J. Org. Chem. 1994, 59, 8015–8022

Mechanism of the Cycloaddition of Isocyanide to Silene: Siliranimine versus Silaziridine

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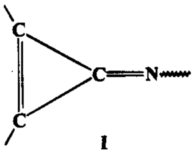
Received June 28, 1994[®]

The model reaction of hydrogen isocyanide and silene ($HN{\equiv}C + CH_2{=}SiH_2$) has been studied by theoretical methods. Geometries of the stationary points have been optimized at the MP2/6-31G** level while relative energies have been estimated using QCISD(T) wave functions in conjunction with the 6-31G** basis and corrected for zero-point energies. The primary cycloadduct, siliranimine, is calculated to be slightly less stable than silaziridine, the isomeric alternative having an exocyclic C=C double bond, in agreement with experiment on substituted systems. The third alternative species with an exocyclic C=Si double bond lies higher in energy. The [2 + 1] cycloaddition of $HN{\equiv}C$ to $H_2C{=}SiH_2$ is a concerted but asynchronous and stereoselective process in which the carbon lone pair of $HN{\equiv}C$ attacks first the Si atom. The favored unimolecular rearrangement siliranimine–silaziridine occurs in two distinct steps involving a four-membered cyclic carbene as the intermediate. The carbene has a relative stability similar to siliranimine, and its formation constitutes the rate-determining step of the entire transformation. Although the carbene is a formal product of a [2 + 2] cycloaddition of HNC + $H_2C{=}SiH_2$, the relevant transition structure could not be located at the levels employed. Some properties of the rings considered including the ring strains, the barriers to nitrogen inversion, and the proton affinities at nitrogen have also been examined.

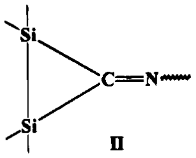
Introduction

In recent years, isocyanides have increasingly been employed as synthons in organic synthesis and as ligands in complexation to metals. The cyanide–isocyanide rearrangement is often involved as an initial step in numerous preparative applications.[1] Isocyanides are also susceptible to attack by nucleophiles, electrophiles, and radicals under various experimental conditions yielding a wide range of primary imine adducts.[2,3a] Owing to the presence of a monocoordinated carbon atom, isocyanides are well suited as 1,1-dipoles in cycloaddition reactions giving different types of heterocycles.[3] As far as the additions to multiple bonds are concerned, isocyanides have been known to undergo [2 + 1] cycloadditions with alkynes.[3a] However the primary cycloadducts, namely cyclopropenimines (**I**), have been isolated only from those reactions involving electron-rich or strained cyclic alkynes.[4] In other cases, fast subsequent reactions occurred giving rise to several secondary products.

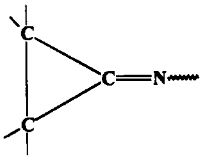
West and co-workers[5] reported a clean reaction of an isocyanide with a stable disilene at room temperature to form the expected disilacyclopropanimine (**II**). The structure of **II** was unambiguously determined by X-ray crystallography. Similar reactivity of isocyanides toward alkenes, ketones, or analogous compounds is not known yet, but the [2 + 1] cycloreversions of cyclopropanimine (**III**) and oxiranimine (**IV**) giving alkene + isocyanide and ketone + isocyanide, respectively, have recently been reported by Quast and co-workers.[6] The fragmentation of cyclopropanimine (**III**) was shown to be possible either in the neutral or ionized state.[6a]



I



II



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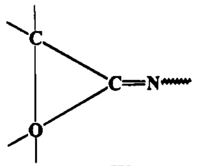

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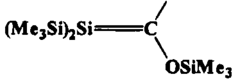
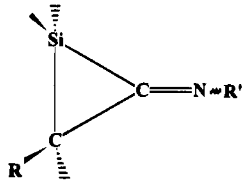
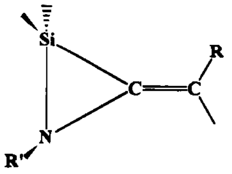
Brook and co-workers[7] studied the reaction of alkyl isocyanides with stable silenes **V** and found that the species formed were not the anticipated siliranimines **VI** but rather the silaziridines **VII** having an exocyclic carbon–carbon double bond. A subsequent kinetic study by these authors[7] carried out at low temperature and



V



VI



VII

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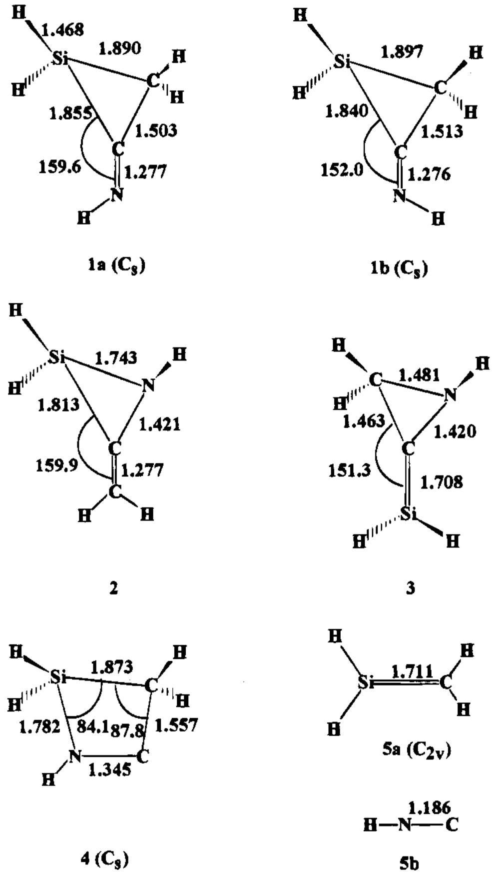
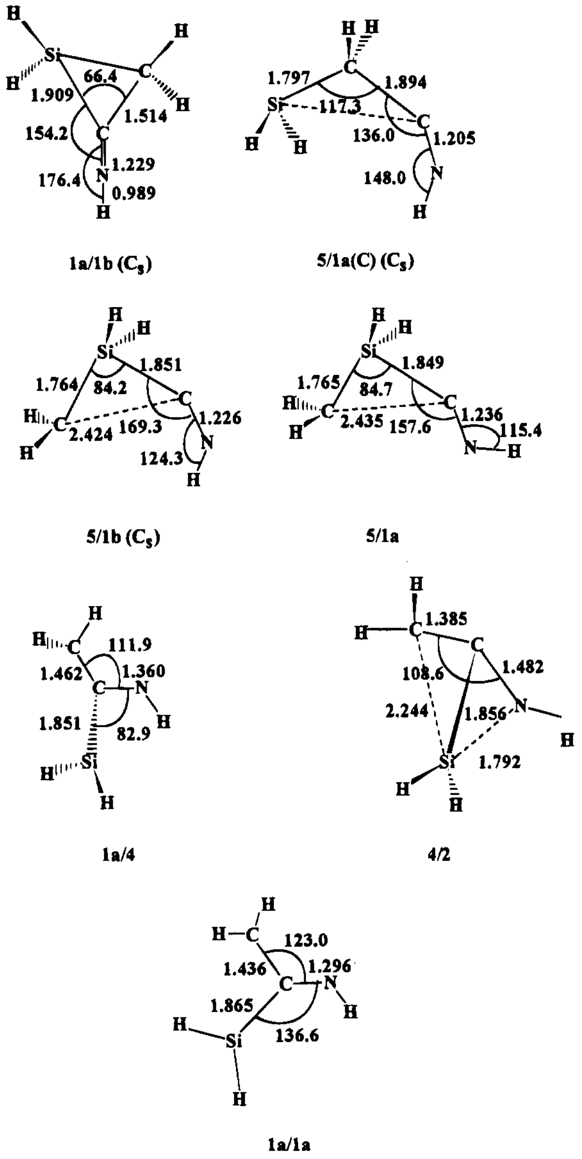


1a (C$_s$) 1b (C$_s$) 2 3 4 (C$_s$) 5a (C$_{2v}$) 5b

Figure 1. Selected MP2/6-31G(d,p) geometrical parameters of the equilibrium structures considered. Bond lengths are given in Å and bond angles in deg.



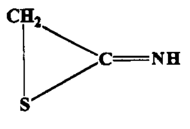
1a/1b (C$_s$) 5/1a(C) (C$_s$) 5/1b (C$_s$) 5/1a 1a/4 4/2 1a/1a

Figure 2. Selected MP2/6-31G(d,p) geometrical parameters of the transition structures relevant to the isomerization, cycloaddition, and rearrangements.

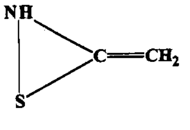
monitored by NMR spectrometric techniques revealed, however, that the primary adduct of the isocyanide plus silene reaction at −70 °C is effectively a siliranimine **VI**, but the latter underwent molecular rearrangement upon warming at −40 °C to give a silaziridine (**VII**) as the observed products (eq 1). These experimental results are

$$V + RN\equiv C \xrightarrow{-70\ °C} VI \xrightarrow{-40\ °C} \mathbf{VII} \qquad (1)$$

rather surprising in many aspects, in particular concerning the relative stability between the isomers **VI** and **VII** and also the ease with which both cycloadditions and rearrangement reactions occurred. They contrast with ab initio molecular orbital results[8] that we have recently obtained for the simplest model sulfur analogous system. As a matter of fact, the unsubstituted thiiranimine (**VIII**)



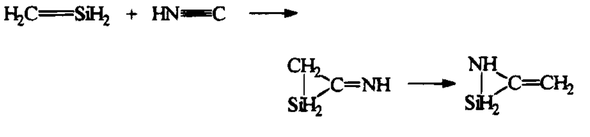
VIII



IX

has been calculated to be more stable than its isomer **IX** (51 kJ/mol at the MP4/6-31G** level).[8c] On the other hand, the barrier height for the [2 + 1] cycloaddition of HNC to $H_2C{=}S$ giving **VIII** was found to be substantial, namely $\Delta H^{\ddagger} = 95$ kJ/mol at 298 K (at a similar level of theory).[8a] In addition, methylenecyclopropanes are known to undergo unimolecular rearrangement only at higher temperatures, with enthalpies of activation of the order of magnitude of 170 kJ/mol.[9]

In an attempt to obtain some useful quantitative information on the structural, energetic and mechanistic aspects related to the silene plus isocyanide addition, we have carried out ab initio molecular orbital calculations on the simplest model system, $H_2Si{=}CH_2$ + HNC. Particular attention has been paid to the mechanism of the siliranimine–silaziridine rearrangement (see eq 2).



(2)

We have found a four-membered cyclic carbene as a

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Table 1. Total Energies (Hartree)[a] and Zero-Point Energies (kcal/mol) of the Stationary Points Considered Using the 6-31G(d,p) Basis Set

structure[a]	MP2(F)[b]	MP4SDTQ	QCISD	QCISD(T)	ZPE[c]
1a (siliranimine)	−422.482 10	−422.515 86	−422.446 39	−422.517 41	38.3
1b (siliranimine)	−422.479 33	−422.513 28	−422.493 88	−422.514 75	38.2
2 (silaaziridine)	−422.494 79	−422.525 98	−422.507 07	−422.527 54	38.4
3 (exo-silene)	−422.446 08	−422.479 39	422.459 10	−422.480 83	38.9
4 (carbene)	−422.478 66	−422.513 32	−422.497 36	−422.516 06	38.8
5 { **5a** $H_2C{=}SiH_2$	−93.142 32	−93.160 77	−93.148 48	−93.159 53	8.9
5b HNC	−329.299 05	−329.321 25	−329.314 62	−329.324 09	24.2
1a/1b	−422.431 72	−422.464 65	−422.444 32	−422.465 32	36.5
5/1a (C)	−422.407 21	−422.450 05	−422.421 98	−422.449 43	35.1
5/1b	−422.432 68	−422.470 66	−422.446 07	−422.471 42	35.6
5/1a	−422.429 52	−422.468 54	−422.443 55	−422.469 77	35.5
1a/4	−422.424 92	−422.457 44	−422.435 71	−422.458 79	38.8
4/2	−422.432 35	−422.464 36	−422.443 52	−422.465 66	38.3
1a/1a (plan)	−422.407 51	−422.449 23	−422.422 98	−422.454 65	37.0

[a] Based on MP2/6-31G(d,p) geometries. The core orbitals are frozen unless otherwise noted. [b] Using full sets of MOs. [c] Zero-point energies calculated from HF/6-31G(d,p) wavenumbers and scaled by 0.9.

Table 2. Relative Energies (kcal/mol) of the Stationary Points Considered at Different Levels Using the 6-31G(d,p) Basis Set

structure	MP2(F)	MP4SDTQ	QCISD	QCISD(T)	QCISD(T) + ZPE
1a	0.0	0.0	0.0	0.0	0.0
1b	1.7	1.6	1.6	1.7	1.6
2	−8.0	−6.3	−6.7	−6.4	−6.3
3	22.6	22.9	23.4	23.0	23.6
4	2.2	1.6	−0.6	0.8	1.3
5 (**5a** + **5b**)	25.6	21.2	20.9	21.2	16.0
1a/1b	31.6	32.1	32.7	32.7	30.9
5/1a (C)	47.0	41.0	46.7	42.7	39.5
5/1b	31.0	28.3	31.6	28.9	26.2
5/1a	33.0	29.7	33.2	29.9	27.1
1a/4	35.9	36.7	38.1	36.8	37.3
4/2	31.2	32.3	33.2	32.5	32.5
1a/1a	46.8	41.8	46.1	39.4	38.1

reaction intermediate. Various properties of the three-membered rings have also been investigated.

Calculation Method

For the sake of comparison with our previous results on the sulfur analogues[8] **VIII**−**IX**, we have adopted the same theoretical approach in the present work. In brief, this involved initial geometry optimizations at the Hartree−Fock (HF) level with the dp-polarized 6-31G(d,p) basis set.[10] The structures located were then subjected to a vibrational analysis at the HF/6-31G(d,p) level in order to characterize them and to estimate their zero-point energies. Geometrical parameters were subsequently refined using correlated wave functions at the second-order Møller−Plesset perturbation (MP2) theory level with the 6-31G(d,p) basis set. No constraints on the degrees of freedom have been imposed during the geometry optimizations. Relative energies between stationary points were obtained using full fourth-order perturbation theory (MP4SDTQ) with the 6-31G(d,p) basis set and MP2-optimized geometries. In addition, the thermochemical parameters relevant to the cycloaddition and rearrangement processes were estimated making use of the quadratic configuration interaction method (QCISD(T)). All calculations were performed using a local version of the GAUSSIAN 90 program.[10]

Results and Discussion

Selected geometrical parameters of the stationary points of interest optimized at the MP2/6-31G(d,p) level of theory are displayed in Figures 1 and 2. The corresponding total and relative energies are listed in Tables 1 and 2, respectively. In general the number *X/Y* stands for a transition structure (TS) connecting both equilibrium structures *X* and *Y*. Energies of some isodesmic reactions relevant to two cyclic species are summarized in Figure 3. Schematic potential energy profiles for the rearrangements are illustrated in Figures 4 and 5. Finally, calculated proton affinities are given in Table 3. Relative energies computed by the MPn and QCI methods are similar both qualitatively and quantitatively; this supports the use of single-reference wave functions for treating most of the structures under consideration. Unless otherwise noted, the relative energies quoted in the text refer to the QCISD(T)/6-31G(d,p) + ZPE values.

Siliranimine. Both forms **1a** and **1b** of siliranimine exhibit C_s symmetry. The *syn* form **1a** in which both atoms Si and H(N) are disposed in a cis-configuration with respect to the C=N bond has a lower energetic content than the *anti*-**1b** (1.5 kcal/mol, Table 2). A similar situation has previously been found for the sulfur analogue **VIII**. Both isomeric forms **1a** and **1b** are connected with each other by the transition structure TS1 shown in Figure 2. The corresponding barrier to nitrogen inversion of 30.2 kcal/mol (relative to **1a**) which is comparable to the barrier height calculated for $H_2C{=}NH$ (about 30 kcal/mol) but significantly larger than that for thiiranimine **VIII** (about 25 kcal/mol).[8] This result suggests that a siliranimine carrying a poorer inverting group at nitrogen could exist in two distinct syn and anti conformers.

The vibrational wavenumber associated with the C=N stretching mode is estimated to be 1754 cm^{-1}, a value comparable to the corresponding values of 1742 cm^{-1} for thiiranimine and 1780 cm^{-1} for cyclopropanimine but larger than that of 1640 cm^{-1} for methylenimine.[8,13] This confirms the trend for an upward shift of the C=N stretching wavenumber when this double bond is coupled with a three-membered ring.

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(13) The C=N stretching wavenumbers are estimated using harmonic wavenumbers at the HF/6-31G(d) level and scaled by a factor 0.863. See ref 8 for details.

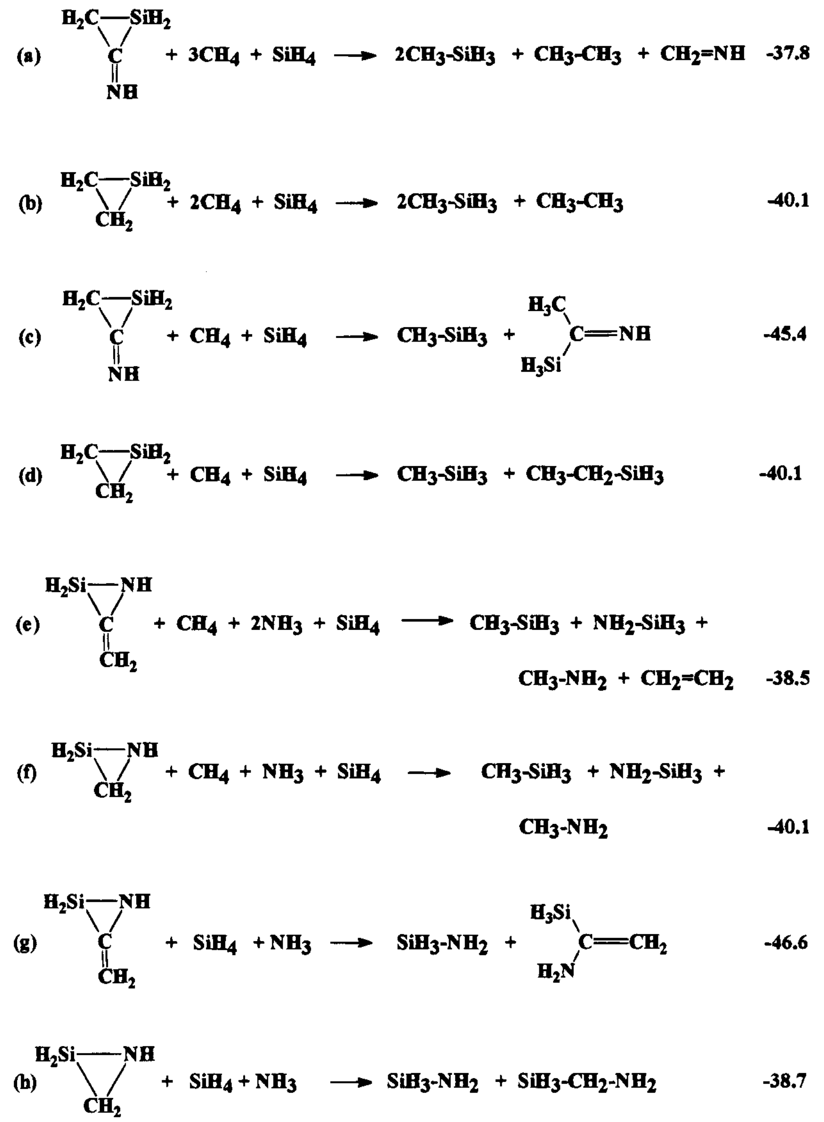


Figure 3. Some isodesmic reactions relevant to the three-membered rings **1a** and **2**. Reaction energies are obtained from MP4/6-31G(d)//HF/6-31G(d) calculations, in kcal/mol.

In order to estimate the ring strain present in siliranimine we have considered some of its possible isodesmic reactions and compared these with the corresponding reactions of silirane. The four reactions examined are shown in Figure 3 along with their energies. Note that the calculated energy ordering is internally consistent within the MPn expansion and the absolute values are not particularly sensitive to the method employed with or without electron correlation.

The bond separation reactions a and b compare the resulting ring strains in the two three-membered cycles with and without, respectively, an exocyclic double bond. It is apparent that the former has a smaller formal ring strain than the latter but the difference amounts to only 2.3 kcal/mol (at the MP4/6-31G(d) level). On the other hand, the energies of both reactions c and d which are essentially determined by a loss in ring strain indicate that the intrinsic ring strain in **1a** is 7.9 kcal/mol larger than that of silirane. Thus, the coupling of a silirane ring with a C=N bond induces an extra stabilization of about 10.2 kcal/mol in favor of the resulting ring. A graphic representation of the isodesmic reactions is given in Chart 1.

Endocyclic Silaziridine. The molecule **2** (Figure 1) contains a silaziridine cyclic structure coupled with an exocyclic C=C double bond. The X-ray structure of a substituted silaziridine has been determined by Brooks and co-workers.[7] In general, our MP2/6-31G(d,p) values for the exocyclic and endocyclic bond distances of the unsubstituted species **2** compare reasonably well with the crystal structure (within differences of ±0.02 Å). Our results also agree with the findings that the terminal carbon atom of the C=C bond has an essentially planar configuration while the nitrogen atom is pyramidal. All atoms of the enamine moiety ($H_2C{=}C{-}N$) in **2** are situated in a plane but the silicon atom lies slightly out of that plane, the dihedral angle SiCCN being in fact 161°.

An inversion of configuration of **2** at the nitrogen center is rather facile. Separate calculations using MP4/6-31G(d,p) wave functions indicate an energy barrier to inversion of less than 1 kcal/mol. Such a barrier height which is similar to that of vinylamine (1.7 kcal/mol) but smaller than those of ammonia (5.9 kcal/mol) or aziridine (12 kcal/mol) points toward an efficient stabilization of the relevant TS by an electron delocalization within the enamine group.

The energies of isodesmic reactions employed to estimate the ring strain of **2** are also given in Figure 3 and illustrated in Chart 1. Again, the reaction e is less

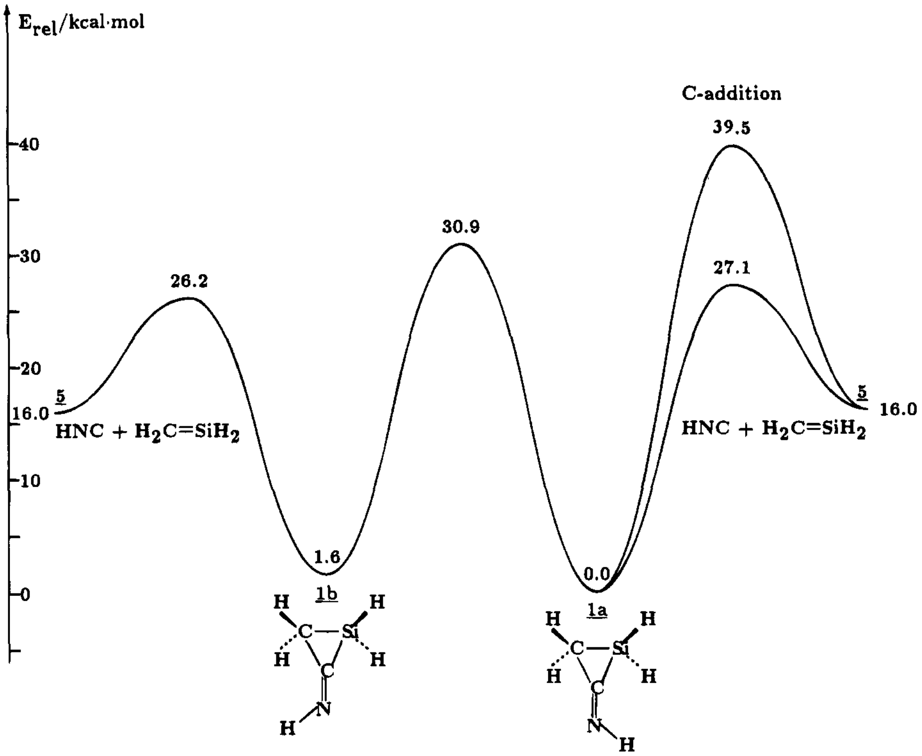


Figure 4. Schematic potential energy profile showing the cycloaddition and isomerization of siliranimine. Energies obtained from QCISD(T)/6-31G(d,p) + ZPE calculations.

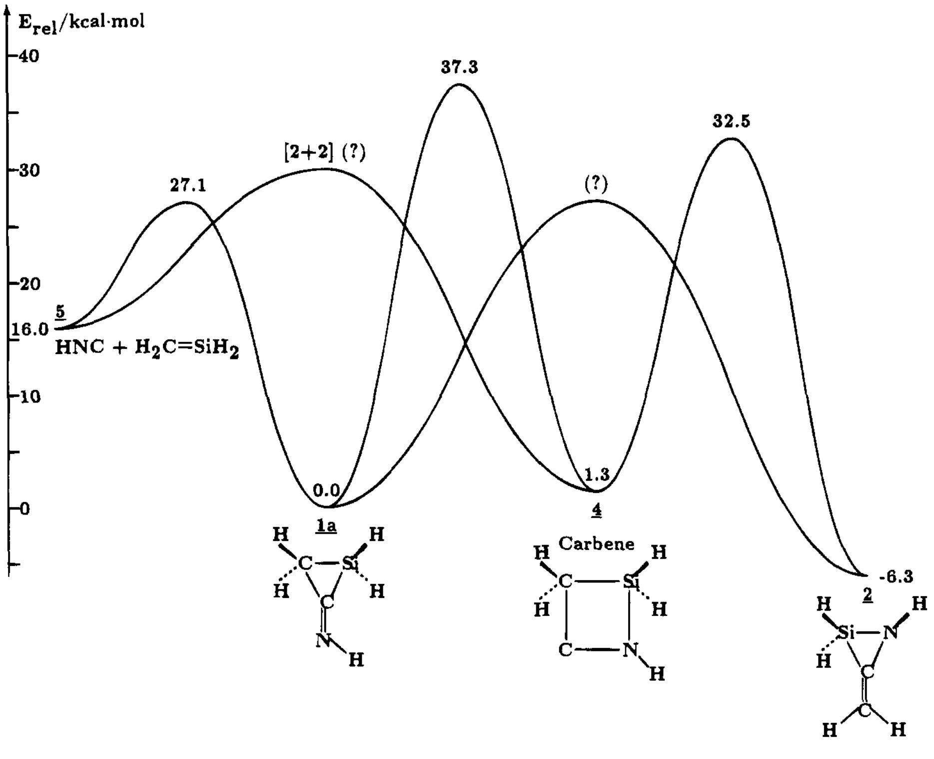


Figure 5. Schematic potential energy profile showing the cycloaddition of $H_2Si{=}CH_2$ + HNC and rearrangement of the adduct. Energies obtained from QCISD(T)/6-31G(d,p) + ZPE calculations.

exothermic than the reaction f by 1.6 kcal/mol, suggesting a smaller formal ring strain for **2**. In contrast, the intrinsic ring strain of **2** is found to be larger by 7.9 kcal/mol than that of the silaziridine ring without an exocyclic system (reactions g and h). Thus, the coupling ring-exocyclic double bond increases the intrinsic ring strain, but the latter is largely compensated by an electronic stabilizing interaction between both moieties. The resulting effect is an apparent reduction of the ring strain.

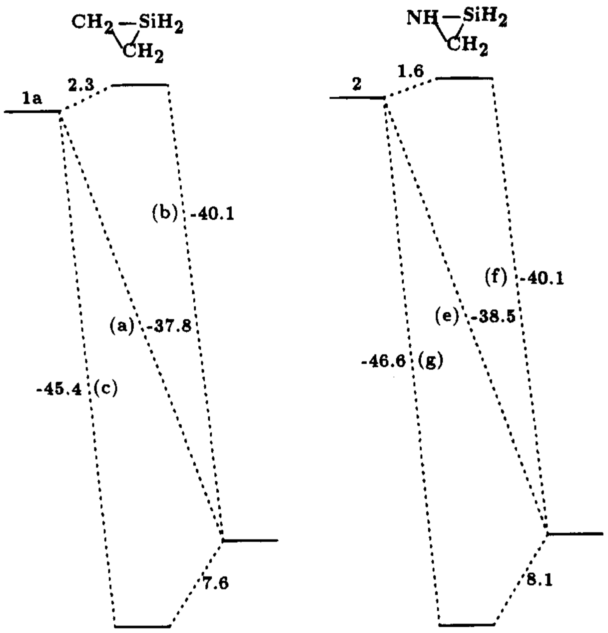
Exocyclic Silaziridine. The third alternative ring system **3** with an exocyclic C=Si bond is calculated to have a pyramidal nitrogen atom and an almost planar heavy atom skeleton (Figure 1). The nitrogen inversion is associated with an energy barrier of 7.4 kcal/mol

Table 3. Proton Affinities at Nitrogen of 1a and 2

	PA[a]			
species	HF	MP2	MP3	MP4
1a	233	226	230	228
2	227	222	226	224

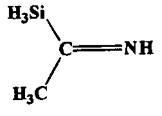
[a] Proton affinities in kcal/mol, using HF/6-31G(d,p)-optimized geometries and the 6-31G(d,p) basis set and including zero-point energies.

Chart 1



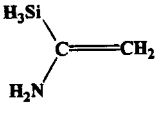
calculated at the MP4/6-31G(d,p) level. Thus, this barrier is larger than that of **2** discussed above, and even larger than that of ammonia, but it is still smaller than that of aziridine. This presumably arises from a lack of efficient interaction within the silenamine moiety of the relevant TS.

Relative Energies between Three-Membered Rings. As seen in Table 2, of the three isomers considered, the endocyclic silaziridine **2** is consistently found to be the most stable form whereas the exocyclic silaziridine **3** is the least stable form. Our best estimate places **2** 6 and 30 kcal/mol below **1a** and **3**, respectively. This result is thus in agreement with the experimental observation of Brooks et al.[7] (eq 1). Note that a reversed energy ordering is observed in the corresponding open form **1O** and **2O**. **1O** is calculated to lie about 6 kcal/mol below **2O** (MP4(6-31G(d)). It is also well known that ethanimine ($H_3CCH{=}NH$) is more stable than its isomer vinylamine ($H_2C{=}CHNH_2$). In this context, the higher stability of **2** over **1a** should arise from the relative strength of the new bonds formed upon ring closure. As a matter of fact, the bond energy terms for both Si−N (in **2**) and Si−C (in **1a**) bonds have been estimated to be 78.3 and 69.3 kcal/mol, respectively.[11] The stronger Si−N bond seemingly tips the energy balance in favor of **2**.



$(H_3Si)(H_3C)C{=}NH$

1O



$(H_3Si)(H_2N)C{=}CH_2$

2O

Proton Affinities. The proton affinities at nitrogen (PA(N)) of both isomers **1a** and **2** have been calculated. The results are summarized in Table 3. It appears that **1a** exhibits a somewhat larger PA(N) (by 4 kcal/mol) making both protonated species closer in energy. Thus, the siliranimine is stabilized following protonation and has therefore a better chance to exist in the iminium cation form than in the neutral imine form.

[2 + 1] Cycloaddition of $H_2C{=}SiH_2$ to HN≡C. This addition is moderately exothermic; the reactants lie about 16 kcal/mol above the primary adduct **1a**. Three transition structures shown in Figure 2 have been located for this additive process. **5/1a** (C) is characterized by short C−C and long C−Si intermolecular distances. The isocyanide fragment becomes bent but the HNC angle remains large (148°). We have not been able to find a TS in which the hydrogen atom of HNC has a *cis* configuration relative to Si. **5/1a** (C) can be seen as the TS for attack on the carbon atom of silene leading to siliranimine **1a**. The barrier height relative to the separated fragments **5** is calculated to be 23.5 kcal/mol.

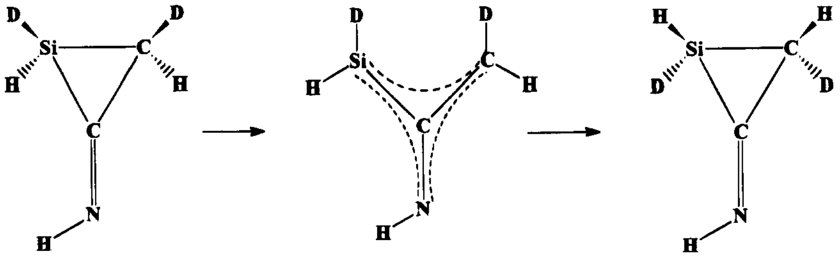
Both structures **5/1a** and **5/1b** which contain short C−Si and long C−C intermolecular distances are, for their part, the TS for attack on the silicon atom. **5/1b** leads the supermolecule to the *anti* cycle **1b** while **5/1a** connects the reactants with the *syn*-**1a**. Except for the conformation around the nitrogen atom, geometrical parameters of both structures are similar. In many aspects, the addition pathway is analogous to the well-established one of a singlet carbene to a multiple bond.[12]

Interestingly, the corresponding energy barriers for Si addition in **5/1a** and **5/1b** of 9.6 and 11.1 kcal/mol, respectively, are much smaller than that for C addition mentioned above. This behavior can be understood in terms of the frontier orbital interaction. The isocyanide plus silene addition is essentially controlled by the HOMO (isocyanide)−LUMO (silene) interaction. The HOMO of isocyanide is the carbon lone pair while the LUMO of sylene is a Π*(C=Si) orbital in which the silicon atom bears the larger MO coefficient, namely $C_i(Si) = 0.81$ and $C_i(C) = -0.66$ (values obtained with the 6-31G(d,p) basis). On the other hand, Si is also the electrophilic center of silene characterized by a large positive charge. As a consequence the initial carbon−silicon approach is energetically favored over the carbon−carbon. Note that the isocyanide group in both TS for Si addition is strongly bent.

Figure 4 displays a schematic energy profile showing the primary addition and isomerization processes. The hydrogen isocyanide plus silene cycloaddition can be seen as stereoselective. The kinetically most favored pathway passes through the TS **5/1b** giving the thermodynamically less stable cycloadduct **1b**. Because the isomerization of the latter to the more stable adduct **1a** requires a larger activation energy, the isomer **1b** could be formed as the primary adduct. Nevertheless, the relative position between the relevant TS could be modified by the substituent effect. A bulky group such as *tert*-butyl or xylyl employed by Brooks et al.[7] in their experiment could tip the balance in favor of **5/1a** whereas a better inverting group at nitrogen may reduce the barrier to inversion.

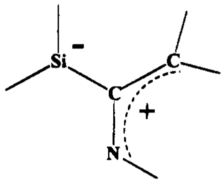
A Mulliken population analysis points out that a small amount of charge is actually transferred from silene to isocyanide in both TS for Si addition. Such a charge transfer is likely to arise from a back donation of the HOMO (silene) to the LUMO (isocyanide). Experimentally,[7] silenes with $SiMe_3$ and $OSiMe_3$ groups have been employed; both are in fact electron donors and thus expected to exert a strong electronic effect reducing

Scheme 1



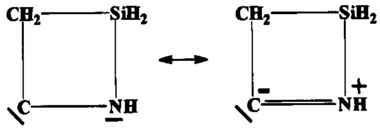
further the (already small) barrier height for cycloaddition. Bear in mind that the experiment[7] was carried out at −70 °C (eq 1).

Siliranimine–Silaziridine Rearrangement. A ring opening via a homolytic cleavage of the carbon–carbon bond can be precluded because this process usually requires a large activation energy.[9] Brooks et al.[7] suggested a heterolytic cleavage of the weaker C–Si bond giving a planar zwitterion of the type **6** as an intermediate. To test this hypothesis, we have considered an open and planar form **1a/1a** whose geometry is also given in Figure 2. At the HF/6-31G(d,p) level, **1a/1a** is characterized as a TS in which the imaginary vibrational mode (ν_i = 477i cm^{-1}, a'' symmetry) corresponds to a racemization of **1a** following a disrotatory ring opening (Scheme 1). **1a/1a** is calculated to lie 38.5 kcal/mol above **1a**. Nevertheless, a vibrational analysis at the MP2/6-31G(d,p) level reveals that **1a/1a** possesses two imaginary wavenumbers (430i and 239i cm^{-1}, a'' symmetry) both corresponding to out-of-plane distorsions of hydrogen atoms. Thus, the validity of single determinant wave functions in treating this type of zwitterion is questioned. The identity of **1a/1a** could only safely be determined by vibrational analysis at an appropriate multireference level. In searching for the TS relevant to the **1a** → **2** isomerization, we have been able to locate **1a/4** (Figure 2) which has a nonplanar configuration and corresponds to a ring opening along the C–Si bond. In order to find out the identity of this TS, we have performed an intrinsic reaction coordinate calculation (IRC). On one side of the IRC path starting from **1a/4**, we have found siliranimine **1a**; on the other side we have found, surprisingly enough, not the silaziridine **2** as the product, but instead the four-membered cyclic carbene **4** as the alternative minimum connected with **1a/4**. The carbene **4** has a CNSiC framework and an aminoethylidene structure. The nitrogen atom has a planar configuration resulting from a strong overlap between the nitrogen lone pair and carbenic empty p-orbital (Scheme 2). The C–N distance in **4** is in fact relatively short (1.345 Å) as compared with typical C–N single bonds. This is presumably responsible for the high thermodynamic stability of **4** which lies only 1.3 kcal/mol above **1a**. From a geometrical viewpoint, **4** is formally a primary product of a [2 + 2] cycloaddition of $H_2C{=}SiH_2$ + HN≡C. In spite of extensive attempts, we have failed to locate a relevant TS. Two apparent reasons for this failure could be mentioned: (i) a TS for a [2 + 2] pathway, if any, probably lies higher in energy than those for the [2 + 1] discussed above, and/or (ii) the use of single reference wave functions may not be appropriate for this reaction pathway. Relative to **1a**, the energy barrier for rearrangement via **1a/4** amounts to 37.3 kcal/mol.

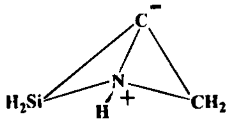


6

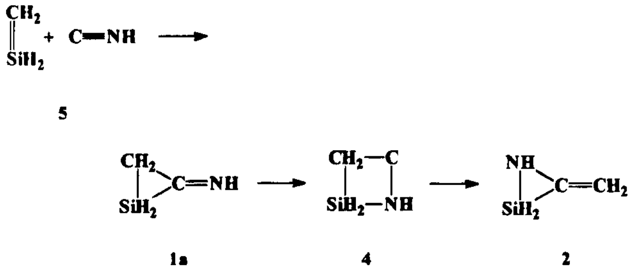
Scheme 2



Extensive calculations have enabled us to locate the structure **4/2** which is confirmed by IRC calculations to be the TS linking both equilibrium structures **4** and **2**. **4/2** lies only marginally lower in energy than **1a/4** (4.8 kcal/mol). In view of the relatively short Si–C distances (1.856 and 2.244 Å), **4/2** could be seen as a nonplanar and tetrahedral zwitterion which is an analogue of the cyclopropylcarbinyl and bicyclobutonium ions. **4/2** has thus an interesting geometry with both ammonium cation and carbanion moieties at the bridgehead positions of a bicyclosilabutane. Such a structure is not particularly destabilized. Figure 5 showing the energy profile from the reactants to the product suggests that the rearrangement **1a** → **4** constitutes the rate-determining step of the entire process, which could be summarized as follows.



4/2



An important fact is that the TS **1a/4** for rearrangement lies about 10.2 kcal/mol above the TS **5/1a** for cycloaddition. Experimentally, this additional step has been achieved by an increase of the temperature by only 30 °C. Thus, the energy difference between both TS of the substituted system should be significantly smaller than our value for the unsubstituted system. Nevertheless, the energy ordering between the TS seems to be consistent with the nonobservation of a carbene intermediate **4**. Proceeding in the opposite direction, namely decomposition of silaziridine **2**, the carbene **4** could eventually be detected.

It should also be stressed that a direct conversion of siliranimine to silaziridine cannot be excluded, even though our extensive searches using HF-based methods have not been successful. That is the sense of the question marks given in Figure 5.

Concluding Remarks

A number of important points emerge from our theoretical study of the [2 + 1] cycloaddition of the model system $H_2C{=}SiH_2$ plus $HN{\equiv}C$:

(1) Of the three possible ring systems, the silaziridine **2** with an exocyclic C=C bond is the most stable form, consistent with experimental observations on substituted systems.

(2) The higher stability of silaziridine **2** is due to an efficient and strong stabilizing interaction between the three-membered ring and the exocyclic bond system which results in a reduction of the ring strain.

(3) The $H_2C{=}SiH_2 + HN{\equiv}C$ reaction is essentially a concerted but asynchronous Si-addition yielding siliranimine as the primary product; the addition is thus stereoselective.

(4) The conversion of siliranimine **1a** to its more stable isomer **2** occurs in two distinct steps with a four-membered cyclic carbene intermediate **4**. The latter has an energetic content comparable to **1a**. The formation of the carbene is calculated to be the rate-determining step of the whole transformation, consistent with the experimental nonobservation of a carbene species.

(5) The identification of the carbene intermediate **4** is perhaps the most intriguing result of the present study. Its high stability renders its observation possible. It could be detected in a reverse transformation starting from silaziridine. However, the possibility of a direct siliranimine–silaziridine conversion as well as a [2 + 2] cycloaddition for which whose transition structures could not be located using single reference wave functions might modify this conclusion.

Acknowledgment. The authors are indebted to the Belgian National Fund for Scientific Research (NFWO), the Belgian Government (Programmatie voor Wetenschapsbeleid), and KULeuven Computing Center.