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Reactions of Silylene with Unreactive Molecules. 2. Nitrogen: Gas-Phase Kinetic and Theoretical Studies

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Time-resolved studies of the reaction of silylene, SiH_2, with N_2 have been attempted at 296, 417, and 484 K, using laser flash photolysis to generate and monitor SiH_2. No conclusive evidence for reaction could be found even with pressures of N_2 of 500 Torr. This enables us to set upper limits of ca. 3×10^{-15} cm^3 molecule^{-1} s^{-1} for the second-order rate constants. A lower limit for the activation energy, E_a, of ca. 47 kJ mol^{-1} is also derived. Ab initio calculations at the G3 level indicate that the only SiH_2N_2 species of lower energy than the separated reactants is the $H_2Si\cdots N_2$ donor−acceptor (ylid) species with a relative enthalpy of −26 kJ mol^{-1}, insufficient for observation of reaction under the experimental conditions. Ten bound species on the SiH_2N_2 surface were found and their energies calculated as well as those of the potential dissociation products: HSiN + NH($^3\Sigma^-$) and HNSi + NH($^3\Sigma^-$). Additionally two of the transition states involving cyclic-SiH_2N_2 (siladiazirine) were explored. It appears that siladiazirine is neither thermodynamically nor kinetically stable. The findings indicate that $Si-N_d$ bonds (where N_d is double-bonded nitrogen) are not particularly strong. An unexpected cyclic intermediate was found in the isomerization of silaisocyanamide to silacyanamide.

Introduction

Silylene, SiH_2, is one of the most reactive species known.[1,2] Its reactions include Si−H bond insertions, C=C and C≡C π-bond additions, and reactions with lone pair donors.[3] Many of these reactions occur at close to the collision rate.[1,2] Examples of measured reaction rate constants from our laboratories (in cm^3 molecule^{-1} s^{-1} at room temperature) include 4.6×10^{-10} ($SiH_2 + SiH_4$[4]), 3.5×10^{-10} ($SiH_2 + C_2H_4$[5]), and 4.2×10^{-10} ($SiH_2 + Me_2CO$[6]). Even the high value of ca. 3.3×10^{-10} has been obtained for $SiH_2 + CO$[7] by extrapolation to high pressures of rate measurements which are relatively slow at normal pressures. For the reaction of $SiH_2 + Me_2O$, a value of 8.1×10^{-10}, which exceeds the conventional collision number, has been obtained by Alexander et al.,[8] suggesting that maybe SiH_2 has an unusual and exceptionally high collision diameter. From this evidence it is clear that SiH_2 must be a good candidate to probe the reactivity of exceptionally unreactive molecules. In part 1 we studied its reaction with CO_2[9] and found that reaction does indeed take place, albeit at less than the collision rate. Rate measurements combined with ab initio studies were consistent with a mechanism of addition of SiH_2 across one of the C=O double bonds to form siloxirone.

In the present study we report our investigations of its reaction with N_2, by both gas-phase kinetics and ab initio calculations. A previous study of $SiH_2 + N_2$ by Chu et al.[10] reported no reaction, but as we have shown[7] for the reaction of $SiH_2 + CO$ (also investigated by Chu et al.), the low pressure (5 Torr) of bath gas (He) employed in their study was inadequate for the third body stabilization of the product. We were further prompted by the knowledge that, in low-temperature matrix isolation studies, Maier et al. have shown that Si atoms (of similar high reactivity to SiH_2) react with both CH_2O[11] and N_2,[12] and also Lalov et al.[13] have detected a complex of $SiCl_2$ with N_2. The first ab initio study of the SiH_2N_2 system by Thomson and Glidewell[14] some 20 years ago concluded that there were no isomers of greater stability than the separated $SiH_2(^1A_1)$ and N_2. In more recent studies of the potential energy (PE) surface for SiH_2N_2, Kawauchi et al.[15] (MP4SDTQ/6-31G** level) concluded that, of 10 possible species on the singlet surface, only the $SiH_2\cdots N_2$ donor−acceptor (or ylid) complex was more stable than $SiH_2 + N_2$.

Experimental Section

Equipment, Chemicals, and Method. The apparatus and equipment for these studies have been described in detail previously.[4,16] Only essential and brief details are therefore included here. SiH_2 was produced by the 193 nm flash photolysis of phenylsilane ($PhSiH_3$) using a Coherent Compex 100 exciplex laser. Photolysis pulses were fired into a variable temperature quartz reaction vessel with demountable windows, at right angles to its main axis. SiH_2 concentrations were monitored in real time by means of a Coherent 699-21 single-mode dye laser pumped by an Innova 90-5 argon ion laser and operating with Rhodamine 6G. The monitoring laser beam was multipassed 36 times along the vessel axis, through the reaction zone, to give an effective path length of ca. 1.0 m. A portion of the monitoring beam was split off before entering the vessel

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for reference purposes. The monitoring laser was tuned to 17 259.50 cm^{-1}, corresponding to a known strong vibration−rotation transition[16,17] in the SiH_2 $A(^1B_1) \leftarrow X(^1A_1)$ absorption band. Light signals were measured by a dual photodiode/differential amplifier combination, and signal decays were stored in a transient recorder (Datalab DL910) interfaced to a BBC microcomputer. This was used to average the decays of up to 15 photolysis laser shots (at a repetition rate of 0.5 or 1 Hz). The averaged decay traces were processed by fitting the data to an exponential form using a nonlinear least-squares package. This analysis provided the values for first-order rate coefficients, k_{obs}, for removal of SiH_2 in the presence of known partial pressures of substrate gas.

Gas mixtures for photolysis were made up, containing between 3.0 and 5.0 mTorr of $PhSiH_3$, and 0−500 Torr of N_2. Pressures were measured by capacitance manometers (MKS, Baratron).

All gases used in this work were thoroughly degassed prior to use. $PhSiH_3$ (99.9%) was obtained from Ventron-Alfa (Petrarch). Nitrogen (OFN, 99.998%) was obtained from British Oxygen. Sulfur hexafluoride, SF_6 (no GC-detectable impurities), was from Cambrian Gases.

Ab Initio Calculations. The electronic structure calculations were performed with the Gaussian 98 software package.[18] All structures were determined by energy minimization at the MP2=Full/6-31G(d) level. Transition state structures were characterized as first-order saddle points by calculation of the Hessian matrix. Stable structures, corresponding to energy minima, were identified by possessing no negative eigenvalues of the Hessian, while transition states were identified by having one and only one negative eigenvalue. The standard Gaussian-3 (G3) compound method[19] was employed to determine final energies for all local minima. For transition states four single-point energy determinations were carried out at the MP2 geometry, viz. QCISD(T)/6-31G(d), MP4/6-31+G(d), MP4/6-31G(2df,p), and optimized MP2=full/GTlarge, and the values were combined according to the G3 procedure.[19] The identities of the transition state structures were verified by calculation of intrinsic reaction coordinates[20] (IRC) at the MP2=Full/6-31G(d) or B3LYP/6-31G(d) levels. Reaction barriers were calculated as differences in G3 enthalpies at 298.15 K. Some additional calculations on the stable species were also carried out at the CBS-QB3 level.[21]

Results

Kinetics. Preliminary experiments quickly established that at ambient temperatures SiH_2 reacts very slowly, if at all, with N_2. This means that the purity requirement of these experiments is very demanding. Since SiH_2 reacts with many species at or close to the collision rate, small quantities of reactive impurities can give misleading results. Fortunately, the supplied source of N_2 was very pure. Nevertheless, even at impurity levels of 20 ppm, contributions to rates at pressures of 500 Torr may not be negligible. An estimate for the SiH_2 decay constant at 500 Torr for N_2 containing an impurity which reacts at every collision is 1.0×10^5 s^{-1}. Given that decay constants lie in the range $(4.3-6.6) \times 10^4$ s^{-1} in the absence of N_2 (values depend slightly on pressure of SF_6 bath gas), this means that decay constants of value up to 1.5×10^5 s^{-1} could be accounted for by reaction with an impurity (although the expected impurities of O_2 and H_2O do not react at every collision). Other preliminary checks showed that, for a given reaction mixture, k_{obs} values were not dependent on the exciplex laser energy (50−80 mJ/pulse, routine variation) or number of photolysis shots (up to 15 shots). The constancy of k_{obs} (5 shot averages) showed no effective depletion of reactants. The sensitivity of detection of SiH_2 was very high but decreased with increasing temperature and pressure. Therefore, slightly higher quantities of $PhSiH_3$ precursor were required under the latter conditions. For the purposes of rate constant measurement at a given temperature $PhSiH_3$ pressures were kept fixed.

TABLE 1: Dependence of First-Order Decay Constants, k_{obs}, on Nitrogen Pressure

T/K	P/Torr	$k_{obs}/10^4$ s^{-1}
296	0	4.6
	103	7.8
	191	8.4
	203	9.6
	501	9.1
417	0	4.6
	200	6.05
	501	9.1
484	0	4.6
	200	6.3
	501	7.15

TABLE 2: Calculated Maximum Values for Second-Order Rate Constants for $SiH_2 + N_2$

T/K	k/cm^3 molecule^{-1} s^{-1}	E_a/kJ mol^{-1}
296	$<(3.0 \pm 0.6) \times 10^{-15}$	>29
417	$<(3.8 \pm 0.4) \times 10^{-15}$	>39
484	$<(2.6 \pm 0.5) \times 10^{-15}$	>47

A set of runs were carried out at 296 K in which N_2 pressures were varied up to ca. 500 Torr. Values for the decay constants are shown in Table 1. Similarly, two runs were carried out at each of 417 and 484 K. The results are also shown in Table 1. It is clear from these data that while the slight increases in decay constant values with N_2 pressure could indicate a direct reaction, they could also be accounted for by a reaction with impurities. Assuming this is not the case, the data of Table 1 may be used to calculate second-order rate constants, k, using the formula, $k = [k(c) - k_0]/c$, where c is the value of $[N_2]$. The values of k are shown in Table 2. Given the possibility of impurity effects, these represent upper limits to the true values. There are no obvious effects of temperature on these limits. Given the minimal indications of reaction even at the highest pressure of N_2 employed, there is no evidence of a pressure dependence effect either. Estimates of minimum activation energies are also shown in Table 2 (see Discussion).

Ab Initio Calculations. Possible species on the SiH_2N_2 surface were investigated in some detail at the G3 level of theory. Twelve potential products or product pairs have been identified. However, relative to the reactant species, only one species, the silylene−nitrogen ylid, has a lower enthalpy, although another species, 2-silacarbodiimide, has a zero enthalpy change. This was confirmed at the CBS-QB3 level. There is no silicon analogue to the relatively stable species, diazomethane, on the CH_2N_2 potential surface. This immediately tells us that stable products of the $SiH_2 + N_2$ reaction are unlikely to be found in practice. Nevertheless, we decided to explore in a limited way the connectivity between some of the species on this energy surface. From analogies with other π-type additions of silylene and also from the analogous methylene reaction surface we investigated the probable pathways for formation and decomposition of siladiazirine. The results from these calculations show that this species has a fairly high barrier to ring opening to diimidosilylene, but almost no barrier to ring opening to the silanitrogen ylid. Since the remaining species have no obvious access to the lowest energy part of the surface and are already higher in energy than the reactants, further

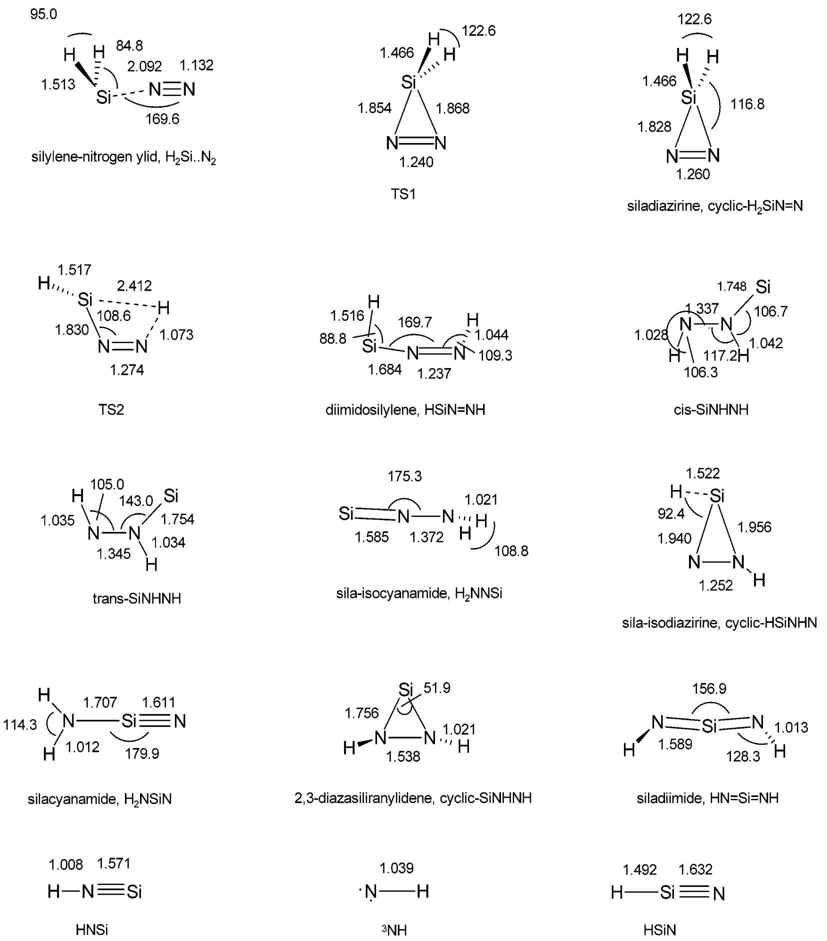


Figure 1. Ab initio (G3) calculated geometries of local minimum structures and two transition states on the SiH_2N_2 energy surface. Selected distances are given in angstroms and angles in degrees.

TABLE 3: Ab Initio Enthalpies of SiH_2N_2 Species from This (G3 Level) and Other Work

molecular species[a]	energy/hartree	relative energy/kJ mol^{-1}		
		this work	TG[b]	KTMSY[c]
$SiH_2 + N_2$	−399.934 427	0	0	0
$H_2Si\cdots N_2$	−399.944 241	−26	97	−14
TS1	−399.912 405	58		
cyclic-$H_2SiN{=}N$	−399.912 060	59	196	92
TS2	−399.875 964	153		
$HSiN{=}NH$	−399.897 596	97	234	143
cis-SiNHNH	−399.853 143	213		262
trans-SiNHNH	−399.854 058	211		254
$H_2NN{=}Si$	−399.927 221	19	656	48
cyclic-HSiNHN	−399.881 865	138		171
$H_2NSi{\equiv}N$	−399.901 750	86	225	101
cyclic-SiNHNH	−399.914 329	53	1316	116
$HN{=}Si{=}NH$	−399.934 366	0	192	78
HSiN + NH[d]	−399.669 584	521		
HNSi + NH[d]	−399.774 711	245		

[a] See Figure 1 for identification. [b] Reference 14 (MP3/6-31G*//3-21G level). [c] Reference 15 (MP4SDTQ/6-31G** level). [d] $^3\Sigma^-$ species (ground state).

exploration of the connectivity of these species was not pursued here (but see Appendix).

The structures of all species are shown in Figure 1 (Cartesian coordinates are listed in the Supporting Information), and their enthalpy values are listed in Table 3 as well as being represented on the potential energy (enthalpy) surface in Figure 2. Dotted lines in Figure 2 indicate possible (but not confirmed) rearrangement pathways.

Discussion

Kinetics. The results reported here represent the second investigation of the reaction of SiH_2 with molecular nitrogen. In the first, Chu et al.[10] studied the reaction in 5 Torr of He (total pressure) and found no reaction at 298 K ($k < 1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}). We have extended the pressure range up to 500 Torr of N_2, as well as explored the temperature dependence, and thereby set a substantially lower maximum value for k (at each of three temperatures). The lack of an observable decay attributable to the reaction under study shows that despite the general reactivity of silylene, nitrogen is inert to its presence. While this lack of reaction can obviously be related to the underlying potential energy surface (see below), it is important to consider the possible kinetic factors which could explain this result, even when an overall reaction is energetically possible. There are three of these.

(i) *The activation energy could be too high*. If we assume an A factor for the reaction, then lower limits for the activation energy, E_a, can be calculated. On the basis that A factors are usually high for SiH_2 reactions, we take the collision number value (2×10^{-10} cm^3 molecule^{-1} s^{-1}). This leads to the three values for E_a shown in Table 2. The highest of these, viz. 47 kJ mol^{-1}, obviously represents the best estimate of the lower limit for E_a.

(ii) *The equilibrium constant may be unfavorable*. If we assume the necessity of a 50% conversion of SiH_2 to product in order to be able to detect clear evidence of reaction, then (at 298 K) a value of $\Delta G° = -1.0$ kJ mol^{-1} is required. Assuming a value for $\Delta S°$ of -150 J K^{-1} mol^{-1} (derived from the

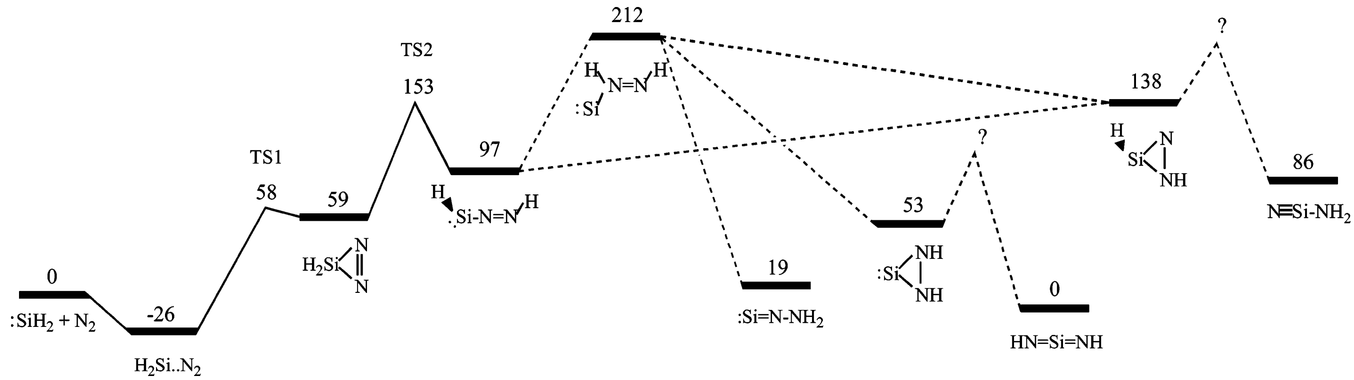


Figure 2. Potential energy (enthalpy) surface for the reaction of $SiH_2 + N_2$. All enthalpies (kJ mol^{-1}) are calculated at the ab inito G3 level.

parameters of the G3 calculations), this gives rise to a value of $\Delta H° = -46$ kJ mol^{-1}. This is the minimum (negative) value necessary for a reaction to be observed. The enthalpy requirement would be for even higher (negative) values at higher temperatures.

(iii) *The third-body stabilization requirement (pressure) may be too high.* The $SiH_2 + CO$ reaction,[7] very similar to the present system, was effectively in its third-order region of pressure dependence, although at pressures in the range 30−500 Torr it was readily amenable to study. Pressure dependences for such reactions may be calculated by RRKM theory, but the key parameter on which they depend is the binding energy of the complex. In the case of $SiH_2 + CO$ a value of $\Delta H°$ of ca. 90 kJ mol^{-1} corresponded to the best fit.[7] Although RRKM calculations have not been carried out on the present system, stabilization of an association complex would fail if the binding enthalpy were significantly less than this.

Thus, the kinetic observations would not rule out either an exothermic reaction with a sufficiently high barrier or an association reaction which formed a sufficiently weakly bound complex.

Ab Initio Calculations. The results obtained in this work are compared with those of previous calculations[14,15] in Table 3. These indicate a similar ordering of the stabilities for each study (relative to $SiH_2 + N_2$) with the higher level G3 calculations carried out here showing lower energies than both those of Kawauchi et al.[15] (MP4SDTQ/6-31G** level) and Thomson and Glidewell[14] (MP3/6-31G*//3-21G level). In agreement with Kawauchi et al.,[15] we have found the $SiH_2\cdots N_2$ ylid to be the only stable species, although our result shows it to be nearly twice as stable as they found. Nevertheless, with a binding enthalpy of only 26 kJ mol^{-1}, it is not stable enough to be formed experimentally under our conditions. In fact, using the thermodynamic approach described above, we calculate that at equilibrium (at 298 K) the conversion of initially formed SiH_2 would be only 0.025%! At higher temperatures it would be even less. Thus, the calculations confirm the observed lack of reaction.

Geometries of the SiH_2N_2 species found by G3 and shown in Figure 1 are generally very similar to those found earlier[15] and are not discussed in detail here. These calculations, however, do reveal some further points of interest which are described below.

(i) The structure of the ylid is interesting with its SiH_2 moiety virtually perpendicular to the $Si\cdots N{\equiv}N$ axis. This indicates clearly that it bears little relation to the planar (C_{2v}) CH_2N_2 analogue, diazomethane. In this respect the situation resembles that of the $SiH_2\cdots C{\equiv}O$ complex,[7] which has a similar structure to $SiH_2\cdots N{\equiv}N$ rather than to ketene (CH_2CO, planar, C_{2v}). The $SiH_2\cdots CO$ molecule, however, is bound by ca. 92 kJ mol^{-1} (G2 level),[7] considerably more than the ca. 26 kJ mol^{-1} (G3 level) found here for the $SiH_2\cdots N_2$ ylid. The comparison with the dissociation energies of CH_2N_2 and CH_2CO, which are significantly larger, is shown in Table 4. The principal difference between the SiH_2 and CH_2 analogues may be put down to the inability of Si to make effective π-bonds with either the N of N_2 or the C of CO. CH_2 and SiH_2 at least resemble one another in the sense that they bind more effectively with CO than N_2, a feature they have in common with most transition metals. Despite the weakness of the $H_2Si\cdots N_2$ ylid, it should be stable enough to be observed at low temperatures (in a matrix), especially bearing in mind that $Cl_2Si\cdots N_2$, which is bound by only 1.2 kJ mol^{-1}, has been observed at 10 K.[13]

TABLE 4: Comparison of Dissociation Enthalpies of MN_2 and MCO Molecules to $MH_2(^1A_1) + N_2(CO)$ (for M = Si, C)

molecular species	dissociation enthalpy/kJ mol^{-1}
$H_2Si\cdots N_2$	25^a
$H_2Si\cdots CO$	92^b
$H_2C{=}N_2$	143^c $(105)^e$
$H_2C{=}CO$	364^d $(326)^e$

[a] This work. [b] Reference 7. [c] Reference 22 and references cited therein. [d] Reference 23 and $\Delta H_f°(CH_2,^1A_1)^c$. [e] Value for dissociation to $CH_2(^3B_1)$.

(ii) Although the simplest cyclic adduct of $SiH_2 + N_2$, viz. siladiazirine, is thermodynamically unstable with respect to its dissociation products, we decided to investigate its kinetic stability. The motivation for this was that although diazirine, cyclo-CH_2N_2, is thermodynamically stable with respect to dissociation,[15,22,24,25] the difluoro derivative, cyclo-CF_2N_2, is not, but it is an isolable compound because it has a substantial energy barrier to decomposition.[25] Our calculation of the transition state, TS1, linking the ylid $SiH_2\cdots N_2$ with siladiazirine, indicates that it lies slightly below the actual molecular siladiazirine energy level. This is an artifact of the G3 calculation, since TS1 obeys the normal criterion of a transition state (at MP2=Full/6-31G-(d) and B3LYP/6-31G(d) levels). What it does signify is that the ring opening of siladiazirine back to the ylid isomer is effectively a barrierless process. The IRC calculation (using B3LYP/6-31G(d)) indicated, as expected, that TS1 connects the ylid with siladiazirine. However, it also revealed an unexpected energy plateau in the minimum-energy pathway. This is indicated in Figure 3, which also shows the geometry of the SiH_2N_2 species in this region. This species, which we call a "plateau species" (being neither a stable molecule nor a transition state), has the structure indicated in Figure 3 and most closely corresponds to a $\pi \rightarrow p$ complex (similar to that found on the $SiH_2 + C_2H_4$ surface[26]). Thus, after all and unlike cyclo-CF_2N_2, it seems that the siladiazirine molecule is too unstable kinetically ever to be made. The alternative rearrangement process to diimidosilylene, HSiN=NH, via TS2 has a substantial barrier of 94 kJ mol^{-1}.

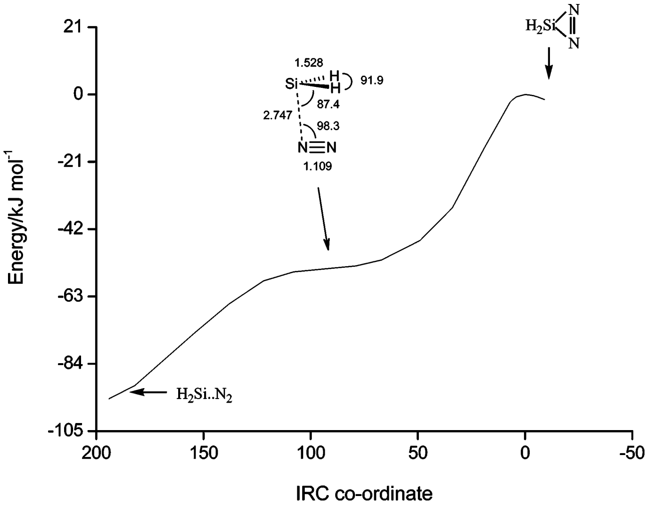
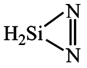
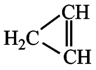
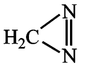
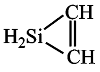


Figure 3. IRC profile for TS1. The IRC coordinate is a combination of Si···N_2 bond stretch and Si···N≡N angle bend.

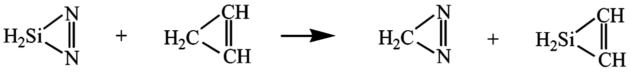
TABLE 5: Thermochemistry of Some Unsaturated Small Ring Compounds

Molecule	ΔH_f^o values/kJ mol^{-1}
	331[a]
	276[b]
	332[c], 255-276[d], 325[e]
	289[f], 272[g]

[a] This work. [b] Reference 29. [c] Reference 30. [d] Reference 24. [e] Reference 22. [f] Reference 31. [g] Reference 32.

The thermodynamic instability of siladiazirine contrasts with the weak stability of cyclic-SiN_2 (in other words, loss of H_2 stabilizes the SiNN ring), with a binding energy of 12 kJ mol^{-1}, found by Maier et al.[12] Si also forms a linear SiNN molecule ($^3\Sigma^-$ ground state). It appears that Si(^{3}P) binds more strongly with N_2 than does SiH_2.

These findings were somewhat surprising to us, in that it is well-known[27] that silicon bonds particularly strongly to electronegative elements. For example, single Si−N dissociation energies lie in the range 408−464 kJ mol^{-1},[27] rather greater than those of C−N bonds (303−355 kJ mol^{-1} [28]). A check as to whether the Si−N_d bonds of siladiazirine have any special strength (where N_d = double-bonded nitrogen) may be made through the thermochemistry of the following isodesmic reaction:



In this reaction ring strain enthalpies should approximately cancel, and the overall enthalpy difference, $\Delta H°$, is given by the following relationship:

$$\Delta H° = [2DH°(\mathrm{Si{-}N_d}) - 2DH°(\mathrm{Si{-}C_d})] - [2DH°(\mathrm{C{-}N_d}) - 2DH°(\mathrm{C{-}C_d})]$$

Although these dissociation enthalpies differ in magnitude, some cancellation is to be expected. The only obvious factor that could lead to a $\Delta H°$ value significantly different from zero would be the special effect of particularly strong Si−N_d bonds caused by electronegativity difference. In that case a positive value for $\Delta H°$ would be expected. The data for $\Delta H_f°$ for these compounds are shown in Table 5. The combination of these numbers leads to a value for $\Delta H°$ lying in the range −80 to +14 kJ mol^{-1}. Using the most recent (theoretical) value for $\Delta H_f°$(diazirine)[22] leads to −10 kJ mol^{-1}. Thus, despite some uncertainty, the value is not highly positive.[38] This result reveals no special strength for Si−N_d bonds unless there is some other factor playing an unexpected role.

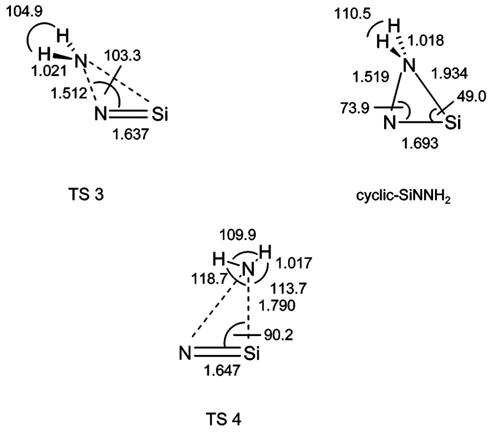


Figure 4. Ab initio (G3) calculated geometries of transition states and intermediates linking H_2NNSi and H_2NSiN.

TABLE 6: Ab Initio Enthalpies of SiH_2N_2 Species on the H_2NNSi to H_2NSiN Isomerization Pathway

molecular species[a]	energy/hartree	relative energy[b]/kJ mol^{-1}
TS3	−399.887 750	123
cyclic-$SiNNH_2$	−399.906 675	73
TS4	−399.863 545	186

[a] See Figure 4 for identification. [b] Relative to SiH_2 + N_2.

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Appendix. Isomerization of Silaisocyanamide to Silacyanamide

In carbon chemistry the isomerization of isocyanides to cyanides is one of the classic unimolecular reactions.[33] Its mechanism may be viewed either as a 1,2 group shift or as a head-to-tail rotation of the NC (to CN) group. We therefore thought that an example of a silicon analogue to this reaction would be worth reporting. This was accomplished as a brief extension to the current study by exploring the surface connecting silaisocyanamide (H_2NNSi) and silacyanamide (H_2NSiN). This ministudy, expected to reveal a single simple transition state, surprised us by producing a further stable species, cyclic-H_2NNSi, and two transition states, TS3 and TS4, connecting it to H_2NNSi and H_2NSiN, respectively. The energies for these species are shown in Table 6 and the structures in Figure 4. (Cartesian coordinates are listed in the Supporting Information.) The energy surface is shown in Figure 5. As has long been known, silaisocyanides are more stable than silacyanides (the reverse of their carbon analogues).[34,35] What was unexpected was a stable intermediate. (There is no intermediate

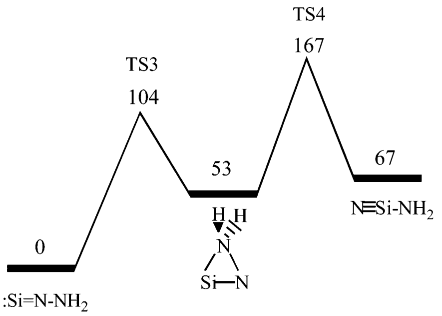

Figure 5. Potential energy (enthalpy) surface for the silaisocyanamide to silacyanamide interconversion at G3 level (enthalpies in kJ mol^{-1}).

in the isomerization of HNSi to HSiN.[36,37]) This is the fourth stable cyclic member of the SiH_2N_2 family which we have found. It appears to have one very long Si−N bond suggestive of a weak donor−acceptor interaction. However, unless there are other reaction channels open to it, it appears to exist in a substantial enough energy well to make its isolation possible.

Supporting Information Available: Tables of Cartesian coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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(38) As an addendum to the present study, we have used G3 to calculate a value for $\Delta H°$ for this reaction of -23 kJ mol^{-1}.