N bond leads to a visible elongation of the Si═C bond by 0.019 Å (by 0.010 Å at the B3LYP/6-31G* level) and to distortion of the planar structure at the silicon atom toward its tetrahedral geometry. The deviation of the silicon atom

---

(17) Gutovsky, H. S.; Chen, J.; Hayduk, P. J.; Keen, J. D.; Emilsson, T. *J. Am. Chem. Soc.* **1989**, *111*, 1901.

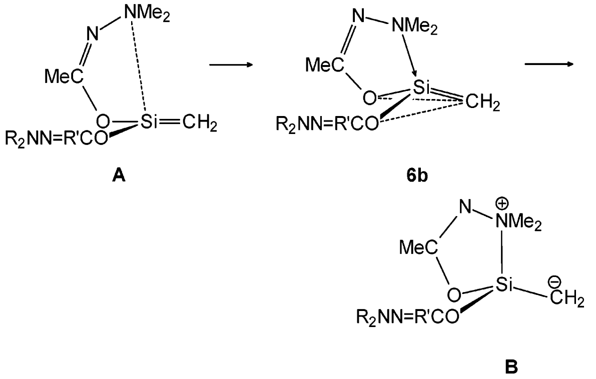
(18) Apeloig, Y. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z.; Patai, S., Eds.; Wiley: New York, 1989; pp 57−225.

(19) Gusel'nikov, L. E.; Avakyan, V. G.; Gusel'nikov, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 662.

from the OCO plane, Δ_{Si}, is about 0.33 Å, and the $\sum_{Si}$ value is 348° (for the tetrahedral atom the sum of three valent angles is 328.5°). Interestingly, the silene carbon remains undistorted ($\sum_C = 360°$).

Analogous changes in geometry about silicon have been observed or computed for a number of intermolecularly and intramolecularly donor-stabilized silenes.[4,5c−f,6] For example, the X-ray data on complexes $Me_2Si{=}C(SiMe_3)(SiMe_2Bu\text{-}t){\cdot}THF$ (**9**), $(Me_2Si{=}C(SiMe_3)(SiMe_2Bu\text{-}t){\cdot}F^-$ (**10**), and $Me_2Si{=}C(SiMe_2Ph)_2{\cdot}NMe_2Et$ (**11**) show that the greatest tetrahedricity of the silicon atom ($\sum_{Si} = 341.7°$) is inherent to adduct **10** possessing the strongest nucleophile.[4c] However, the dependence of the geometry of silene complexes on the degree of additional D→Si bonding was rather suggested than strongly established.

To follow the trends in changing d(Si═C) and Δ_{Si} upon N→Si bond formation, a modeling of the reaction 1 of intramolecular nucleophilic addition to the double bond Si═C in **6a** seems to be instructive. Indeed, mono-chelate **6b** can be considered as a stable intermediate that lies on the reaction pathway linking prereaction state **A**, in which one of the nitrogen atoms occupies an advantageous position for attack on a *tricoordinate* silicon, with the product **B**, having ylide-like structure with a *tetracoordinate* silicon.



(1)

Within the RHF/6-31G* method, we simulated a part of this reaction pathway by scanning the intramolecular distance Si···N, d(Si−N), of **6b** with 0.1 Å steps in the range of 2.3−1.7 Å (d(Si−N) = 1.7 Å is close to a lower limit of the length of a covalent Si−N bond). At each fixed d(Si−N) value, all other geometrical parameters were optimized. The obtained results reveal unambiguously that the shortening d(Si−N) leads to concerted elongation of the Si═C double bond and increasing silicon pyramidality and in so doing brings mono-chelate **6b** actually to ylide **B** (see Figure 2). This resembles the trends in similar changes in geometry of the carbon coordination center of carbonyl compounds in their reactions with nucleophiles found by methods of structural correlations and quantum chemistry.[20]

Some experimental and theoretical studies show that a coordination bond of many TBP complexes of primordially sp^3-hybridized silicon[21] and the silene adduct $H_2C{=}SiH_2{\cdot}OMe_2$ (**12**)[4d] is shorter in the condensed phases than in the gas phase. As applied to donor-stabilized silenes, it may produce an appreciable distinction between the solid-state and gas-phase distances of their Si═C bond. The question of whether and to what extent the environment may affect the structure of chelate **6b** is of general interest.

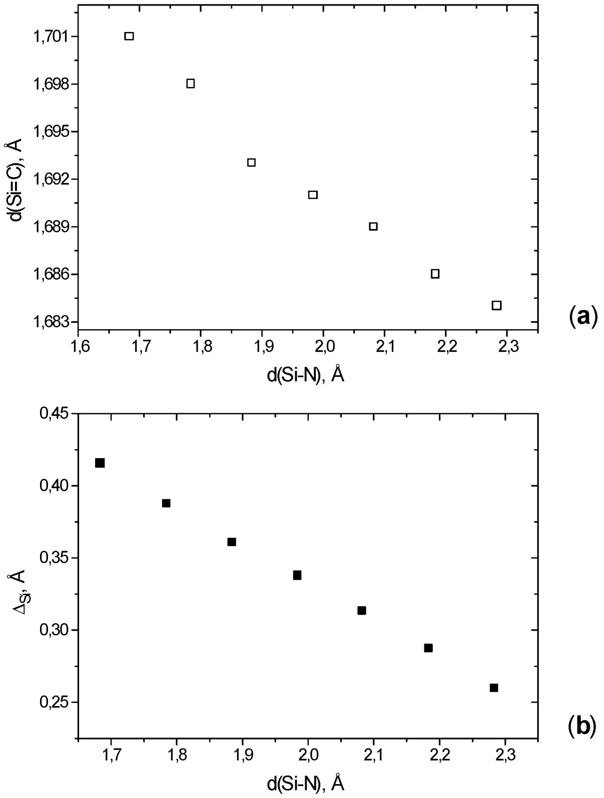


Figure 2. Influence of the Si←N bond distance on (a) the Si═C bond distance and (b) the displacement of the silicon atom from the CO^{1}O^2 plane (Δ_{Si}) calculated at the RHF/6-31G* level.

It is assumed that the solid-state geometry of DA complexes is very close to their geometry in highly polar solution.[21,22] Our RHF/6-31G* computations using the SCRF model predict that the length of most bonds of mono-chelate **6b** in polar solution (with dielectric constant ϵ equal to 45.0) should be near those in the gas phase (see Table 2). The corresponding differences do not exceed several thousandths of an angstrom, a standard interval for covalent bonds.[23] The maximal change of about 0.01 Å (0.04 Å in the PCM model) is inherent to the N→Si(sp^2) bond. But even these values are 30−40 times less than those calculated in a similar manner for the N→Si bond in 1-fluorosilatrane, $FSi(OCH_2CH_2)_3N$ (**13**) (~0.3 Å),[21e] and estimated for the

---

[20] (a) Bürgi, H. B.; Dunitz, J. D.; Shefter, E. *J. Am. Chem. Soc.* **1973**, *95*, 5065. (b) Bürgi, H. B.; Dunitz, J. D.; Lehn, J. M.; Wipff, G. *Tetrahedron* **1974**, *30*, 1563.

[21] (a) Voronkov, M. G.; Brodskaya, E. I.; Reich, P.; Shevchenko, S. G.; Baryshok, V. P.; Frolov, Yu. L. *J. Organomet. Chem.* **1979**, *164*, 35. (b) Voronkov, M. G.; Pestunovich, V. A.; Baukov, Yu. I. *Metalloorgan. Khim*. **1991**, *4*, 1210; *J. Organomet. Chem. USSR* (*Engl. Transl.*) **1991**, *4*, 593. (c) Sidorkin, V. F.; Balakhchi, G. K.; Voronkov M. G.; Pestunovich, V. A. *Dokl. Akad. Nauk SSSR* **1987**, *296*, 113; *Dokl. Phys. Chem. (Engl. Transl.)* **1987**, *296*, 400. (d) Boggs, J. E.; Peng, Ch.; Pestunovich, V. A.; Sidorkin, V. F. *J. Mol. Struct. (THEOCHEM)* **1995**, *357*, 67. (e) Schmidt, M. W.; Windus, T. L.; Gordon, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 7480. (f) Pestunovich, V.; Kirpichenko, S.; Voronkov, M. G. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, 1998; pp 1447−1537.

[22] Jonas, V.; Frenking, G.; Reetz, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 8741.

[23] (a) Wong, M. W.; Frisch, M. J.; Wiberg, K. B. *J. Am. Chem. Soc.* **1991**, *113*, 4776. (b) Wong, M. W.; Wiberg, K. B.; Frisch, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 523 (c) Wong, M. W.; Wiberg, K. B.; Frisch, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 1645.

Table 2. Differences (Δd) between Selected Solution (RHF/6-31G* − SCRF, $\epsilon = 45.0$)[a] and Gas-Phase (RHF/6-31G*) Bond Distances (Å) for 6b and 6c

	Δd				
species	Si(2)═C(1)	Si(2)−N(8)	Si(2)−O(3)	C(5)═N(7)	N(7)−N(8)
6b	0.003	−0.012	−0.002	0.000	0.001
6c	0.004	−0.011	0.001	0.001	0.000

[a] The Onsager radii of **6b** (5.07 Å) and **6c** (5.34 Å) were calculated quantum chemically using the procedure in ref 24.

O→Si bond in the silene-ether complex $H_2C{=}SiH_2 \cdot OMe_2$ in ether solution (0.389 Å)[4d] by the B3LYP/6-311+G(2df,p) method using the SCIPCM approach. In accordance with the known trends for various DA complexes,[21,22] smaller medium-induced structural changes imply a stronger coordinative bond in **6b**. Naturally, the above results do not exclude a more pronounced medium effect on the geometry of silene complexes **2**−**4** and **11**, which possess a weaker N→Si bond and/or a less polar Si═C bond due to substitution by σ-donor groups.

Computations on the bis-chelate form **6c** give the first information about a possible structure of silene complexes bearing a pentacoordinate silicon. The formation of the second N→Si(sp^2) bond in **6c** results in “pulling” the silicon atom into the COO plane and in further elongation of the Si═C bond (Table 1). Two competing N→Si bonds are equal in length and 0.199 and 0.109 Å longer at the RHF/6-31G* and B3LYP/6-31G* levels, respectively, than the only N→Si bond in **6b**. The chelate cycles in **6c** are similar to that in **6b** and have an envelope form. The silicon atom is 0.6 Å deviated from the OCNN planes.

At first glance, a silicon polyhedron in **6c** predicted by computations seems to be surprising. Unlike most pentacoordinate organosilanes, which possess a distorted trigonal bipyramidal (TBP) structure,[7] bis-chelate **6c** has a slightly distorted square pyramidal (SP) geometry about the silicon with an apical location of the carbon and a basal disposition of two nitrogen and two oxygen atoms. A similar silicon polyhedron is characteristic of only a few spirosilicates[7,25] and, what is more important, of bis-chelate organylbis[(*N*-dimethylamino)-imidato-*N*,*O*]siliconium derivatives, $\{RSi[OC(R'){=}NNMe_2]_2\}^+X^-$ (**14**).[8] As compared to the latter, bis-chelate **6c** has more obtuse (by 10−12°) NSiC angles and sharper (by 20−27°) NSiN angles. The bite angles in **6c** are 4° smaller than in **14**. Interestingly, the coordination bonds of a doubly bonded silicon in **6c** are longer than those of a positively charged silicon in **14** (1.93−1.97 Å).[8] The RHF/6-31G* computations using the SCRF model[13] predict that the geometry of bis-chelate **6b** in a polar solution with a dielectric constant $\epsilon = 45.0$ should be almost the same as that in the gas phase (see Table 2).

Electronic and MO Structure. Selected results of the topological analysis of the electron density ρ in species **6a**−**c** within the Bader approach[15] at the RHF/6-31G* and B3LYP/6-31G* levels are shown in Table 3. In the framework of the AIM theory, the high values of the calculated parameter of the ellipticity, $\epsilon = 0.778$ (**6a**), 0.584 (**6b**), and 0.541 (**6c**), indicate a double-bond character of their Si═C bond which decreases with increasing the silicon coordination number. Recall that the parameter ϵ is equal to 0.45 for the double bond C═C in ethylene and close to 0 for the single and triple bonds with cylindrical symmetry.[15] The covalent nature of the Si═C bond is undoubtedly proved by the negative value of the electron energy density $E(\mathbf{r}_c)$ in the related bond critical point, bcp(Si═C) (ionic bonds are characterized by $E(\mathbf{r}_c) > 0$).[26] This bond is highly polarized, as judged from the small absolute value of $E(\mathbf{r}_c)$ and the positive sign of its Laplacian, $\nabla^2\rho$, at the bcp(Si═C). These results are fully consistent with generally used conceptions concerning the nature of Si═C bond in silenes.[2,18]

Bader analysis confirms the N→Si(sp^2) bonding in **6b** and **6c** species by detection of new (noncharacteristic of **6a**) critical points: (3, −1) points, bcp(N→Si), of their N→Si bonds and (3, 1) ring critical points, rcp, of the chelate cycles. The bcp(N→Si) properties describe the N→Si bonding as a highly polarized bond with sufficient covalent interaction. Compared to a single bond (i.e., Si−O), the N→Si bonds in **6b** and **6c** are characterized by very high ϵ values. This may show that the π-component of the Si═C bond is involved in the formation of N→Si bond(s). At the same time, the data collected in Table 3 indicate that an increase in the silicon coordination number from 4 to 5 has little, if any, effect on the nature of the Si═C and N→Si bonds.

The following should be noted. When passing from **6a** to **6b** and **6c**, the progressive elongation of the Si═C bond is accompanied, contrary to the structural trends known for usual silenes,[18] by an increase in its polarity, $\Delta q = q_{Si} - q_C$. The related changes in the RHF/6-31G* Δq values for **6b** and **6c** were estimated to be 0.17 and 0.26 e using the Mulliken technique of charge calculation and 0.08 and 0.76 e within the Bader approach, respectively. However, a comparison of the square roots of the ratios of the sums of the squares of coefficients at the carbon and silicon atomic orbitals forming the occupied π MOs ($r = [(\sum_i c_i^2(C))/(\sum_i c_i^2(Si))]^{1/2}$, where the sum is taken over the occupated π MOs; $i = 1$ and 2 for non-chelate **6a** and bis-chelate **6c**, respectively) demonstrates that the π-polarity of the Si═C bond in bis-chelate **6c** ($r = 1.22$) is lower than in non-chelate **6a** ($r = 1.30$). Perhaps, it is precisely the decrease in the π-polarity of the Si═C bond that leads to its lengthening with a subsequent increase of the silicon coordination number in **6a**−**c**. Meanwhile, the corresponding RHF/6-31G* $|E(\mathbf{r}_c)/\rho|$ values, which are linear with the electron energy of a bond,[27] increase from 0.560 for **6a** to 0.570 and 0.573 for **6b** and **6c**, respectively, thus indicating a small strengthening of the Si═C bond. Interestingly, a recent computational study on a set of Si-substituted silenes $R_2Si{=}CH_2$ bearing mono-dentate substituents R also showed a striking growth in energy of the Si═C π-bond upon its lengthening.[19]

Figure 3 shows how one can represent, according to the RHF/6-31G* calculations, a scheme of the formation of MOs of the N→Si═C fragment of **6b** from the nitrogen

---

[24] Wong, M. W.; Wiberg, K. B.; Frisch, M. J. *J. Chem. Phys.* **1991**, *95*, 8991.

[25] Holmes, R. R. *Chem. Rev.* **1996**, *96*, 927.

[26] (a) Cremer, D.; Kraka, E. *Croat. Chem. Acta* **1984**, *57*, 1259. (b) Cremer, D.; Kraka, E. *Angew. Chem.* **1984**, *96*, 612. (c) Ritchie, J. P.; Bachrach, S. M. *J. Am. Chem. Soc.* **1987**, *109*, 5909.

[27] Grimme, S. *J. Am. Chem. Soc.* **1996**, *118*, 1529.

Table 3. Electron Density (ρ, e/a$_0^3$), Laplacian ($\nabla^2\rho$, e/a$_0^5$), Ellipticity (ϵ), and Energy Density ($E(\mathbf{r}_c)$, hartree/a$_0^3$) at Bond (3, −1) and Ring (3, 1) Critical Points of 6a−c Calculated at the RHF/6-31G* and B3LYP/6-31G* Levels of Theory

		properties of critical points								
			ρ		$\nabla^2\rho$		ϵ		$E(\mathbf{r}_c)$	
		critical point	HF	DFT	HF	DFT	HF	DFT	HF	DFT
6a	bcp	C(1)═Si(2)	0.153	0.148	0.689	0.589	0.778	0.720	−0.085	−0.086
		Si(2)−O(3)	0.127	0.125	1.097	0.913	0.025	0.068	−0.011	−0.025
6b	bcp	C(1)═Si(2)	0.151	0.148	0.634	0.557	0.584	0.592	−0.086	−0.088
		Si(2)−O(3)	0.108	0.107	0.808	0.647	0.035	0.039	−0.011	−0.025
		Si(2)−N(8)	0.074	0.075	0.279	0.143	0.147	0.166	−0.024	−0.034
	rcp	Si(2)−N(8)−N(7)−C(5)−O(3)	0.037	0.033	0.232	0.200			0.007	0.007
6c	bcp	C(1)═Si(2)	0.150	0.147	0.612	0.537	0.541	0.563	−0.086	−0.087
		Si(2)−O(3)	0.106	0.098	0.788	0.536	0.026	0.022	−0.011	−0.024
		Si(2)−N(8)	0.050	0.062	0.116	0.067	0.430	0.128	−0.018	−0.029
		Si(2)−N(16)	0.050	0.062	0.116	0.067	0.430	0.128	−0.018	−0.029
	rcp	Si(2)−N(8)−N(7)−C(5)−O(3)	0.034	0.032	0.209	0.191			0.006	0.007
		Si(2)−N(16)−N(15)−C(13)−O(11)	0.034	0.032	0.209	0.191			0.006	0.007

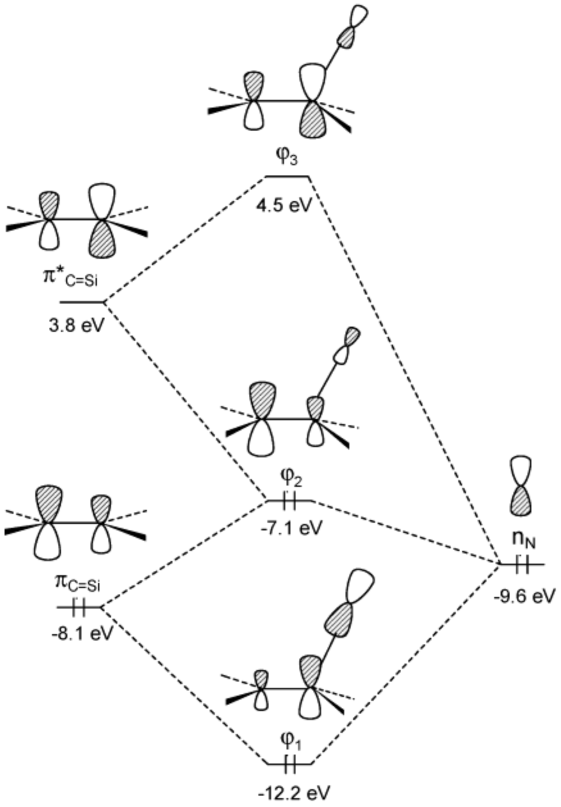


Figure 3. Scheme of forming MOs in the fragment C═Si−N of mono-chelate **6b** calculated at the RHF/6-31G* level.

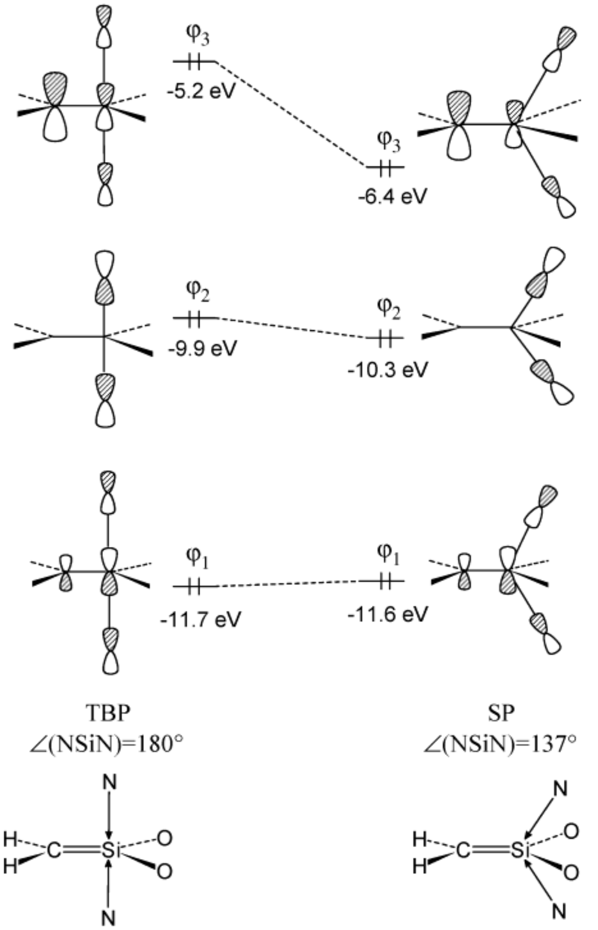


Figure 4. Walsh diagram for the transformation of **6c** from a TBP to a SP structure.

LEP orbital (n_N) and the π-type MOs of the Si═C bond in the prereaction state **A**. Structure **A** was constructed from **6a** by 42° and 52° clockwise rotations around the Si−O and C−O bonds, respectively, in one of the SiOC(Me)═NNMe$_2$ fragments without geometry optimization. The φ_1, φ_2, and φ_3 orbitals of the mono-chelate form **6b** were found on the basis of analysis of their amplitudes and node properties. Among occupied molecular orbitals, this analysis did not reveal a composite orbital associated solely with the $n_N,\pi^*_{Si=C}$ conjugation. An important stabilizing role of the latter consists probably in a considerable decrease in the destabilizing contribution of the $n_N,\pi_{Si=C}$ four-electron interaction. Further progress in the silicon pyramidality, Δ_{Si}, with shortening of the N−Si distance (see Figure 2) should finally destroy the π-bond Si═C and transform the φ_1 and φ_2 orbitals of mono-chelate **6b** into the bonding orbital of an N−Si bond and a lone-pair orbital on the carbon of zwitterion **C**.

The MO structure of bis-chelate **6c** is more interesting. According to the symmetry of the C═SiO$_2$N$_2$ coordination center, the lone pairs of two nitrogen atoms and π-component of the Si═C bond have to form three common occupied molecular orbitals. Figure 4 gives a schematic illustration and the energies of these orbitals calculated at the RHF/6-31G* level for the transformation of hypothetical (with a fixed angle NSiN of 180°) trigonal-bipyramidal to inherent (fully optimized) square-pyramidal **6c**. Essensially, the composite orbital φ_3 is completely *antibonding as applied to the N→Si←N fragment* in both TBP and SP geometries. One can see that the merits of the latter geometry exhibiting a lesser angle NSiN (137°) are provided first of all by stabilization of the φ_3 MO due to the decreasing extent of unfavorable overlapping between the p-type AOs of the Si and N atoms.

The aforesaid allows the classification of the bonding in the $C{=}SiN_2$ fragment of a pentacoordinate doubly bonded silicon of bis-chelate **6c** as four-center six-electron (4c-6e). The principle difference between the latter and the well-known 3c-4e bonding in the axial fragment of TBP complexes of silanes[21f,28] is in the different number of electrons (2 and 0, respectively) occupying the φ_3 MO.

Energies of the 6a−c Forms and the Origin of Donor-Stabilization of Silenes. The computations predict a higher thermodynamic stability of bis-chelate **6c** compared to non-chelate **6a** and, what is more interesting, even to mono-chelate **6b**. Our B3LYP/6-31G* calculations (including the ZPE corrections) found 26.8 and 31.4 kcal/mol energetic advantages of chelates **6b** and **6c**, respectively, over non-chelate **6a**. The RHF/6-31G* energy differences between the chelate and non-chelate forms (ΔE) were found to be −32.4 kcal/mol for **6b** and −36.3 kcal/mol for **6c**. Related ΔE values calculated by Gusel'nikov's group at the MP2/6-31G* level of theory with full geometry optimization and ZPE corrections appeared to be −37.3 and −48.4 kcal/mol for **6b** and **6c**, respectively, whereas the MP4/6-311G*//MP2/6-31G* single-point calculations changed the above values to −35.1 and −43.5 kcal/mol, respectively.[29]

The presented data testify that the B3LYP method underestimates the Si←N bonding as compared with the MP2 method. This is manifested also in the fact that the B3LYP/6-31G* values of $d_{\mathrm{Si-N}}$ in **6b**,**c** exceed the corresponding MP2/6-31G* values by about 0.07 Å.

The enhanced stability of the bis-chelate **6c** over mono-chelate **6b** persists at $T = 298$ K. The B3LYP/6-31G* differences of their enthalpies (ΔH_{298}) and free energies (ΔG_{298}) are equal to −5.0 and −2.2 kcal/mol, respectively, and the MP2/6-31G* calculations[29] lead to $\Delta H_{298} = -11.5$ kcal/mol and $\Delta G_{298} = -9.9$ kcal/mol.

For **6b** and **6c**, the ΔE magnitudes are a measure of energy of their N→Si bonds. Hence, the calculated ΔE values imply that the energy of each of the two N→Si bonds in bis-chelate **6c** is about half as large as that of the only N→Si bond in **6b**. The ΔE value for **6b** is nearly twice as large as that for silene complexes **5** and $(MeO)_2Si{=}CH_2{\cdot}NH_3$[6] and at least four times larger than the energy of the formation of the intermolecular coordinative bonds in complexes $Me_2Si{=}CH_2{\cdot}NH_3$[6] and $H_2Si{=}CH_2{\cdot}OMe_2$.[4d]

The large difference between the energies of the coordinative bond formation is the most obvious reason for the above-mentioned distinction in sensitivity of the geometry of complexes **6b** and $H_2Si{=}CH_2{\cdot}OMe_2$ to the medium polarity. A similar argument cannot be used for the explanation of the corresponding distinction in solvent effect on the geometries of **6b** and **13** since the direct ab initio estimation of the N→Si bond energy for the latter compound failed.[21e] In this situation it is instructive to compare the potential function of the N→Si bond deformation of medium-unaffected mono-chelate silene **6b** with that known for medium-dependent 1-fluorosilatrane **13**.[21e] Both functions calculated at the RHF/6-31G* level of theory by scanning the potential energy of these species along the N→Si coordinate are shown in Figure 5. A sharper potential demonstrates that the N→Si bond deformation in **6b** demands a larger energy cost. Thus, the foregoing energy estimations explain the distinction in extent of the medium effect on the coordinative bond length in **6b**, **12**, and **13**.

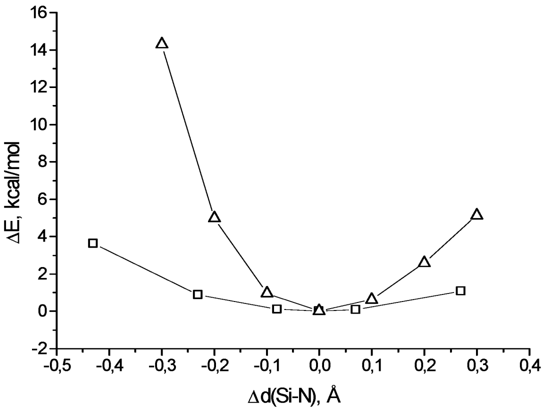


Figure 5. RHF/6-31G* potential functions of the Si←N bond deformation for mono-chelate **6b** (△) and 1-fluorsilatrane **13** (□).[21e]

The enhanced kinetic stability of intermolecularly and intramolecularly donor-stabilized silenes is usually explained by the large energy of the D→Si bond dissociation at the rate-limiting step of their cyclodimerization reaction.[2b] A possible alternative explanation can consist in *steric hindrances* and *orientational demands* for nucleophilic attack at a four-coordinate (or five-coordinate) silicon, decreasing its nucleophilicity. If the developed conception of silene reactivity[2,18] is also valid for their complexes, an additional reason for increased barrier to dimerization of the latter can lie in the aforesaid lower π-polarity of their Si═C bond. Obviously, the resultant barrier cannot exceed the energy or, more precisely, the energy of activation of dissociation of a D→Si bond. Otherwise, cyclodimerization of donor-stabilized silenes should proceed via dissociation of the coordinative bond. Elucidation of an intrinsic reaction pathway and relative contribution of the steric and electronic effects in the kinetic stabilization of silene complexes calls for further study.

Whatever the pathway may be, the stability and conditions of observation and isolation of donor-stabilized silenes depend primary on the D→Si bond strength. It was clearly demonstrated by Wiberg and co-workers,[4c] who found a growth of kinetic stability of intermolecular complexes of silenes with increasing donor nucleophilicity (and hence the complex formation energy). From this point of view, the desired intramolecular complexes **6b**,**c**, despite a high polarity of their Si═C double bond, should be more kinetically stable than hypothetical species **5** and intermolecular adduct **12**, which was recently observed at a low temperature.[4d] Therefore, 1,1-

---

(28) (a) Sidorkin, V. F.; Pestunovich, V. A.; Voronkov, M. G. *Dokl. Akad. Nauk SSSR* **1977**, *235*, 1363; *Dokl. Phys. Chem. (Engl. Transl.)* **1977**, *235*, 850. (b) Pestunovich, V. A.; Sidorkin, V. F.; Voronkov, M. G. In *Progress in Organosilicon Chemistry*; Marciniec, B., Chojnowski J., Eds.; Gordon and Breach: New York, 1995; pp 69−82.

(29) Avakyan, V. G.; Gusel'nikov, S. L.; Gusel'nikov, L. E. Private communication.

bis[*N*-(dimethylamino)acetimidato]silene (**6**) seems to be a challenging target for the experimentalists.

Conclusions

1,1-Bis[*N*-(dimethylamino)acetimidato]silene (**6**) has been found to have three stationary states corresponding to its non-chelate (**6a**) and two intramolecularly N-donor-stabilized forms, mono-chelate (**6b**) and bis-chelate (**6c**), with three-, four-, and five-coordinate doubly bonded silicon, respectively. On going from **6a** to **6b** and **6c**, the silicon structure transforms from planar to distorted tetrahedral and square-pyramidal structures, whereas the Si═C double bond becomes longer (from 1.674 Å to 1.693 and 1.704 Å and from 1.691 Å to 1.701 and 1.713 Å at the RHF and B3LYP levels, respectively) and more polar. The RHF and B3LYP lengths of a N→Si bond in **6b** (1.988 and 2.031 Å) are shorter than in **6c** (2.187 and 2.140 Å). In the framework of the AIM theory, the N→Si bond in chelates **6b**,**c** is described as a highly polar covalent one. Analysis of the geometry and the MO structure of bis-chelate **6c** suggests the four-center, six-electron (4c-6e) bonding of silicon in the $N_2Si{=}C$ moiety. Energetic advantages of the chelate **6b** and **6c** forms over **6a** were estimated to be 26.8 and 31.4 kcal/mol at the B3LYP/6-31G* level including the ZPE correction and 32.4 and 36.3 kcal/mol at the RHF/6-31G* level. The B3LYP, MP2, and MP4 calculations suggest that intramolecular N-donor stabilization may be sufficient to observe silene **6** under relatively mild conditions. Therefore, this compound seems to be a challenging target for the experimentalists.

Acknowledgment. We are grateful to Prof. R. W. F. Bader for a copy of the AIMPAC package of programs and to Prof. V. A. Lopyrev for assistance with computations using the Gaussian programs as well as to Prof. L. E. Gusel’nikov, Dr. V. G. Avakyan, and Dr. S. L. Gusel’nikov, who put the MP2 data at our disposal before publishing. We thank all these people and Prof. M. Gordon and Prof. N. Auner for fruitful discussions. Financial support of our work by the International Association for the Promotion of Cooperation with Scientists from the New Independent States of the Former Soviet Union (INTAS) and Russian Foundation for Basic Research (RFBR) is gratefully acknowledged (Grants INTAS-RFBR 0070, RFBR 01-03-33034, and INTAS 03-51-4164).

Supporting Information Available: Tables containing Cartesian coordinates and total energies of all structures reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

OM034364M