**Directed Gas-Phase Formation of Aminosilylene (HSiNH2; X1A') - the Simplest Silicon Analogue of an Aminocarbene - under Single-Collision Conditions**

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**ABSTRACT**

The aminosilylene molecule (HSiNH2, X1A') - the simplest representative of an unsaturated nitrogen-silylene - has been formed under single collision conditions via the gas phase elementary reaction involving the silylidyne radical (SiH) and ammonia (NH3). The reaction is initiated by the barrierless addition of the silylidyne radical to the non-bonding electron pair of nitrogen forming an HSiNH3 collision complex, which then undergoes unimolecular decomposition to aminosilylene (HSiNH2) via atomic hydrogen loss from the nitrogen atom. Compared to the isovalent aminomethylene carbene (HCNH2, X1A'), by replacing a single carbon atom with silicon, a profound effect on the stability and chemical bonding of the isovalent methanimine (H2CNH) – amino­methylene (HNCH2) and aminosilylene (HSiNH2) - silan­imine (H2SiNH) isomer pairs is shown, i.e., thermodynamical stabilities of the carbene versus silylene are reversed by 220 kJ mol-1. Hence, the isovalency of the main group XIV element silicon was found to exhibit little similarities with the atomic carbon revealing a remarkable effect not only on the reactivity, but also on the thermochemistry and chemical bonding.

**1. INTRODUCTION**

   In recent decades, the similarities and disparities between the carbon chemistries and the silicon chemistries have intrigued chemists with special attention devoted to the formation, chemical bonding, and electronic structure of carbenes (CRR’) versus silylenes (SiRR’) with R and R’ representing (organic) substituents or hydrogen atoms.[1](#_ENREF_1),[2](#_ENREF_2) Carbenes are defined by a divalent carbon atom plus two unshared electrons resulting in an electron deficient, six-electron valance shell.[3](#_ENREF_3),[4](#_ENREF_4) The simplest carbene – methylene (CH2) - holds a triplet 3B1 electronic ground state, and its first excited singlet state 1A1 is higher by about 38 kJ mol-1.[5](#_ENREF_5),[6](#_ENREF_6) Triplet carbenes have two unpaired electrons, whereas singlet carbenes are spin-paired and are characterized by a sp2 hybridization of the carbon atom. With the exception of, for instance, the linear pentadiynylidene (HCCCCCH; X3Σg−),[7](#_ENREF_7) most carbenes have a bent triplet ground state unless when bonded to a nitrogen, oxygen, sulfur, and/or halogen substituents. The latter donate an elec­­tron pair to the carbon atom empty p orbital at the carbene center thus stabilizing the singlet ground state. The singlet state will become the ground state if the energy is sufficiently reduced by the interaction of a non-bonding electron pair with the carbon atom empty p orbital.[1](#_ENREF_1),[8](#_ENREF_8) Overall, the electron sextet along with the coordinative unsaturation classifies gas phase car­be­nes as highly reactive transient species.[9](#_ENREF_9) However, the first report of an isolatable (phosphi­no)carbene [λ3-phosphinocarbene-λ5-phosphaacetylene] by Bertrand *et al*.[10](#_ENREF_10) and of a stable *N*-heterocyclic carbene (NHC) [1,3-di(adamantyl)imidazol-2-ylidene] by Ardu­engo *et al.*[11](#_ENREF_11) revoluti­o­nized the preparation of acyclic and N-heterocyclic car­be­nes with critical implications to meta­thesis catalysis and organo catalysis.[12-14](#_ENREF_12)

     The isovalent silylenes can be formally derived from the silylene stem compound (SiH2) by replacing the hydrogen atom(s) by substituents.[15](#_ENREF_15) Unlike carbenes, which do exist in triplet *and* singlet ground states, silylene derivatives hold exclusively singlet ground states with a lone (non-bonding) electron pair and empty 3p orbital centered at the silicon atom.[16](#_ENREF_16) The electronic structure of silylene is characterized by sp2 hybridization on the silicon atom.[17](#_ENREF_17) Like carbe­nes, free gas phase silylenes have been classified as highly reactive and short-lived intermediates [2](#_ENREF_2) until West and co-workers reported the first *N*-heterocyclic silylene (NHSi) – the isovalent class of *N*-heterocyclic carbene (NHC) – 1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazasilol-2-ylidene stable at ambient temperature.[18](#_ENREF_18) This work stimulated extensive research into room temperature stable *N*-heterocyclic silylenes through the exploitation of the concept of kinetic stabilization through sterically hindered substituents like bulky alkyl groups at the nitrogen atom in the ring along with electronic stabilization through nitrogen lone pair π-donation into the empty 3p orbital at the divalent silicon.[19](#_ENREF_19) Recently, stable acyclic silylenes were synthesized by Rekken *et al*. with a S-Si-S angle of 90.52o along with a HOMO-LUMO gap of 411 kJ mol-1 and by Protchenko *et al.* with a HOMO-LUMO gap of 197 kJ mol-1 together with a B-Si-N angle of 109.7 o.[20](#_ENREF_20),[21](#_ENREF_21)

However, despite the impressive progress in preparing stable acyclic and *N*-heterocyclic silylenes, little atten­tion was devoted to the directed gas phase formation and characterization of the simplest unsaturated nitrogen-silylene amino­silylene (HSiNH2; 1A'). Amino­silylene has previously been detected using argon matrix at 12 K after photolysis of silyl azide (H3SiN3)[22](#_ENREF_22) and mixing ablated silicon atoms with ammonia;[23](#_ENREF_23) the mechanism involving the formation of aminosilylene was proposed by Beach *et al.* via laser induced photochemistry of silane (SiH4) − ammonia (NH3) mixtures.[24](#_ENREF_24) In 2010, rotational spectra of amino­silylene were preliminarily studied within the discharge of silane − ammonia mixtures.[25](#_ENREF_25) Since a unified picture of the underlying gas phase chemistry and chemical bonding of the isovalent imines and aminocarbenes such as methanimine (H2CNH; 1A') and aminomethylene (HCNH2; 1A') is beginning to emerge,[26-29](#_ENREF_26) as the silicon isovalent counterpart of an aminocarbene, free gas phase aminosilylene (HSiNH2; 1A') represent the simplest, but least explored representative of a key class of silicon-bearing reactive intermediates due to its high reactivity and inherent short lifetime. Here, we provide an exceptional peek into the elusive gas phase formation of aminosilylene (HSiNH2; 1A') – the simplest silicon analogues of aminocarbene – via the elementary reaction of the D1-silylidyne radical (SiD; *X*2Π) with D3-ammonia (ND3; *X*1A1) and ammonia (NH3; *X*1A1)under single collision conditionsexploiting crossed molecular beam experiments merged with electronic structure calculations. The studies are conducted at the most microscopic and fundamental level, shedding light on the underlying reaction mechanisms leading to a clean gas phase formation of the simplest aminosilylene *without* successive reactions thus providing new insights on the underlying reaction dynamics of one of the most elusive representatives of a rather obscure class of highly reactive silylenes: aminosilylene (HSiNH2; 1A').

**2. RESULTS**

**2.1 LABORATORY FRAME**

      Considering the inherent background of 12CO2+ and 13CO2+ in the detector, data at m/z = 44 and 45 cannot be detected. To explore both atomic deuterium and molecular deuterium loss channels, fully deuterated reactants (SiD-ND3) are employed first. For the SiD (30 amu) - ND3 (20 amu) reaction, reactive scattering signal was observed at m/z = 48 (28SiND3+, 30SiND2+) and 46 (28SiND2+, 30SiND+) with signal at m/z = 46 accumulated at a 37 ± 3 % level compared to m/z = 48. Considering the silicon natural isotope abundaces (28Si (92.2 %), 29Si (4.7%), 30Si (3.1%)) and that the time-of-flight (TOF) spectra of m/z = 48 and 46 are identical after scaling, we conclude that a single reaction channel exists in the experiment, i.e., the reaction of D1-silylidyne (SiD, 30 amu) with D3-ammonia (ND3, 20 amu) forming SiND3 (48 amu) along with atomic deuterium (D, 2 amu) (reaction (1)). The signal at m/z = 46 originates from dissociative electron impact ionization of parent SiND3 product in the ionizer, but due to the overlapping TOFs at m/z = 48 and 46 not from the molecular deuterium loss (reaction (2)). No ion counts were detected at m/z = 50 (28SiND4+, 30SiND3+) and 49 (29SiND3+); these findings suggest that no 28SiND4 adducts survive the flight time of 411 µs from the collision center to the ionization region of the detector and that neither 29Si- nor 30Si-substituted SiND3 isotopologues were formed in sufficient high yields to be detected under our experimental conditions. Consequently, the laboratory data alone reveal that SiND3 isomer(s) are formed via the elementary reaction of the D1-silylidyne with D3-ammonia through the D1-silylidyne versus atomic deuterium exchange pathway (reaction (1)). The angular resolved TOF spectra were then accumulated at m/z = 48 and scaled to the TOF recorded at the center-of-mass angle to yield the laboratory angular distribution (LAD). The latter distribution spreads 35o within the scattering plane and shows a maximum at the CM angle (Figure 1). The nearly forward-backward symmetry with regard to the CM angle of the distribution suggests indirect reaction dynamics involving SiND4 reaction intermediate(s).[30](#_ENREF_30) It is important to stress that the quadrupole mass spectrometer works in time of flight mode, i.e. this device records the flight time of a product molecule at a well-defined mass-to-charge ratio from the interaction region to the electron impact ionizer; our instrument does not record classical mass spectra of the formed products.

1. SiD + ND3 → SiND3 (48 amu) + D (2 amu)
2. SiD + ND3 → SiND2 (46 amu) + D2 (4 amu)

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**Figure 1**. Laboratory angular distribution (a, c) and TOF spectra (b, d) for the reaction of the D1-silylidyne radical with D3-ammonia (data collected at m/z = 48 (a, b)) and with ammonia (data collected at m/z = 46 (c, d)). The solid circles define the experimental distribution; the open circles represent the experimental data; the red lines depict the best fits. Colors of the atoms: nitrogen, blue; silicon, purple; hydrogen, white and deuterium, light blue.

In fully deuterated SiD-ND3 reaction, atomic deuterium can be emitted from the D1-silylidyne and/or from D3-ammonia reactant(s). For more information, the reaction of D1-silylidyne (SiD, 20 amu) with ammonia (NH3, 17 amu) was also explored (Figure 1; reactions (3) and (4)). Signal at m/z = 46 should originate from the hydrogen atom loss from the ammonia reactant (reaction (3)); two loss channels can contribute to signal at m/z = 45: atomic deuterium loss from the D1-silylidyne reactant in reaction (4) and dissociative electron impact ionization of the hydrogen atom loss product (SiNDH2) of reaction (3). In the experiment, scattering signal was observed at m/z = 46; background interference from 13CO2+ (m/z = 45) prevented detection of reaction (4). Therefore, in the SiD-NH3 reaction, the hydrogen atom originated at least from the ammonia reactant leading to SiNDH2. Similar to the D1-silylidyne – D3-ammonia system, the resulting LAD for the D1-silylidyne – ammonia system is also forward-backward symmetric with regard to the CM angle; compared to the ejected deuterium atom (reaction (1)), the lighter hydrogen atom (reaction (3) leads to the narrower LAD distribution for the D1-silylidyne – ammonia reaction (spans only 30o within the scattering plane).

(3) SiD + NH3 → SiNDH2 (46 amu) + H (1 amu)

(4) SiD + NH3 → SiNH3 (45 amu) + D (2 amu)

**2.2 CENTER-OF-MASS FRAME**

      To elucidate the nature of the SiND3 and SiNDH2 isomers formed via the atomic deuterium and hydrogen losses, respectively, the laboratory data were transformed into CM reference frame. This procedure yields two distributions, i.e., the CM translational energy *P(E*T*)* and angular *T(θ)* flux distribution.[31](#_ENREF_31),[32](#_ENREF_32) In both systems, the laboratory data could be fit with a single channel, i.e., D loss channel (SiND3 (48 amu) plus D (2 amu); reaction (1)) and H loss channel (SiNDH2 (46 amu) plus H (1 amu); reaction (3)) (Figure 2). In detail, for products formed without internal excitation, considering the law of energy conservation, the maximum translational energy (Emax) of 14 ± 6 kJ mol-1 and 18 ± 6 kJ mol-1, which can be derived from the*P(E*T*)*,represents the sum of the reaction exoergicity and the collision energy (15.9 ± 0.4 kJ mol-1; 14.9 ± 0.4 kJ mol-1). This suggests that the SiD-ND3 and SiD-NH3 reactions are essentially thermo neutral within the error limits (2 ± 6 kJ mol-1; -3 ± 6 kJ mol-1).

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**Figure 2**. Center-of-Mass translational energy (a, d), angular flux distributions (b, e) and the corresponding flux contour map (c, f) for the reaction of D1-silylidyne with D3-ammonia (data collected at m/z = 48 (a, b, c)) and with ammonia (data colleced at m/z = 46 (d, e, f)). The red lines represent the best-fit; shaded areas depictthe error limits of the best fits.

Further, the *P(E*T*)* distribution peak at 9 ± 3 kJ mol-1 and 8 ± 2 kJ mol-1 suggesting rather loose exit transition states together with simple bond rupture processes forming upon decomposition of the reaction intermediates via atomic deuterium and hydrogen loss, respectively. Finally, in both systems, the CM angular distributions reveal non-zero intensity from 0o to 180o along with a forward-backward symmetry. These findings provide compelling evidence of indirect reaction dynamics involving long lived SiND4 and SiNDH3 intermediate(s), holding lifetime longer than their rotational periods.[30](#_ENREF_30),[33](#_ENREF_33) These findings are also reflected in the flux contour maps, which depict the reactive scattering products flux intensityas a function of the CM scattering angle and product velocity, contain the information of the reactive scattering process.[30](#_ENREF_30)

**3. DISCUSSION**

   Having proved the gas phase formation of the SiND3 isomer(s) in the SiD-ND3 system and of SiNDH2 isomer(s) in SiD-NH3 system, we are now merging the electronic structure calculations with experimental results to untangle the nature of the product isomer(s) formed and the underlying reaction mechanisms. The accurate electronic structure calculations were conducted with the relative energies of the local minima and transition states are predicted within 8 kJ mol-1 and the overall reaction energies within 3 kJ mol-1 (Figure 3; Figure S1). The electronic structure calculations identified four SiNH3 (**p3, p4, p6, p7**) and three SiNH2 isomers (**p1, p2, p5**) formed via atomic and molecular hydrogen loss, respectively. Among the atomic hydrogen loss products, aminosilylene (HSiNH2, **p3**, *Cs*, X1A') represents the most stable isomer followed by silanimine (H2SiNH, **p4**, *Cs*, X1A'), silylidyneammonia (SiNH3, **p6**, *C3v*, X3A1), and imidogensilyl (H3SiN, **p7**, *C3v*, X3A1). The overall reaction energies of 2, 72, 196, and 281 kJ mol-1 reveal that under collision energy of 15 kJ mol-1, only aminosilylene (HSiNH2, **p3**, *Cs*, X1A') is energetically accessible. With respect to the molecular hydrogen loss channel, the doublet radicals aminosilylidyne (SiNH2, **p1**, *C2v*, X2B2), imidogensilylene (HSiNH, **p2**, *Cs*, X2A'), and imidogensilyl (H2SiN, **p5**, *C2v*, X2B2) can be formed in bimolecular reactions with reaction energies of -117, -43, and +90 kJ mol-1, respectively. The relative energies of the products are in excellent agreement with earlier computational studies.[23](#_ENREF_23),[34](#_ENREF_34),[35](#_ENREF_35) These data reveal that imido­gensilyl (H2SiN, **p5**, *C2v*, X2B2) is energetically not accessible. Therefore, the consecutive discussion centers on the channels forming **p1** to **p3**.

   For the SiD-ND3 system, the calculations reveal that the D1-silylidyne radical (SiD) adds barrierlessly to the non-bonding electron pair of nitrogen forming a silicon-nitrogen single bond (212.2 pm) and the initial collision complex **i1** on the doublet surface (Figure 3). All attempts to locate insertion pathways of D1-silylidyne into the nitrogen-deuterium bond to intermediate **i2** failed and resulted in intermediate **i1**. Intermediate **i1** can isomerize to intermediate **i2**, which represents the global minimum of the SiND4 potential energy surface (PES), through a barrier located 17 kJ mol-1 above the separated reactants. Alternatively, the initial collision complex can undergo unimolecular decomposition to D3-aminosilylene (DSiND2, **p3**, *Cs*, X1A'), i.e., the thermodynamically most stable SiND3 isomer. Intermediate **i2** can undergo unimolecular decomposition to D2-aminosilylidyne (SiND2, **p1**, *C2v*, X2B2) through molecular deuterium loss or to D3-aminosilylene (DSiND2, **p3**, *Cs*, X1A') via atomic deuterium loss. Intermediate **i2** can also isomerize via a deuterium shift to **i3**, which then emits molecular deuterium yielding D2-imidogensilylene (DSiND, **p2**, *Cs*, X2A'). The experimental collision energy of 15.9 ± 0.4 kJ mol-1 is slightly lower than the isomerization barrier of **i1** (DSiND3, *Cs*, 2A'') → **i2** (D2SiND2, *Cs*, 2A'). If intermediate **i2** is formed, unimolecular decomposition of the latter should result in a molecular deuterium loss (forming **p1** and/or **p2**) – which was experimentally not observed - as well as atomic deuterium loss (forming **p3**). On the other hand, atomic deuterium loss from **i1** **could** yield exclusively D3-aminosilylene (DSiND2, **p3**, *Cs*, X1A'). Based on the aforemen­tioned considerations, the reaction dynamics are indirect through the involvement of SiND4 complexes and initiated by the barrierless addition of D1-sylilydene to the non-bonding electron pair of D3-ammonia forming **i1** (DSiND3, *Cs*, X2A''), which then eliminated a deuterium atom from the nitrogen atom yielding the thermodynamically most stable SiND3 isomer D3-aminosilylene (DSiND2, **p3**, *Cs*, X1A'). The lack of any molecular deuterium product channel suggests that the barrier to isomerization from **i1** to **i2** cannot be overcome, a conclusion which is in line of the computed barrier of 17 kJ mol-1, which is slightly higher than the collision energy in our experiments. The computed reaction energy of +7 ± 3 kJ mol-1 forming D3-aminosilylene (**p3**) agrees very well with the experimental reaction energy of +2 ± 6 kJ mol-1. These conclusions are also supported by the SiD-NH3 system (Figure 3). Here, the atomic hydrogen loss from i1 – also formed via barrierless addition of the D1-silylidyen radical to ammonia – leads to D1-aminosilylene (DSiNH2, **p3**, *Cs*, X1A') in a thermoneutral reaction, which matches the experi­mental reaction energy of -3 ± 6 kJ mol-1.

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**Figure 3.** Potential energy surface (PES) for the reaction of the D1-silylidyne radical with D3-ammonia (a) and with ammonia (b). A complete PES is presented in Figure S1. Colors of the atoms: nitrogen, blue; silicon, purple; hydrogen, white and deuterium, light blue.

Overall, the crossed molecular beam experiments merged with electronic structure calculations provide compelling evidence on the first directed gas phase formation of D3- and D1-aminosilylene (DSiND2/DSiNH2, **p3**, *Cs*, X1A') under single collision conditions.

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**Figure 4**. Geometries, point groups, electronic ground state wave functions, relative energies (kJ mol-1), bond distances (Å), and selected bond angles (degrees) of methanimine (1, H2CNH) and aminomethylene (2, HCNH2) along with their isovalent species of aminosilylene (3, HSiNH2) and silanimine (4, H2SiNH). Colors of the atoms: nitrogen, blue; silicon, purple; carbon, gray and hydrogen, white.

The thermodynamical differences in the stability between carbene and silylene are reflected by comparing the aminosilylene with the isovalent aminomethylene (HCNH2) molecules. The profound effect by replacing a single carbon atom by silicon is depicted in Figure 4. The molecular geometries of methanimine (1) and aminomethylene (2) including the relative energies, bond distances and angles were extracted from the literature.[36-39](#_ENREF_36)

**4. CONCLUSIONS.**

     Our combined experimental and theoretical study provides compelling evidence on the directed gas phase formation of aminosilylene (HSiNH2; **p3**) - the simplest silicon analogue of an aminocarbene - under single collision conditions – via the silylidyne (SiH) - ammonia (NH3) reaction. To start with, the barrierless addition of the silylidyne radical to the non-bonding electron pair of nitrogen will lead toan HSiNH3 collision complex, which then undergoes unimolecular decomposition to aminosilylene (HSiNH2; **p3**) via atomic hydrogen loss from the nitrogen atom. The distinct chemical bondings of silicon-nitrogen versus the isovalent carbon-nitrogen compounds are well expressed, when contemplating aminosilylene (**3**) and silanimine (**4**) with their carbon analogues methanimine (**1**) and aminomethylene (**2**) (Figure 4).[34](#_ENREF_34),[36-40](#_ENREF_36) Methanimine (H2CNH, **1**) represents the global mini­mum and is thermodynamically more stable by 150 kJ mol-1 compared to the carbene structure amino­methylene (HNCH2, **2**). The sequence of stability is reversed when replacing a carbon atom by silicon with aminosilylene (HSiNH2, **3**) corresponds to the global minimum and silan­imine (H2SiNH, **4**) lying 70 kJ mol-1 higher in energy. The enhanced stability of (**3**) compared to (**4**) can be rationalized through a favorable π-type back-donation of the non-bonding electron pair of nitrogen into the empty pz orbital at the silicon atom; this in turn stabilizes the silylene structure (**3**) and results in a close to 900 hydrogen-silicon-nitrogen angle, i.e. no hybridization of the silicon atom, whereas the sp2-hybidized carbon atom in aminomethylene (**2**) is consistent with the hydrogen-carbon-nitrogen angle of 106o. This electronic structure of aminosilylene is illustrated by its molecular orbitals shown in Figure 5; for instance, the HOMO-1 corresponds to the π-type back-donation from nitrogen to silicon; the absence of hybridization between the s and p orbitals of the silicon atoms is also clearly evident (Figure 5). Overall, as the silicon analogue of the simplest aminocarbene - aminomethylene (**2**) - aminosilylene (**3**) represents a previously elusive key reac­tion intermediate in the gas phase inorganic silicon chemistry revealing that crossed molecular beam experiments carry advantages such as a gas phase formation of aminosilylene (HSiNH2). This species represents a benchmark of one of the most elusive representatives of a rather obscure class of highly reactive silylenes, which can be formed in gas phase with the primary reaction products “flying away” undisturbed *without* successive reactions. This clean bimolecular gas phase reaction might represent a uni­versal template toward the formation of even substituted aminosilylenes (HSiNHR) with R be­ing an organic group through reactions of silylidyne radicals



**Figure 5.** Valence molecular orbitals of aminosilylene (HSiNH2, **3**).

with primary amines (NH2R) thus shedding light on the previously obscure chemistry of aminosilylenes.

**5. EXPERIMENTAL AND COMPUTATIONAL**

**5.1. EXPERIMENTAL**

       The reaction of the D1-silylidyne radical (SiD; *X*2Π) with D3-ammonia (ND3; *X*1A1) and ammonia (NH3; *X*1A1) were conducted exploiting a crossed molecular beams machine.[41](#_ENREF_41) The D1-silylidyne pulsed supersonic beam was formed *in situ* in the primary chamber by laser ablation of a rotating silicon rod with 266 nm pulses (4-8 mJ per pulse; 30 Hz) and entrainment of the ablated species in a 1:1 mixture of deuterium gas (D2, >99.7%; Linde) and neon (Ne; 99.999%; Matheson) released by a pulsed piezoelectric valve with 4 atm backing pressure, 60 Hz repetition rate.[42](#_ENREF_42) D1-silylidyne beam was optimized at a unique mass-to-charge value of m/z = 31 (29SiD+) for intensity, considering the natural silicon isotope abundances (28Si (92.2 %), 29Si (4.7%), 30Si (3.1%)). The primary D1-silylidyne beam was first skimmed and then velocity-selected by a high stable four-slot chopper wheel (120 Hz) controlled by a precision motion system.[42](#_ENREF_42) The chopped section of the D1-silylidyne beam is defined by a peak velocity (*v*p) of 1200 m s-1 and speed ratio (*S*) of 6 (Table S1). It should be noted that no higher molecular weight silicon-deuterium bearing species were detected in the primary beam in the experiment. Considering the 18 µs travel time from the ablation to the interaction region along with a lifetime of 500 ns for electronically excited (*A*2Δ of) D1- silylidyne, potentially excited D1-silylidyne radicals should relax to their ground state.[43](#_ENREF_43) The primary beam crossed perpendicularly with the secondary D3-ammonia (ND3; Sigma-Aldrich; 99 D %) or ammonia (NH3; Matheson; 99.99 %) beam released by a pulsed piezo valve with a backing pressure of 550 Torr. The velocities of the crossing segment of the secondary beams as compiled in Table S1 resulted in collision energies (*EC*) of 15.9 ± 0.4 kJ mol-1 for the SiD-ND3 and 14.9 ± 0.4 kJ mol-1 for the SiD-NH3 reaction, respectively. Reactively scattering products were ionized by an electron impact ionizer (80 eV, 2 mA), mass filtered according to distinct mass-to-charge ratios (m/z) exploiting a quadrupole mass spectrometer (Extrel, QC 150), and ultimately recorded by a Daly type ion counter.[44](#_ENREF_44),[45](#_ENREF_45) The detector assembly is located in a differentially pumped ultrahigh vacuum (UHV) chamber operated routinely at 710-12 Torr. The recorded labora­tory data were transformed into the CM reference frame to obtain reaction dynamics information using a forward-convolution routine.[32](#_ENREF_32),[46](#_ENREF_46),[47](#_ENREF_47) User-defined CM angular *T(θ)* and translational energy *P(E*T*)* flux distributions are optimized until a best fit of the laboratory frame angular distribution and TOF spectra is achieved. The reactive differential cross section *I(u, θ) ≈ P(u) × T(θ)* is **then** derived with the velocity *u* and CM angle *θ*.

**5.2. COMPUTATIONAL**

We employed density functional theory (DFT) within the frame of the hybrid B3LYP[48](#_ENREF_48),[49](#_ENREF_49) method and with the 6-311G(d,p) basis set to optimize the geometric structures of the reactants, products, intermediates, and transition states taking part in the reaction of silylidyne with ammonia. Next, the same B3LYP/6-311G(d,p) method was used to compute vibrational frequencies of all stationary structures, while considering the particular isotopic composition of the 28Si14NDxH4-x species involved in the SiH + NH3/SiD + ND3/SiD + NH3 reactions. For the reactants and the critical transition state for the H atom migration **i1**-**i2**, geometry optimization was also carried out at the doubly hybrid DFT B2PLYPD3/6-311G(d,p) level of theory[50](#_ENREF_50),[51](#_ENREF_51)with a dispersion correction[52](#_ENREF_52) and at the coupled clusters CCSD/6-311G(d,p) level.[53-56](#_ENREF_53) For the B2PLYPD3/6-311G(d,p) optimized structures, vibrational frequencies were recalculated using the same method. Further refinement of single-point energies was performed at the explicitly correlated coupled clusters CCSD(T)-F12 level[57](#_ENREF_57),[58](#_ENREF_58) with single and double excitations and perturbative treatment of triple excitations, with the cc-pVQZ-f12 basis set[59](#_ENREF_59) for most structures. Additionally, for the reactants and the critical i1-i2 transition state, the calculations were also carried out with the cc-pVTZ-f12 basis set and then, the energies were extrapolated to the complete basis set (CBS) limit using the two-point formula, ECBS = Ecc-pVQZ-f12 + (Ecc-pVQZ-f12 – Ecc-pVTZ-f12)×0.69377.[60](#_ENREF_60) For the critical species**,** the CCSD(T)-F12/CBS energieswere evaluated at three different optimized geometries obtained with B3LYP, B2PLYPD3, and CCSD. Moreover, to incorporate the core electron correlation effects, the energies of these species were further improved using CCSD(full,T)-F12 calculations, which included, when handling the electronic correlation, all core electrons except 1s of Si atoms,with the cc-pCVTZ-f12 and cc-pCVQZ-f12 basis sets[61](#_ENREF_61)and extrapolated to the CBS limit. Calculations of anharmonic frequencies were executedat the B3LYP/6-311G(d,p) levelusing vibrational perturbation theory to the second order (VPT2)[62](#_ENREF_62)with the goal to assess anharmonicity corrections to zero-point vibrational energies.TheGAUSSIAN 09 package[63](#_ENREF_63)was employed for all B3LYP and B2PLYPD3 calculations as well as CCSD geometry optimizations and VPT2 computations of anharmonic frequencies. Alternatively, theMOLPRO 2010package[64](#_ENREF_64) was utilized for the CCSD(T)-F12 calculations. Noteworthy, the CCSD(T)-F12/CBS relativeenergies of the i1-i2 transition state including the core correlation and anharmonic ZPE corrections with its geometry optimized usingall three different methods agreed with its CCSD(T)-F12/cc-pVQZ-f12//B3LYP/6-311G(d,p) + ZPE(B3LYP/6-311G(d,p)) energy with harmonic ZPE in the margins of 1-2 kJ mol-1.

**SUPPORTING INFORMATION**

Experimental details of Si-NH3/ND3 reactions, complete potential energy diagram (Figure S1), the experimental parameters (Table S1), optimized geometric structures in the form of Cartesian coordinates and vibrational frequencies for all stationary structures involved in the reactions (Table S2).

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**Conflict of interest**

The authors declare no conflict of interest.

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