Organometallics **1999,** *18,* 4692−4699

Intramolecular N-Donor-Stabilized Silenes: An ab Initio MO Study of 1-Methylene-5-methyl-5-aza-2,8-dioxa-1-silacyclooctane†

V. G. Avakyan,*,‡ L. E. Gusel'nikov,*,§ V. A. Pestunovich,‖
A. A. Bagaturyants,‡ and N. Auner⊥

Photochemistry Center of Russian Academy of Sciences, Novatorov 7A, Moscow, Russia; A. V. Topchiev Institute of Petrochemical Syntheses of Russian Academy of Sciences, Leninsky 29, Moscow, Russia; Irkutsk Institute of Chemistry, Siberian Branch of Russian Academy of Sciences, Favorsky 1, 664033 Irkutsk, Russia; and Institut für Anorganische Chemie, Marie-Curie-Strasse 11, 60439 Frankfurt am Main, Germany

Received December 10, 1998

Ab initio calculations with full geometry optimization were performed to predict the structure of 1-methylene-5-methyl-5-aza-2,8-dioxa-1-silacyclooctane (MADS), a compound with an intramolecular Si←N donor−acceptor bond between a sp^2-hybridized silicon and a nitrogen atom. Calculations were carried out at the RHF/6-31G(d)//6-31G(d) and MP2/6-31G(d)//MP2/6-31G(d) levels of theory. The MADS structure with the shortest intramolecular Si···N distance (2.105 Å) appears to be of C_s symmetry, whereas that with a long (3.695 Å) Si···N distance belongs to the symmetry group C_1. Both structures are represented by a *boat*−*boat* conformation of the eight-membered cycle and correspond to local minima on the potential energy surface, the former being the global minimum. The energy of the intramolecular Si←N donor−acceptor bond (19.7 kcal/mol) was calculated as the difference between the total energies of the two MADS structures with short and long Si···N distances representing the structures *with* and *without* Si←N bonding, respectively. The NBO indices and the electron density maps of the HOMOs support the conclusion that the intramolecular Si←N donor−acceptor bond is characteristic for MADS with the short Si···N distance. The results obtained for MADS are compared with data calculated for some model compounds, such as 1,1-dimethylsilene, 1,1-dimethoxysilene, their hydrogenated derivatives, the corresponding silanes, and Lewis base/acid complexes of the silenes and silanes with ammonia possessing intermolecular Si←N donor−acceptor bonds. On the basis of the energy of the dehydrogenation of 1,5-dimethyl-5-aza-2,8-dioxa-1-silacyclooctane into MADS, which was calculated at the MP2/6-31G(d)//MP2/6-31G(d) level, the stabilization for the Si═C double bond was estimated to be 18.0 kcal/mol due to the formation of an intramolecular Si←N bond. For complexes of ammonia with silenes, in which the silicon atom remains in the sp^2 valence state, the complex formation energy is considerably higher compared to complexes of NH_3 with the corresponding silanes.

Introduction

The ability to increase the coordination number at silicon centers from four to five and six by both the inter- and intramolecular coordination to various base compounds and by electron-donating substituents in the coordination sphere is well documented for sp^3 hybridized silicon.[1] Moreover, the ability to stabilize silylium ions by formation of inter- and intramolecular complexes and solvates with n- and π-donors was studied by theory[2a−c] and experiment[1f,2d−h] only recently. In contrast, much less is known about the increase of the coordination number at a sp^2-hybridized doubly bonded silicon. Only a few examples of donor complexations are described, including adducts of silenes and silaneimines intermolecularly attached to O- and tert-N-donor bases (Si←O and Si←N coordination[3]) and, furthermore, intramolecular complexes of silanediyl, silanethione and dibenzosilafulvene derivatives of (dimethylaminometh-

---

† First reported at the International Memorial I. Postovsky Conference on Organic Chemistry, March 17-20, 1998, Ekaterinburg, Russia.

‡ Photochemistry Center of Russian Academy of Sciences. E-mail: avak@mx.icp.rssi.ru. Fax: +7 095 9361255.

§ A. V. Topchiev Institute of Petrochemical Syntheses of Russian Academy of Sciences. E-mail: leguselnikov@glas.apc.org. Fax: +7 095 2302224.

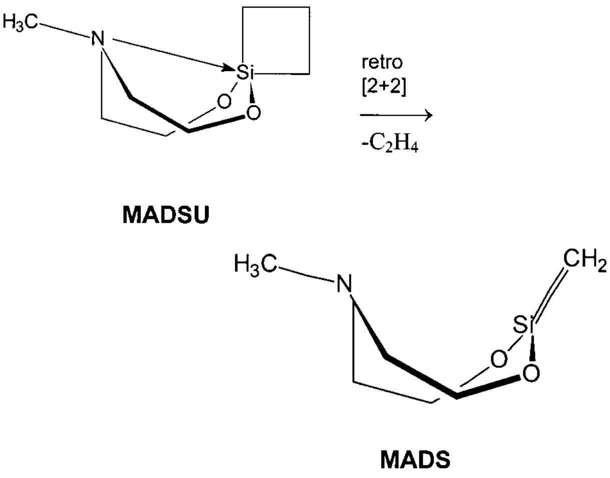
‖ Irkutsk Institute of Chemistry, Siberian Branch of Russian Academy of Sciences. E-mail: vadim@irioch.irkutsk.ru. Fax: +7 3952 356 046.

⊥ Institut für Anorganische Chemie. E-mail: Auner@chemie.uni-frankfurt.de. Fax: +49-69798-29188.

(1) (a) Tandura, S. N.; Voronkov, M. G.; Alekseev, N. V. *Top. Curr. Chem.* **1986**, *131*, 99. (b) Chuit, C. R.; Corriu, J. P.; Reye, C. J.; Young, C. *Chem. Rev.* **1993**, *93*, 1371. (c) Holmes, R. R. *Chem. Rev.* **1996**, *96*, 927. (d) Lukevic, E.; Pudova, O. *Khim. Geterotsykl. Soed.* **1966**, 1605. (e) Kost, D.; Kalikhman, I. In *The Chemistry of Organic Silicon Compounds, Vol. 2*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; pp 1339−1446. (f) Chuit, C.; Corriu, R. J. P.; Reye, C. In *Chemistry of Hypervalent Compounds*; Akiba, K.-Y., Ed.; Wiley-VCH: New York, 1999; pp 81−146. (g) Pestunovich, V.; Kirpichenko, S.; Voronkov, M. In *The Chemistry of Organic Silicon Compounds, Vol. 2*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; pp 1447−1537.

10.1021/om9810089 CCC: $18.00

yl)arylsilenes (Si$\leftarrow$N coordination[1b,3f,4]). In this paper we report about ab initio calculations on the molecular structure of 1-methylene-5-methyl-5-aza-2,8-dioxa-1-silacyclooctane (MADS), a silene unit containing an intramolecular Si$\leftarrow$N donor bond. According to eq 1, this compound might be generated by a retro 2+2 process from 8-methyl-8-aza-5,11-dioxa-4-silaspiro[3,7]undecane (MADSU).



(1)

Only recently has MADSU been experimentally prepared, and as expected the transannular Si$\leftarrow$N donor bond was spectroscopically proved.[5] One may suggest that an electrophilic unsaturated sp^2 silicon atom will be even more readily involved in donor–acceptor interactions than an sp^3 silicon center, and as a result, an even stronger "donor stabilization" effect onto the Si=C double bond is predictable. To analyze the chelate and substituent effects on the structure and properties of MADS, ab initio calculations of the geometrical and electronic structure of MADS were performed and compared with intermolecular interacting donor–acceptor complexes of 1,1-dimethyl- and 1,1-dimethoxysilenes (DMS and DMOS) with ammonia as model compounds. These calculations allow an estimation of the energies of both the strength of the intramolecular Si$\leftarrow$N donor bond and the donor stabilization of the Si=C double bond in MADS.

Computational Methods

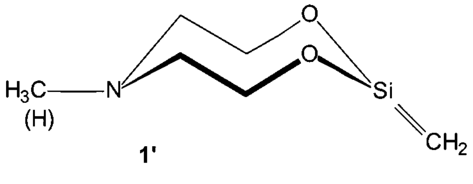
All calculations were performed with full geometry optimization using the standard 6-31G(d) basis set[6] at the RHF and MP2 levels (preliminary geometry search was performed with the 3-21G(d) basis set[7]). Notably, these basis sets are the same as used only recently for structure calculations on silatranes and to study the nature of the Si$\leftarrow$N donor bonds.[8,9] The calculations were carried out using the GAMESS program.[10,18]

For all structures, their correspondence to local minima on the potential energy surface (PES) was confirmed by calculations of the Hessian eigen values.

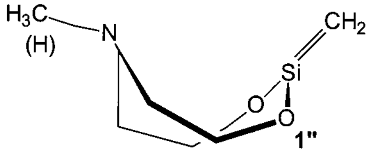
1-Methylene-5-methyl-5-aza-2,8-dioxa-1-silacyclooctane (MADS) and 1,5-Dimethyl-5-aza-2,8-dioxa-1-silacyclooctane (DADS, the Hydrogenation Product of MADS). Sufficient physical criteria for the existence of a donor–acceptor Si···N bond are (i) an interatomic Si···N distance shorter than the sum of the van der Waals radii (3.5 Å) and longer than a covalent Si–N bond (1.7–1.8 Å); (ii) a higher bond energy than the energy of a nonvalence interaction; and (iii) a directional character of the interaction. Hence, studying the ability to form a transannular Si$\leftarrow$N bond in MADS consists of several steps: (i) calculation and conformational search for the geometry of MADS with the shortest Si$\leftarrow$N distance; (ii) estimation of the Si$\leftarrow$N bond energy; and (iii) calculation of model silene–ammonia complexes to compare their geometric and energetic features with those of MADS.

The energy of an intermolecular donor–acceptor Si$\leftarrow$N bond is usually calculated from the difference between the total energies of the complex and the isolated donor and acceptor subunits. This approach is not valid for MADS, since its donor and acceptor moieties belong to the same molecule. One may estimate the energy of the Si$\leftarrow$N bond in MADS as a difference of the total energies of the two conformations, e.g., **1′** and **1″**, having a short (**1″**) and a long Si···N distance (**1′**), the former being considered as a structure *with* a bond but the latter being a structure *without* a bond.

The conformational search for the structures **1′** and **1″** was preliminary started with the 3-21G calculation of the N-hydride derivative of MADS. While the structure **1′** resembled *a "crown"* conformation of the eight-membered cycle, the *pseudo*-atrane structure **1″** exhibits the required Si$\leftarrow$N donor–acceptor bond.



1'



1"

The geometry optimization of **1′** and **1″** at the 3-21G level of theory showed the structure with the short Si···N distance

---

(2) (a) Olsson, L.; Ottosson, C.-H.; Cremer, D. *J. Am. Chem. Soc.* **1995**, *117*, 7460. (b) Ottosson, C.-H.; Cremer, D. *Organometallics* **1996**, *15*, 5309. (c) Maerker, C.; Schleyer, P. v. R. In *The Chemistry of Organic Silicon Compounds, Vol. 2*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; pp 513–555. (d) Lickiss P. D. In *The Chemistry of Organic Silicon Compounds, Vol. 2*; Rappoport, Z.; Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; pp 557–594. (e) Chauhan, M.; Chuit, C.; Corriu, R. J. P.; Mehdi, A.; Reye, C. *Organometallics* **1996,** *15,* 4326. (f) Belzner, J.; Schär, D.; Kneisel, B. O.; Herbst-Irmer, R. *Organometallics* **1995,** *14*, 1840. (g) Steinber, H.-U.; Müller, T.; Auner, N.; Maerker, C.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 626. (h) Maerker, C.; Kapp, I.; Schleyer, P. v. R. In *Organosilicon Chemiytry II. From Molecules to Materials*; Auner, N., Weis, J., Eds.; VCH: Weinheim 1996; p 330.

(3) (a) Wiberg, N.; Schurz, K. *J. Organomet. Chem.* **1988**, *341*, 145. (b) Wiberg, N.; Koepf, H. *J. Organomet. Chem.* **1986**, *315*, 9. (c) Wiberg, N.; Scurz, K. *Chem. Ber.* **1988**, *121*, 681. (d) Wiberg, N.; Joo, K.-S.; Polborn, K. *Chem. Ber.* **1993,** *126*, 67. (e) Wiberg, N. In *Organosilicon Chemistry II. From Molecules to Materials*; Auner, N., Weis, J., Eds.; VCH: Weinheim, 1996; p 367. (f) Zemlyanskii, N.; Borisova, I. V.; Shestakova, A. K.; Ustynyuk, Y. A.; Chernyshev, E. A. *Izv. Akad. Nauk, Ser. Khim.* **1998**, 491.

(4) Lanneau, G. F. *Main Group Chem. News* **1993**, *1*, 16.

(5) (a) Gusel'nikov, L. E.; Buravtsev, N. N.; Volkova, V. V.; Zubarev, Yu. E.; Buravtseva, E. N.; Pestunovich, V. A.; Lazareva, N. F. *30th Organosilicon Symposium*; University of Western Ontario, May 30–31, 1997, London, Canada, Abstracts A-24. (b) Pestunovich, V. A.; Lazareva, N. F.; Kozyreva, O. V.; Gostevskii, B. A.; Albanov, A. I.; Gusel'nikov, L. E.; Avakyan, V. G.; Volkova, V. V.; Auner, N. *International Memorial I. Postovsky Conference*, March 17–20, 1998**,** Ekaterinburg, Russia, Program and Abstracts, pp 177, IS-24.

(6) Pople, J. A.; Binkley J. S.; Seeger, R. *Int. J. Quantum Chem.* **1976**, *S10*, 1.

(7) Hehre, W. J.; Ditchfield R.; Pople, J. A. *J. Chem. Phys.* **1972**, *67*, 2257.

(8) Gordon, M. S.; Carroll, M. T.; Jensen, J. H.; Davis, L. P.; Burggraf L. W.; Guidry, R. M. *Organometallics* **1991**, *10*, 2657.

(9) Schmidt, M. W.; Windus T. L.; Gordon, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 7480.

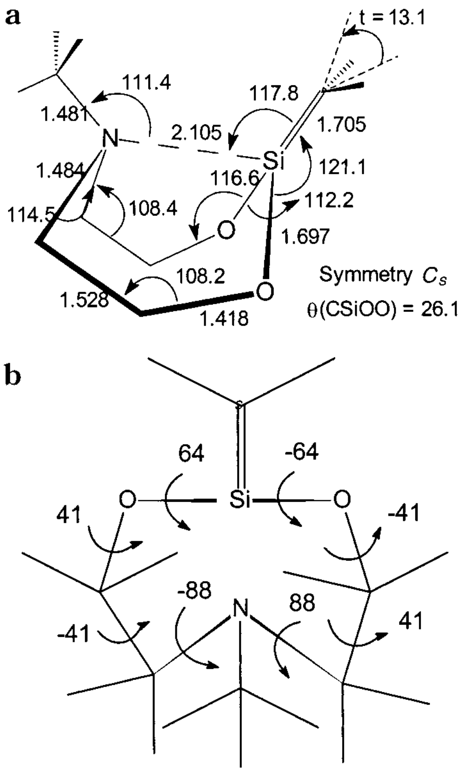


Figure 1. (a) MP2/6-31G(d) geometry of the symmetric conformer of MADS, *boat*–*boat* conformation. (b) Dihedral angles (deg) in the C_s conformer of MADS (top view).

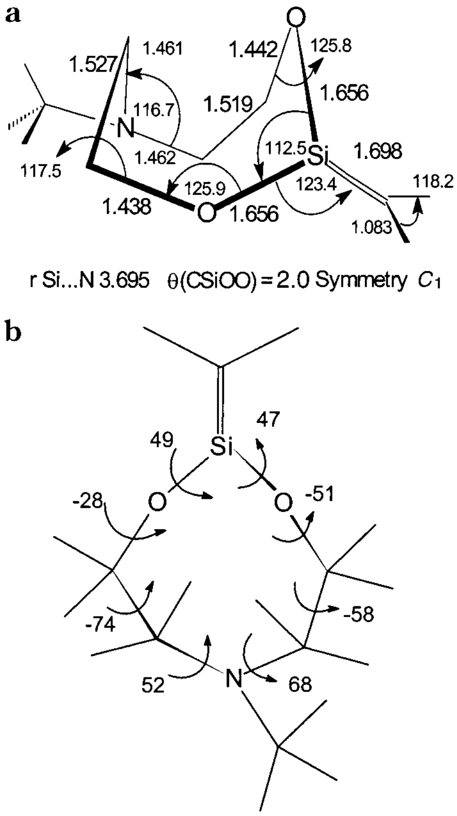


Figure 2. (a) MP2/6-31G(d) geometry of the asymmetric conformer of MADS, *boat*–*boat* conformation. (b) Dihedral angles (deg) in the C_1 conformer of MADS (top view).

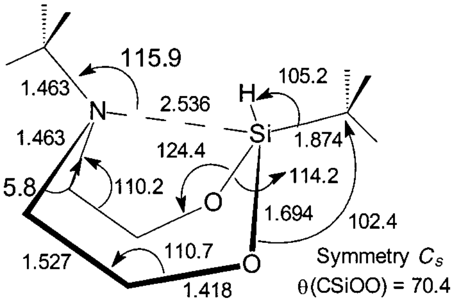


Figure 3. MP2/6-31G(d) geometry of the C_s symmetric *boat*–*boat* conformer of DADS.

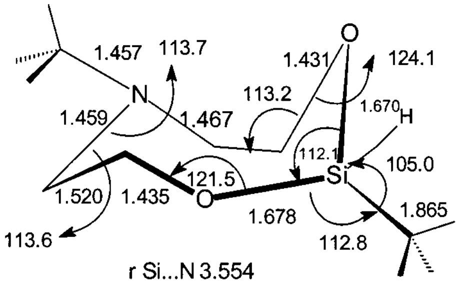


Figure 4. MP2/6-31G(d) geometry of the C_1 symmetric *boat*–*chair* conformer of DADS.

(r(Si···N) 2.045 Å) to be 22 kcal/mol energetically more favorable than that with the longer Si···N distance (r(Si···N) 3.186 Å). Thus, a first rough estimation reveals that the transannular Si←N donor bond interaction exists and its energy is considerably high. However, the verification of the preliminary results by use of the more sophisticated quantum-chemical methods could not be attuned easily.

Surprisingly, the full geometry optimization of both conformers at the RHF/6-31G(d)//6-31G(d) and the MP2/6-31G(d)//MP2/6-31G(d) levels of theory results in an equivalent structure description, both resembling the conformer **1**″, with a short intramolecular Si···N distance of 2.126 and 2.105 Å (Figure 1a), respectively.[19] Thus, conformer **1a** is the most appropriate structure of MADS *with* an intramolecular Si←N donor bond. The molecule belongs to the C_s symmetry group, and it is the most stable conformer of MADS.

The molecular structure of MADS possessing a long Si···N distance, taken as a model for a compound *without* any Si←N donor contact, was found to be asymmetric, belonging to the C_1 symmetry group. It is best described by a *boat*–*boat* conformation, the Si···N distance being 3.695 Å. According to the Hessian eigen values, it corresponds to a local minimum of the PES. The results of the final structure calculations for the two MADS conformers carried out at the MP2/6-31G(d)//MP2/6-31G(d) level are shown in Figures 1a and 2a; the dihedral angles are depicted in Figures 1b and 2b. The C_s and C_1 conformations of 1,5-dimethyl-5-aza-2,8-dioxa-1-silacyclooctane (DADS), the hydrogenation products of the symmetric and asymmetric conformeres of MADS, were both optimized at the MP2/6-31G(d) level of theory (Figures 3 and 4).

Model Adducts. For a comparison of the electronic influences of an intra- or intermolecularly interacting donor atom on the silene's electrophilic silicon center or onto the Si=C π-bond, respectively, calculations were also carried out for a pair of model silenes, 1,1-dimethylsilene and 1,1-dimethoxysilene, and their complexes with ammonia. Historically, 1,1-dimethylsilene (DMS) was the first spectroscopically characterized and chemically trapped compound with a silicon–carbon double bond,[11] and 1,1-dimethoxysilene (DMOS) might be a suitable model compound, having an electronic surrounding of the silicon atom similar to that in MADS. The hypo-

---

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

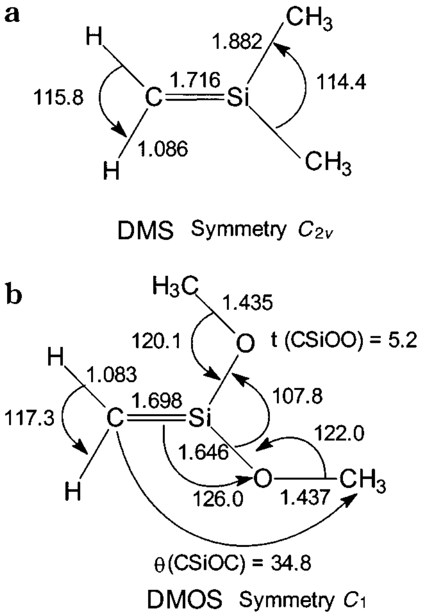
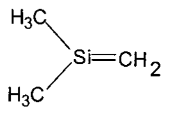
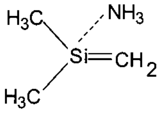
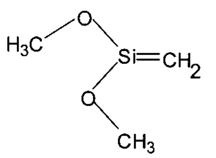


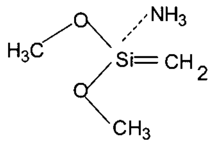
Figure 5. MP2/6-31G(d) geometry of dimethylsilene and dimethoxysilene.

thetical complexes of these silenes with ammonia, DMS·NH$_3$, and DMOS·NH$_3$, respectively, were used to model an intermolecular donor−acceptor bond between a sp^2-hybridized silicon atom and the electron-donating nitrogen.[20]


DMS


DMS·NH$_3$


DMOS


DMOS·NH$_3$

The calculated structures for DMS and DMOS are shown in Figure 5. Other conformers for DMOS were found to be locally unstable and converged to the geometry of the C_1 conformer.

The structures of the DMS·NH$_3$ and DMOS·NH$_3$ complexes were calculated using the MP2/6-31G(d) basis set, and they are shown in Figure 6.

The calculated total energies for the molecules, the Si=C and Si←N bond lengths, the atomic charges on the Si, C(=CH$_2$), and the N atoms, and the natural bond order (NBO) indices on the Si=C and Si←N bonds are summarized in Table 1. The ammonia-complexing energies, ΔE_c, of the model silenes and their hydrogenation products are given in Table 2. The latter were calculated as the difference between the total energies of the complex and the sum of E_{total} of silene (silane) and NH$_3$.

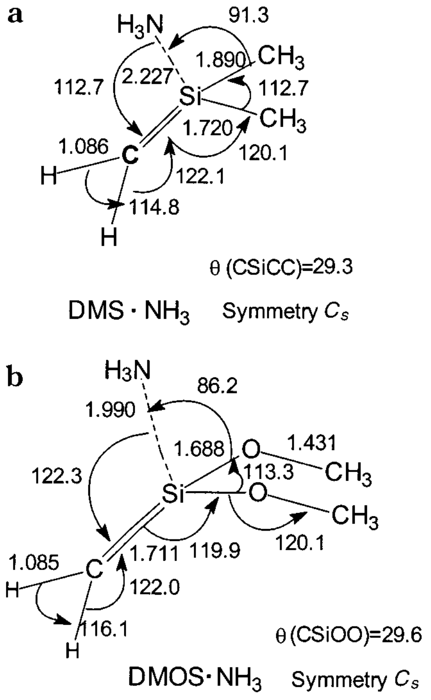


Figure 6. MP2/6-31G(d) geometries of DMS·NH$_3$ and DMOS·NH$_3$.

Results and Discussion

Model Silenes and Their Ammonia Complexes. A comparison of the data obtained for the geometry of DMS with those data available in the literature proves the HF/6-31G(d) calculations to be fairly reliable. Thus, the calculated Si=C double-bond length in DMS (1.696 Å) resembles strongly that value determined by microwave spectroscopic methods (1.692 Å).[12] The Si=C bond length in the parent silene, H$_2$Si=CH$_2$, was earlier predicted at the RHF/DZ+d (1.691 Å), SDCI/DZ+d (1.703 Å),[13a] B3LYP/6-311(d,p) (1.704 Å),[13b] and MP2/6-31G(d) (1.714 Å)[13c] levels of theory. The now calculated DMS Si=C bond length (1.716 Å) is in convincing agreement with the value determined by X-ray diffraction for Me$_2$Si=C(SiMe$_3$)SiMe(Bu-t)$_2$ (1.702 Å[14]), although it looks somewhat overestimated.[21]

A comparison of the Si=C bond lengths calculated for the model silenes with those of the parent silene (1.714 Å[13c]) shows that the introduction of two methyl groups at the silicon atom elongates the Si=C bond by 0.002 Å, whereas oxygen-containing substituents shorten it by 0.016 Å (cf. 1.716 Å for DMS and 1.698 Å for DMOS). This is in good agreement with earlier theoretical predictions.[15]

In agreement with experimental data for adducts of silenes with N- and O-donor bases,[3] the computational calculations of the intermolecular ammonia donor complexes DMS·NH$_3$ and DMOS·NH$_3$ predict that the formation of a Si←N coordination results in a visible distortion of the planar silicon and an elongation of the Si=C double-bond length in the silene subunit (Figure 6). The out-of-plane angles are 29.3° and 29.6°, respectively, and correspond to the sum of angles of sp^2 nodes at silicon, 352.9° and 353.1°, in DMS·NH$_3$ and DMOS·NH$_3$, respectively. These data may be compared with those values obtained from the structure analysis of the adduct Me$_2$Si=C(SiMe$_2$Ph)$_2$·NEtMe$_2$ (349° [3d]). However,

---

(11) (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. (c) Gusel'nikov, L. E.; Nametkin, N. S. In *Advances in Organosilicon Chemistry*; Voronkov, M. G., Ed.; Mir Publishers: Moscow, 1985; p 69. (d) Gusel'nikov, L. E.; Avakyan, V. G. *Sov. Sci. Rev., B, Chem.* **1989**, *13*, 39.

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

Table 1. Total Energies, Atomic Charges, Si···N and Si═C Distances, and NBO Analysis of Molecules and Complexes

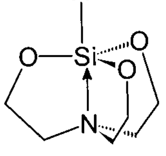
molecule	basis set	E_{total}, au	E_{MP2}, au	atomic charges, a.u. Si	C	N	r (Si···N), Å (NBO)	r (Si═C), Å (NBO)
MADS 1″	3-21G(d)	−685.255808		1.295	−0.927	−0.852	2.045	1.693
MADS 1′	3-21G(d)	−685.220347		1.157	−0.848	−0.796	3.186	1.681
C_s, boat−boat	6-31G(d)	−727.870256		1.080	−0.731	−0.716	2.126	1.693
C_s, boat−boat	MP2/6-31G(d)	−729.256152	−1.390223	0.828	−0.648	−0.539	2.104	1.705
							(0.330)	(1.719)
C_1, boat−boat	MP2/6-31G(d)	−729.224724	−1.383691	0.994	−0.655	−0.559	3.695	1.698
							(<0.05)	(1.789)
DADS, C_s, boat−boat	6-31G(d)	−729.095369						
	MP2/6-31G(d)	−730.479706	−1.390468				2.536	1.874
DADS, C_1, boat−chair	MP2/6-31G(d)	−730.47797	−1.385576	1.148	−0.740	−0.561	3.554	1.865
							-	(0.938)
$Me_2Si{=}CH_2$	6-31G(d)	−407.131303		0.606	−0.617		-	1.696
	MP2/6-31G(d)	−407.607953	−0.477348	0.462	−0.523		-	1.7160
								(1.823)
$(MeO_2)Si{=}CH_2$	6-31G(d)	−556.896418		1.017	−0.706		-	1.680
	MP2/6-31G(d)	−557.719501	−0.826873	0.798	−0.614		-	1.698
								(1.737)
$Me_2Si{=}CH_2{\cdot}NH_3$	6-31G(d)	−463.322979		0.724	−0.692	−1.030	2.260	1.708
	MP2/6-31G(d)	−463.974176		0.523	−0.588	−0.941	2.226	1.720
							(0.221)	(1.797)
$(MeO_2)Si{=}CH_2{\cdot}NH_3$	6-31G(d)	−613.110368		0.976	−0.740	−0.979	1.983	1.703
	MP2/6-31G(d)	−614.111560		0.723	−0.642	−0.910	1.990	1.711
							(0.436)	(1.745)
NH_3	6-31G(d)	−56.184356				−0.996	-	-
NH_3	MP2/6-31G(d)	−56.354212	−0.170392			−0.951	-	-

Table 2. Si←N Donor−Acceptor Energy in MADS and DADS and Complex Formation Energies, ΔE_c, kcal/mol,[a] of Silenes and Silanes with Ammonia

complex	SCF/6-31G(d)	MP2/6-31G(d)
MADS		−19.7
DADS		−1.7
$Me_2Si{=}CH_2{\cdot}NH_3$	−4.59	−7.5
$(MeO)_2Si{=}CH_2{\cdot}NH_3$	−18.56	−23.8
$(MeO)_2MeSiH{\cdot}NH_3$	−1.97	−4.1
$Me_3SiH{\cdot}NH_3$	−1.62	−3.2

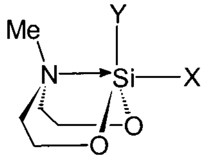
[a] Energy of the complex formation with NH_3, $\Delta E_c = E_{total}(\text{sila(e)ne}{\cdot}NH_3) - \Sigma(E_{total}(\text{sila(e)ne}) + E_{total}(NH_3))$, kcal/mol.

the calculated Si═C bond lengths in $DMS{\cdot}NH_3$ and $DMOS{\cdot}NH_3$ appear to be smaller (by 0.004 and 0.013 Å, correspondingly) than those found for Wiberg's adduct ($\Delta = 0.06$ Å [3d]). Presumably, this discrepancy may result form the comparison of calculated gas-phase structures of the model complexes with that in the solid state. As can be stated for silatranes (**2**),[17] the geometry of the coordination silicon center may depend on the kind of aggregation. Thus, the Si←N bond distance (2.45 Å) in 1-methylsilatrane (**2**, X = CH_3) in the gas phase is 0.28 Å longer than that determined for the solid state.[17a]



2

Structure of MADS and the Si←N Coordination Bond Energy. The present results from ab initio calculations confirm a significant intramolecular Si←N coordination in MADS. The calculated Si←N bond length of 2.105 Å (Figure 1) is shorter than the Si···N distances in 1,1-disubstituted silocanes (**3**) (2.3−2.9 Å[1d]) in the solid state and shorter than those determined for 1-fluorosilatranes (**2**, X = F, 2.32 Å[17b]) in the gas phase.



3

The shortest Si←N bond distance in this series found for MADS obviously indicates a strong intramolecular coordination of the donor nitrogen to the sp^2-hybridized silicon. A comparison of the MP2/6-31G(d) total energies for structures with short (2.105 Å) and long (3.695 Å) Si···N distances (Table 1) proves the energy of the intramolecular Si←N donor−acceptor bond to be 19.7 kcal/mol. This value is close to that calculated for $DMOS{\cdot}NH_3$ (23.8 kcal/mol), the complex with the strongest complex formation energy (see Tables 1 and 2). Simultaneously, the difference between the MP2/6-31G(d) energies of two DADS conformations (Figures 3 and 4) with a short (2.536 Å) and a long (3.554 Å) Si···N distance is only 1.7 kcal/mol, thus confirming a considerably weaker acceptor ability of the sp^3-hybridized silicon in a similar geometrical surrounding compared to its sp^2-hybridized counterpart.

A comparison of the structures and NBO indices at the Si←N and Si═C units in both conformers of MADS is of basic interest. From Figures 1a and 2a it is evident that shortening of the Si···C distance results in a small lengthening of the Si═C bond. While MADS with the short Si···N distance (**1a**) exhibits a Si═C double-bond length of 1.705 Å, the conformer **2a** shows a Si═C double-bond length of 1.698 Å. Not surprisingly, the latter value is very close to that calculated for DMOS, because both molecules possess the same substituent pattern at the silicon atom. Thus, the lengthening of

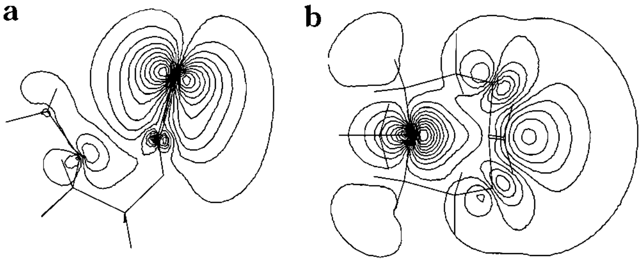


Figure 7. Electron density maps of the HOMO in the MADS conformer with the short Si···N distance (**1a**; 2.105 Å). N is on the left, the Si═C unit is on the right side: (a) side view; (b) top view. The lone pair of the N atom is stretched into the direction of the π-orbital of the Si atom.

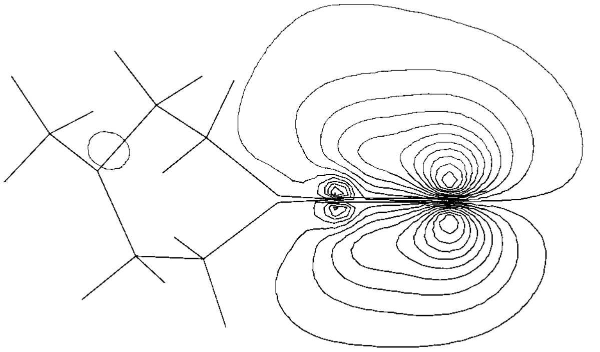


Figure 8. Electron density map of the HOMO in the MADS conformer with the long Si···N distance (**2a**; 3.695 Å). N is on the left, the Si═C unit is on the right side, top view. The HOMO is a nearly pure π-orbital of the Si═C double bond. The negligible participation of the nitrogen lone pair indicates the nonbonding interaction between the N and Si atoms.

the Si═C bond is indicative for a silicon π-orbital involvement in the bonding interaction with the nitrogen lone pair. The electron density maps of the HOMOs for both MADS conformers are shown in Figures 7 and 8. The MADS conformer **1a** (Figure 7) shows a recognizable overlap between the n(N)- and π(Si═C)-orbital. The NBO index of the Si←N donor−acceptor bond is 0.330.

A comparison of the electron density plots with those of silatranes[9] shows that in the latter case only the nitrogen n-orbital contributes to the bonding area.

From Figure 8 it becomes obvious that the HOMO of the MADS conformer **1a** does not indicate any bond interaction between the N and Si atoms and both the nitrogen n- and the Si═C π-orbital are differently directed, the NBO index being less than 0.05.

In the MADS conformer with C_s symmetry, the Si←N coordination (**1a**, $d_{SiN} = 2.105$ Å), the NBO Index (0.33) and the out-of-plane angle of 26.1° at the Si sp^2 node (corresponding to the sum of the trigonal angles around the silicon atom equal to 354.4°) relate directly to the strength of the Si←N donor bond. These values are just intermediate compared to the Si←N bond distances, NBO indices, and angles in DMS·NH$_3$ (2.227 Å, 0.221, and 29.3° (352.9°)) and DMOS·NH$_3$ (1.990 Å, 0.436, and 29.6° (353.1°)). Consequently one may also expect the energy of a Si←N coordination in MADS to be intermediate between the formation energies of the corresponding complexes, but being somewhat closer to the energy of DMOS·NH$_3$, which was calculated to be −23.8 kcal/mol [for comparison: DMS·NH$_3$ −7.5 kcal/mol (Table 2)]. Indeed, the calculated value for the energy of the transannular Si←N donor bond in MADS (−19.7 kcal/mol) fits well to this assumption.[22]

From the comparison of the distances and energies of the coordinative Si←N bond in model silene−ammonia complexes and in a trimethylsilylium−ammonia (+1) complex, which both contain an sp^2-hybridized silicon atom, a shorter Si−N bond length and a stronger Si−N bond in the latter complex should be expected due to the positive charge on silicon. And, in fact, the Si−N bond length (1.957 Å) and the bond energy (56.6 kcal/mol) in a trimethylsilylium−ammonia (+1) complex[2a] differ from those of both DMS and DMOS complexes (cf. 2.227 and 1.99 Å; 4.6 and 18.6 kcal/mol). Both calculations were performed at the same level of theory (RHF/6-31G(d)); notably, the calculation at the 6-31G(d) level is likely to underestimate the Si←N donor bond energy.

The magnitude of the Si←N bond energy (19.7 kcal/mol) considerably exceeds usual conformational energies of cyclic compounds and explains the absence of a stable symmetric MADS conformer with a long Si···N distance.

Due to the remarkably large difference between the total energies calculated for the two MADS configurations, one may predict that the conformer with the transannular (Si···N) bond should be preferred under conventional conditions. As the thermodynamically less stable conformer **2a** is also characterized by a local minimum on the PES, its existence may be presumably suggested at some nonconventional conditions. On the contrary, due to only a small difference in the energies of the two conformers of DADS (1.7 kcal/mol), the existence of two conformers with a short (2.536 Å) and a long (3.554 Å) Si···N distance is assumable; the ratio is 95:5% according to the Boltzmann factor.

Donor−Acceptor Stabilizing Effect on Si═C Double Bonds Resulting from Si←N Coordination. For an estimation of donor−acceptor stabilizing effects on Si═C double bonds resulting from Si←N coordination, a comparison of the standard reaction heats was used. In particular, the difference in the total energies, E_{total}, of the silanes and the corresponding silenes was considered. The dehydrogenation energy ΔE_{dehydr} corresponds to E_{total}(silane) − E_{total}(silene) − E_{total}(H$_2$) of the reactions in eq 2 and eq 3 and seems to be a good

$$R_2SiH{-}CH_3 + \Delta E_{dehydr} = R_2Si{=}CH_2 + H_2 \quad (2)$$

$$R_2SiH{-}CH_3{\cdot}NH_3 + \Delta E_{dehydr} = R_2Si{=}CH_2{\cdot}NH_3 + H_2 \quad (3)$$

measure for the relative thermodynamic stability of noncoordinated simple silenes and their N-donor-stabilized counterparts. Furthermore, ΔE_{dehydr} gives the energy needed to form a silene from the corresponding silane. Consequently, the higher the amount of dehydrogenation energy calculated, a silene of less stability is predicted and vice versa. From this it is concluded that the donor−acceptor stabilization of a Si═C double bond resulting from Si←N coordination in the model complexes may be calculated from the difference between the dehydrogenation energies of any particular silene and its ammonia complex counterparts.

$$[(\Delta E_{stabil} = \Delta E_{dehydr}\,(\text{eq }2) - \Delta E_{dehydr}\,(\text{eq }3)]$$

Table 3. Total Energy, au, of H_2, Silenes, Silanes, and Ethene−Ethane Necessary for the Calculation of the Hydrogenation Energies

molecule[a]	SCF/3-21G	MP4/6-311G(d,p)
H_2	−1.12296	−1.16770
C_2H_6	−78.85801	−79.61672
C_2H_4	−77.66496	−78.38497
$H_3Si{-}CH_3$	−328.65049	−330.62054
$H_2Si{=}CH_2$	−327.41810	−329.34344

molecule[b]	SCF/6-31G(d)	MP2/6-31G(d)
H_2	−1.126828	−1.144141
Me_3SiH	−408.364587	−408.842341
$(MeO)_2MeSiH$	−558.139793	−558.966422
$Me_3SiH{\cdot}NH_3$	−464.551527	−465.201632
$(MeO)_2MeSiH{\cdot}NH_3$	−614.327285	−615.327213

[a] Data from ref 13d. [b] This work.

Table 4. Dehydrogenation Energies to Form Unsaturated Compounds, Ethene, MADS, and Silenes, ΔE_{dehydr}, kcal/mol[a]

molecules[b]	SCF/3-21G	MP4/6-311G(d,p)
$C_2H_6 \rightarrow C_2H_4$	43.98	40.19
$Me_3SiH \rightarrow H_2Si{=}CH_2$	68.66	68.64

molecules[c]	SCF/6-31G(d)	MP2/6-31G(d)
DADS, long R(Si⋯N) → $MADS_l$	61.67	67.86
DADS, short R(Si⋯N) → $MADS_s$		49.83
$(MeO)_2SiH{-}CH_3 \rightarrow (MeO)_2Si{=}CH_2$	73.12	64.49
$(MeO)_2SiH{-}CH_3{\cdot}NH_3 \rightarrow (MeO)_2Si{=}CH_2{\cdot}NH_3$	66.79	44.87
$Me_3SiH \rightarrow Me_2Si{=}CH_2$	63.81	56.63
$Me_3SiH{\cdot}NH_3 \rightarrow Me_2Si{=}CH_2{\cdot}NH_3$	56.53	52.28

[a] $\Delta E_{dehydr} = E_{total}(\text{silane}) - E_{total}(\text{silene}) - E_{total}(H_2)$. [b] Calculated from data of ref 13d. [c] This work.

The dehydrogenation energies of a series of silanes and their corresponding ammonia complexes such as trimethylsilane and trimethylsilane·NH_3, dimethoxymethylsilane, and dimethoxymethylsilane·NH_3, and the two conformers of DADS (Figures 3 and 4) were estimated at both the MP2/6-31G(d) and the RHF/6-31G(d) levels of theory. Dehydrogenation of these silanes and their complexes formally yields the corresponding silenes, DMS and DMOS, and their ammonia adducts, DMS·NH_3 and DMOS·NH_3, respectively, as well as the two conformers of MADS (Figures 1 and 2).

The total energies for H_2, the silanes, and the corresponding compounds ethane−ethene and methylsilane−silene,[13d] necessary to estimate ΔE_{dehydr}, are summarized in Table 3, and the dehydrogenation energies are given in Table 4. From ΔE_{dehydr} obtained for ethane and methylsilane it is obvious that the energy difference is about 25 and 28 kcal/mol for the small and the extended basis set, respectively, indicating the low energetic profit forming a sp^2-hybridized silicon center as compared to the carbon analogue.

In the series studied, the MADS conformer **2a**, e.g., the silene *without* Si←N coordination, appears to be the least stable one (ΔE_{dehydr} 67.9 kcal/mol), whereas the complex of DMOS with ammonia is the most stable derivative (ΔE_{dehydr} 44.9 kcal/mol). The other compounds are characterized to have intermediate values of ΔE_{dehydr} (Table 4).

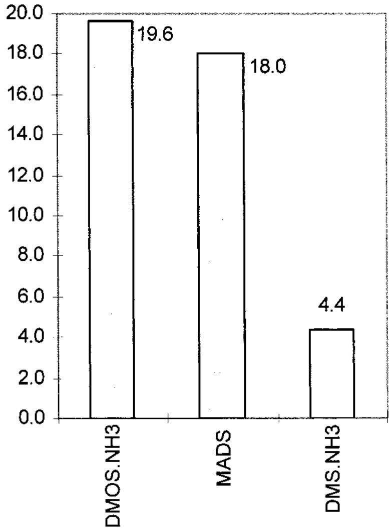


Figure 9. Donor−acceptor stabilization energies, ΔE_{stabil}, kcal/mol, of silene ammonia complexes and of MADS due to Si←N coordination.

With respect to Si←N donor−acceptor interactions the stabilization energy for silenes was determined from the differences between the dehydrogenation energies of corresponding compounds *with* and *without* Si←N coordination. Thus, from subtraction of ΔE_{dehydr} (MADS C_s, **1a**) from ΔE_{dehydr} (MADS C_1, **2a**), ΔE_{dehydr} (DMOS·NH_3) from ΔE_{dehydr} (DMOS), and ΔE_{dehydr} (DMS·NH_3) from ΔE_{dehydr} (DMS), ΔE_{stabil} was calculated as Si=C donor−acceptor stabilization energy. Due to the intramolecular Si←N donor−acceptor interaction, this energy was calculated to be 18.0 kcal/mol for MADS, 19.6 kcal/mol for DMOS·NH_3, and 4.4 kcal/mol for DMS·NH_3 (Figure 9).

Notably, the energy for the intramolecularly donor stabilized MADS is very close to that of the most stable model complex, DMOS·NH_3.

From these calculations it can be concluded that (i) the formation of the Si←N coordination stabilizes the Si=C double bond and (ii) the introduction of two oxygen atoms attached to silicon considerably enhances this effect, because it still increases the acceptor ability of the silene's electrophilic silicon atom. Consequently, the Si←N coordination and the stabilization energy of the Si=C double bond in DMOS·NH_3 are considerably higher than that in DMS·NH_3. Similar results were found carrying out the calculations at the RHF/6-31G(d) level.

Polarity of the Si=C Double Bonds and Reactivity of Si←N Donor−Acceptor Coordinated Silenes. Silenes are known to be highly reactive compounds, and the reactivity is mainly dominated by the substitution pattern at the Si=C moiety. A direct description of the silene reactivity may be estimated by calculating the reaction path for cycloaddition reactions including the formal [2+2] cyclodimerization. However, for silenes having N-donor atoms in their coordination sphere such calculations are a rather complex many-body task. In such cases the polarity of the silicon carbon double bond might give a rough approximation of the silene reactivity.[15] In general it is suggested that an increase in the

---

(13) (a) Colvin, M. E.; Kobayashi, J.; Bicerano J.; Schaefer, H. F., III. *J. Chem. Phys.* **1986**, *85*, 4563. (b) Bailliux, S.; Bogey, M.; Breidung, J.; Burger, H.; Fajgar, R.; Liu, Y.; Pola, J.; Senzlober M.; Thiel, W. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2513. (c) Gordon M. S.; Truong, T. N. *Chem Phys. Lett.* **1987**, *142*, 110. (d) Schmidt, M. W.; Truong, T. N.; Gordon, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 5217.

polarity of the Si=C double bond leads to lower reaction barriers and, consequently, to higher rates for addition reactions. To estimate the reactivity of the silenes discussed in this paper, the Si=C charge distributions before and after formation of Si←N donor coordination are compared.

One would expect that the electron donation into the π^*-orbital of silenes in intramolecular donor complexes such as MADS will result in a decrease of the positive charge at silicon and to an overall decrease of the polarity of the Si=C double-bond moiety. This trend is evident from MP2/6-31G(d) calculations on MADS conformers with long (**2a**, 3.695 Å) and short (**1a**, 2.105 Å) Si···N distances. On approach of a N-donor atom to silicon, both the positive charge at the silicon center (+0.994 vs +0.828 e) and the negative charges at the nitrogen and carbon atoms (−0.559 vs −0.539 and −0.655 vs −0.648 e, respectively) are lowered (see Table 1), the overall polarity of the Si=C double bond being decreased. On going from DMOS to DMOS·NH_3, the positive charge at silicon decreases by 0.076 e, while the negative charge at carbon increases by 0.028 e, the overall polarity of the Si=C double bond being also decreased.

In contrast, the electron density at silicon decreases and the negative charge at carbon increases by 0.061 and 0.065 e for DMS and DMS·NH_3, respectively (Table 1), the overall polarity of the Si=C double bond being unchanged. Therefore, from the charge distribution in the series MADS, DMOS, and DMS one may predict the following order of reactivity of silenes *with* and *without* Si←N donor coordination:

$$\text{MADS } (r(\text{Si}\cdots\text{N})\ 3.695\ \text{Å}) > \text{MADS } (r(\text{Si}\cdots\text{N})\ 2.105\ \text{Å})$$

$$\text{DMOS} > \text{DMOS}\cdot\text{NH}_3$$

$$\text{DMS} \cong \text{DMS}\cdot\text{NH}_3$$

Conclusions

The ab initio calculations on silene ammonia complexes and MADS indicate strong inter- and intramolecular Si←N coordination between the sp^2-hybridized silicon atom and nitrogen in the gas phase. The Si←N bond in MADS is found to be shorter than that in the saturated counterpart of MADS and in silatranes. The participation of the sp^2 silicon in the Si←N donor−acceptor bond is accompanied by an elongation and an increase of the polarity of the silicon−carbon double bond, and only a small distortion of the planarity of both doubly bonded atoms is found. With respect to the difference in the enthalpies for dehydrogenation reactions, which is smaller for silene donor coordinated complexes and for MADS with a short Si···N distance, one may conclude that Si←N coordination stabilizes the silicon−carbon double bond in silenes.

Acknowledgment. The financial support from 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 (Grant INTAS-RFBR-95-0070 and Grant RFBR 96-03-33906). The authors are grateful to A. A. Granovsky for granting updated versions of the PC GAMESS program, and to Dr. A. A. Safonov for assistance in calculations. N.A. thanks Dr. Th. Müller for fruitful discussions.

OM9810089

---

(14) Wiberg, N.; Wagner, G.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 229.

(15) (a) Apeloig, Y. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons Ltd.: New York, 1989; Chapter 2. (b) Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M.-B.; Apeloig Y.; Karni, M. *J. Am. Chem. Soc.* **1986**, *108*, 270. (c) Apeloig, Y.; Karni, M. *J. Chem. Soc., Chem. Commun.* **1984**, 768.

(16) Brodskaya, E. I.; Voronkov, M. G. *Bull. Acad. Sci. USSR, Chem Sci. (Engl. Transl.)* **1986**, 1546.

(17) (a) Shen, Q.; Hilderbrandt, R. L. *J. Mol. Struct.* **1980**, *64*, 257. (b) Forgacs, G.; Kolonits, M.; Hargittai, I. *J. Struct. Chem.* **1990**, *1*, 245.

(18) Some calculations were made with the PC GAMESS version by Alex A. Granovsky, Moscow State University.

(19) The structure **1′** obtained with the 3-21G(d) basis set appears to be the artifact of the small basis set and the symmetric path of the conformation conversions leads to the single structure **1″**.

(20) In reality the interaction of ammonia with silenes *in statu nascendi* leads to the formation of aminosilanes, which undergo subsequent reactions.[11]

(21) The same trend was observed for r(Si=C) (1.714 Å) of the parent silene[13c] calculated at the MP2/6-31G(d) level. At the MCSCF level this overestimation may reach to the higher value (1.743 Å in $H_2Si{=}CH_2$).[13d]

(22) The calculated formation energy of DMOS·NH_3 is considerably higher than that for the $SiF_4\cdot NH_3$ complex (10 and 8.6 kcal/mol) but falls into the range of Si←N donor bond energies in silatranes (13−22 kcal/mol).[16]