

Synthesis of the Silaisocynoacetylene Molecule

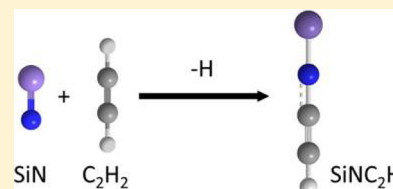
Dorian S. N. Parker,[†] Antony V. Wilson,[†] Ralf I. Kaiser,^{*,†} Tais Labrador,[‡] and Alexander M. Mebel^{*,‡}

[†]Department of Chemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822, United States

[‡]Department of Chemistry and Biochemistry, Florida International University, Miami, Florida 33199, United States

S Supporting Information

ABSTRACT: The hitherto elusive silaisocynoacetylene molecule (HCCNSi)—a member of the silaisocyanide family—has been synthesized for the first time through the reaction of the silicon nitride radical (SiN) with acetylene (C₂H₂) in the gas phase under single collision conditions. Compared to the isoelectronic reaction of the cyano radical (CN) with acetylene, the replacement of the carbon atom in the cyano group by an isovalent silicon atom has a pronounced effect on the reactivity. Whereas the silicon nitride radical was found to pass an entrance barrier and adds with the nitrogen atom to the acetylene molecule, the cyano radical adds barrierlessly with the carbon atom forming the HCCH(NSi) and HCCH(CN) intermediates, respectively. These structures undergo hydrogen loss to form the linear silaisocynoacetylene (HCCNSi) and cyanoacetylene molecules (HCCCN), respectively. Therefore, the isovalency of the silicon atom was found to bear little resemblance with the carbon atom having a dramatic effect not only on the reactivity, but also on the reaction mechanism, thermochemistry, and chemical bonding of the isoelectronic silaisocynoacetylene and cyanoacetylene products, effectively reversing the thermodynamical stability of the nitrile versus isonitrile and silanitrile versus isosilanitrile isomer pairs.



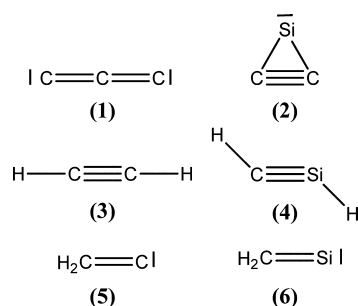
1. INTRODUCTION

The concept of isoelectronicity was introduced by Langmuir in 1919¹ and has been instrumental in advancing innovative synthetic chemistry, in developing modern concepts of chemical bonding, in understanding the reactivity of isoelectronic systems, and in rationalizing basic concepts of molecular structure.^{2–5} For almost a century particular attention has been devoted to comparing silicon chemistry with the analogous carbon chemistry. Residing in main group 14, both carbon and silicon have four valence electrons and hence are isovalent.⁶ Nevertheless, their chemical bonding can be quite distinct. For instance, the tricarbon molecule (C₃, 1) is linear and belongs to the *D*_{∞h} point group (Scheme 1); on the other hand, the isoelectronic silicon dicarbide molecule (2), where a single carbon is replaced by a silicon atom, has a C_{2v}-symmetric cyclic structure (c-SiC₂).⁷ The diverse chemical bonding of carbon and silicon is also reflected in a comparison of the C₂H₂ and

SiCH₂ systems. Whereas the linear acetylene molecule (H–C≡C–H, 3) represents the thermodynamically most stable C₂H₂ isomer with the vinylidene carbene structure (H₂C=C, 5) less stable by 186 kJ mol^{–1},⁸ the sequence of stability is reversed for the SiCH₂ isomers. Here, the silavinylidene molecule (H₂C=Si, 6) represents the global minimum and is thermodynamically favored by 151 kJ mol^{–1} compared to the bent isomer silaacetylene (HCSiH, 4).⁹ This can be contributed to the finding that silicon does not “like” to form triple bonds with the isovalent carbon atom.

However, although significant research has been conducted in comparing carbon–hydrogen-bearing molecules with their isoelectronic silicon-bearing species, a detailed comparison of the chemistries and bonding of carbon–hydrogen–nitrogen (CHN)-bearing molecules with isoelectronic species, in which a single carbon atom is replaced by a silicon atom, is still in its infancy. Here, both carbon and silicon form isoelectronic radicals with atomic nitrogen: the cyano radical (CN; X²Σ⁺) and the silicon nitride radical (SiN; X²Σ⁺) with bond energies of 435 and 372 kJ mol^{–1} and bond distances of 1.17 and 1.57 Å, respectively. From here, the chemical character of the silicon nitride and the cyano radicals starts to diverge. Despite the tetravalent characters of carbon and silicon, the higher electronegativity difference between nitrogen (3.04) and silicon (1.90) compared to nitrogen (3.04) and carbon (2.55) is reflected in a preferential localization of the unpaired electron at the nitrogen atom in the silicon nitride radical. Further, the refractory nature of silicon nitrides such as the Si₃N₄ parent compound has made investigations of gas phase reactions of the

Scheme 1. Structures of Isoelectronic Carbon-, Hydrogen-, and Silicon-Bearing Molecules

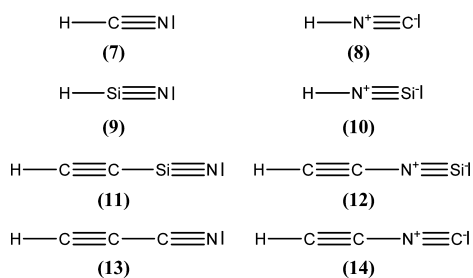


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diatomic silicon nitride radical (SiN ; $X^2\Sigma^+$) fraught with difficulties with studies limited largely to theoretical examinations.^{10–12} In contrast, the simplest closed-shell carbon- and nitrogen-bearing molecule, i.e., cyanogen C_2N_2 , exists as a gas at room temperature. Also, reactions of the isoelectronic cyano radicals (CN ; $X^2\Sigma^+$) with simple hydrocarbons like acetylene have been extensively studied theoretically and experimentally utilizing the crossed molecular beam approach.^{13,14} Under single collision conditions, these bimolecular gas phase reactions lead to the formation of nitriles (RCN), i.e., organic molecules carrying the cyano group (CN), which is connected with its carbon atom to the organic group R ; the corresponding isonitrile isomers (RNC) were not synthesized under bimolecular collisions in the gas phase. On the other hand, no experimental study has been conducted on the synthesis of the silicon analogous molecules, i.e., silanitriles (RSiN) and silaisonitriles (RNSi). Schaefer et al. investigated the relative stabilities of their simplest representatives (HSiN and HNSi).¹⁵ Whereas for the isoelectronic HCN – HNC isomer pair, hydrogen cyanide (HCN , **7**) is more stable by 63 kJ mol^{-1} than the hydrogen isocyanide molecule (HNC , **8**),¹⁶ the trend is clearly reversed, when a carbon atom is replaced by the isovalent silicon atom. The silaisocyanide (HNSi , **10**) was computed to be thermodynamically favored by 271 kJ mol^{-1} compared to the silahydrogencyanide isomer (HSiN , **9**). Considering organic silanitriles and silaisonitriles, a single theoretical study¹² suggested that the silaisocynoacetylene (HCCNSi , **12**) should be more stable by 230 kJ mol^{-1} compared to the silacyanoacetylene (HCCSiN , **11**), i.e., the corresponding silicon-analogous molecules of cyanoacetylene (HCCCN , **13**) and isocyanoacetylene (HCCNC , **14**, Scheme 2). Nevertheless, the synthesis of any silanitrile or silaisonitrile has remained elusive so far.

Scheme 2. Structures of Nitriles, Isonitriles, and Their Sila-Analogous Compounds ($\text{R} = \text{H}, \text{CCH}$)



Here, we report on the first synthesis of the hitherto elusive silaisocynoacetylene (HCCNSi) molecule under single collision conditions in the gas phase by reacting silicon nitride radicals (SiN) with acetylene (HCCH) utilizing the crossed molecular beam method.¹⁷ The latter presents a powerful experimental technique to conduct chemical reactions in the gas phase and to observe the outcome of the reaction of a single silicon nitride radical with only one acetylene molecule, and to form highly reactive molecules in the gas phase, which are difficult to synthesize by classical organic chemistry. This is done here to identify the first member of the silaisocyanide family: the silaisocynoacetylene molecule.

2. EXPERIMENTAL SECTION

The reaction between the silicon nitride radical (SiN ; $X^2\Sigma^+$) and acetylene (C_2H_2 ; $X^1\Sigma_g^+$) was conducted in the gas phase at the

molecular level under single collision conditions utilizing a crossed molecular beam machine.¹⁷ A pulsed, supersonic beam of silicon nitride was prepared *in situ* by laser ablation of a silicon rod at 266 nm ¹⁸ and subsequently entraining the ablated silicon atoms in nitrous oxide (N_2O , 99.99%; Matheson) gas. The nitrous oxide acted as a seeding and a reactant gas most likely forming the silicon nitride radical via nitrogen abstraction by atomic silicon from nitrous oxide; no other silicon–nitrogen-bearing molecules were present in our beam. Note that the silicon nitride radicals are expected to be in their ground electronic state ($X^2\Sigma^+$); the first excited state ($A^2\Pi$) is located about 24 kJ mol^{-1} higher than the ground state.¹⁹ Based on the excited-state lifetimes of the isoelectronic boron monoxide $\text{BO}(A^2\Pi)$ ²⁰ and cyano $\text{CN}(A^2\Pi)$ ²¹ species, of about 2 and 11 μs , respectively, the $A^2\Pi$ state of silicon nitride is expected to hold a lifetime shorter than the traveling time of the silicon nitride radicals from the ablation center to the interaction region of the scattering chamber, which is about 20 μs . The silicon nitride beam perpendicularly intersected a supersonic beam of pure acetylene gas (C_2H_2 ; 99.99%; Matheson) in the scattering chamber at a collision energy of $35.7 \pm 3.5 \text{ kJ mol}^{-1}$. The reaction products were monitored by a rotatable quadrupole mass spectrometer after electron impact ionization of the neutral products at 80 eV in an ultra-high-vacuum chamber. The velocity distributions of the products were collected through the angular-resolved time-of-flight (TOF) technique, that is, recording the arrival time of ions at well-defined mass-to-charge ratios (m/z) of the ionized products, at different scattering angles (Figure 1).¹⁷ The TOF spectra at each angle were then integrated to obtain the laboratory angular distribution.

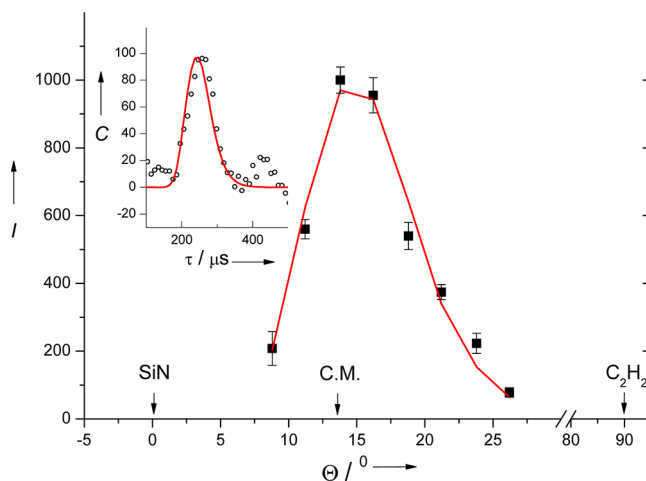


Figure 1. Laboratory angular distribution at $m/z = 67$ of the C_2HSiN product from the reaction of the silicon nitride radical with acetylene; the direction of the silicon nitride radical beam is defined as 0° , that of the acetylene beam as 90° . The solid line represents the angular distribution obtained from the best-fit center-of-mass angular and translational energy distributions, the black squares represent the experimental data (I , integrated counts; Θ , laboratory angle; τ , time-of-flight; C , counts). The time-of-flight spectrum recorded at the center-of-mass angle is shown as an inset (open circles, experimental data; solid line, best fit from the center-of-mass functions).

The TOF spectra were collected at $m/z = 67$ (SiNC_2H), which corresponds to the formation of a species with the molecular formula SiNC_2H . Our objective is not only to assign the chemical formula of the reaction product, but also to rationalize the chemical structure and the underlying reaction mechanism involved in the formation of this novel organo-silicon molecule. To complete these goals, it is vital to extract information on the chemical dynamics from the experimental data. This is accomplished by exploiting a forward convolution fitting technique to simulate the laboratory data (TOF spectra, laboratory angular distribution) of the SiNC_2H product at $m/z = 67$. This approach produces two “best-fit” functions: the center-of-mass

translational energy flux distribution $P(E_T)$ and the angular flux distribution $T(\theta)$ (Figure 2).²²

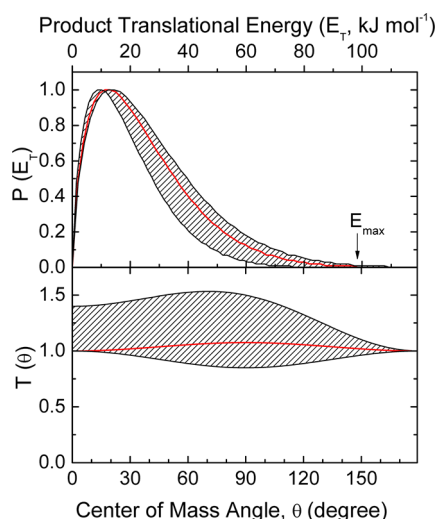


Figure 2. Best-fit center-of-mass angular ($T(\theta)$, lower) and translational energy ($P(E_T)$, upper) flux distributions of the reaction of the silicon nitride radical with acetylene to form the silaisocynoacetylene (HCCNSi) molecule plus atomic hydrogen. The red lines are the best fits; the shaded areas delimit the acceptable upper and lower error limits. E_{\max} indicates the maximum translational energy.

3. RESULTS AND DISCUSSION

Considering the center-of-mass translational energy flux distribution, $P(E_T)$, the maximum translational energy ($E_{\max} = 90 \pm 20 \text{ kJ mol}^{-1}$) of the products helps to identify the nature of the SiNC₂H isomer. For molecules born without rovibrational excitation, E_{\max} represents the sum of the reaction exoergicity plus the collision energy. Therefore, if we subtract the latter from E_{\max} , the reaction to form SiNC₂H plus atomic hydrogen is exoergic by $54 \pm 22 \text{ kJ mol}^{-1}$. The SiNC₂H isomer formed can be elucidated by comparing the experimentally determined reaction exoergicity with the theoretical energetics

obtained from electronic structure computations for distinct SiNC₂H isomers. Here, geometries of various species involved in the reaction were optimized at the hybrid density functional B3LYP level^{23,24} with the 6-311G** basis set and vibrational frequencies were calculated using the same B3LYP/6-311G** method. Two transition states, for the initial silicon nitride addition to acetylene by the nitrogen end and the hydrogen atom loss from H₂CCNSi, do not exist at the B3LYP level of theory, but were located using higher level quadratic configuration interaction²⁵ QCISD/6-311G** calculations. For these TSs, vibrational frequencies were also computed at the QCISD/6-311G** level. Relative energies were then refined employing the coupled cluster CCSD(T) method^{26–28} with Dunning's correlation-consistent cc-pVDZ, cc-pVTZ, cc-pVQZ, and cc-pVSZ basis sets.^{29,20} The total CCSD(T) energies were extrapolated to the complete basis set (CBS) limit by fitting the following equation,³⁰ $E_{\text{tot}}(x) = E_{\text{tot}}(\infty) + B e^{-Cx}$, where x is the cardinal number of the basis set (2, 3, 4, and 5 for cc-pVDZ, cc-pVTZ, cc-pVQZ, and cc-pVSZ, respectively) and $E_{\text{tot}}(\infty)$ is the CCSD(T)/CBS total energy. Spin-restricted coupled cluster RCCSD(T) calculations were used for open-shell structures. All ab initio and density functional calculations were performed using the GAUSSIAN-09³¹ and MOLPRO 2010³² program packages. The CCSD(T)/CBS + ZPE(B3LYP/6-311G** or QCISD/6-311G**) relative energies are expected to be accurate within $\pm 5 \text{ kJ mol}^{-1}$.

At the CCSD(T)/CBS level of theory, the calculations suggest the existence of two SiNC₂H isomers in the singlet ground states: the linear HCCNSi and the HCCSiN structures. These represent the silaisocynoacetylene and silacyanoacetylene molecules, respectively (Figure 3). The computations indicate further that silaisocynoacetylene (HCCNSi) is more stable by 226 kJ mol^{-1} compared to the silacyanoacetylene (HCCSiN) isomer. The preferential stability of silaisocynoacetylene compared to silacyanoacetylene correlates nicely with a previous computational study by Schaefer et al. on the silahydrogencyanide (HSiN)–silaisohydrogencyanide (HNSi) system, which suggested that the latter is thermodynamically favored by 270 kJ mol^{-1} .¹⁵ Our calculations suggest further that the reaction to form silaisocynoacetylene plus atomic

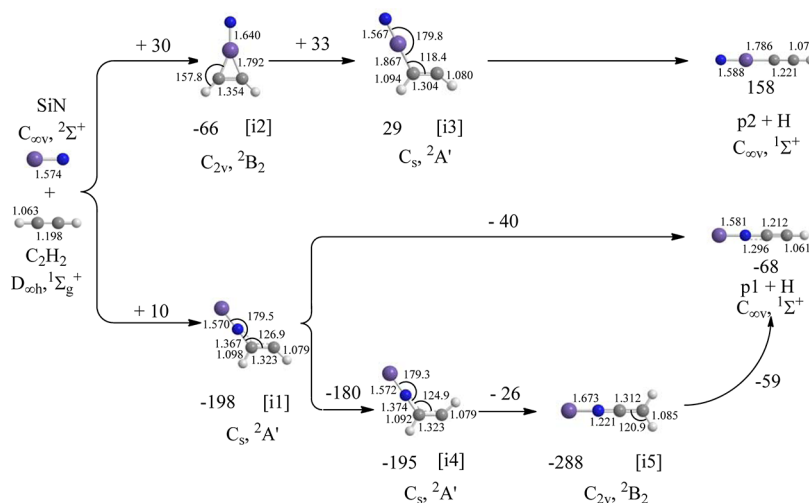


Figure 3. Schematic representation of the potential energy surface of the reaction of the silicon nitride radicals with acetylene. Energies calculated at the CCSD(T)/CBS level are shown in kJ mol^{-1} and are relative to the energy of the separated reactants. The point groups of the reactants, intermediates, and products are also shown as are the symmetries of their electronic wave functions. The geometries of the transition states, reactants, intermediates, and products are compiled in the Supporting Information.

hydrogen is exoergic by 68 kJ mol^{-1} ; these data agree very well with the experimentally determined reaction exoergic of $54 \pm 22 \text{ kJ mol}^{-1}$. The silacyanoacetylene (HCCSiN) isomer is energetically not accessible under single collision conditions; the computed reaction endoergic of 158 kJ mol^{-1} could not be compensated by the collision energy of about 36 kJ mol^{-1} . Therefore, we can conclude that the silaisocynoacetylene (HCCNSi) is the sole reaction product formed at $m/z = 67$. Note that if the first excited state of the SiN radical ($A^2\Pi$) reacts with acetylene, the reaction would occur on the first excited surface. We calculated three possible structures of this molecule in the first excited triplet state, linear SiNC_2H ($C_{\infty v}$, $^3\Sigma^-$), bent NSiC_2H (C_s , $^3A'$), and cyclic NSiC_2H (C_s , $^3A'$). However, the calculations show that these products reside 185, 267, and 374 kJ mol^{-1} higher in energy than the reactants, respectively, and thus cannot be formed in the present experiment. Therefore, we can conclude that our experiments synthesized and observed for the first time a molecule of the hitherto elusive silaisocyanide family.

Finally, we would like to untangle the reaction mechanism forming the silaisocynoacetylene (HCCNSi). For this, we inspect the angular flux distribution $T(\theta)$. Here, the center-of-mass function depicts flux over the complete scattering range from 0° to 180° ; this is indicative of an indirect reaction mechanism and the formation of a reaction intermediate of the chemical formula $\text{C}_2\text{H}_2\text{NSi}$ in the reaction of the silicon nitride radical with acetylene.³³ Further, the “best fit” depicts a symmetric profile around 90° (Figure 2); this finding indicates that the lifetime of the reaction intermediate, i.e., a $\text{C}_2\text{H}_2\text{NSi}$ isomer, which decomposes to the silaisocynoacetylene (HCCNSi) via an atomic hydrogen elimination, is longer than its rotational period. The center-of-mass translational energy distribution provides important additional information on the reaction mechanisms leading to silaisocynoacetylene (HCCNSi). Here, the center-of-mass translational energy distribution shows a distribution maximum of $7\text{--}21 \text{ kJ mol}^{-1}$; this maximum suggests the existence of an exit barrier and a tight transition state, when the hydrogen atom is leaving the decomposing $\text{C}_2\text{H}_2\text{NSi}$ intermediate to yield the silaisocynoacetylene (HCCNSi) product.³³ This also suggests a significant geometry and electron density rearrangement from the fragmenting $\text{C}_2\text{H}_2\text{NSi}$ species to the final products. Considering the concept of microscopic reversibility,³⁴ in the case of the reversed reaction of an addition of a hydrogen atom to the silaisocynoacetylene (HCCNSi), an entrance barrier to addition of this order of magnitude is expected. Considering that the hydrogen atom adds to a closed shell molecule, the existence of an entrance barrier is reasonable. For instance, entrance barriers of an addition of atomic hydrogen to a carbon–carbon triple and double bond in acetylene and ethylene have been documented to be 18 and 12 kJ mol^{-1} , respectively.³⁵

We would like to combine now these findings with electronic structure calculations and propose the structure of the reaction intermediate(s) and the inherent reaction mechanism(s) to synthesize the silaisocynoacetylene (HCCNSi) molecule in the gas phase as a result of a bimolecular collision between the silicon nitride radical and acetylene. Our computations indicate that the silicon nitride radical interacts with the carbon–carbon triple bond of the acetylene molecule and adds either to a single carbon atom or to two carbon atoms via its nitrogen or silicon atom, respectively, to yield intermediates [i1] and [i2], respectively. These pathways are associated with entrance

barriers of 10 and 30 kJ mol^{-1} , respectively. Considering our collision energy of about 36 kJ mol^{-1} , both entrance channels are open. However, the cyclic intermediate [i2] can only ring-open to [i3]; a hydrogen loss from the latter can only form the silacyanoacetylene (HCCNSi) molecule; recall that based on the overall endoergic of the reaction ($+158 \text{ kJ mol}^{-1}$), the formation of silacyanoacetylene (HCCSiN) is closed. Therefore, if formed, the intermediates [i2] and [i3] will eventually decompose back to the reactants, and the addition of the silicon nitride with its silicon atom to acetylene—although energetically feasibly—de facto results in “recycling” of the reactants. On the other hand, the acyclic intermediate [i1] formed via addition of the silicon nitride radical with its nitrogen atom to the acetylenic carbon atom resides in a deep potential energy well located 198 kJ mol^{-1} below the energy of the separated reactants. This intermediate can either decompose via atomic hydrogen loss through a tight exit transition state located 28 kJ mol^{-1} above the final products to form silaisocynoacetylene (HCCNSi). Alternatively, this molecule can be formed from [i1] via trans–cis isomerization to [i4], hydrogen shift to [i5], and decomposition of the latter via a tight exit transition state located 9 kJ mol^{-1} above the final products. Consequently, both experiments and theoretical calculations correlate nicely. In summary, the silicon nitride radical reacts with acetylene via an indirect reaction mechanism via addition with its nitrogen atom through a barrier of only 10 kJ mol^{-1} to the π electron density at one carbon atom of acetylene forming a $\text{C}_2\text{H}_2\text{NSi}$ intermediate [i1]. The latter either fragments by hydrogen loss to the silaisocynoacetylene (HCCNSi) or—after isomerization—rearranges via [i4] to [i5], which eventually undergoes unimolecular decomposition to silaisocynoacetylene (HCCNSi). Both channels form silaisocynoacetylene (HCCNSi) via tight transition states.

It is fascinating to compare the reaction mechanism of the silicon nitride radical (SiN ; $X^2\Sigma^+$) plus acetylene with the isoelectronic reaction between the cyano radical (CN ; $X^2\Sigma^+$) and acetylene studied earlier in our group.¹³ Here, the reaction was suggested to proceed indirectly via a barrier-less addition of the cyano radical with its carbon atom to one carbon atom of the acetylene molecule forming the $\text{HCCH}(\text{CN})$ intermediate. The latter emits a hydrogen atom through a tight exit transition state forming the cyanoacetylene molecule (HCCCN). Alternatively, the initial reaction intermediate undergoes a hydrogen migration to H_2CCCN prior to the decomposition of the latter via a tight exit transition state yielding also cyanoacetylene (HCCCN). No isocynoacetylene isomer (HCCNC), which is less stable by 107 kJ mol^{-1} compared to the cyanoacetylene molecule (HCCCN), was formed.

Consequently, the substitution of a tetravalent carbon atom by an isoelectronic silicon atom in the cyano radical has a profound effect on the reactivity of the silicon nitride radical and on the stability of the products. A comparison of the reactivity of the cyano (CN ; $X^2\Sigma^+$) and the silicon nitride radical (SiN ; $X^2\Sigma^+$) with acetylene indicates that a replacement of the carbon by a silicon atom shifts the product spectrum from a cyanoacetylene molecule (HCCCN) to a silaisocynoacetylene molecule (HCCNSi). Both reactions follow an indirect mechanism and are initiated by addition of the radical to the acetylene molecule, but the addition side switches from the carbon atom in the cyano radical to the nitrogen atom in the silicon nitride radical. Further, the addition of the cyano radical has no entrance barrier, whereas a barrier of 10 kJ mol^{-1} was computed for the silicon nitride addition. Therefore, we can

conclude that the reactivity of the silicon nitride radical cannot be simply derived from the reactivity of its isoelectronic system, i.e. the cyano radical. Fundamental differences in the chemical reactivity between the silicon nitride radical and the cyano radical exists, which leads not only to an intense change in the product spectrum, but also in an inversed stability of the silaisocynoacetylene (HCCNSi)–silacyanoacetylene (HCCSiN) versus isocynoacetylene (HCCNC)–cyanoacetylene (HCCCN) isomer pairs.

4. CONCLUSIONS

In summary, our study ascertained for the first time the formation of a representative of the hitherto elusive silaisonitrile family—here silaisocynoacetylene (HCCNSi)—in the gas phase as a result of a bimolecular reaction of a silicon nitride radical with acetylene. This versatile protocol of a reaction of a silicon nitride radical with an unsaturated hydrocarbon opens up an unconventional path to access the previously obscure class of silaisonitrile molecules. By an intelligent combination of crossed molecular beam experiments and electronic structure calculations, this will help to further understand the chemical reactivity and molecular structures in the silaisonitrile family. Although the isoelectronicity with the reactions of the cyano radicals represents itself in similar dynamical behavior (addition reaction, indirect scattering dynamics via complex formation), the dissimilarity in chemical reactivity of the isoelectronic cyano and silicon nitride radicals are expected to be quite pronounced. It is clear that further experimental and theoretical studies of these systems under single collision conditions are warranted to fully expose the unique reactivity of the silicon nitride radicals and the formation of the new class of silaisonitrile molecules.

■ ASSOCIATED CONTENT

Supporting Information

All molecular structures and their rotational constants, Cartesian coordinates, and calculated vibrational frequencies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

ralfk@hawaii.edu; mebela@fiu.edu

Notes

The authors declare no competing financial interest.

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