

Dihalodimethylsilanes from silicon atoms and methyl halides: a combined matrix-spectroscopic and density functional theory study[☆]

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Abstract

The reaction of silicon atoms with methyl halides **6a–d** has been studied in an argon matrix at 10 K. It is shown that the product formation depends on the relative methyl halide/argon ratio. In the initial step triplet *n*-adducts **T-5** are formed. **T-5a–c** can be identified spectroscopically. The next step can be induced photochemically. The primary photoproducts are the halomethylsilylenes **S-1a–c**. In case of methyl iodide **6d** the reaction with silicon atoms leads spontaneously to silylene **S-1d**. In a diluted argon matrix all silylenes **1a–d** can further be photoisomerized to the corresponding halosilenes **2a–d**. In the presence of an excess of a methyl halide complexes of type **7a–d** are formed. Longer irradiation transforms these adducts into the dihalodimethylsilanes **8a–d**. The generation of the silanes **8a–d** starting from silicon and a methyl halide images the results of the Rochow-Müller synthesis. The relevance of our findings to this important technical process is discussed. The structural elucidation of all new species is based on the comparison of the experimental observations with density functional theory calculations.

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1. Introduction

During the past 6 years, we have studied the reactions of thermally generated silicon atoms with a variety of low molecular weight reactants in an argon matrix. The reaction products were identified by means of IR and UV-vis spectroscopy, aided by comparison with calculated spectra. The method turned out to be very versatile and successful [1]. The selected substrates were mainly molecules with isolated, conjugated or aromatic π bonds, and compounds containing π bonds and at the same time free electron pairs.

Of special interest are molecules possessing *n* electrons only in combination with σ bonds. The reactions of silicon atoms with target molecules of this type are relevant for the understanding of the Rochow-Müller (R.-M.) synthesis [2]. In a recent essay Seyferth describes

the enormous importance of this ‘direct synthesis’ of dichlorodimethylsilane by reaction of a silicon/copper alloy with methyl chloride [3]. At the same time he points out, as has also been argued by Pachaly and Weis [4], that even today, more than 60 years after its discovery in 1940, the mechanism of this process is still not fully understood. It was our hope that investigation on the behavior of Si atoms in a matrix may perhaps throw some light upon the fundamental reactions occurring on the surface of the Si/Cu contact mass used in the R.-M. synthesis. Therefore we started a project dealing with reactions of silicon atoms with substrates like water, methanol, dimethyl ether, and methyl halides [5].

In the first paper of an anticipated series dealing with the reactions of silicon atoms with ($\sigma+n$) systems the results with dimethyl ether as the substrate molecule are discussed [1e]. This study reveals that matrix isolation techniques cannot only be applied to uncover the *intramolecular* transformations of the *n*-adduct, which is formed in the reaction of a Si atom with a single molecule of dimethyl ether, to methoxymethylsilylene. If the concentration of the target molecule is raised, also

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mic (5–25 kcal mol⁻¹) reaction. The next higher candidates are the *n*-adducts **T-5a–d**. The first three members **T-5a–c** are stabilized compared to the starting materials Si(³P) atoms and methyl halides **6a–c**, which are the zero levels of our energy scale. The same is probably also true for methyl iodide **6d**. Its *n*-adduct **T-5d** is listed 0.9 kcal mol⁻¹ higher in energy than the two components. But this is presumably due to the fact, that in the iodine series the basis set SDD was used for the iodine atom. This basis set does not include polarization or diffuse functions. When the same method was applied to methyl bromide the *n*-adduct **T-5c** was also calculated to lie above (+2.2 kcal mol⁻¹) the base line for Si(³P) atom and methyl bromide **6c**. So, the value of +0.9 kcal mol⁻¹ for *n*-adduct **T-5d** does not indicate, that methyl iodide may behave differently from the other methyl halides.

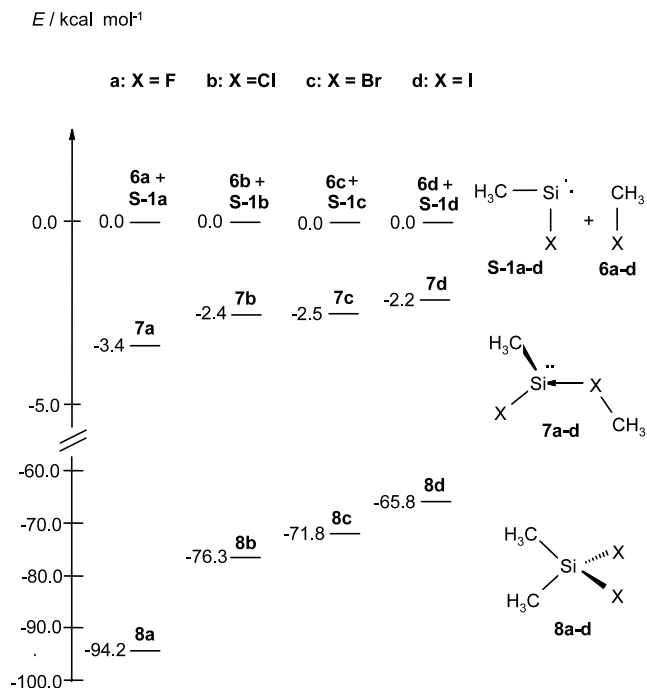
In order to get some information about the fate of silylenes **S-1a–d** in the presence of a second molecule of methyl halide **6a–d** we checked whether silylenes **S-1a–d** can experience stabilization by donor/acceptor interaction with **6a–d**. Indeed, the two partners form weak donor/acceptor complexes **7a–d**. That means: If **S-1a–d** is created in a matrix at very low temperature in the presence of an excess of a methyl halide **6a–d**, complexes like **7a–d** should be present. Such a solvation might be the prerequisite for the direct synthesis of silanes **8a–d**. These compounds represent the global minima on the C₂H₆SiX₂ energy hypersurfaces and are expected to be generated from the two educt molecules **S-1a–d** and methyl halide **6a–d** in rather exothermic ($\Delta H_r = 65$ –95 kcal mol⁻¹) processes (Table 2) (Scheme 2). According to calculations the complexes **7a–d** are nonplanar. The methyl group on the silicon lies above the plane of the cisoid sequence X–Si–X–CH₃.

4. Matrix experiments

In the standard experiments a gaseous mixture of a methyl halide **6a–d** and argon was deposited together with silicon atoms, generated by resistive heating of a

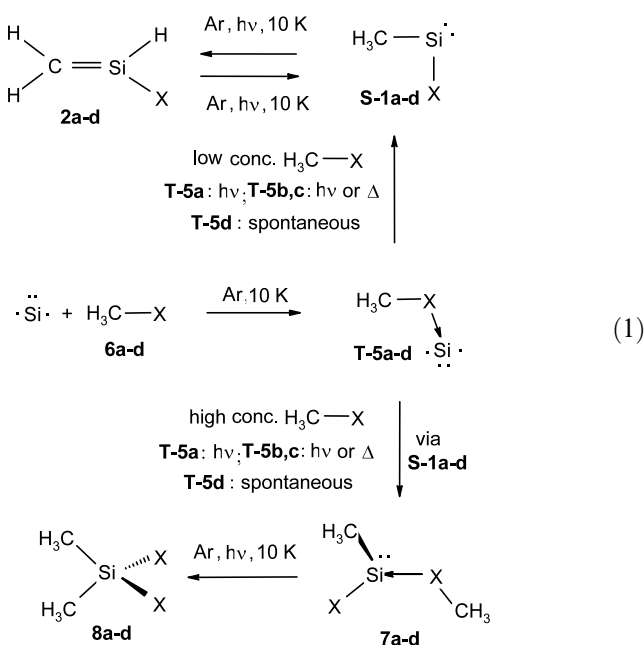
Table 2
Calculated energies of some C₂H₆SiX₂ isomers (B3LYP/6-311+G**, extra basis set SDD for iodine)

Halogen	Species (pointgroup, state), energy, ZPE included [hartrees]			
F	8a (C _s , ¹ A')	S-7a (C ₁ , ¹ A ₁)	CH ₃ SiF ₂ +3	S-1a+6a
	-569.202531	-569.057946	-569.061842	-569.052473
Cl	8b (C _s , ¹ A ₁)	S-7b (C ₁ , ¹ A ₁)	CH ₃ SiCl ₂ +3	S-1b+6b
	-1289.878482	-1289.760688	-1289.756874	-1289.756874
Br	8c (C _s , ¹ A ₁)	S-7c (C ₁ , ¹ A ₁)	CH ₃ SiBr ₂ +3	S-1c+6c
	-5517.715268	-5517.604774	-5517.587711	-5517.600846
I	8d (C _s , ¹ A ₁)	S-7d (C ₁ , ¹ A ₁)	CH ₃ SiI ₂ +3	S-1d+6d
	-392.224219	-392.123499	-392.041087	-392.119392



Scheme 2. Calculated relative energies of some C₂H₆SiX₂ isomers (X = F, Cl, Br: B3LYP/6-311+G**; X = I: B3LYP/SDD).

silicon rod to a temperature of ca. 1380 °C, onto a CsI window at 10 K. FT-IR and UV–vis spectra were taken of the matrices. Subsequent photochemical transformations were initiated by irradiating the matrices with light of the appropriate wavelength. Many experiments have been necessary to reveal all the facets of the Si/methyl halide systems. Only a few typical runs, uncovering some special features, are discussed explicitly (Eq. (1)).



4.1. Reactions with methyl fluoride

The basic idea of matrix isolation technique is to have isolated guest molecules in the surrounding of a huge amount of atoms forming the host lattice, in order to avoid any reaction between the entrapped species. Therefore, it is the ideal method for the study of *intramolecular* processes. In so far it is a contradiction per se to apply matrix isolation for the investigation of *intermolecular* reactions. If one wants to enforce intermolecular reactions it is necessary to raise the concentration of the reaction partners. According to our experience this situation is already reached with a ratio **6a**:Ar = 1:250. Under these conditions a new species showing a strong, sharp IR band at 960.7 cm^{-1} , together with 4 weak absorptions in the range $1440\text{--}2950\text{ cm}^{-1}$, is detected (Fig. 1; Table 3). The comparison between the calculated (Table 3) and experimental bands leaves no doubt that the primarily formed product is triplet *n*-adduct **T-5a**. Silylene **S-1a** cannot yet be detected.

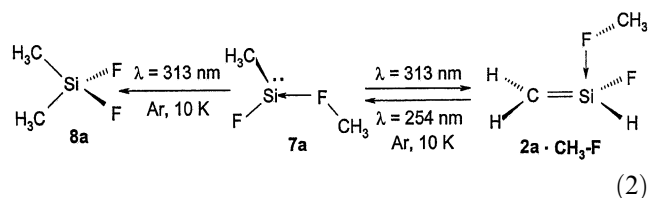
For our purpose it was important to know whether the IR spectra can help to find out whether **T-5a** can experience any change by solvation with an additional molecule of methyl fluoride **6a**. It turned out that this effect is less pronounced than with the other *n*-adducts **T-5b–5d**. If the amount of **6a** is raised (**6a**:Ar = 1:10) the band of **T-5a** at 960.7 cm^{-1} is broadened and the other lines have disappeared (Table 3).

The UV spectrum of *n*-adduct **T-5a** shows in the diluted matrix a strong maximum around 240 nm (Fig. 2). In case of the higher concentrated matrix an additional weak absorption of **T-5a** at roughly 360 nm is detectable (Fig. 4, curve a). The short wavelength band explains why **T-5a** is easily photoisomerized upon irradiation with 254 nm-light, but very slowly with longer (313, 366 nm) wavelengths.

Irradiation of *n*-adduct **T-5a** in a diluted argon matrix (**6a**:Ar = 1:250) with $\lambda = 254\text{ nm}$ leads to a complete isomerization into fluoromethylsilylene **S-1a** (Fig. 1; Table 4). This compound shows a strong IR band at 824.4 cm^{-1} and 4 weaker ones between 650 and 1450 cm^{-1} . In the UV region **S-1a** shows an absorption at 375 nm (Fig. 2). As a result of this silylene undergoes a secondary photoisomerization when irradiated with light of the wavelength 366 nm. The product is fluorosilene **2a**, as indicated by its IR spectrum (Fig. 3; Table 5), showing four strong bands at 689.4 , 839.2 , 872.3 and 1030.1 cm^{-1} . In the UV spectrum of **2a** a broad absorption around 260 nm can be detected. This absorption is responsible for the photochemical back reaction of **2a** to **S-1a** upon irradiation with 254 nm-light. Such a reversible silene/silylene photoisomerization has been described by us for the parent compounds already in 1984 [7] and can be taken as a kind of structural proof for the involved species.

If the concentration of methyl fluoride was increased (**6a**:Ar = 1:10) and the matrix containing the *n*-adduct **T-5a** irradiated for 10 min with short wavelength light (254 nm) the formation of fluoromethylsilylene **S-1a** could again be observed. But in this case additional IR bands at 722.2 , 798.2 and 1219.8 cm^{-1} (Table 6) indicated that besides free silylene **S-1a** some complexed silylene **7a** was present. This interpretation is supported by the UV spectra (Fig. 4). In addition to the absorption of free silylene **S-1a** around 370–375 nm a second band, which can be assigned to the methyl fluoride-complexed silylene **7a**, is visible at 310 nm. According to this difference depending on the concentration of **6a** it is possible to excite **S-1a** and **7a** separately by using specific wavelengths. With 366 nm **S-1a** is transferred into silene **2a**, with 313 nm complex **7a** forms an adduct **2a**·CH₃–F between the silene and methyl fluoride as indicated by IR bands at 837.3 , 877.2 and 2271.2 cm^{-1} (Table 7) and a UV absorption at 260–290 nm. This photoreaction is also reversible with 254 nm-light.

The spontaneous stabilization of the primarily generated silylene **S-1a** by addition of an additional molecule of methyl fluoride giving complex **7a** explains, why difluorodimethylsilane **8a** (identified by comparison with an authentic sample; IR: 1268.3 , 1266.9 , 934.7 , 929.1 , 903.3 , $820.0\text{ (vs cm}^{-1})$; no UV maximum) can—in addition to **S-1a** and **7a**—also be detected after *simultaneous* irradiation of the cocondensation product with 254 and 313 nm-light. After longer irradiation all **7a** is transferred into silane **8a** (Fig. 4, Eq. (2)).



Considering all the results found in an argon matrix it was the logical consequence to carry out the same kind of experiments in the absence of any argon. A matrix of pure solid methyl fluoride **6a** provides two advantages: On the one hand the *n*-adduct **T-5a** is only surrounded by methyl fluoride molecules (perfect solvation), an ideal prerequisite for intermolecular reactions. On the second hand the methyl fluoride matrix softens at a much higher temperature than solid argon, and therefore allows studies over a wider temperature range. Unfortunately, reactions in pure methyl fluoride matrices at 10 or 40 K gave no clear-cut results. But weak IR bands of difluorodimethylsilane **8a** were detected when the spectroscopic window was irradiated with 254 nm-light during cocondensation of pure **6a** and silicon atoms

Taking into account all these observations one understands that the best way to silane **8a** is the

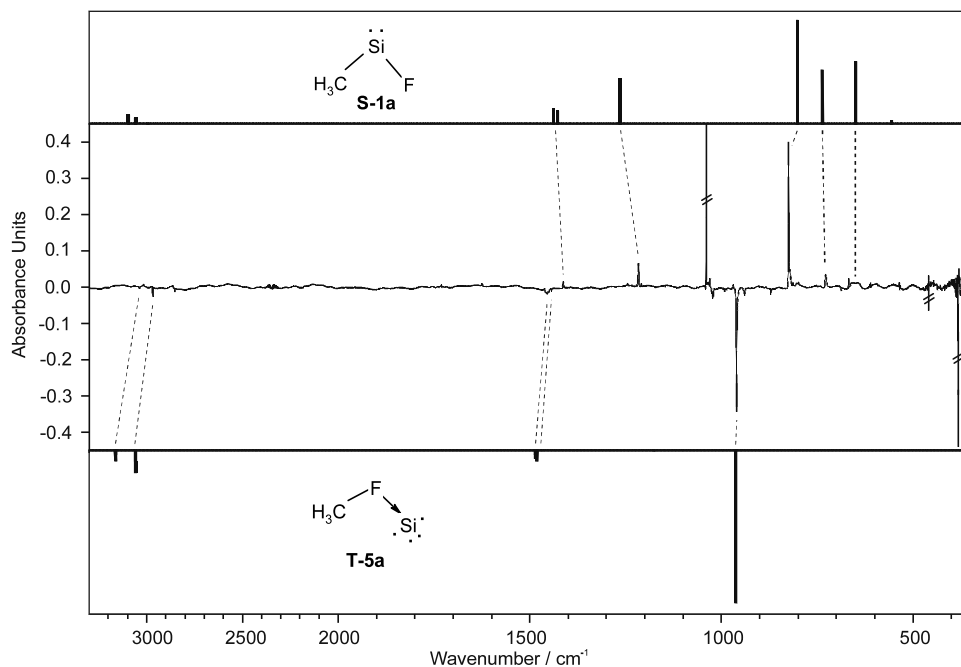


Fig. 1. Top: calculated (B3LYP/6-311+G**) IR spectrum of singlet fluoromethylsilylene **S-1a**; center: difference FT-IR spectrum originating from the photoreaction **T-5a** → **S-1a** (obtained by subtraction of the spectra before and after irradiation with 254 nm for 10 min); bottom: calculated (B3LYP/6-311+G**) IR spectrum of triplet *n*-adduct **T-5a**. The crossed-out bands belong to methyl fluoride **6a**.

irradiation of *n*-adduct **T-5a** in a matrix with a high concentration of methyl fluoride. The amount of complex **7a**—formed from **S-1a** in the first photochemical step by association with a second molecule of methyl fluoride—determines the yield of the final product **8a** in the second photochemical step.

This hypothesis will be confirmed below by comparison with the results with the other methyl halides **6b–d**. The methyl fluoride series is not the best example for silane formation. The generation of the corresponding

silanes **8b–8d** is much more convincing. On the other hand methyl fluoride system represents a peculiar case in so far that all expected intermediates **T-5a**, **S-1a**, **7a** and the end products silene **2a** and silane **8a** can be identified. Even more important: the study of the fluorine derivatives gave us the first hint on the importance of the activation energy for the insertion of the silicon into the CH₃–F bond on the way from *n*-adduct **T-5a** to silylene **S-1a**. This aspect will be discussed in more detail in the next section.

Table 3
Calculated (B3LYP/6-311+G**) and experimental IR spectrum of CH₃FSi isomer **T-5a**

No.	Sym.	Approx. description	Calculation	Experiment	
				CH ₃ F/Ar 1:250	CH ₃ F/Ar 1:10
ν_1	a ₁	Torsion	54.8(0.7)	–	–
ν_2	a ₁	CFSi bend.	108.1(0.8)	–	–
ν_3	a ₁	SiF str.	167.8(38.1)	–	–
ν_4	a ₁	CF str.	961.8(169.2)	960.7(vs)	960.7(m)
ν_5	a ₁	CH ₃ rock.	1176.6(1.2)	–	–
ν_6	a ₁	CH ₃ rock.	1177.4(0.7)	–	–
ν_7	a ₁	CH ₃ s-def.	1467.8(0.9)	–	–
ν_8	a ₁	CH ₃ d-def.	1481.4(12.2)	1443.5(m)	–
ν_9	a ₁	CH ₃ d-def.	1485.6(9.3)	1450.9(w)	–
$2 \times \nu_8$	a ₁		2962.8(–)	2852.6(m)	–
ν_{10}	a ₁	CH ₃ s-str.	3059.9(25.1)	2968.7(m)	–
ν_{11}	a ₁	CH ₃ d str.	3160.6(10.9)	3040.0(w)	–
ν_{12}	a ₁	CH ₃ d-str.	3162.8(12.2)	3040.0(w)	–

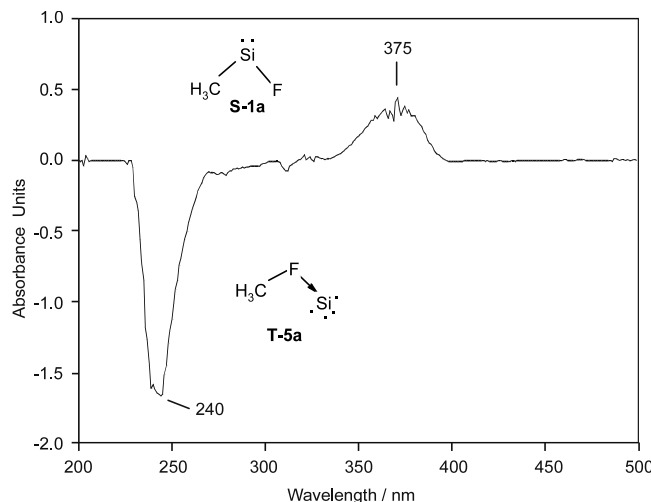


Fig. 2. Difference UV-vis spectrum originating from the photoreaction $T-5a \rightarrow S-1a$ (obtained by subtraction of the spectra of a diluted argon matrix ($6a:Ar = 1:250$) before and after irradiation with 254 nm for 10 min).

Table 4

Calculated (B3LYP/6-311+G**) and experimental IR spectrum of fluoromethylsilylene **S-1a**

Sym.	Approx. description	Calculation	Experiment	
			CH_3F/Ar 1:250	CH_3F/Ar 1:50
a_1	Torsion	77.7(0.2)	–	–
a_1	CSiF bend.	274.2(10.8)	–	–
a_1	CH_3 rock.	556.1(4.1)	–	–
a_1	SiC str.	649.7(68.6)	660.8(m)	660.6(m)
a_1	CH_3 rock. + SiF str.	736.7(59.1)	727.7(m)	727.0(m)
a_1	CH_3 rock. + SiF str.	801.7(114.1)	824.4(vs) ^a	824.1(vs) ^a
a_1	CH_3 s-def.	1264.3(50.1)	1216.3(s)	1216.9(s)
a_1	CH_3 d-def.	1427.7(14.1)	–	–
a_1	CH_3 d-def.	1438.1(16.1)	1412.6(m)	1412.6(m)
a_1	CH_3 s-str.	2994.4(1.4)	–	–
a_1	CH_3 d str.	3057.8(6.6)	–	–
a_1	CH_3 d-str.	3094.5(10.0)	–	–

^a The $^{29}Si^{19}F$ -band was observed at 818.7 cm^{-1} (1:250), the $^{30}Si^{19}F$ -band at 813.2 cm^{-1} (1:250) or 813.0 cm^{-1} (1:50).

Methyl fluoride is practically never discussed as a candidate for the R.-M. synthesis. Rochow mentions this possibility only in a footnote [8]. A corresponding citation in a review article [9] is misleading.

4.2. Reactions with methyl chloride

Since the R.-M. synthesis is based on methyl chloride **6b** most of our efforts were directed towards this substrate. If silicon atoms are cocondensed at 10 K

with a mixture **6b**:Ar = 1:250 the primary product is *n*-adduct **T-5b**. Already at 10 K a thermal transformation of **T-5b** into **S-1b** takes place. This thermal instability makes it difficult to identify **T-5b** spectroscopically. The C–Cl stretching vibration of **T-5b** is found at 679.1 cm^{-1} (Fig. 5) and corresponds to the calculated value at 667.3 cm^{-1} (Table 8). A second band with less intensity (1/3; ^{37}Cl isotopomer) is found at 673.9 cm^{-1} . The UV absorption which can be attributed to **T-5b** lies at 260 nm (Fig. 6). In addition **T-5b** must possess an absorption in the long wavelength region at around 580 nm, since *n*-adduct **T-5b** disappears slowly upon irradiation with 578 nm-light. But according to the IR spectrum the main component of the directly formed reaction product is chloromethylsilylene **S-1b**, which is characterized by strong IR bands at 484.4 and 1219.8 cm^{-1} (Fig. 7; Table 9). In the UV region **S-1b** absorbs at 405 nm (Fig. 6). Similar as it was described above for **S-1a** also **S-1b** can be transferred (light of wavelengths $> 385\text{ nm}$) into chlorosilene **2b**, as shown by the IR spectrum (Fig. 7; Table 10) and its UV absorption at 250 nm. The back reaction needs 254 nm-light. The spectroscopic data for **S-1b** and **2b** confirm our results of an earlier study [7].

If the concentration of methyl chloride is raised (**6b**:Ar = 1:10) no IR bands of *n*-adduct **T-5b** or silylene **S-1b** can be detected. But **T-5b** has to be present in the matrix since in the UV spectrum the band at 260 nm (strong) is observable, together with a second absorption at 330 nm (weak), which we also attribute to *n*-adduct **T-5b** (Fig. 8). Upon irradiation with 330 nm the band at 260 nm disappears. At the same time a new absorption, again at 330 nm, can be detected. If one compares with the IR results (see below), it has to be concluded that this band belongs to adduct **7b**, which is formed from the primarily generated uncomplexed silylene **S-1b**. Upon irradiation of the matrix with 330 nm-light the IR bands of and dichlorodimethylsilane **8b** appear (Fig. 9). As discussed above, during irradiation a sufficient amount of **T-5b** is isomerized to **S-1b**. In the concentrated matrix the silylene exists mainly as the complex **7b**, which in a subsequent photoreaction generates silane **8b**. If one uses 254 nm-light the final detectable product is also silane **8b**. If one wants to get comparable amounts of **S-1b** and **7b** the most suitable ratio of **6b**:Ar is in the range 1:50. Under these conditions IR bands at 753.0 and 1222.0 cm^{-1} , belonging to **7b**, can be registered (Table 11).

Many attempts were made to find out whether the reaction in pure methyl chloride **6b** can be used for preparative runs at higher temperatures. It could be shown that cocondensation of silicon atoms in solid methyl chloride at 10, 40 or 60 K followed by irradiation with 254 nm ends up with the appearance of the IR bands of silane **8b**. That means that at temperatures up to 60 K the methyl chloride-complexed silylene **7b** is

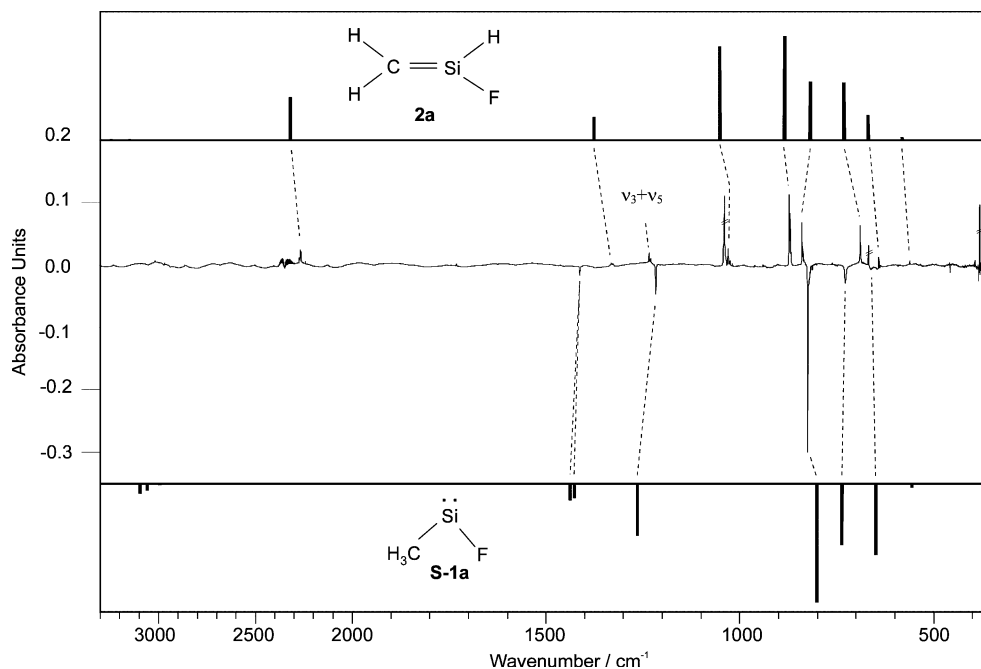


Fig. 3. Top: calculated (B3LYP/6-311+G**) IR spectrum of 1-fluorosilene **2a**; center: difference FT-IR spectrum originating from the photoreaction **S-1a** → **2a** (obtained by subtraction of the spectra before and after irradiation with 366 nm for 1 h); bottom: calculated (B3LYP/6-311+G**) IR spectrum of singlet fluoromethylsilylene **S-1a**. The crossed-out bands belong to methyl fluoride **6a** and CO₂.

stable in the methyl chloride matrix. This is no more the case at 77 K.

No better results were achieved when a neopentane matrix, which should be inert against silicon atoms [1i], was applied. Cocondensation of methylchloride **6b** and neopentane at 60 K in the ratio 1:100 and subsequent

irradiation with 254 nm-light gave only small signals of silane **8b**.

Being aware of the thermal instability of *n*-adduct **T-5b** it was tempting to test whether there is a better chance to get silane **8b** if the Si atoms and methyl chloride **6b** are trapped together on the spectroscopic

Table 5
Calculated (B3LYP/6-311+G**) and experimental IR spectrum of 1-fluorosilene **2a**

No.	Sym.	Approx. description	Calculation	Experiment	
				CH ₃ F/Ar 1:250	CH ₃ F/Ar 1:50
ν_1	a'	CH ₂ rock.	259.6(13.6)	–	–
ν_2	a''	CH <i>cis</i> wag.	346.6(23.3)	–	–
ν_3	a''	CH <i>trans</i> wag.	580.6(3.0)	561.8(w)	561.8(w) ^a
ν_4	a'	CH ₂ rock.	668.4(23.9)	641.2(m)	640.9(m)
ν_5	a''	CH ₂ wag.	731.0(55.4)	689.4(s)	689.1(s)
ν_6	a'	SiF str.	818.0(56.4)	839.2(s) ^b	838.9(s) ^b
ν_7	a'	CH rock.	883.8(100.0)	872.3(s) ^c	872.0(s) ^c
ν_8	a'	SiC s-str.	1051.6(90.4)	1030.1(s) ^d	– ^d
$\nu_3 + \nu_5$			1311.0	1233.6(w)	1233.6(w)
ν_9	a'	CH ₂ s-def.	1376.1(22.1)	1331.8(w)	1331.6(w)
ν_{10}	a'	SiH s-str.	2318.7(41.2)	2266.6(m) ^[e]	2266.1(m) ^e
ν_{11}	a'	CH s-str.	3147.9(0.9)	–	–
ν_{12}	a'	CH a-str.	3243.9(0.8)	–	–

^a IR-absorption of additional matrix site at 559.6 cm⁻¹.

^b IR-absorptions of additional matrix sites at 834.4 and 831.7 (1:250) or 831.5 cm⁻¹ (1:50).

^c IR-absorptions of additional matrix sites at 870.1 and 867.1 cm⁻¹ (1:250) or 869.8 and 867.2 cm⁻¹ (1:50).

^d ²⁹Si¹²C-str. band absorbs at 1025.4 cm⁻¹, ³⁰Si¹²C-str. band at 1019.3 cm⁻¹.

^e IR-absorption of additional matrix site at 2272.8 cm⁻¹ (1:250) or 2272.4 cm⁻¹ (1:50).

Table 6
Calculated (B3LYP/6-311+G**) and experimental IR spectrum of CH₃F-complex of fluoromethylsilylene **7a**

Sym.	Approx. description	Calculation	Experiment CH ₃ F/Ar 1:50	CH ₃ F/Ar 1:10
a ₁	CFSiF ip def.	32.1(6.2)	–	–
a ₁	Torsion (MeF)	70.6(0.5)	–	–
a ₁	Torsion (SiMe)	84.5(4.2)	–	–
a ₁	CFSiF ip bend.+torsion (SiMe)	109.8(2.1)	–	–
a ₁	CFSiF oop bend.+torsion (SiMe)	122.2(2.8)	–	–
a ₁	SiF str. (MeF)	150.6(30.2)	–	–
a ₁	CFSi bend. (MeF)	174.2(2.0)	–	–
a ₁	CSiF bend.	279.4(10.6)	–	–
a ₁	CH ₃ rock.+SiC str.	601.5(17.9)	–	–
a ₁	CH ₃ rock.+SiC str.	667.2(33.2)	653.5(w)	–
a ₁	CH ₃ rock.+SiF str.	715.5(95.4)	720.8(m)	722.2(m)
a ₁	CH ₃ rock.+SiF str.	784.6(77.4)	803.8(m)	798.2(m)
a ₁	CF str.	965.9(170.0)	969.4(m)	–
a ₁	CH ₃ rock. (MeF)	1176.8(0.9)	–	–
a ₁	CH ₃ rock. (MeF)	1187.9(0.5)	–	–
a ₁	CH ₃ s-str. (SiMe)	1265.8(47.2)	1217.2(m) ^a	1219.8(m)
a ₁	CH ₃ d str. (SiMe)	1434.6(15.0)	–	–
a ₁	CH ₃ d-str. (SiMe)	1443.5(12.3)	–	–
a ₁	CH ₃ s-def. (MeF)	1469.5(1.3)	–	–
a ₁	CH ₃ d-def. (MeF)	1483.7(6.9)	–	–
a ₁	CH ₃ d-def. (MeF)	1495.1(6.0)	–	–
a ₁	CH ₃ s-str. (SiMe)	2992.0(4.6)	–	–
a ₁	CH ₃ s-str. (MeF)	3059.4(31.1)	2941.8(w)	–
a ₁	CH ₃ d-str. (SiMe)	3063.4(11.2)	2941.8(w)	–
a ₁	CH ₃ d-str. (SiMe)	3099.3(12.6)	2978.1(w) ^b	–
a ₁	CH ₃ d-str. (MeF)	3154.4(15.7)	3045.1(w) ^b	–
a ₁	CH ₃ d-str. (MeF)	3166.3(4.5)	–	–

^a Shoulder close to the strong IR absorption of fluoromethylsilylene **S-2a** at 1216.9 cm⁻¹.

^b Shoulders close to the strong IR absorptions of the CH₃ a-str. band at 3017.5 cm⁻¹ and the absorptions of the Fermi pair (CH₃ s-str. and 2 × CH₃ d-def.) at 2968.3 and 2863.2 cm⁻¹ of unreacted methyl fluoride (1:50).

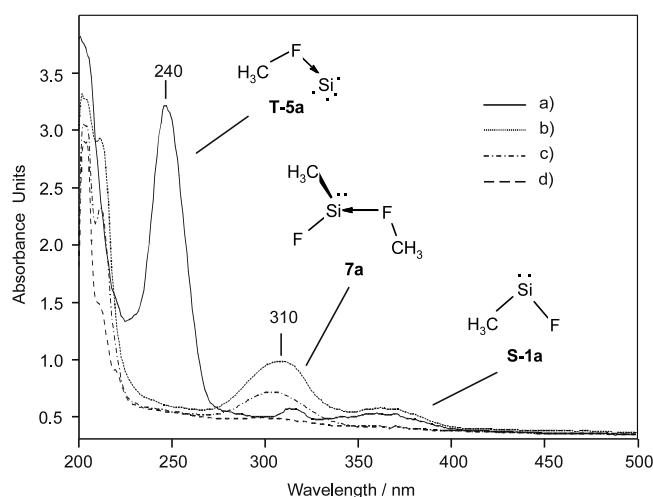


Fig. 4. UV-vis spectrum of the cocondensation product of silicon atoms and methyl fluoride (**6a**:Ar = 1:10); curve a: after cocondensation; curve b: after irradiation with 254 nm for 30 nm; curve c: after simultaneous irradiation with 254 and 313 nm for 2 h; curve d: after irradiation with 254 and 313 nm for 10 h.

window and the condensate is simultaneously irradiated. If the concentration of methyl chloride is high enough each newly formed *n*-adduct molecule should immediately be transformed into silane **8b**. Indeed, the amount of dichlorodimethylsilane **8b** is much higher if the cocondensation of silicon atoms and pure methylchloride **6b** is carried out under simultaneous irradiation with 254 nm-light (Fig. 9, curve d).

4.3. Reactions with methyl bromide

The behavior of methyl bromide **6c** is very similar to that of methyl chloride. Again the primarily formed *n*-adduct **T-5c** is not stable in the argon matrix and undergoes even at 10 K the insertion reaction leading to silylene **S-1c**. That means, the original reaction mixture generated in a dilute (**6c**:Ar = 1:500) matrix shows at the same time the spectra of **T-5c** (UV: 260 nm (Fig. 10); IR: 1288.2, 1418.4 cm⁻¹ (Table 12)) and **S-1c** (UV: 425 nm (Fig. 10); IR: 386.0, 1219.5 cm⁻¹ (Fig. 11; Table 13)).

Like the other silylenes also **S-1c** can be isomerized to the corresponding silene **2c** by irradiation with suited

Table 7
Calculated (B3LYP/6-311+G**) and experimental IR spectrum of CH₃F-complex of 1-fluorosilene **2a**·MeF

Sym.	Approx. description	Calculation	Experiment	
			CH ₃ F/Ar 1:50	CH ₃ F/Ar 1:10
a ₁	Torsion	28.6(4.0)	—	—
a ₁	CSiF bend.	52.1(1.2)	—	—
a ₁	CH ₃ rock.	65.6(7.0)	—	—
a ₁	SiC str.	87.2(2.4)	—	—
a ₁	CH ₃ rock.+SiF str.	112.5(27.6)	—	—
a ₁	CH ₃ rock.+SiF str.	144.8(1.1)	—	—
a ₁	CH ₃ s-def.	262.9(13.7)	—	—
a ₁	CH <i>cis</i> wag.	389.0(40.2)	—	—
a ₁	CH <i>trans</i> wag.	576.5(9.0)	—	—
a ₁	CH ₂ rock.	667.2(22.2)	641.3(w)	—
a ₁	CH ₂ wag.	716.2(41.7)	—	—
a ₁	SiF str.	807.7(50.7)	838.9(m)	837.3(vw)
a ₁	CH rock.	880.1(97.4)	876.2(m)	877.2(w)
a ₁	CF str. (MeF)	996.7(158.3)	986.9(m)	—
a ₁	SiC str.	1045.5(97.0)	—	—
a ₁	CH ₃ rock.	1180.9(0.8)	—	—
a ₁	CH ₃ rock.	1185.3(0.4)	—	—
a ₁	CH ₂ scissor.	1374.7(23.6)	—	—
a ₁	CH ₃ s-def.	1472.4(1.6)	—	—
a ₁	CH ₃ d-def.	1486.2(7.4)	—	—
a ₁	CH ₃ d-def.	1493.7(6.3)	—	—
a ₁	SiH str.	2330.5(41.7)	2278.3(w) ^a	2271.2(vw)
a ₁	CH ₃ s-str.	3050.1(32.0)	—	—
a ₁	CH ₃ d str.	3139.0(22.0)	—	—
a ₁	CH ₂ s-str.	3146.8(0.4)	—	—
a ₁	CH ₃ d-str.	3150.1(12.5)	—	—
a ₁	CH ₂ a-str.	3241.1(0.1)	—	—

^a An IR-peak of an additional matrix site was observed at 2274.0 cm⁻¹ (1:50).

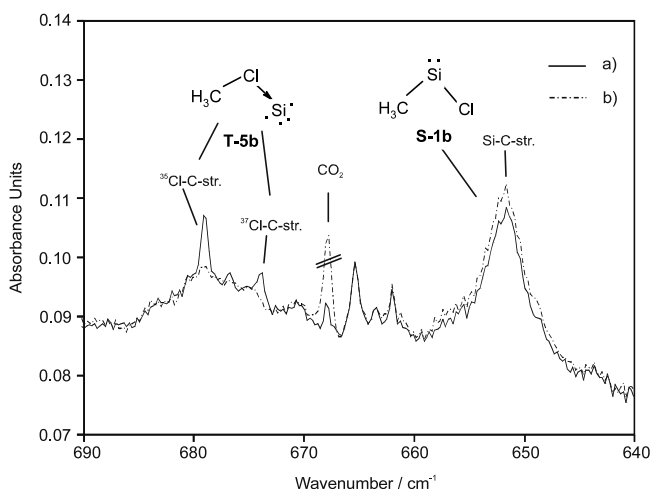


Fig. 5. FT-IR spectrum (cut-out) of the cocondensation product of silicon atoms and methyl chloride (**6b**:Ar = 1:250); curve a: after cocondensation; curve b: after irradiation with 254 nm.

Table 8
Calculated (B3LYP/6-311+G**) and experimental IR spectrum of CH₃ClSi isomer **T-5b**

Sym.	Approx. description	Calculation	Experiment	
			CH ₃ Cl/Ar 1:250	CH ₃ Cl/Ar 1:50
a ₁	Torsion	53.2(0.0)	—	—
a ₁	CCiSi bend.	101.4(1.7)	—	—
a ₁	SiCl str.	142.6(21.4)	—	—
a ₁	CCl str.	667.3(27.2)	679.1(w) ^a	678.8(w) ^a
a ₁	CH ₃ rock.	1029.4(12.9)	1011.8(vw)	1012.1(vw)
a ₁	CH ₃ rock.	1032.1(1.1)	—	—
a ₁	CH ₃ s-def.	1378.9(9.1)	1334.3(vw)	1334.2(vw)
a ₁	CH ₃ d-def.	1466.1(12.8)	1428.7(vw)	1428.3(vw)
a ₁	CH ₃ d-def.	1471.0(9.5)	1433.2(vw)	1433.2(vw)
a ₁	CH ₃ s-str.	3077.2(17.4)	—	2954.8(vw)
a ₁	CH ₃ d str.	3186.3(1.3)	—	—
a ₁	CH ₃ d-str.	3189.8(1.2)	—	—

^a ¹²C³⁷Cl str. band was observed at 673.8 (1:250) or 674.0 cm⁻¹ (1:50).

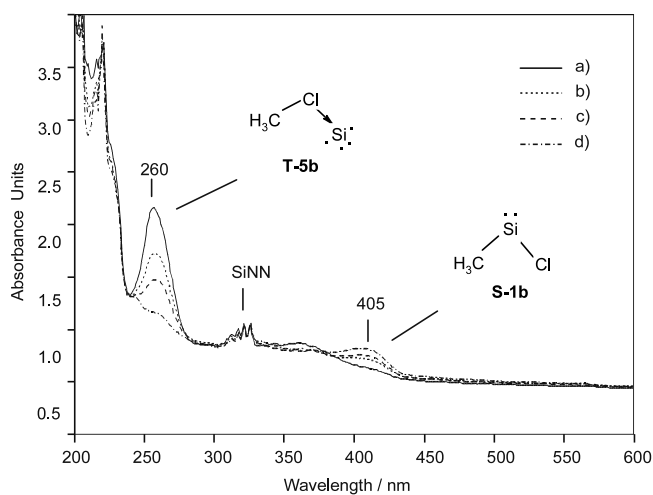


Fig. 6. UV-vis spectrum of the cocondensation product of silicon atoms and methyl chloride (**6b**:Ar = 1:50); curve a: after cocondensation; curve b: after irradiation with 578 nm for 2 h; curve c: after 4 h (578 nm); curve d: after 20 h (578 nm).

wavelengths (436 or > 385 nm). 1-Bromosilene **2c** is characterized by a very strong IR band at 833.6 cm⁻¹ (Fig. 11; Table 14). Silene **2c** absorbs in the UV at 252 nm (Fig. 12) and reforms therefore silylene **S-1c** upon irradiation with 254 nm-light.

If the original matrix is irradiated at 10 K with 578 nm the isomerization **T-5c**→**S-1c** is induced. So, *n*-adduct **T-5c** must have a second, long wavelength-absorption around 580 nm. Due to the strong absorption at 260 nm the photochemical transformation of *n*-

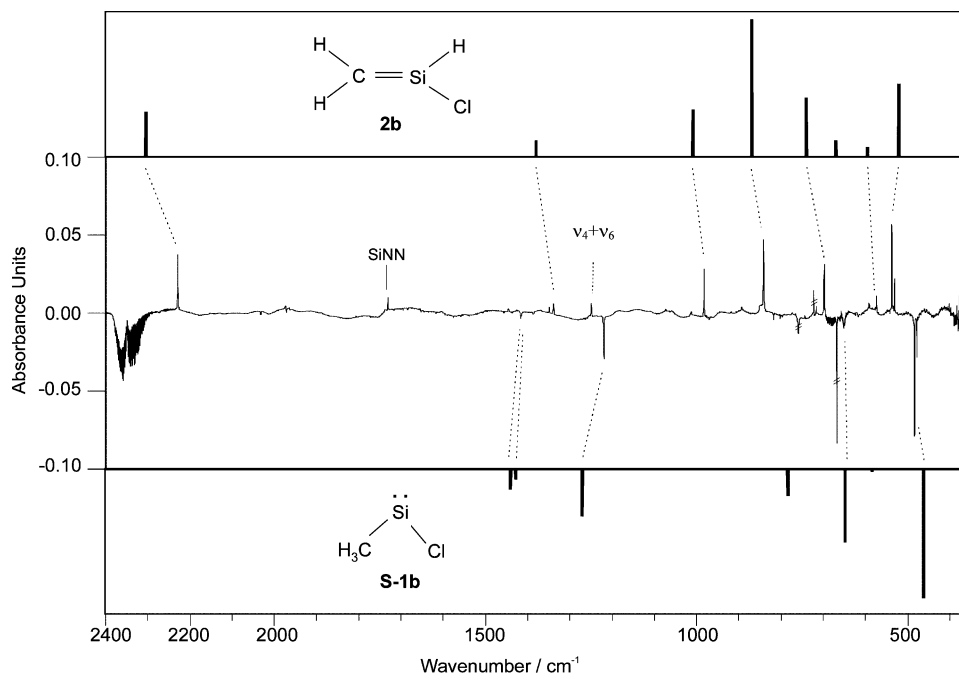


Fig. 7. Top: calculated (B3LYP/6-311+G**) IR spectrum of 1-chlorosilene **2b**; center: difference FT-IR spectrum originating from the photoreaction **S-1b** → **2b** (obtained by subtraction of the spectra before and after irradiation with $\lambda > 385$ nm for 1 h); bottom: calculated (B3LYP/6-311+G**) IR spectrum of singlet chloromethylsilylene **S-1b**. The crossed-out bands belong to methyl chloride **6b** and CO₂.

adduct **T-5c** is much easier to carry out with light of the wavelength 270 or 254 nm. Under these conditions the bands of traces of dibromodimethylsilane **8c** appear in the IR spectrum. The direct precursor for silane **8c**, silylene-complex **7c** with an attached methyl bromide molecule, is detectable if the concentration of methyl bromide is raised (**6c**:Ar = 1:10; broad bands at 754.5 and 1222.4 cm⁻¹ (Table 15)). Upon irradiation of **7c** strong bands (428.6, 682.2, 804.0, 815.0, 845.6, 1181.7, 1255.1 cm⁻¹) of dibromodimethylsilane **8c** can be registered.

4.4. Reactions with methyl iodide

The fate of methyl iodide **6d** in the presence of silicon atoms is principally in accordance with the observations described for other methyl halides. Nevertheless, a certain trend is quite obvious, if one compares the methyl fluoride and methyl iodide system. With methyl fluoride the relevant intermediates, **S-1a**, and **7a** can be isolated and clearly identified. But it is difficult to reach the final goal, namely the formation of silane **8a**. The contrary is true for methyl iodide **6d**. In this series it is

Table 9
Calculated (B3LYP/6-311+G**) and experimental IR spectrum of chloromethylsilylene **S-1b**

Sym.	Approx. description	Calculation	Experiment		Ref. [7]
			CH ₃ Cl/Ar 1:250	CH ₃ Cl/Ar 1:50	
a ₁	Torsion	88.0(0.0)	–	–	–
a ₁	CSiCl bend.	231.2(4.8)	–	–	–
a ₁	SiCl str.	462.0(112.4)	484.4(s) ^a	484.4(s)	485.0(w)
a ₁	CH ₃ rock.	584.7(2.6)	–	–	–
a ₁	SiC str.	647.8(63.8)	651.8(m)	651.8(w)	–
a ₁	CH ₃ rock.	783.9(23.2)	759.5(m)	759.5(m)	–
a ₁	CH ₃ s-def.	1270.4(41.2)	1219.8(s)	1219.8(s)	1223.0(m)
a ₁	CH ₃ d-def.	1428.4(9.0)	–	–	–
a ₁	CH ₃ d-def.	1440.2(18.0)	1416.2(m)	1416.0(m)	–
a ₁	CH ₃ s-str.	3000.1(1.0)	–	–	–
a ₁	CH ₃ d str.	3066.8(4.4)	–	–	–
a ₁	CH ₃ d-str.	3091.8(9.6)	–	–	–

^a ²⁸Si-³⁷Cl str. band was observed at 478.6 cm⁻¹.

Table 10
Calculated (B3LYP/6-311+G**) and experimental IR spectrum of 1-chlorosilene **2b**

No.	Sym.	Approx. description	Calculation	Experiment		Ref. [7]
				CH ₃ Cl/Ar 1:250	CH ₃ Cl/Ar 1:50	
ν_1	a'	CH ₂ rock.	220.1(7.0)	—	—	—
ν_2	a''	CH <i>cis</i> wag.	317.6(9.7)	—	—	—
ν_3	a'	SiCl str.+CH ₂ rock.	521.0(68.9)	537.7(m) ^a	537.7(m) ^a	539.0(w)
ν_4	a''	CH <i>trans</i> wag.	595.4(9.4)	574.4(w)	574.4(w)	—
ν_5	a'	CH ₂ rock.	669.9(15.8)	—	—	—
ν_6	a''	CH ₂ wag.	740.6(56.2)	697.4(m)	697.5(m)	699.0(w)
ν_7	a'	CH rock.	869.7(129.7)	841.8(s)	841.8(s)	843.0(vs)
ν_8	a'	SiC s-str.	1009.2(44.6)	982.6(m) ^b	982.6(m) ^b	984.0(m)
$\nu_4 + \nu_6$			1336.0	1249.4(w)	1249.4(w)	—
ν_9	a'	CH ₂ s-def.	1380.3(15.4)	1339.4(w)	1339.4(w)	—
ν_{10}	a'	SiH s-str.	2304.4(42.9)	2228.7(m)	2228.7(m)	2230.0(w)
ν_{11}	a'	CH s-str.	3145.2(0.5)	—	—	—
ν_{12}	a'	CH a-str.	3242.8(0.6)	—	—	—

^a ²⁸Si³⁷Cl band absorbs at 531.0 cm⁻¹.

^b ²⁹Si¹²C-isotopomer absorbs at 976.8 (1:250) or 976.8 cm⁻¹ (1:50). ³⁰Si¹²C. band absorbs at 971.3 (1:250) or 971.0 cm⁻¹ (1:50).

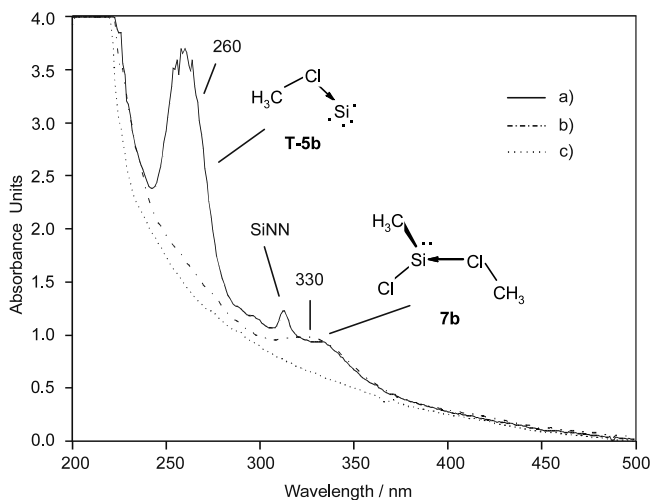


Fig. 8. UV-vis spectrum of the cocondensation product of silicon atoms and methyl chloride (**6b**:Ar = 1:10); curve a: after cocondensation; curve b: after irradiation with 330 nm for 30 min; curve c: after irradiation with 330 nm for 11 h.

quite easy to generate silane **8d**, the problem is here to get reliable information about the species on the way between the starting materials to the final product **8d**.

For instance, when methyl iodide **6d** is cocondensed with silicon atoms in a diluted argon matrix (ratio **6d**:Ar = 1:500) only bands belonging to iodomethylsilylene **S-1d** (IR: 1218.8 cm⁻¹ (Fig. 13; Table 16); UV: 242, 465 nm (Fig. 14)) are observed. This fact indicates, that *n*-adduct **T-5d** is absent since it isomerizes spontaneously to **S-1d** even at 10 K in a rather fast reaction.

As in the other cases **S-1d** is transformed into 1-iodosilene **2d** upon irradiation. This reaction has been initiated with light of the wavelength > 405, or 436, or

460 nm. Silene **2d** shows its strongest IR band at 833.6 cm⁻¹ (Fig. 13; Table 17). It has an UV absorption at 266 nm (Fig. 14). Therefore the back reaction **2d** → **S-1d** occurs upon irradiation with light of the wavelength 254 or 290 nm.

Parallel to the formation of silene **2d** during the irradiation (405, or 436, or 460 nm) of the original matrix diiododimethylsilane **8d** (1256.3, 1251.3, 845.5, 807.7 and 788.8 cm⁻¹) is also generated, in spite of the low concentration of methyl iodide **6d**.

When higher concentrations (ratio **6d**:Ar = 1:50 or 1:10) were used no bands indicating the presence of **T-5d** or **S-1d** could be detected. But a UV absorption at 370 nm (Fig. 15) and broad IR bands at 754.4 and 1220.6 cm⁻¹, which tentatively can be assigned to complex **7d**, could be observed (Table 18). Irradiation of such a matrix (Fig. 16, curve a) with 366 nm gave in a fast and clean photoreaction silane **8d** (Fig. 16, curve b), as confirmed by comparison with authentic material.

In logical continuation of these promising results pure methyl iodide was cocondensed with silicon atoms at 40 K under simultaneous irradiation with 366 nm-light. The only detectable product was diiododimethylsilane **8d**, as indicated by appearance of its IR bands (Fig. 16, curve c). No UV absorption in the region > 320 nm could be observed. The same outcome was achieved at 80 K (Fig. 16, curve d). These experiments show that under the described conditions methyl iodide **6d** and silicon atoms generate silane **8d** in a very selective and direct way.

This finding is of special interest in so far that—to the best of our knowledge—there are no substantial reports on the application of methyl iodide in the R.-M. synthesis. Again Rochow only mentions in a footnote that **6d** may form methyl iodosilanes on sintered copper-

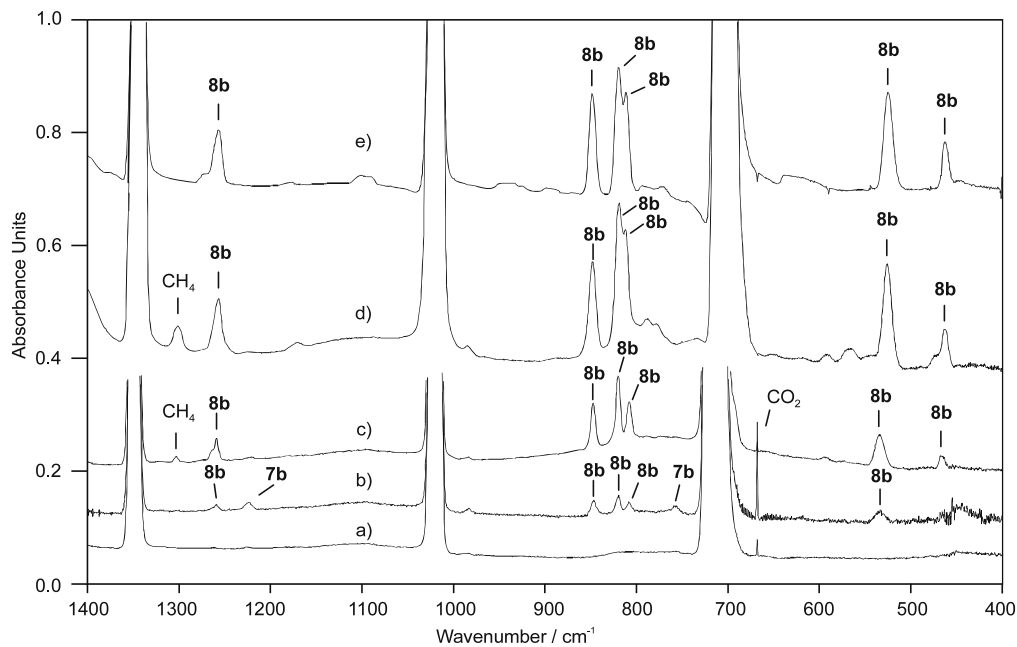


Fig. 9. FT-IR spectrum of the cocondensation product of silicon atoms and methyl chloride (**6b**:Ar = 1:10); curve a: after cocondensation; curve b: after irradiation with 330 nm for 30 min; curve c: after irradiation with 330 nm for 11 h; curve d: after cocondensation of pure methyl chloride **6b** under simultaneous irradiation with 254 nm at 40 K; curve e: authentic sample of **8b** in **6b** (ratio 1:200). The three unmarked, very strong bands belong to methyl chloride **6b**.

Table 11

Calculated (B3LYP/6-311+G**) and experimental IR spectrum of CH₃Cl-complex of chloromethylsilylene **7b**

Sym.	Approx. description	Calculation	Experiment	
			CH ₃ Cl/Ar 1:50	CH ₃ Cl/Ar 1:10
a ₁	CCSiCl oop def.	16.0(4.5)	—	—
a ₁	CCSiCl ip def.	71.7(5.8)	—	—
a ₁	Torsion	76.0(0.3)	—	—
a ₁	CH ₃ rock. (MeCl)+CSiCl bend.	78.7(2.3)	—	—
a ₁	SiCl str.(MeCl)	111.8(12.4)	—	—
a ₁	CCSi bend.	128.7(0.7)	—	—
a ₁	torsion (SiMe)	133.2(4.0)	—	—
a ₁	CSiCl bend.	232.7(3.9)	—	—
a ₁	SiCl str.	433.2(97.6)	—	444.0(w)
a ₁	CH ₃ rock. +SiC str.	603.9(23.8)	—	—
a ₁	CH ₃ rock. (SiMe)	672.4(31.0)	—	—
a ₁	CCl str.	687.4(34.5)	—	—
a ₁	CH ₃ rock. (SiMe)	782.2(22.6)	753.0(w)	756.6(w)
a ₁	CH ₃ rock. (MeCl)	1033.9(1.9)	—	—
a ₁	CH ₃ rock. (MeCl)	1040.7(8.6)	—	—
a ₁	CH ₃ s-def. (SiMe)	1271.7(39.8)	1222.0(m)	1223.5(m)
a ₁	CH ₃ s-def. (MeCl)	1385.1(7.2)	—	—
a ₁	CH ₃ d-def. (SiMe)	1431.2(9.6)	—	—
a ₁	CH ₃ d-def. (SiMe)	1443.5(15.6)	—	—
a ₁	CH ₃ d-def. (MeCl)	1475.1(4.9)	—	—
a ₁	CH ₃ d-def. (MeCl)	1480.2(5.1)	—	—
a ₁	CH ₃ s-str. (SiMe)	2994.2(2.6)	—	—
a ₁	CH ₃ d str. (SiMe)	3066.3(9.3)	—	—
a ₁	CH ₃ s-str. (MeCl)	3075.2(18.7)	—	—
a ₁	CH ₃ d-str. (SiMe)	3106.2(6.5)	—	—
a ₁	CH ₃ d str. (MeCl)	3179.2(0.1)	—	—
a ₁	CH ₃ d-str. (MeCl)	3185.1(2.3)	—	—

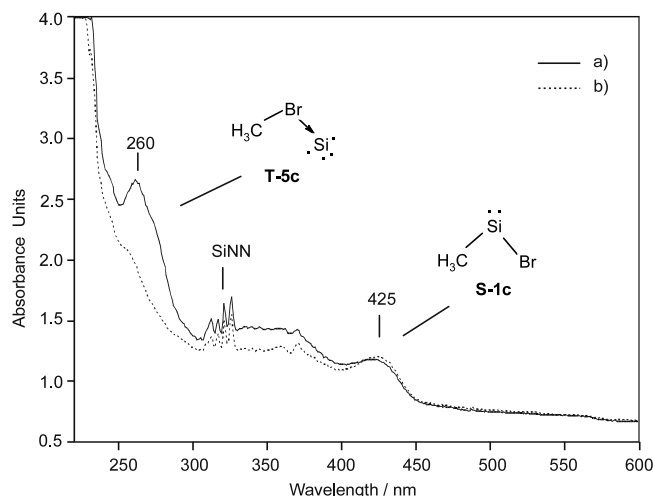


Fig. 10. UV-vis spectrum of the cocondensation product of silicon atoms and methyl bromide (**6c**:Ar = 1:500); curve a: after cocondensation; curve b: after irradiation with 578 nm for 15 min.

Table 12
Calculated (B3LYP/6-311+G**) and experimental IR spectrum of CH₃BrSi isomer **T-5c**

Sym.	Approx. description	Calculation	Experiment	
			CH ₃ Br/Ar 1:250	CH ₃ Br/Ar 1:50
a ₁	Torsion	54.7(0.0)	–	–
a ₁	CBrSi bend.	85.3(1.1)	–	–
a ₁	SiBr str.	145.8(6.7)	–	–
a ₁	CBr str.	528.5(11.1)	–	–
a ₁	CH ₃ rock.	956.1(20.0)	– ^a	– ^a
a ₁	CH ₃ rock.	959.9(1.7)	–	–
a ₁	CH ₃ s-def.	1321.9(16.7)	1288.2(w)	1288.3(w)
a ₁	CH ₃ d-def.	1457.7(12.9)	1418.4(w)	1418.8(w)
a ₁	CH ₃ d-def.	1464.1(7.7)	–	–
a ₁	CH ₃ s-str.	3079.1(12.9)	– ^a	– ^a
a ₁	CH ₃ d str.	3195.7(0.4)	–	–
a ₁	CH ₃ d-str.	3202.9(0.3)	–	–

^a Covered by strong IR absorptions of unreacted methyl bromide.

silicon pellets, but thermal decomposition allows only poor yields [8].

4.5. Reaction pathways from triplet *n*-adducts **T-5a–d** to singlet silylenes **S-1a–d**

4.5.1. Reactions with methyl fluoride

According to Scheme 1 the attack of a silicon atom at the fluorine atom of **6a** is less exothermic than in the cases of **6b** and **6c**. At the same time the stabilization energy of silylene **S-1a** is much higher than that of **S-1b** or **S-1c**. Therefore, one would expect that *n*-adduct **T-5a** should be less stable than **T-5b** or **T-5c**. As discussed above, experiment shows the opposite. This fact de-

manded a calculation of the transition states of these processes. It turned out, that indeed *n*-adduct **T-5a** is expected to have the highest activation barrier (Scheme 3). Another finding is: the *n*-adducts **T-5a–d** can use two different pathways for the insertion. For instance, starting from **T-5a** the concerted mode leads in the first step under spin conservation to triplet silylene **T-1a**. Intersystem crossing then yields **S-1a**. The alternative reaction path proceeds via the breakage of the methyl–halogen bond and is—this statement is valid for all systems—preferred compared with the synchronous process. In case of *n*-adduct **T-5a** the splitting into a methyl radical and a radical SiF is exothermic ($\Delta H_r = -23.3 \text{ kcal mol}^{-1}$), but is governed by a barrier of $11.0 \text{ kcal mol}^{-1}$. Recombination of the two fragments can lead to triplet silylene **T-1a** ($\Delta H_r = -48.4 \text{ kcal mol}^{-1}$) or in a more exothermic reaction ($\Delta H_r = -91.7 \text{ kcal mol}^{-1}$) directly to **S-1a**. The concerted pathway would afford an activation energy of even 19 kcal mol^{-1} .

4.5.2. Reactions with methyl chloride

It is probably the low activation barrier (barrier of $4.3 \text{ kcal mol}^{-1}$) for the radical decay type transition of *n*-adduct **T-5b** into silylene **S-1b** that governs the methylchloride system (Scheme 3). This process is expected to be faster than the insertion in the methyl fluoride case. This prediction is in agreement with the observation that the lifetime of **T-5b** at 10 K is so small that the insertion of the silicon atom into the CH₃–Cl bond of **6b** occurs spontaneously even at this very low temperature. Naturally it is better to use photochemical activation (especially with 254 nm-light).

Summarizing all these informations one gets the impression that the key step in the generation of silane **8b** from silicon atoms and methyl chloride **6b** is the transformation of *n*-adduct **T-5b** into silylene **S-1b** via the diradical pathway. This aspect can probably transferred from the atomic/molecular into the macroscopic dimension (R.-M. synthesis).

4.5.3. Reactions with methyl bromide

According to calculations (Scheme 3) the behavior of methyl bromide should be similar to methyl chloride. The activation barrier for the radical type decay is predicted to be still smaller. No wonder that it is difficult to trap and to identify *n*-adduct **T-5c**.

4.5.4. Reactions with methyl iodide

As in the methyl bromide series the activation barrier for the isomerization of *n*-adduct to silylene following the radical decay mechanism is calculated (Scheme 3) to be very low ($1.8 \text{ kcal mol}^{-1}$). Similar to methyl bromide methyl iodide **6d** should be the ideal candidate for a spontaneous formation of silylene **S-1d**.

If one looks at Schemes 1 and 3 one may be surprised that the *n*-adduct **T-5d** of methyl iodide is higher in

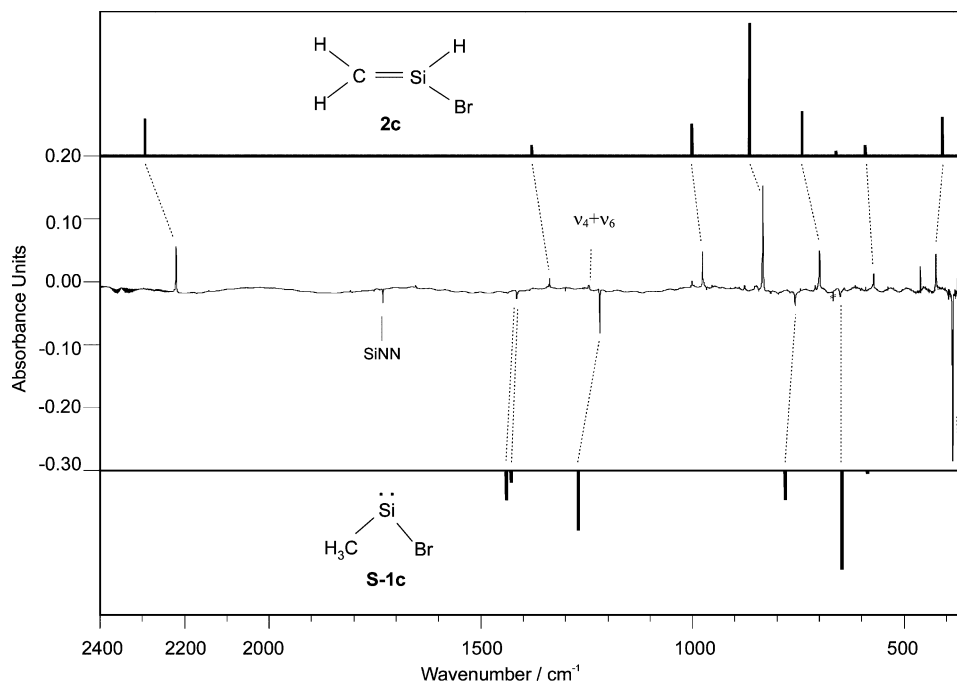


Fig. 11. Top: calculated (B3LYP/6-311+G**) IR spectrum of 1-bromosilene **2c**; center: difference FT-IR spectrum originating from the photoreaction **S-1c** → **2c** (obtained by subtraction of the spectra of a diluted argon matrix (**6c**:Ar = 1:500) before and after irradiation with 436 nm for 10 h); bottom: calculated (B3LYP/6-311+G**) IR spectrum of singlet bromomethylsilylene **S-1c**. The crossed-out band belongs to CO₂.

Table 13

Calculated (B3LYP/6-311+G**) and experimental IR spectrum of bromomethylsilylene **S-1c**

Sym.	Approx. description	Calculation	Experiment	
			CH ₃ Br/Ar 1:250	CH ₃ Br/Ar 1:50
a ₁	Torsion	79.2(0.0)	–	–
a ₁	CSiBr bend.	201.9(2.8)	–	–
a ₁	SiBr str.	370.1(76.6)	386.0(s) ^a	–
a ₁	CH ₃ rock.	586.6(2.1)	–	–
a ₁	SiC str.	646.2(63.0)	650.9(m)	650.3(m)
a ₁	CH ₃ rock.	780.4(18.7)	757.6(m)	757.1(m)
a ₁	CH ₃ s-def.	1269.6(38.2)	1219.5(s)	1219.5(s)
a ₁	CH ₃ d-def.	1428.4(7.7)	–	–
a ₁	CH ₃ d-def.	1439.3(19.1)	1415.5(m)	1415.2(m)
a ₁	CH ₃ s-str.	3001.2(1.0)	–	–
a ₁	CH ₃ d str.	3069.7(3.7)	–	–
a ₁	CH ₃ d-str.	3088.2(9.6)	–	–

^a The ²⁸Si⁸¹Br band was observed at 384.7 cm⁻¹.

energy than the starting materials Si atoms and **6d**. Probably this is an artefact caused by the necessity to use an effective core potential basis set SDD for the iodine atom. To confirm this assumption we calculated with the same method the bromine series and found a trend to higher energies for all species (**T-5c**: +2.2 instead of -7.6 kcal mol⁻¹; **4c**+**3**: -7.8 instead of -18.0 kcal mol⁻¹). But the activation energy for the diradical pathway remained practically constant (1.9 instead of 1.8 kcal mol⁻¹).

4.5.5. Secondary insertion reactions

The existence of two alternative pathways for the first insertion (transformation of the *n*-adducts **T-5a–d** into the singlet silylenes **S-1a–d**) is in principle also possible for the second insertion into the C,X bond of the respective methyl halide (formation of the silanes **8a–d** from the complexes **7a–d**). Calculations showed that only in the case of **7a** the diradical-type decay generating a methyl radical **3** and the radical CH₃SiF₂ is exothermic (by 2.5 kcal mol⁻¹). For the other complexes **7b–d** this process is endothermic and therefore has not to be considered.

The experimentally observed growing tendency from **7b** via **7c** to **7d** to isomerize to the corresponding final silane is probably governed by the increasing nucleophilicity of the involved halogen atom.

4.6. Structural features of the new species

According to the calculations the *n*-adducts **T-5a–d** possess a nonlinear geometry. The complexation is weak, as documented by relatively long Si–X bond distances, if compared to the Si–X bond lengths in the sp³-hybridized dihalodimethylsilanes (**8a**: 1.626; **8b**: 2.085; **8c**: 2.258; **8d**: 2.504 Å). At the same time the C–X bonds are weakened, as indicated by prolongation in relation to the corresponding methyl halides (**6a**: 1.395; **6b**: 1.806; **6c**: 1.966; **6d**: 2.183 Å). There is no bonding interaction between the silicon and the methyl groups, the Si–C distances are too long. The Si–X–C

Table 14
Calculated (B3LYP/6-311+G**) and experimental IR spectrum of 1-bromosilene **2c**

No.	Sym.	Approx. description	Calculation	Experiment	
				CH ₃ Br/Ar 1:250	CH ₃ Br/Ar 1:50
ν_1	a'	CH ₂ rock.	198.2(4.3)	–	–
ν_2	a''	CH <i>cis</i> wag.	306.5(6.8)	–	–
ν_3	a'	SiBr str. + CH ₂ rock.	408.8(47.9)	425.9(m) ^a	425.9(m) ^a
ν_4	a''	CH <i>trans</i> wag.	591.8(13.5)	572.3(w)	572.5(w)
ν_5	a'	CH ₂ rock.	660.5(6.8)	–	–
ν_6	a''	CH ₂ wag.	740.9(55.2)	699.4(m)	699.7(m)
ν_7	a'	CH rock.	865.3(162.0)	833.6(vs) ^b	833.4(vs) ^b
ν_8	a'	SiC s-str.	1001.0(39.6)	976.1(m) ^c	975.8(m) ^c
$\nu_4 + \nu_6$			1332.7	1245.2(w)	1245.0(w)
ν_9	a'	CH ₂ s-def.	1379.6(13.6)	1338.1(w)	1338.1(w)
ν_{10}	a'	SiH s-str.	2294.1(45.5)	2220.0(m)	2220.4(m)
ν_{11}	a'	CH s-str.	3142.6(0.4)	–	–
ν_{12}	a'	CH a-str.	3241.9(0.7)	–	–

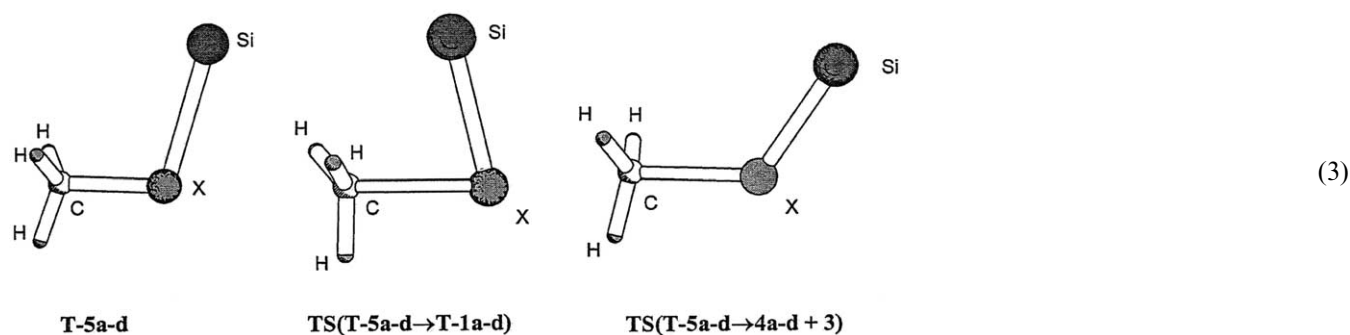
^a ²⁸Si:⁸¹Br band absorbs at 424.6 cm⁻¹.

^b Additional absorptions were observed at 876.8 and 716.7 cm⁻¹.

^c ²⁹Si:¹²C-isotopomer absorbs at 970.4 (1:250) or 970.3 cm⁻¹ (1:50), ³⁰Si:¹²C band absorbs at 965.0 (1:250) or 964.9 cm⁻¹ (1:50).

angle drops from 123.3° (**T-5a-d**) to 101.8° (**T-5d**) (Table 19, Eq. (3)).

and dissociation occurs mainly after having passed this stage (Table 21, Eq. (3)).



In the transition states **TST-5a-d** → **T-1a-d** of the concerted insertion reactions **T-5a-d** → **T-1a-d** the Si–X bonds become stronger, the C–X bonds are loosened, and the Si–C bonds reach bonding distances. The closer contact between the silicon and the methyl groups is imaged by very small angles Si–X–C (Table 20, Eq. (3)).

The transition states **TST-5a-d** → **3** + **4a-d** of the diradical decay of *n*-adducts **T-5a-d** into a methyl radical **3** and a SiX radical **4a-d** the Si–X bonds are stronger than in the alternative case. The Si–X–C angles are widened and are even larger than in the *n*-adducts. The prolongation of the C–X bonds is much less pronounced. This may be due to the fact that the transition state lies very early on the reaction coordinate

4.7. Spectroscopic trends

It is tempting to test whether it is possible to reveal some systematic trends if one compares series of species bearing different substituents X. For instance, this is possible for the silenes **2a-d**. The decreasing strength of the double bond going from **2a** to **2d** is reflected in the experimental SiC and SiH stretching frequencies (Table 22).

In a similar manner the SiC stretching vibration is influenced in the singlet silylenes **S-1a-d** (Table 23). The bathochromic shift of the UV maxima in going from X = F to X = I is in accordance with the calculated values (Table 23).

Table 15
Calculated (B3LYP/6-311+G**) and experimental IR spectrum of
CH₃Br-complex of bromomethylsilylene **7c**

Sym.	Approx. description	Calculation	Experiment	
			CH ₃ Br/Ar 1:50	CH ₃ Br/Ar 1:10
a ₁	CBrSiBr oop def.	14.7(3.1)	–	–
a ₁	CBrSiBr ip. def.	54.9(1.0)	–	–
a ₁	Torsion	71.3(0.0)	–	–
a ₁	CSiBr bend. (MeBr)	75.6(7.0)	–	–
a ₁	CbrSi bend.	98.9(8.0)	–	–
a ₁	SiBr str. (MeBr)	136.1(4.7)	–	–
a ₁	Torsion (SiMe)	142.9(2.3)	–	–
a ₁	CSiBr bend.	203.6(2.7)	–	–
a ₁	SiBr str.	347.8(62.4)	–	–
a ₁	CBr str. (MeBr)	569.4(16.3)	–	–
a ₁	SiC str. +CH ₃ rock.	607.7(30.3)	–	–
a ₁	CH ₃ rock. (SiMe)	679.2(22.5)	–	–
a ₁	CH ₃ rock. (SiMe)	779.2(17.5)	–	754.5(vw)
a ₁	CH ₃ rock. (MeBr)	969.2(3.0)	–	–
a ₁	CH ₃ rock. (MeBr)	976.1(13.7)	–	–
a ₁	CH ₃ s-def. (SiMe)	1273.0(35.9)	1224.3(w)	1222.4(m)
a ₁	CH ₃ s-def. (MeBr)	1333.7(11.9)	–	–
a ₁	CH ₃ d-def. (SiMe)	1432.8(8.8)	–	–
a ₁	CH ₃ d-def. (SiMe)	1443.7(16.2)	–	–
a ₁	CH ₃ d-def. (MeBr)	1465.9(3.1)	–	–
a ₁	CH ₃ d-def. (MeBr)	1472.6(4.7)	–	–
a ₁	CH ₃ s-str. (SiMe)	2996.4(2.6)	–	–
a ₁	CH ₃ d str. (SiMe)	3065.2(9.2)	–	–
a ₁	CH ₃ s-str. (MeBr)	3077.0(13.3)	–	–
a ₁	CH ₃ d-str. (SiMe)	3106.6(4.9)	–	–
a ₁	CH ₃ d str. (MeBr)	3187.5(1.3)	–	–
a ₁	CH ₃ d-str. (MeBr)	3199.6(0.4)	–	–

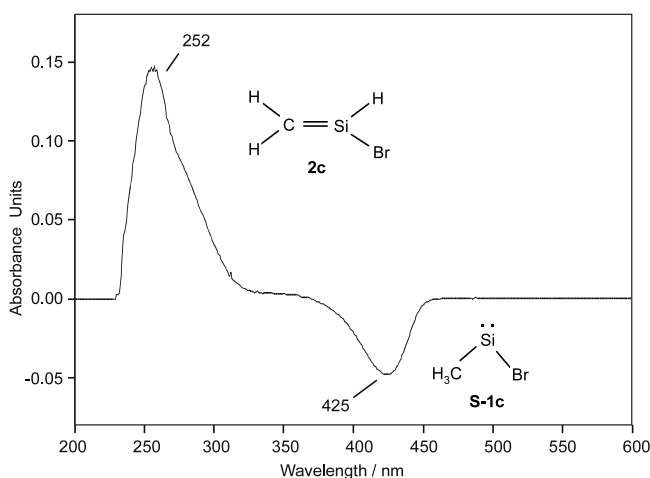


Fig. 12. Difference UV-vis spectrum originating from the photoreaction **S-1c** → **2c** (obtained by subtraction of the spectra of a diluted argon matrix (**6c**:Ar = 1:500) before and after irradiation with 436 nm for 10 h).

4.8. Relevance to the mechanism of the R.-M. synthesis

Several summaries [10] cover the efforts which have been made until 1998 to reveal the mechanism of the R.-M. synthesis. The first investigation was already carried out by Hurd and Rochow [11]. They discussed the possibility that a volatile and unstable copper methyl or even free methyl radicals may play a decisive role. As a key step the methyl radicals were believed to react with SiCl centers on the surface of the catalyst (Scheme 4a).

Later on the 'radical mechanism' was questioned [10a,b]. A new hypothesis was developed according to which the direct synthesis of dihalodimethylsilane should be treated as a heterogeneous catalytic process in which the chemisorption of the methyl halide on the surface of the contact mass is of the utmost importance [10a,b]. Assuming that the reaction takes place on a surface that consists of adjacent copper and silicon atoms it was proposed that the first step is a dissociative adsorption in which the methyl group becomes attached to the copper and the halogen to the silicon (addition at two centers; Scheme 4b). The chemisorption is then followed by migration of the methyl group. The opposite orientation (Scheme 4c) of the methyl halide was also discussed. A decision is difficult to make since the polarity of the Cu,Si bond is not known. This is also true for the most discussed reactive site, the η-phase Cu₃Si. Numerous reports have appeared dealing with the 'chemisorption mechanism' before [10] and after 1998. Nevertheless, there is still no satisfying final answer to all questions. Agreement only exists in so far that the heterogeneous mechanism involves as the first step the chemisorption of the methyl halide onto the contact mass. The subsequent splitting into a methyl radical and a chlorine atom finds support in the observation that co-adsorption of these separately generated two fragments on a Cu₃Si surface leads to chloromethylsilanes [12]. But in spite of all the modern surface studies on the catalytic influence of Cu/Si alloys the subtle effects on the selectivity, the structure of the active sites, the kinetics (rate-determining step), the further reaction of the initial intermediate with a second methyl halide molecule, the formation of side products, the influence of promoters and inhibitors, etc. are still not completely revealed.

Being confronted with such a complex system one should keep in mind that the formation of dichlorodimethylsilane from silicon and methyl chloride does not necessarily need the presence of copper. For instance, it was reported already in 1966 that *pyrophoric* silicon, when suspended in paraffin oil, reacts at 200 °C in the absence of any catalyst with methyl chloride under generation of chloromethylsilanes [13]. From this observation it can be derived that besides activation by copper and structural features of the surface grain size is also an important factor. A good illustration is the

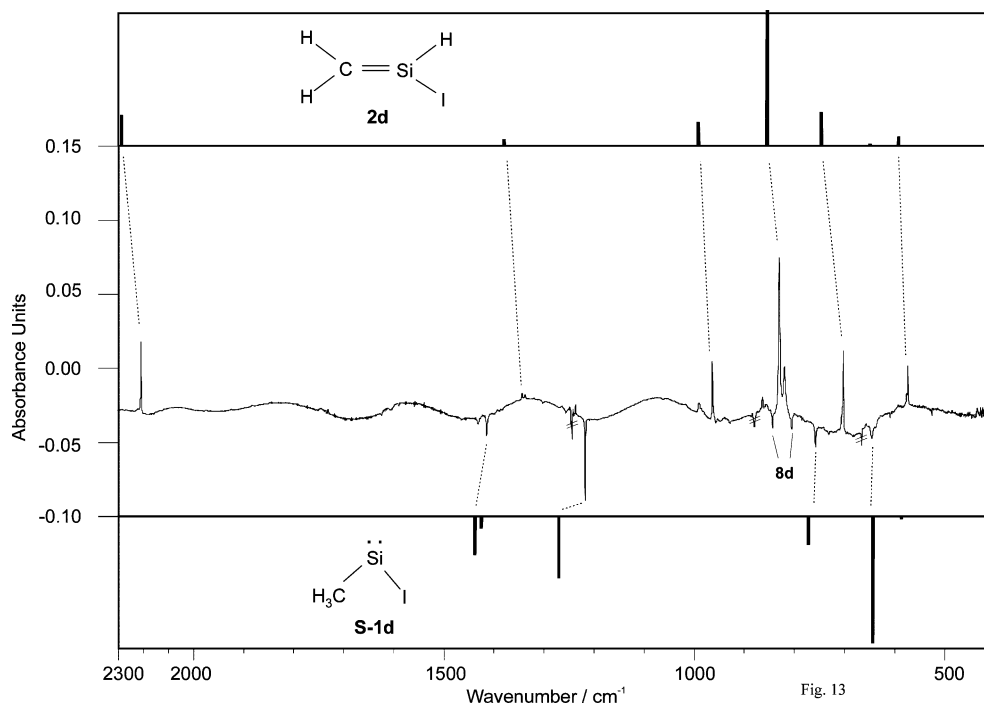


Fig. 13. Top: calculated (B3LYP/6-311+G**) IR spectrum of 1-iodosilene **2d**; center: difference FT-IR spectrum originating from the photoreaction **2d**→**S-1d** (obtained by subtraction of the spectra of an argon matrix (**6d**:Ar = 1:50) after and before irradiation with 290 nm for 30 min); bottom: calculated (B3LYP/6-311+G**) IR spectrum of singlet iodomethylsilylene **S-1c**. The crossed-out bands belong to methyl iodide **6d** and CO₂.

Table 16

Calculated (B3LYP/6-311+G**) and experimental IR spectrum of iodomethylsilylene **S-1d**

Sym.	Approx. description	Calculation	Experiment	
			CH ₃ I/Ar 1:250	CH ₃ I/Ar 1:50
a ₁	Torsion	80.9(0.0)	–	–
a ₁	CSiI bend.	180.5(3.5)	–	–
a ₁	SiI str.	306.3(55.0)	–	–
a ₁	CH ₃ rock.	589.4(1.6)	591.1(w)	–
a ₁	SiC str.	646.3(67.1)	648.0(m)	–
a ₁	CH ₃ rock.	774.9(14.9)	760.3(m)	759.2(w)
a ₁	CH ₃ s-def.	1272.4(32.7)	1218.8(s)	1218.8(s)
a ₁	CH ₃ d-def.	1426.6(6.4)	–	–
a ₁	CH ₃ d-def.	1439.2(20.4)	1415.5(m)	1415.5(m)
a ₁	CH ₃ s-str.	2997.9(0.6)	–	–
a ₁	CH ₃ d str.	3067.6(2.6)	–	–
a ₁	CH ₃ d-str.	3082.4(7.8)	–	–

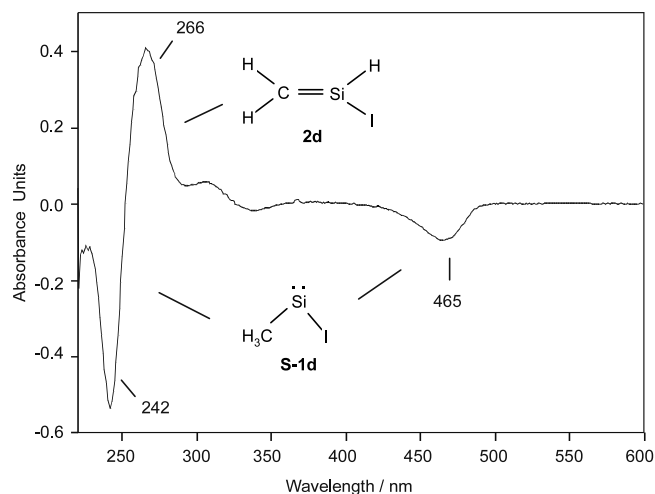


Fig. 14. Difference UV-vis spectrum originating from the photoreaction **S-1d**→**2d** (obtained by subtraction of the spectra of an argon matrix (**6d**:Ar = 1:50) before and after irradiation with 436 nm for 10 h).

technical application of *atomized* silicon (particle sizes in the range 0.1–1 μm) [14]. No wonder that pure silicon was also tested in recent mechanistic studies. Methyl chloride undergoes dissociative adsorption on Si(1 0 0) with high probability below room temperature to produce methyl radicals and chlorine atoms [15]. For a Si(1 0 0)-2 × 1 surface even the energetic of this process could be determined [16]. The similarity with our view for the molecular dimension is striking.

One conclusion can be drawn from the many studies devoted to obtaining an understanding of the mechanism of the R.-M. synthesis: The process proceeds by way of surface-confined chloromethylsilylene [17]. There is even direct chemical evidence for CH₃SiCl as an intermediate. Clarke and Davidson have detected 1-chloro-1-methyl-1-silacyclopent-3-ene upon injection of a mixture of methyl chloride and 1,3-butadiene into a fixed bed of copper-activated silicon [18]. They argued

Table 17
Calculated (B3LYP/6-311+G**) and experimental IR spectrum of 1-iodosilene **2d**

No.	Sym.	Approx. description	Calculation	Experiment	
				CH ₃ I/Ar 1:250	CH ₃ I/Ar 1:50
ν_1	a'	CH ₂ rock.	183.1(3.2)	–	–
ν_2	a''	CH <i>cis</i> wag.	283.1(3.6)	–	–
ν_3	a'	SiI str. + CH ₂ rock.	342.3(32.9)	–	–
ν_4	a''	CH <i>trans</i> wag.	594.7(14.4)	575.7(w)	575.9(w)
ν_5	a'	CH ₂ rock.	650.5(4.0)	–	–
ν_6	a''	CH ₂ wag.	748.7(51.6)	704.2(m)	704.5(w)
ν_7	a'	CH rock.	856.4(206.7)	833.6(s) ^a	833.2(s)
ν_8	a'	SiC s-str.	993.4(36.2)	965.8(m) ^b	965.6(m)
$\nu_4 + \nu_6$			1332.7	– ^c	– ^c
ν_9	a'	CH ₂ s-def.	1380.8(10.1)	1338.7(w)	1338.7(w)
ν_{10}	a'	SiH s-str.	2286.1(46.6)	2207.8(m)	2207.8(m)
ν_{11}	a'	CH s-str.	3134.9(0.3)	–	–
ν_{12}	a'	CH a-str.	3235.1(0.9)	–	–

^a Additional bands were observed at 821.6, 865.6 and 1344.5 cm⁻¹.

^b ²⁹Si¹²C-isotopomer absorbs at 960.1 cm⁻¹, ³⁰Si¹²C band absorbs at 955.2 cm⁻¹.

^c The combination band, which is visible in the IR-spectra of the other homologues silenes is hidden underneath the strong IR absorptions of methyl iodide.

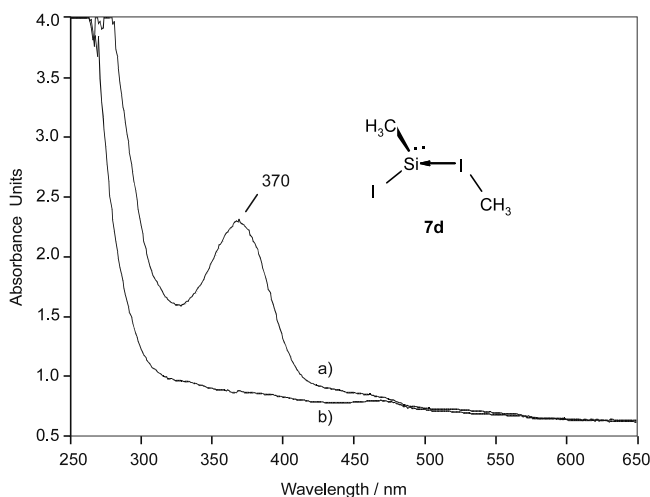


Fig. 15. UV-vis spectrum of the cocondensation product of silicon atoms and methyl iodide (**6d**:Ar = 1:10); curve a: after cocondensation; curve b: after irradiation with 366 nm for 1 h.

that CH₃SiCl is present in the gas phase during the R.-M synthesis. A similar experiment was carried out by Ono and co-worker [19]. They also found a mixture of 1-silacyclopent-3-enes besides chloromethylsilanes. These authors speculate that the silanes are formed from surface-embedded chloromethylsilylene by further reaction with methyl radicals and chlorine or hydrogen atoms. More reasonable models for the secondary reaction, the addition of methyl chloride to surface-bound chloromethylsilylene, have been proposed by Podgorny et al. [10b][20]. The basic idea is the generation of donor-acceptor complexes by nucleophilic

Table 18
Calculated (B3LYP/6-311+G**) and experimental IR spectrum of CH₃I-complex of iodomethylsilylene **7d**

Sym.	Approx. description	Calculation	Experiment	
			CH ₃ I/Ar 1:50	CH ₃ I/Ar 1:10
a ₁	CISiI oop def.	25.7(2.3)	–	–
a ₁	CISiI ip def.	42.8(0.3)	–	–
a ₁	CSiI bend. (MeI)	72.9(8.1)	–	–
a ₁	torsion (MeI)	79.1(1.3)	–	–
a ₁	CH ₃ rock. (MeI)	84.0(2.8)	–	–
a ₁	CH ₃ rock. + SiF str.	136.2(7.9)	–	–
a ₁	CH ₃ rock. (SiMe)	155.9(1.1)	–	–
a ₁	torsion (SiMe)	184.8(3.5)	–	–
a ₁	Si-I str.	288.8(42.9)	–	–
a ₁	C-I str.	497.9(9.1)	–	–
a ₁	CH ₃ rock. (SiMe)	609.1(31.3)	–	–
a ₁	CH ₃ rock. (SiMe)	679.5(25.4)	–	–
a ₁	CH ₃ rock. (SiMe)	773.6(14.5)	754.3(vw)	754.4(w)
a ₁	CH ₃ rock. (MeI)	914.6(3.4)	–	–
a ₁	CH ₃ rock. (MeI)	921.6(17.3)	–	–
a ₁	CH ₃ s-def. (SiMe)	1275.8(31.2)	1219.8(w)	1220.6(m)
a ₁	CH ₃ s-def. (MeI)	1297.1(19.6)	–	–
a ₁	CH ₃ d-def. (SiMe)	1431.3(8.6)	–	–
a ₁	CH ₃ d-def. (SiMe)	1443.4(17.5)	–	–
a ₁	CH ₃ d-def. (MeI)	1461.0(2.2)	–	–
a ₁	CH ₃ d-def. (MeI)	1467.6(3.9)	–	–
a ₁	CH ₃ s-str. (SiMe)	2992.4(2.1)	–	–
a ₁	CH ₃ d str. (SiMe)	3060.3(7.5)	–	–
a ₁	CH ₃ s-str. (MeI)	3075.3(10.2)	–	–
a ₁	CH ₃ d-str. (SiMe)	3103.7(3.9)	–	–
a ₁	CH ₃ d str. (MeI)	3191.1(2.1)	–	–
a ₁	CH ₃ d-str. (MeI)	3206.9(0.2)	–	–

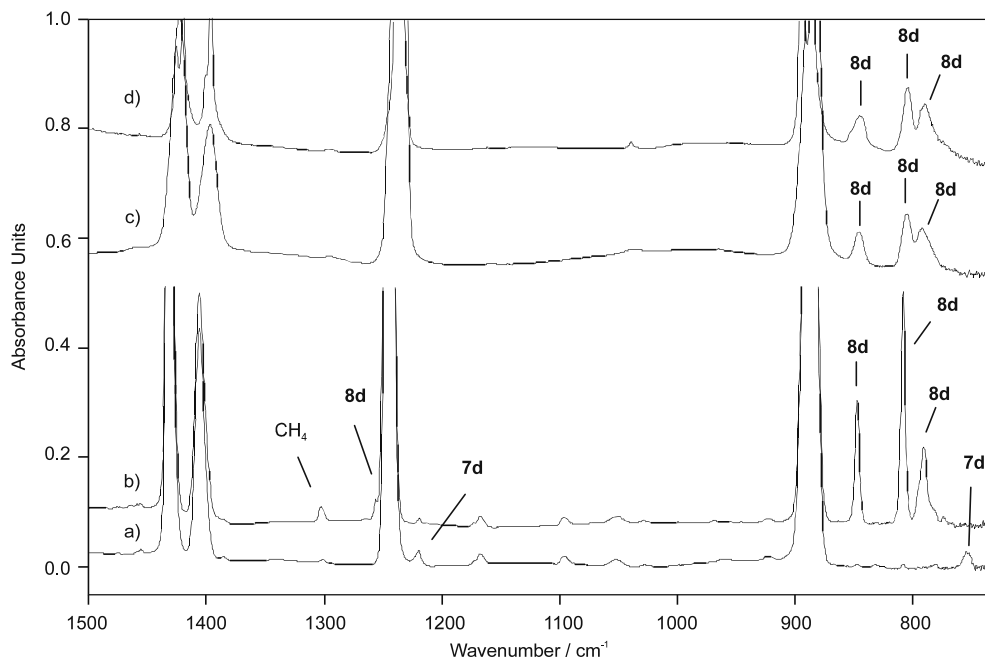
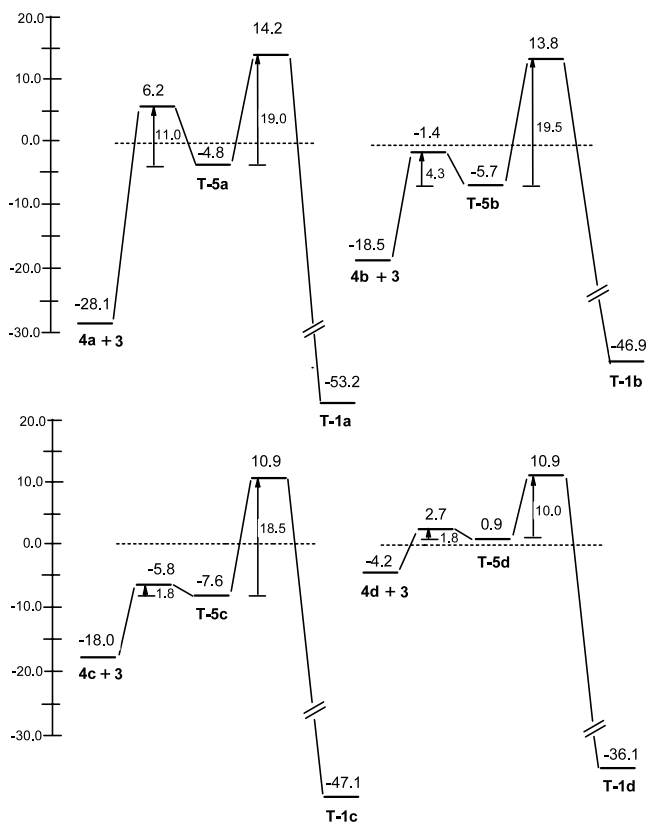


Fig. 16. FT-IR spectra of the cocondensation products of silicon atoms and methyl iodide **6d** in high concentration; curve a: after cocondensation of silicon atoms and methyl iodide (**6d**:Ar = 1:10) at 10 K; curve b: after irradiation with 366 nm for 1 h.; curve c: after cocondensation of pure methyl iodide **6d** at 40 K under simultaneous irradiation with 366 nm; curve d: same reaction (formation of silane **8d**) at 80 K. The four unmarked, very strong bands belong to methyl iodide **6d**.



Scheme 3. Calculated transition states **TST-5a–d/SiX 4a–d+3** for the diradical type and **TST-5a–d/T-1a–d** for the concerted isomerization of *n*-adducts **T-5a–d** (X = F, Cl, Br: B3LYP/6-311+G**; X = I: B3LYP/SDD).

attack of methyl chloride at the surface silicon species followed by migration of the methyl group within the sphere of a highly coordinated silicon.

Is there anything we can learn in regard to the R.-M. synthesis from the results of our matrix studies? Surely, it is daring to compare the reactions of silicon atoms with those on the surface of the contact mass. There are obvious analogies. The physisorption state on the surface [16] corresponds to *n*-adduct **T-5b**, the more stable chemisorption state [16] is comparable with radical pair **4b+3**. The dissociative chemisorption on the surface probably occurs by a nucleophilic attack of methyl chloride **6b** to a silicon atom positioned at the surface of the contact mass. It is also possible, that the next step, the formation of the surface-bound silylene, follows a pathway similar to the sequence **T-5b** → methyl radical **3+4b** → **S-1b**. The rate-determining step should be the fragmentation of the surface-bound methyl chloride **6b** into a methyl radical **3** and surface-embedded SiCl. That means that the mechanism of the R.-M. synthesis has to be looked at as a combination of the ‘radical mechanism’ in the sense of Rochow and the ‘chemisorption mechanism’. Last but not least the addition of the second methyl chloride may be comparable to the reaction path **S-1b** → **7b** → **8b**.

The modified model is summarized in Scheme 5. It has to be pointed out, that the influence of copper is completely omitted in our consideration. It is mainly this part, which deserves further investigation.

Table 19

Some calculated (B3LYP/6-311+G**) structural features of the *n*-adducts **T-5a–d** of atomic silicon with methylhalides **6a–d**

T-5a		T-5b		T-5c		T-5d	
Si–F	2.378	Si–Cl	2.676	Si–Br	2.698	Si–I	2.941
C–F	1.421	C–Cl	1.821	C–Br	1.986	C–I	2.202
Si–C	3.375	Si–C	3.599	Si–C	3.714	Si–C	4.019
C–H	1.089	C–H	1.086	C–H	1.086	C–H	1.085
Si–F–C	123.3	Si–Cl–C	104.7	Si–Br–C	103.9	Si–I–C	101.8
H–C–F	107.6	H–C–Cl	107.4	H–C–Br	106.6	H–C–I	106.3

Distances are given in Å, angles in degrees.

Nevertheless, there is an obvious relationship between our results and the prognosis for the behavior of a certain educt molecule in the R.-M. synthesis. From our point of view the decisive mark is the activation energy for the radical decay of the *n*-adduct (molecular dimension) on the one hand and for the dissociative chemisorption of the adsorbed methyl halide (macroscopic dimension) on the other. The reaction of methyl chloride on the surface of the contact mass is sufficiently catalyzed to occur at temperatures $>250\text{ }^{\circ}\text{C}$. If one takes the methylchloride system in Scheme 3 as the standard, it can be predicted, that methyl fluoride **6a** should be a bad candidate (higher activation barrier for radical type decay) for the R.-M. synthesis, the opposite should in principle be true for methyl bromide **6c** and methyl iodide **6d** (lower barrier). Their application is hindered by other factors. For dimethyl ether, which we also studied [11], a behavior similar to methyl fluoride is expected. In this case the relative energy of the *n*-adduct lies at $-13.2\text{ kcal mol}^{-1}$, the activation barrier for the radical decay at $+18.7\text{ kcal mol}^{-1}$, and the sum of the methyl radical **3** and radical SiOCH_3 is positioned at $-28.9\text{ kcal mol}^{-1}$ (recent calculation). The activation energy for the corresponding concerted pathway is expected to be even higher ($41.5\text{ kcal mol}^{-1}$). So it is no surprise that dimethyl ether cannot be used for the R.-M. synthesis. The opposite prediction can be made for methanol. It forms with silicon atoms in a spontaneous reaction methoxysilylene without offering a chance to detect the corresponding *n*-adduct matrix-spectroscopically [1e]. This observation makes it likely

that methanol can be used in R.-M. type syntheses. This is indeed the case [21].

5. Conclusion

A direct synthesis of dihalodimethylsilanes **8a–d** can be achieved by the reaction of silicon atoms with solid methyl halides **6a–d** under concurrent irradiation with UV light (254 nm). Studies in argon matrices at 10 K uncovered all the details of these processes. The basic reactions are now well understood. The crucial step is the radical decay of the primarily formed *n*-adducts **T-5a–d** into a methyl radical and the corresponding Si–X radical. Hopefully, these studies can contribute to a better understanding of the decisive steps in the R.-M. synthesis.

6. Experimental

The cryostat for matrix isolation was a helium closed-cycle refrigeration system (compressor unit RW2 with coldhead base unit 210 and extension module ROK) from Leybold. The matrix IR spectra were measured (CsI window) using a FT-IR instrument IFS 85 or IFS 55 from Bruker, the UV–vis spectra were taken (BaF₂ window) with a Hewlett Packard HP 8453 diode-array spectrophotometer. The light sources used were a mercury high pressure lamp (HBO 200 from Osram) with a monochromator (Bausch and Lomb) and a

Table 20

Some calculated (B3LYP/6-311+G**) structural features of the transition states **TST-5a–d** → **T-1a–d** of the concerted isomerization of *n*-adducts **T-5a–d** into triplet silylenes **T-1a–d**

X = F		X = Cl		X = Br		X = I	
Si–F	1.936	Si–Cl	2.450	Si–Br	2.597	Si–I	2.854
C–F	1.779	C–Cl	2.185	C–Br	2.307	C–I	2.512
Si–C	2.803	Si–C	2.845	Si–C	2.870	Si–C	2.922
C–H	1.081	C–H	1.082	C–H	1.082	C–H	1.082
Si–F–C	97.9	Si–Cl–C	75.5	Si–Br–C	71.4	Si–I–C	65.6
H1/2–C–F	105.5	H1/2–C–Cl	108.6	H1/2–C–Br	109.3	H1/2–C–I	109.6
H3–C–F	89.7	H3–C–Cl	89.7	H3–C–Br	90.1	H3–C–I	89.9

Distances are given in Å, angles in degrees.

flask, containing a degassed suspension of 8.0 g (0.077 mol) dry ZnF_2 in 15 ml hexachlorobutadiene. The reaction flask was allowed to warm up to room temperature (r.t.) under stirring. The volatile crude silane **8a** was condensed in a trap at -196°C . The dimethyldifluorosilane was purified by further trap to trap distillation as described earlier [24]. This procedure gave a yield of 80%, based on the initial amount of **8b**.

Preparation of dimethyldihalosilanes **8c** and **8d** [23]: 50 mg aluminum bromide (iodide) was added in a the reaction apparatus equipped with cooler and gas inlet tubing to 5 g (0.024 mol) degassed dimethyldiphenylsilane (Aldrich, 97%). A stream of dry HBr (HI) was allowed to bubble through the magnetically stirred solution until the initially exothermic reaction abated. The solution was stirred for some additional hours at r.t. The crude silanes **8c** and **8d** were separated from benzene by distillation (80% yield).

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