Gas-Phase Reactions

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Gas-Phase Synthesis of 1-Silacyclopenta-2,4-diene

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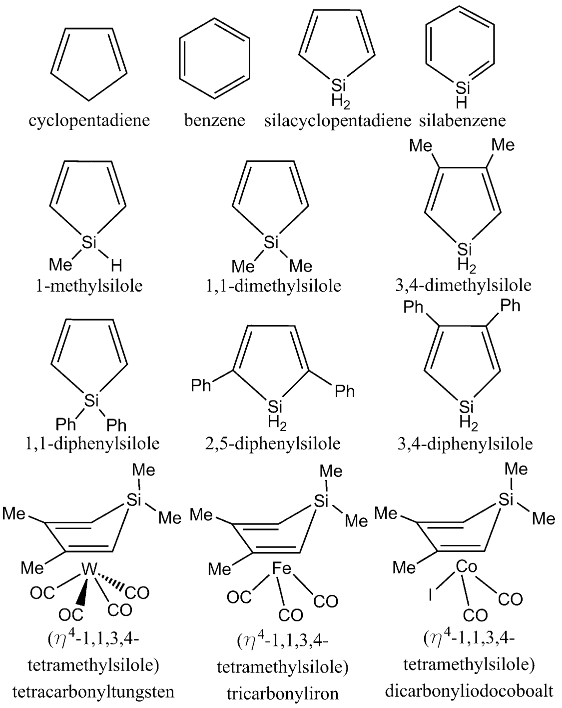
Abstract: *Silole (1-silacyclopenta-2,4-diene) was synthesized for the first time by the bimolecular reaction of the simplest silicon-bearing radical, silylidyne (SiH), with 1,3-butadiene (C_4H_6) in the gas phase under single-collision conditions. The absence of consecutive collisions of the primary reaction product prevents successive reactions of the silole by Diels–Alder dimerization, thus enabling the clean gas-phase synthesis of this hitherto elusive cyclic species from acyclic precursors in a single-collision event. Our method opens up a versatile and unconventional path to access a previously rather obscure class of organosilicon molecules (substituted siloles), which have been difficult to access through classical synthetic methods.*

Since Langmuir coined the concept of isoelectronicity almost 100 years ago,[1] the viability of replacing a single tetravalent carbon atom by an isovalent silicon atom within cyclic molecules has captivated both the theoretical and synthetic chemistry communities from the fundamental point of view of the electronic structure, reactivity, and stability of exotic organosilicon molecules (Scheme 1).[2,3] Siloles (silacyclopentadienes), formally derived from cyclopentadiene (c-C_5H_6) by substituting the methylene (CH_2) group by a silylene (SiH_2) moiety, have received particular attention as building blocks of conjugated π systems owing to their electroluminescence and highly efficient electron transportation at the molecular level.[4–11] Although siloles carrying multiple bulky phenyl (C_6H_5) substituents on carbon as well as silicon are stable as monomers at room temperature,[12–14] siloles substituted by less bulky methyl (CH_3) group(s) tend to dimerize by cycloaddition through [4+2] Diels–Alder reactions (Scheme 1).[14–17] Recent studies reported a novel method for synthesizing siloles through a [2+2+1] cycloaddition.[18,19] Considering the difficulties in preparation, their sensitivity to air, short lifetimes, and the tendency to form dimers, free siloles represent one of the least explored classes of organosilicon molecules. Despite indirect evidence for the formation of silole as a transient intermediate through the detection of its [4+2] adduct and its catalytic hydrogenation[20–23] along with matrix-isolation studies,[24,25] the isolation of the parent silole (1-silacyclopenta-2,4-diene) in the gas phase has eluded synthetic chemists for the last five decades.



Scheme 1. Structures of prototype cyclic hydrocarbons and their silicon analogues, mono-, dimethyl-, and diphenyl-substituted siloles, as well as metal complexes of η^4-siloles indicating the roles of siloles as ligands with transition metals.

Herein, we provide a rare glimpse into the chemistry of the cyclic silole molecule and report on its first gas-phase synthesis under single-collision conditions in a bimolecular reaction involving two acyclic precursors, namely the simplest silicon-bearing radical silylidyne (SiH, $X^2\Pi$) and 1,3-butadiene (C_4H_6, X^1A_g), exploiting the crossed-molecular-beams method. An investigation at the molecular level provides fundamental insights into the reaction mechanisms through which highly reactive molecules such as siloles are synthesized. As the primary reaction product does not undergo consecutive reactions, successive dimerization reactions of the silole are prevented, thus enabling the versatile and clean gas-phase synthesis of this hitherto elusive cyclic species. This system is also interesting from the viewpoint of a physical-organic chemist as such compounds represent benchmarks to unravel the chemical reactivity, bond-breaking processes, and synthesis of cyclic organosilicon molecules from acyclic

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precursors, thus opening up an unconventional path to access the rather obscure class of organosilicon molecules (substituted siloles).

The reactive scattering signals from the silylidyne radical (SiH, $X^2\Pi$) with 1,3-butadiene (C_4H_6, X^1A_g) were monitored considering the natural abundances of carbon (^{13}C: 1.1 %; ^{12}C: 98.9 %) and silicon (^{30}Si: 3.10 %; ^{29}Si: 4.67 %; ^{28}Si: 92.23 %), considering mass-to-charge ratios of $m/z = 86$–81 for the adducts ($^{30}Si^{13}CC_3H_7^+$: m/z 86; $^{29}Si^{13}CC_3H_7^+/^{30}SiC_4H_7^+$: m/z 85; $^{29}SiC_4H_7^+/^{28}Si^{13}CC_3H_7^+$: m/z 84; $^{28}SiC_4H_7^+$: m/z 83) along with products corresponding to the loss of one hydrogen atom ($^{30}Si^{13}CC_3H_6^+$: m/z 85; $^{29}Si^{13}CC_3H_6^+/^{30}SiC_4H_6^+$: m/z 84; $^{29}SiC_4H_6^+/^{28}Si^{13}CC_3H_6^+$: m/z 83; $^{28}SiC_4H_6^+$: m/z 82) and species corresponding to the loss of molecular hydrogen ($^{30}Si^{13}CC_3H_5^+$: m/z 84; $^{29}Si^{13}CC_3H_5^+/^{30}SiC_4H_5^+$: m/z 83; $^{29}SiC_4H_5^+/^{28}Si^{13}CC_3H_5^+$: m/z 82; $^{28}SiC_4H_5^+$: m/z 81). The strongest signal was observed at m/z 82 (for the time-of-flight (TOF) spectra and laboratory angular distribution, see Figure 1). These data could be fit with a single channel originating from the reaction of silylidyne (^{28}SiH; 29 amu) with 1,3-butadiene forming $^{28}SiC_4H_6$ (hereafter: SiC_4H_6; 82 amu) isomers along with atomic hydrogen (H; 1 amu). Signals at higher mass-to-charge ratios depicted less favorable signal-to-noise ratios owing to the less abundant silicon and carbon isotopes; TOF spectra taken at these mass-to-charge ratios were superimposable after scaling, indicating that these signals actually stem from reactions of the isotopically substituted counterparts of the silylidyne (^{30}Si, ^{29}Si) and 1,3-butadiene reactants (^{13}C). No evidence for any adduct could be obtained under our experimental conditions, suggesting that the lifetime of any SiC_4H_7 intermediate is shorter than the flight time from the interaction region to the ionizer. The TOFs recorded at m/z 81 also overlap with those at m/z 82 after scaling, suggesting that the signal at m/z 81 originates from dissociative electron impact ionization of the parent molecules in the ionizer; consequently, any molecular hydrogen loss channel is closed. Therefore, we can conclude that the reaction of the silylidyne radical with 1,3-butadiene involves the formation of SiC_4H_6 isomers in a silylidyne versus atomic hydrogen exchange pathway. The associated laboratory angular distribution depicts a distribution maximum close to the center of mass (C.M.) angle of 38.4° ± 0.7° and spans a scattering range from 24.0° to 52.5°. These results indicate a complex formation reaction mechanism (indirect scattering dynamics) involving SiC_4H_7 intermediate(s).[26] As the hydrogen atom can be ejected from the silylidyne moiety and/or from the 1,3-butadiene reactant, we also studied the reactions of the monodeuterated silylidyne radical (SiD; $X^2\Pi$) with 1,3-butadiene (C_4H_6; X^1A_g) and of the silylidyne radical (SiH; $X^2\Pi$) with [D$_6$]-1,3-butadiene (C_4D_6; X^1A_g) and [D$_2$]-1,3-butadiene ($C_4H_4D_2$; X^1A_g) to identify the position of the atomic hydrogen loss. A detailed analysis of the TOF spectra provides convincing evidence that the hydrogen atom is (dominantly) lost from one of the chemically equivalent terminal CH_2 moieties of the 1,3-butadiene reactant (see the Supporting Information, Figures S1 and S2).

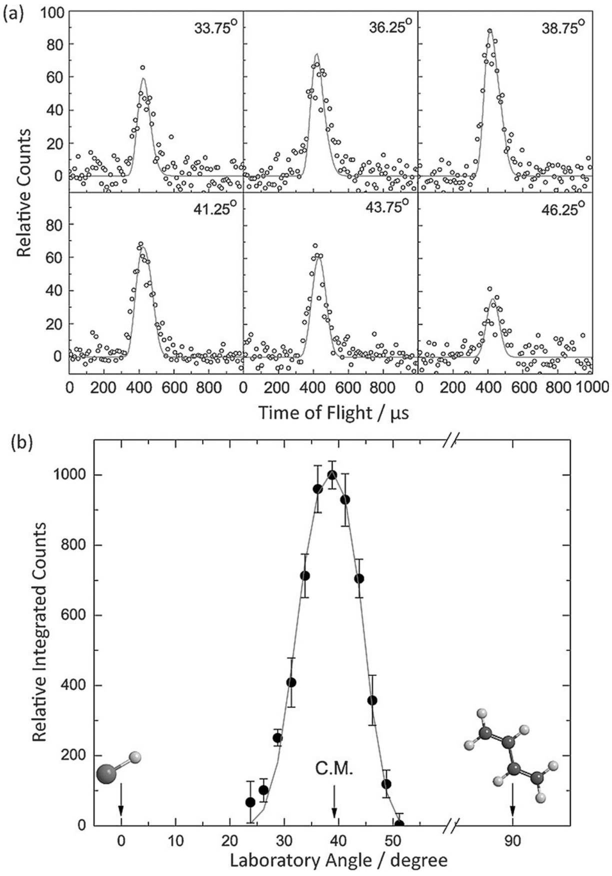


Figure 1. a) Time-of-flight spectra and b) laboratory angular distribution recorded at m/z 82 ($SiC_4H_6^+$) for the reaction of the silylidyne radical with 1,3-butadiene. The circles represent the experimental data points while the solid lines represent the best fits.

However, the ultimate goal of our study was not only to elucidate the molecular formula of the reaction product (SiC_4H_6), but also to unravel the structure of the isomer(s) along with the underlying reaction mechanism for the formation of these unusual organosilicon molecules. To achieve these goals, it was crucial to obtain information on the chemical dynamics from the experimental data. This was carried out by utilizing a forward-convolution routine[27,28] and transforming the laboratory data (TOF spectra, laboratory angular distribution) of the SiC_4H_6 product(s) at m/z 82 into the center-of-mass reference system. This approach results in two "best-fit" center-of-mass functions: the translational energy flux distribution, $P(E_T)$, and the angular flux distribution, $T(\theta)$, (Figure 2). Considering the center-of-mass translational energy flux distribution, $P(E_T)$, the maximum translational energy ($E_{max} = 92 \pm 18\ kJ\,mol^{-1}$) of the products assists in the identification of the nature of the SiC_4H_6 isomer(s) formed. For molecules born without rovibrational excitation, E_{max} represents the sum of the collision energy and the absolute value of the reaction exoergicity. Consequently, if we subtract the collision energy from E_{max}, the reaction to form SiC_4H_6 and atomic hydrogen is found to be exoergic by $-58 \pm 19\ kJ\,mol^{-1}$. Furthermore, the $P(E_T)$ graph depicts a distribution maximum far away from zero translational energy at $20 \pm 5\ kJ\,mol^{-1}$, which indicates a tight-exit transition state and thus repulsive bond rupture upon unimolecular decomposition of the SiC_4H_7 complex, forming SiC_4H_6 isomer(s) by atomic hydrogen elimination. This finding is also

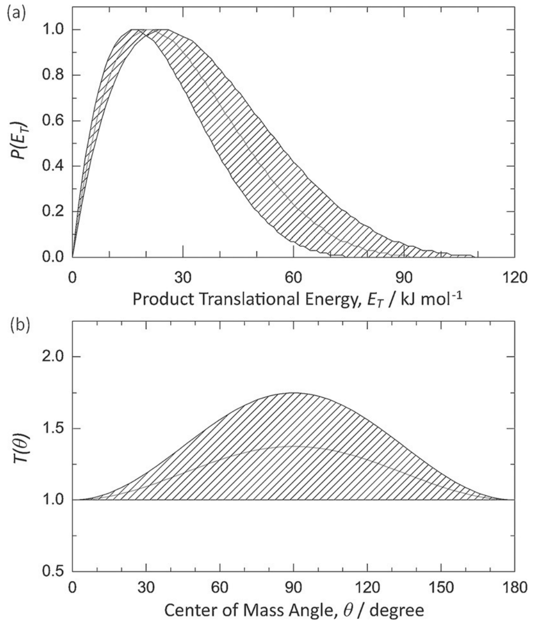


Figure 2. a) The center-of-mass translational energy distribution, $P(E_T)$, and b) the angular distribution, $T(\theta)$), for the reaction of the silylidyne radical with 1,3-butadiene forming SiC_4H_6 isomer(s) by atomic hydrogen emission. The hatched areas indicated the experimental error limits.

supported by the shape of the center-of-mass angular flux distribution, $T(\theta)$, depicting flux over the complete scattering range from 0° to 180°.[26] The best-fit $T(\theta)$ function depicts a symmetric forward–backward profile, suggesting that the lifetime of the decomposing complex is longer than its rotational period.[29] Finally, the maximum intensity at $\theta = 90°$ imposes geometrical constrains on the decomposition of the SiC_4H_7 complex, with the preferred direction of hydrogen emission being almost parallel to the total angular momentum vector and hence nearly perpendicular to the rotational plane of the decomposing complex.[29]

The nature of the synthesized SiC_4H_6 isomer(s) can be elucidated through a comparison of the experimentally determined reaction exoergicity (-58 ± 19 kJ mol^{-1}) with the reaction energies obtained from electronic-structure calculations for distinct SiC_4H_6 isomers. The geometries of various species involved in the reaction were investigated by electronic-structure calculations (see the Supporting Information). These theoretical investigations indicate the existence of 18 singlet SiC_4H_6 isomers (**p1** to **p18**; Figure S3). Among them, only four isomers are energetically accessible at a collision energy of 33.7 ± 1.0 kJ mol^{-1} (**p1**–**p4**). These are 1-silacyclopenta-2,4-diene (silole, **p1**, -57 kJ mol^{-1}), 2-methylene-1,2-dihydrosilete (**p2**, 16 kJ mol^{-1}), 1-silacyclopent-3-en-1-ylidene (**p3**, 22 kJ mol^{-1}), and 1-silacyclopenta-1,3-diene (**p4**, 26 kJ mol^{-1}; Figure 3). All energetically accessible products are cyclic isomers, with only silole being formed in an overall exoergic reaction (-57 ± 8 kJ mol^{-1}). The preferential stability of silole correlates well with earlier computations by the groups of Maier[25] and Denis[30] conducted at the B3LYP/6-311+G** and G4+CCSD(T)/CBS(cc-PV(n+d)Z, $n = 2$–6) levels of theory, which predicted this reaction to be exoergic by 32 ± 10 kJ mol^{-1} and 84 ± 9 kJ mol^{-1}, respectively. A comparison of the experimental reaction energy (-58 ± 19 kJ mol^{-1}) with our computed energetics suggests that at least the thermodynamically most stable silole isomer (**p1**) is formed (-57 ± 8 kJ mol^{-1}). Consequently, we can conclude that we have, for the first time, synthesized and observed the silole molecule (c-SiC_4H_6) in the gas phase under single-collision conditions.

Having identified the silole isomer (**p1**) as a reaction product, we wanted to untangle the reaction mechanism of its formation and also elucidate to what extent the thermodynamically less stable structures (**p2** to **p4**) contribute to the reactive scattering signal. This was accomplished by combining our experimental findings with the electronic-structure calculations (Figure 3). In principle, the silylidyne radical can add to one or to two carbon atoms of the 1,3-butadiene reactant. The computations reveal that a barrier-free addition to one of the terminal carbon atoms (C1/C4) leads to a resonance-stabilized doublet radical *trans*-**i1**, which is bound by 94 kJ mol^{-1} with respect to the separated reactants. The intermediate *trans*-**i1** can undergo a *trans*–*cis* isomerization to *cis*-**i1** with a barrier of only 34 kJ mol^{-1}, which then isomerizes by ring closure through a low barrier of only 30 kJ mol^{-1} to **i2**. This cyclic intermediate can rearrange through a hydrogen migration from one of the CH_2 moieties

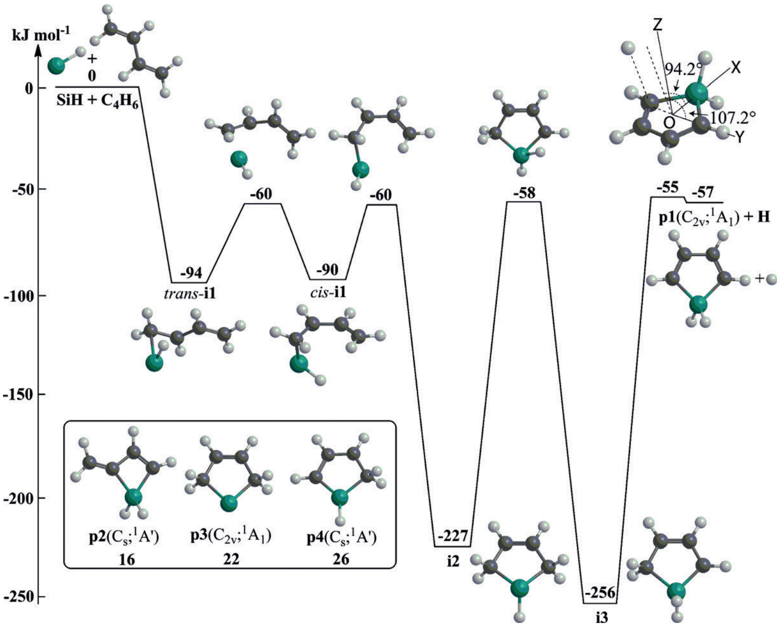
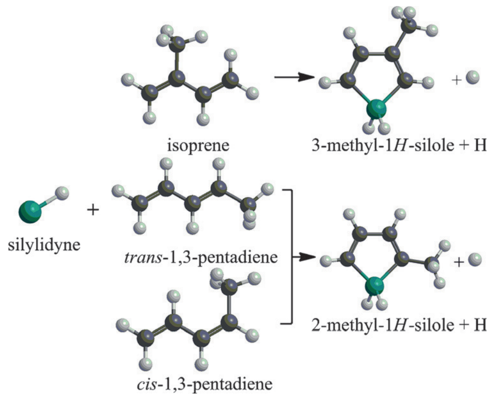


Figure 3. Potential energy surface of SiC_4H_7 for the reaction of the silylidyne radical with 1,3-butadiene leading to **p1** (silole; c-SiC_4H_6) and atomic hydrogen. Three energetically accessible product isomers, **p2**–**p4**, are shown along with the point groups and symmetries of the electronic wave functions. The energies are given in kJ mol^{-1} with respect to the initial reactant system. Carbon black, hydrogen light gray, silicon dark green.

to the silicon atom to give **i3**. The latter represents the global minimum of the SiC_4H_7 potential energy surface (PES) and is stabilized by 256 $kJ\,mol^{-1}$ with respect to the initial reactants. Eventually, the doublet radical intermediate **i3** undergoes unimolecular decomposition by atomic hydrogen loss through an exit transition state located 2 $kJ\,mol^{-1}$ above the energy of the separated products to form the silole molecule (**p1**) in an overall exoergic reaction, with the decomposition being mainly driven by the reformation of the conjugated carbon–carbon double bonds. Please note that the addition of silylidyne to the C1−C2 or C2−C3 bond eventually leads only to the endoergic formation of products that are energetically not accessible under our experimental conditions (see the Supporting Information). Based on the energetics of the reactions and the forward-convolution routine, the energetically accessible products **p2**, **p3**, and **p4** are formed, if at all, in less than 5%.

The theoretically predicted reaction pathway to silole is well supported by our experimental findings. The indirect reaction pathway is reflected in the center-of-mass angular distribution depicting intensity over the whole scattering range; likewise, the off-zero peaking of the center-of-mass translational distribution ($20\pm5\,kJ\,mol^{-1}$) suggests the existence of an exit transition state, which was also confirmed by the electronic-structure calculations. According to the principle of microscopic reversibility, the reverse reaction of the addition of a hydrogen atom to the carbon–carbon double bond of a closed-shell silole molecule should also be afflicted with an entrance barrier that is similar in magnitude to typical barriers for the addition of hydrogen atoms to olefins and dienes (10–30 $kJ\,mol^{-1}$).[31,32] This in turn translates into the ejection of the hydrogen atom nearly perpendicularly to the rotational plane of the decomposing complex, resulting in a center-of-mass angular distribution peaking at 90° as observed experimentally. As evident from the geometry of the exit transition state (Figure 3), the electronic-structure calculations propose angles of hydrogen emission with respect to the principal axes O-X and O-Y of 94.2° and 107.2°, respectively, thus confirming the aforementioned concepts. Finally, the experiments with (partially) deuterated reactants are in line with the theoretically predicted reaction pathway to form silole (**p1**), and clearly confirm that the emitted hydrogen/deuterium atom solely originates from the CH_2/CD_2 moieties (Figure S4). Therefore, the silylidyne radical adds to the π electron density at one of the terminal carbon atoms of 1,3-butadiene in a barrier-free complex-forming (indirect) reaction mechanism. The initial complex *trans*-**i1** undergoes *trans–cis* isomerization to *cis*-**i1** followed by rearrangement through cyclization (**i2**) and hydrogen shift (**i3**), eventually forming silole (**p1**) in an overall exoergic reaction (experiment: $-58\pm19\,kJ\,mol^{-1}$; theory: $-57\pm8\,kJ\,mol^{-1}$).

In summary, our combined experimental and theoretical investigations on the bimolecular gas-phase reaction of the silylidyne radical with 1,3-butadiene have revealed the facile formation of silole —the simplest representative of isoelectronically silicon-substituted cyclopentadiene ($c\text{-}C_5H_6$)— under single-collision conditions exploiting the crossed-molecular-beams technique. This barrier-free route to form cyclic silole through the reaction of the simplest silicon-bearing radical silylidyne with an unsaturated hydrocarbon (1,3-butadiene) can be considered as a benchmark study to synthesize even more complicated, hitherto elusive substituted siloles in the gas phase by directed synthesis, thus opening up an unconventional path to access previously poorly studied classes of siloles, such as alkyl-substituted siloles (Scheme 2), which are difficult to obtain by "classical" synthesis. Therefore, further experimental and theoretical studies of these systems under single-collision conditions are clearly warranted to fully explore the unique reactivity of the silylidyne radical and the formation of novel siloles to gain a comprehensive understanding of their electronic structures, chemical bonding, and stabilities. This might also be of potential relevance to organometallic chemists by expanding the synthesis of organosilicon molecules and their η^4-type transition-metal carbonyl complexes of, for instance, tungsten, iron, and cobalt (Scheme 1).[12]



Scheme 2. Potential pathways for the formation of singly substituted siloles through the reaction of silylidyne with alkyl-substituted 1,3-butadienes, such as isoprene and 1,3-pentadiene, in the gas phase.

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Keywords: gas-phase reactions · mass spectrometry · reaction dynamics · silole · single-collision conditions

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