Silicon Compounds

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Preparation of a Silanone through Oxygen Atom Transfer to a Stable Cyclic Silylene

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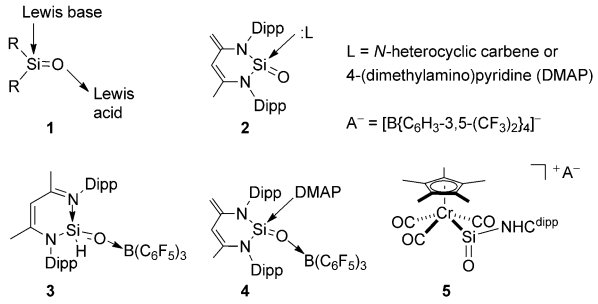
Abstract: *We report the evaporation of a stable cyclic silylene and its oxidation (with ozone or N_2O) through oxygen atom transfer to form the corresponding silanone under matrix isolation conditions. As uncomplexed silanones are rare owing to their very high reactivity, this method provides an alternative route to these sought-after molecules. The silanone, as well as a novel bicyclic silane with a bridgehead silicon atom derived from an intramolecular silylene C–H bond insertion, were characterized by comparison of high-resolution infrared spectra with density functional theory (DFT) computations at the M06-2X/cc-pVDZ level of theory.*

Although carbonyl compounds are among the most important building blocks in organic chemistry, analogous compounds having a Si=O double bond (silanones) not stabilized by Lewis acid/Lewis base coordination are rare.[1] Attempts to synthesize compounds with Si=O bonds were made as early as the 19th century by Friedel and Crafts[2] and at the beginning of the 20th century by Dilthey[3] and Kipping et al.[4] These groups reported the synthesis of compounds having an RR′SiO unit, which were named silicones to denote their analogy to ketones. However, based on their high boiling points and a reactivity that is very different from ketones, Kipping and co-workers concluded that the synthesized glue-like materials were not monomers but were trimers of formula $(RR'SiO)_3$. Kipping did not envision the enormous potential of such oligomers and was pessimistic about the future of silicon chemistry.[5] However, his work led to the seminal discovery of polysiloxanes that are now among the most important building blocks for organic–inorganic hybrid polymers.[6] The term silicone remained and is applied to any compound with an $[R_2SiO]_n$- backbone.

A major problem that prevents the isolation of silanones is their high propensity for dimerization and oligomerization.[1b,7] This reactivity results primarily from the high polarity of the Si=O bond (Pauling electronegativity values: Si = 1.9, O = 3.4) which leads to a zwitterionic bonding character ($Si^{\delta+}$–$O^{\delta-}$) with a small contribution from π bonding,[8] which is significantly larger than that of silanethiones with a Si=S bond.[9]

Such dimerization or oligomerization reactions are suppressed in solid noble-gas matrices at low temperatures owing to their high viscosity and high dilution of the target compounds. This technique led to the detection of several silanones that were produced mainly by oxygenation of silanes, and were characterized by IR spectroscopy through their diagnostic Si=O stretching vibration in the range ν = 1150–1300 cm^{-1} (see Table S1 in the Supporting Information).[10] Another common procedure is the formation of transient silanones through pyrolysis of precursor molecules, such as silapyranes or 7-oxa-8-silabicyclo[2.2.2]octadiene.[11] The parent compound H_2Si=O was first detected in the gas phase in 1985[12] and was identified by its chemiluminescent emission[12,13] and by a millimeter-wave rotational spectrum.[13a] The assignments were supported by ab initio computations at the CCSD/TZ2P(f,d) levels of theory.[13b]

The preparation of a silanone through transfer of a well characterized room-temperature-stable silylene to the cold matrix window and subsequent oxidation has not been reported yet but provides a viable alternative strategy for the preparation of silanones. This is the main focus of this work.



Scheme 1. Reported silanones stabilized by Lewis acids or bases. Dipp = 2,6-*i*$Pr_2C_6H_3$; NHC^{DIPP} = 1,3-bis(2,6-*i*$Pr_2C_6H_3$)imidazolin-2-ylidene.

Although isolable "genuine" R_2Si=O compounds (R = alkyl, aryl) are still unknown under ambient conditions, significant advancements have been made recently in the synthesis and isolation of compounds containing Si=O bonds

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that are stabilized by coordination of the Si atom to Lewis bases or an organometallic fragment and of the oxygen atom to Lewis acids (Scheme 1, compounds **1**–**5**).[1b,c,14] Significant progress was recently achieved through the isolation of the cationic chromiosilanone **5** featuring a trigonal-planar-coordinated silicon center.[1c]

Compounds with Si double bonds to the heavier elements of Group 16 (S, Se, and Te) were synthesized from a stable cyclic dialkyl silylene (specifically from the silylene synthesized by Kira et al.)[15] and Ar(Tbt)Si (Tbt = 2,4,6-tris-[bis(trimethylsilyl)methyl]phenyl)[9b] and were characterized by X-ray crystallography.[9b,15c,16] All compounds are kinetically stabilized by bulky substituents. However, attempts to isolate the silanone from Kira's silylene failed, leading instead to the formation of its dimer.[7f] Formation of Si=E bonds (E = O, S, Se) through the reaction of silylenes (R_2Si:) with oxirane, thiirane, and selenirane was suggested.[17] The corresponding reaction mechanisms were studied computationally and were found to be highly exothermic displaying low reaction barriers.[17] A computational study[18] of the formation of Si=E bonds through the reaction of the silylene[15a,b] with Me_3P=E showed that there is a low reaction barrier for the oxidation (E = O) of the silylene while the reaction is spontaneous and follows the order E = O < S < Se ≪ Te.[18] Hence, the key goal of the present study is the preparation of a novel silanone under noble gas matrix isolation conditions. This goal is achieved through oxygen atom transfer from O_3 or N_2O,[1b,c,7h,10a–c,19] to the stable dialkyl silylene **6** of Kira et al.[15a,b] to form the desired silanone **10** (Scheme 2).

In addition to the desired formation of silanone **10** we also report the isomerization of **6** to silene **7** via a [1,2]$SiMe_3$ shift, previously detected in solution by Kira et al.,[15a,b,20] and the hitherto unobserved intramolecular C–H bond insertion reaction of the silylene precursor **6** to give **9**.

Kira et al. have shown that **6** converts in hexane solution at 60 °C ($t_{1/2}$ = 1 h) through a [1,2]$SiMe_3$ migration[15a,b] into cyclopentasilene (**7**).[15a,b] Subsequent irradiation of **7** with light of wavelength $\lambda > 320$ nm yields the thermodynamically more stable silacyclopentene **8**, which was spectroscopically fully characterized (Scheme 2, upper set of reaction conditions).[20] The unimolecular reaction kinetics of the rearrangement were followed by UV/Vis absorption spectroscopy. Without irradiation **7** is persistent for at least 25 days at 90 °C in benzene solution.[20]

Herein we find that in an Ar matrix at 12 K silylene **6** does not convert into silene **7** even when irradiated. Silene **7** forms thermally under ambient conditions from **6**,[20] and isomerizes upon irradiation to **8** also under matrix conditions. Additionally, under matrix conditions upon irradiation **6** forms a novel silabicyclic structure that has a silicon atom in the bridgehead position (**9**). Note that irradiation of the matrix is the only way to provide energy to isolated molecular species as heating is precluded, but this does not imply exclusive photochemical reactions. Most importantly, upon reaction with O_3 or N_2O silylene **6** produces, through oxygen atom transfer, the desired new silanone **10** (Scheme 2). Silylene **6**[15a,b] was evaporated at 53 °C (at 1.2×10^{-6} mbar) onto a CsI matrix window (at about 16 K) forming a yellow layer. The sample was shielded from light to exclude photochemical reactions and the IR spectra were recorded at 12 K (Figure 1).

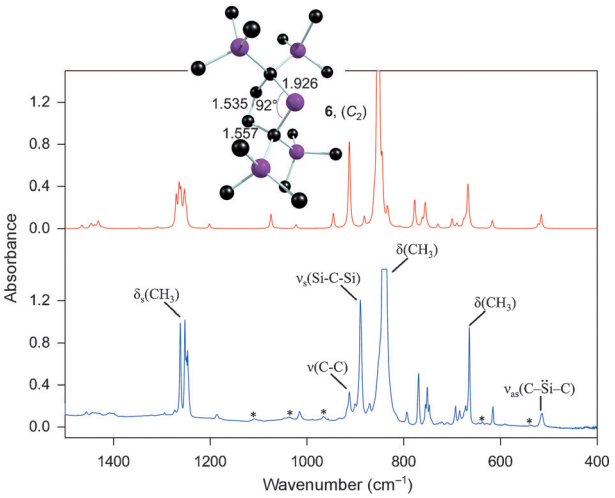
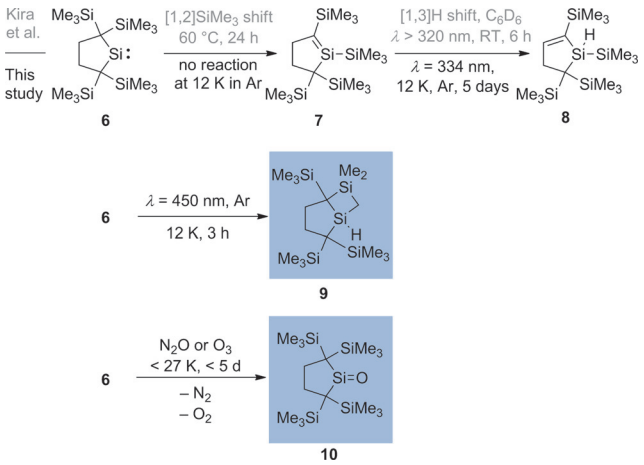


Figure 1. Experimental IR spectrum of matrix-isolated **6** (bottom) and its computed spectrum (top; unscaled) in the 400–1500 cm^{-1} range. Selected bond lengths [Å] and angles [°] of the optimized geometry of the structure are shown and hydrogen atoms are omitted for clarity. Asterisks show small amounts of the thermally generated by-product **7**. See Figure S1 for the full spectrum.



Scheme 2. Reactions of silylene **6** under matrix isolation conditions under Ar at 12 K (conditions given in black below the reaction arrows) to form silanone **10** and silabicyclic compound **9**. Conditions given in gray (above the reaction arrows) are for transformations of silylene **6** in solution.[15a,b,20] New compounds prepared are shown in blue boxes.

The agreement of the IR data for **6** with the frequency computations at the M06-2X/cc-pVDZ level of theory is excellent, and the very small broad bands at 1108 cm^{-1} and 1036 cm^{-1} (marked by asterisks in Figure 1) indicate the formation of only a small amount of **7**, the thermal [1,2]silyl shift product of **6** (the full matrix-isolated IR spectrum of **7** is shown in Figure S1). In view of the relatively facile thermal [1,2]silyl shift at a somewhat higher temperature of 60 °C[20] the detection of nearly pure **6** is remarkable. Shorter evaporation times further reduce the abundance of byproduct

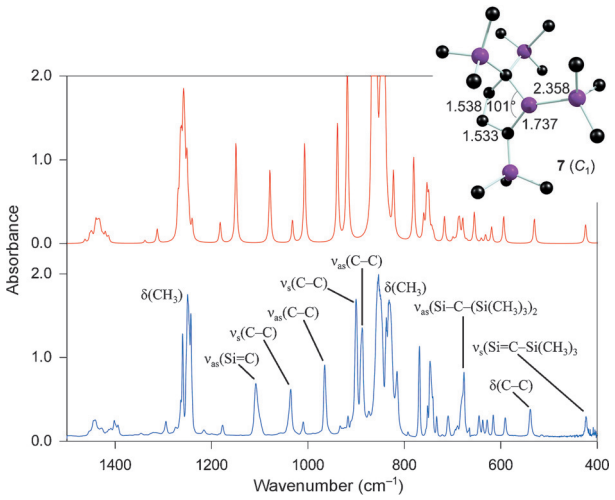


Figure 2. Experimental IR spectrum of matrix-isolated **7** (bottom) and its computed spectrum (top; unscaled) in the 400–1500 cm^{-1} range. Selected bond lengths [Å] and angles [°] of the optimized geometry of the structure are given and hydrogen atoms are omitted for clarity. See Figure S5 for the full spectrum.

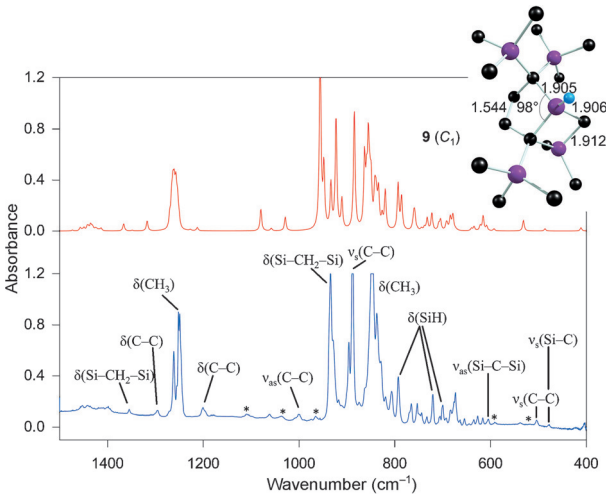


Figure 3. Experimental IR spectrum of matrix-isolated **9** (bottom) and its computed spectrum (top; unscaled) in the 400–1500 cm^{-1} range. Asterisks show small amounts of **7** as a side product formed during deposition of **6**. Selected bond distances [Å] and angles [°] of the optimized geometry of the structure are shown and only pertinent hydrogen atoms are presented. See Figure S14 for the full spectrum. There is also a broad band at ν(Si–H) = 2090–2150 cm^{-1}.

7. Silene **7** can be obtained cleanly on the CsI matrix window by keeping **6** at room temperature for about two weeks followed by evaporation at 63 °C (Figure 2; for the full matrix isolation IR spectrum see Figures S5–S7). The UV/Vis absorption spectrum (Figure S41) of matrix-isolated compound **6** shows a low intensity wavelength maximum at λ = 438 nm that compares well with the absorption at 440 nm in solution.[15a,b] The peak at λ = 260 nm detected in solution could not be discerned in the matrix owing to the absorption bands of the CsI window. The peak at λ = 330 nm is likely attributable to **7** that shows a maximum at λ = 338 nm in solution.[15a,b,20]

Upon irradiation at λ = 334 nm, silene **7** can be photochemically converted quantitatively within five days into **8**[21] (Scheme 2) through a symmetry-allowed [1,3]H shift. Prolonged irradiation with λ = 185–313 nm showed no spectral changes. The conversion of **7** into **8** gives rise to, in addition to a broad ν(Si–H) = 2034–2079 cm^{-1} band, the appearance of a new band at ν(C=C) = 1559 cm^{-1} (see Figure S7 for the IR spectrum of matrix-isolated **8**). In addition to the appearance of this new band, the bands at ν_{as}(Si=C) = 1108 cm^{-1} and ν_s(=CH–CH_2) = 1036 cm^{-1} disappear upon conversion of **7** into **8**.

Irradiation of **6** at wavelengths λ = 313–579 nm (with a typical maximum of λ = 450 nm) leads to the hitherto unreported bicyclic structure **9** (Figure 3) by an intramolecular insertion of the silylene into a C–H bond of one of the trimethylsilyl groups[22] (Scheme 2). The absorption bands at ν(Si–H) = 2129 cm^{-1} (Figure S21) and that for the isolated CH_2 group at 934 cm^{-1} of the newly formed four-membered ring are strong and correlate well, as does the remainder of the IR spectrum, with the computed spectrum (Figure 3). Compound **9** is photochemically stable and does not rearrange upon irradiation with light of wavelengths down to λ = 254 nm.

To oxidize **6** by single oxygen atom transfer, we employed N_2O or O_3 as oxidizers that were co-deposited in the matrix.[10a–c,19] Mixtures of argon and the oxidizer had concentrations of 1.0–2.6 % N_2O or O_3. To allow bimolecular reactions that are typically suppressed in the matrix, the window temperature was raised to 27 K to enable diffusion over short distances; it was then recooled to 12 K before acquisition of the spectra. After deposition of **6** in the matrix, silanone **10** (Figure 4) formed over a period of five days in

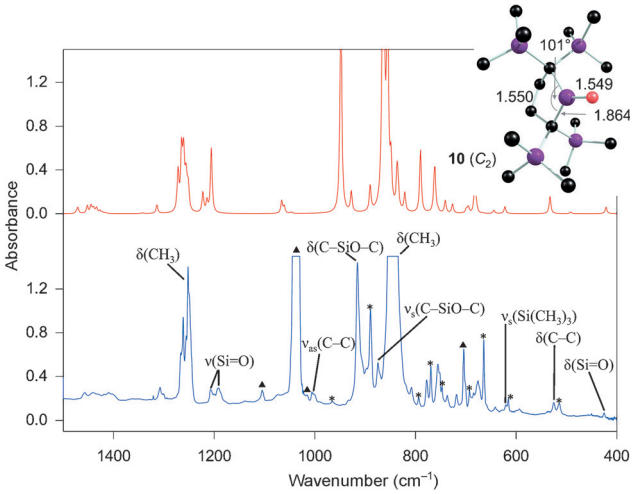


Figure 4. Experimental IR spectrum of matrix-isolated **10** (bottom) and its computed spectrum (top; unscaled) in the 400–1500 cm^{-1} range. Structure **10** was prepared from oxygen atom transfer from O_3 (bands marked with ▲) within five days at increasing temperatures from 12–27 K. Selected bond distances [Å] and angles [°] of the optimized geometry of the structure are shown and hydrogen atoms omitted for clarity. Asterisks show small amounts of starting material **6**. See Figure S22 for the full spectrum.

a temperature range from 12 to 27 K in the presence of co-deposited O_3. The typical temperature-interval procedure involved 11 h at 20 K, 43 h at 25 K, and 3 h at 27 K, followed by recooling to 12 K with subsequent spectrum acquisition. The largest increase in the relative intensity of the silanone bands was achieved during the first 4 h of each annealing step. Irradiation experiments with light at various wavelengths did not lead to significant changes, except for the formation of the bridgehead silane **9** as a side product upon irradiation at $\lambda \leq$ 579 nm. Each experiment with co-deposited oxidizer showed the formation of silanone **10** during the evaporation process. It was found that altering the experimental setup through, for example, increasing the distance between the sample vial and the cold window, only led to reduced signal intensities, which were low already owing to the very low concentration of **10**.

The use of $^{18}O_3$ (prepared through reaction of $^{18}O_2$ in a microwave plasma; see the Experimental Section for details) led to a significant isotopic shift of the Si=O signal of 38.0 cm^{-1} ($\Delta\nu = 1193.9$–1155.9 cm^{-1}), which compares favorably with the computed isotopic shift (at the M06-2X/cc-pVDZ level of theory) of 37.5 cm^{-1} ($\Delta\nu = 1196.5$–1159.0 cm^{-1}). These isotopic shifts compare very well to those for the parent silanone $H_2Si{=}O$ ($\Delta\nu = 40$ cm^{-1}),[10a] MeHSi=O ($\Delta\nu = 38$ cm^{-1}),[10b,h] and $Me_2Si{=}O$ ($\Delta\nu = 35$ cm^{-1}).[10b,f,h,19a,23] Other relevant isotopic shifts can be found in Table S1.[10g–i,24] Experiments conducted with N_2O led to the appearance of new bands at 1208 cm^{-1}, 1200 cm^{-1}, and 1195 cm^{-1}. As the broad N_2O bands at 1245 cm^{-1} and 1163 cm^{-1} are closer than the O_3 signals to the silanone bands, ozone turned out to be the more suitable oxidizer.

In addition to aiding the spectral assignments, our DFT computations (see the Experimental Section) also help rationalize the relative energy changes associated with the observed rearrangements of singlet silylene **6** to **7** and **8** (Scheme 2), the intramolecular silylene C–H bond insertion to **9**, and the oxidation of **6** to the desired silanone **10**. The singlet–triplet energy separation (ΔE_{ST}) of **6** is +32.0 kcal mol^{-1}, which is considerably larger than that of parent SiH_2 (computed $\Delta E_{ST} = +19.5$ kcal mol^{-1}; experimental $\Delta E_{ST} = +18.3 \pm 0.7$ or $+21.4 \pm 0.7$ kcal mol^{-1}[25]). We therefore assume that we observe closed-shell reactivity throughout. The thermochemically initiated rearrangement of **6** to **7** is slightly endothermic by +7.5 kcal mol^{-1} (ΔH_0),[26] which is remarkably small considering that **6** is an electron-deficient sextet species.[27] The rearrangement of **7** to **8**, a [1,3]H thermally suprafacially forbidden reaction converting a C=Si bond into a C=C bond, is exothermic by −19.2 kcal mol^{-1}. As the thermal barriers are sizable ($\Delta H_0^{\neq}(\mathbf{TS_{6\rightarrow 7}}) = +28.8$ kcal mol^{-1} [28]; $\Delta H_0^{\neq}(\mathbf{TS_{7\rightarrow 8}}) = +42.3$ kcal mol^{-1} [21]), it is understandable why all these species can be detected at the very low temperature of the matrix isolation conditions and that they require considerable activation, which our experiments provide through light irradiation. Irradiation of **6** yields the novel silabicyclic compound **9**. Although the intramolecular C–H bond insertion reaction of **6** to yield bicyclic **9** displays the largest exothermicity of −21.8 kcal mol^{-1}, it has not been detected before, most likely because of the sizable barrier for its formation ($\Delta H_0^{\neq}(\mathbf{TS_{6\rightarrow 9}}) = +37.4$ kcal mol^{-1}) in a thermally initiated reaction. The computed reaction profiles for the thermal conversion of **6**→**9**, **6**→**7**, and **7**→**8** are shown in Figure S42.

The oxidation reaction of **6** with O_3 to silanone **10** (with $^1\Sigma_g$ O_2 as product) is highly exothermic (−97.6 kcal mol^{-1}) so that we were unable to find a barrier for this reaction, which is expected to be extremely small. Hence, the concept of using a stable silylene as starting material for the preparation of a silanone through oxidation with O_3 (or N_2O) is energetically very favorable, indicating that the silanone is thermodynamically very stable and that its elusiveness results from kinetic instability.

The DFT-computed Si=O bond length in **10** is 1.549 Å, similar to the 1.542 Å for $(CH_3)_2Si{=}O$. As in other silanones, the Si=O bond in **10** is highly polar; the natural population analysis (NPA)[29] charges are +2.10 (Si) and −1.10 (O). The Si=O Wiberg bond index (WBI)[30] in **10** is 1.35 (for comparison, the WBI of the Si–O single bond in $(CH_3)_3SiOSi(CH_3)_3$ is 0.56). This value indicates that, as in other silanones, this bond is best described as a highly polarized $Si^{\delta+}$–$O^{\delta-}$ zwitterionic bond which has a significant contribution from Si=O π bonding. Note that the β-silyl substituents in **10** slightly weaken the double-bond nature of the Si=O bond. Thus, the Si=O WBI in **10** (1.35) is smaller than in $(CH_3)_2Si{=}O$ (1.44) or in the analogous β-tetramethyl derivative (**10**-Me; WBI = 1.45). This is due to the more effective β-σ(C–Si)–π*(Si=O) interactions (each second-order perturbation interaction is worth 3.5 kcal mol^{-1}) in **10** compared to the β-σ(C–Si)–π*(Si=O) interactions (1.3 kcal mol^{-1} each) in **10**-Me (for molecular orbital renderings, see Figure S42).

We have demonstrated the preparation of a novel uncomplexed cyclic silanone **10** by oxygen atom transfer from O_3 or N_2O to stable silylene **6** and have characterized it by IR spectroscopy. En route to realizing this approach, we also identified a photochemical reaction of silylene **6** yielding a new bicyclic bridgehead silane **9** resulting from intramolecular C–H bond insertion. The excellent matching of experimental (under matrix isolation conditions) and DFT-computed IR spectra corroborate our results.

Experimental Section

Matrix isolation experiments: Standard procedure for the performed experiments used Ar as the host gas. The experiments consumed 45–130 mbar of the host gas from a 2 L storage bulb, with typical gas flow rates of approximately 0.5–0.7 mbar min^{-1}. To regulate the flow rates needle valves between the inlet of the experimental system and the storage bulb were used. All IR measurements were made at 12 K. Silylene **6** was filled under an Ar atmosphere into an airtight tube with a Teflon plug and was attached to the matrix isolation apparatus. The entire filling process was performed in a glove box with O_2 and H_2O levels lower than 3 ppm. The matrix isolation apparatus was evaporated with a Leybold Trivac type D1 6B (1.6 m^3h^{-1}, 4×10^{-4} mbar ultimate pressure) and a Leybold Turbovac 50 PT50 regulated by Leybold Turbotronik NT 50 IKR 020 to a level below 4×10^{-6} mbar. We utilized a Balzers TPG 300 total pressure controller with a Balzers TPR 010 element. An APD DE202 and HC-2 closed-cycle refrigerator system produced the required temperatures of 12 K. To ensure exact temperature values the matrix head bears a Si diode near to the CsI cold window and the Scientific Instruments Inc 9600-1 thermocontroller. To control the temperature for the evaporation process, a Herastat, Heraeus-Wittmann Heidelberg type

TR500, was used. Additionally, the temperature was measured with a NiCr–Ni thermo element directly connected to the sample tube. The evaporation temperature was achieved with a heating wire wrapped around the sample tube. The vacuum shroud consists of the sample alignment, a sapphire window, and two KBr windows.

Deposition of silylene **6**: The silylene experiment consumed 130 mbar Ar in 3.5 h with an averaged evaporation temperature of 53 °C. The matrix showed a yellow coloration.

Cyclopentasilene **7**: Silene **7** was prepared by keeping **6** at room temperature in the dark for about two weeks. Thereafter, **7** was evaporated at a temperature of 63 °C onto a cold window. This differs from the experiment carried out by Kira et al. where **6** completely isomerized to **7** within 24 h in benzene at 60 °C.[15a,b,20] Similarly to the findings of Kira and co-workers, **7** rearranges to silacyclopentene **8** when exposed to light ($\lambda > 320$ nm) also in a matrix.

Silacyclopentene **8**: Irradiation of cyclopentasilene **7** with wavelengths of $\lambda = 254$ nm and 334 nm gives silacyclopentene **8** within 5 days. The irradiations were performed with mercury lamps.

Bridgehead silane **9**: Based on the silylene experiment, the bridgehead silane was prepared by 3 h irradiation of **6** with $\lambda =$ 450 nm at 12 K.

Silanone **10**: Target **10** was generated from an argon mixture with 1.9 % of the oxygen atom transfer agents (O_3 or N_2O) which was coevaporated with **6**. The evaporation temperatures were the same as for the deposition of **6**. Optimization of the tempering steps from 12–27 K over 5 days produced the largest amount of **10**.

Infrared spectra: All IR spectra were recorded on a Bruker IFS55 IR spectrometer with a spectral range of 4500–370 cm^{-1} and a resolution of 0.6 cm^{-1} (2.4 mm aperture), a SiC globar MIR radiation source, a KBr beamsplitter, and a DTGS detector. Each spectra accumulated 50 scans.

UV/Vis absorption spectra: UV/Vis spectra were recorded with a JASCO V-670 instrument.

Irradiation experiments: Experiments were carried out using a Bausch and Lomb high-intensity monochromator (1350 Grooves/mm, 300 nm blaze) and mercury SP200 light source give wavelengths ≥ 254 nm. Wavelength $\lambda < 254$ nm were achieved with a Gräntzel Suprasil (180–254 nm, 250 mA). Schott optical filter glasses assured radiation with the desired wavelength.

Chemicals: Silylene **6** was prepared according to the method of Kira et al.[15a,b] N_2O was purchased from Fluka Analytical ($\geq$ 99.998 %) and used without further purification. Ozone was generated from oxygen from Praxair with a product quality of 2.5. The isotopic experiment were performed with 97.1 % $^{18}O_2$ enriched oxygen from Eurisotop and used without further purification.

Ozone preparation: For the synthesis of ozone, a RAYTHEON microwave power generator was used. The plasma was persistent at a pressure range of 0.4–2.5 mbar. The generated ozone was collected as a deep-blue liquid. Within 4 h, the experimental system yielded about 10 mbar pure ozone, which was purified through various evaporation and liquefaction steps. Mixtures of O_3 with argon were stored in a 2 L flask to ensure the necessary concentrations of 1.0–2.5 %.

Computations: We employed the M06-2X[31] DFT functional in combination with a cc-pVDZ[32] basis set for all geometry optimizations and the characterizations of stationary points as minima (no imaginary frequencies) or transition structures (one imaginary frequency) as well as for all vibrational frequency computations. All computations were performed with the Gaussian09 electronic structure code.[33]

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Keywords: density functional calculations · IR spectroscopy · matrix isolation · oxygen atom transfer · silicon

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