

Nonclassical complex of dichlorosilylene with CO: direct spectroscopic detection*

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A complex between SiCl₂ and CO of the 1 : 1 composition with coordination of the silylene to the C atom of carbon monoxide is detected in Ar matrices using FTIR spectroscopy. A positive shift of the $\nu(\text{CO})$ band of the complex relative to the corresponding band of free CO and a theoretical analysis of the nature of the complex indicate that it is a nonclassical carbonyl complex. It is the first experimentally detected nonclassical carbonyl complex of any silylenes. The main direction of photoinduced transformations of the complex is its decomposition into the starting reactants. The potential energy surface of the SiCl₂ + CO system was explored theoretically. It is shown that further thermal transformations of the primary complex are energetically unfavorable.

Key words: dichlorosilylene, carbon monoxide, donor-acceptor complex, matrix isolation, FTIR spectroscopy, quantum chemical calculations.

Activation of small molecules with derivatives of the Groups 13 and 14 low-coordinated elements is one of the most actively developing areas of modern organoelement chemistry.¹ It is aimed at finding an alternative to the use of expensive and rather toxic derivatives of transition metals as catalysts for the production of chemically valuable products from simple and accessible compounds and is based on the existence of a certain analogy between the electronic structure and chemical properties of transition metal complexes and these derivatives.

To date, the activation of small molecules by silylenes, derivatives of divalent silicon, is the most studied.¹ In particular, it is found that some stable silylenes are very reactive towards carbon monoxide and react with it, forming polycyclic products containing bound with one another carbon atoms of initial CO molecules.^{2–4} It was established in time resolved gas-phase kinetic studies that prototypical labile silylene, SiH₂, also actively reacts with CO,^{5,6} and the kinetics of this interaction in the microsecond time scale is completely determined by the primary complexation between the reactants.⁶ Recently, the synthesis of the first stable carbonyl complexes of silylenes was reported.^{7,8} Labile complexes of SiH₂,^{9,10} SiMe₂,^{11,12} SiMePh,¹³ SiMes₂,¹² Si(OC₆H₃(Prⁱ)₂₋₆)Mes,¹² Si(Bu^t)Mes,¹² and SiCp*₂¹⁴ (Cp* is pentamethylcyclopentadienyl) with CO were detected using IR^{9–11,13,14} and UV spectroscopy^{9–13} in low-temperature inert (argon,^{9–11,13} nitro-

gen,¹¹ and hydrocarbon^{11,12}) matrices and in xenon solutions.¹⁴

Carbonyl complexes represent one of the most studied and widely used classes of transition metal compounds.¹⁵ Therefore, the established ability of silylenes to form carbonyl complexes considerably extends the analogy between the transition metal chemistry and the chemistry of divalent silicon derivatives. As a rule, the metal atoms are coordinated to the carbon atoms of the CO molecules in carbonyl complexes of transition metals. At the same time, a number of less stable complexes of both transition and non-transition metals are known, in which metal atoms are coordinated to oxygen atoms of the CO molecules.¹⁵ The ability of the CO molecule to coordinate due to both its carbon and oxygen atoms is also demonstrated in the complexation with proton-donating molecules such as H₂O,^{16,17} HF,¹⁸ HCl,¹⁹ and so on. In all the cases, carbonyl complexes with coordination due to the oxygen atom of CO were weaker than those with coordination due to the carbon atom. All known complexes of silylenes with CO were identified as complexes with coordination to the CO carbon atom.

There are two types of carbonyl complexes of transition metals: classical and nonclassical. They differ in the contribution of the σ donation and the π back-donation to the formation of the bond between the metal atom and the CO carbon atom, which affects their chemical behavior.¹⁵ A good indicator of the belonging of a carbonyl complex to one or another type is the value of the $\nu(\text{CO})$ vibration frequency of the CO moiety. In the case of classi-

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cal complexes, this value is usually considerably lower than the corresponding frequency of free CO molecule, whereas in the case of nonclassical complexes, it is always higher than the latter.¹⁵ According to this concept, all reported complexes of silylenes with CO should be attributed to the classical type since the frequencies of their $\nu(\text{CO})$ vibrations vary from 2065 to 1908 cm^{-1} ,^{7,8,9–11,13,14} which is significantly lower than the CO molecule vibration frequency measured in the gas phase²⁰ and liquid Xe¹⁴ (2143 cm^{-1}) or in Ar (2138 cm^{-1})²¹ and N₂ matrices (2140 cm^{-1}).²² Theoretical analysis of the electronic structure of stable silylene complexes^{7,8} and the H₂Si • CO complex⁷ shows that they are characterized by the presence of substantial π back-donation, which is responsible for lowering their $\nu(\text{CO})$ frequencies and determines their attribution to the classical type.

At the same time, labile carbonyl complexes of heavier carbene analogs, viz., of SnCl₂, PbF₂, PbCl₂, and PbBr₂, were detected in Ar matrices using IR spectroscopy.²³ According to the obtained $\nu(\text{CO})$ values (2175.5, 2176.4, 2174.5, 2161.2 cm^{-1} , respectively),²³ they are nonclassical complexes. Consequently, it seemed interesting to find out whether SiCl₂ forms a complex with CO, and, if it does, what type it belongs to. In the framework of systematic studies of complexation of SiCl₂ with different weak Lewis bases,^{24–28} we investigated the interaction of SiCl₂ with CO with the use of matrix-isolation IR spectroscopy and quantum chemical calculations. Here we report the obtained results.

Experimental

Matrices were prepared by co-deposition of mixtures of CO ($\geq 99.9\%$, LLC BC Group, Russian Federation) with Ar (99.998%, Mechel Mining, Moscow Coke and Gas Plant, Russian Federation) of predetermined composition with products of vacuum pyrolysis of a suitable SiCl₂ precursor on a mirror copper plate located inside a vacuum cryostat (at a residual pressure of $\sim 10^{-6}$ Torr) and cooled to 10–12 K. The cryostat was equipped with windows of KBr for IR measurements and CaF₂ for irradiation of matrices with UV and visible light. A Displex closed-cycle refrigeration system CSW-208R (APD Cryogenics, Inc.) was used to cool the plate. The CO : Ar molar ratio was varied within (3–50) : 1000. 1,1-Dichloro-1-silacyclopent-3-ene (SCP) prepared according to the known procedure²⁶ and Si₂Cl₆ (98%, LLC Impulse, Russian Federation) were used as SiCl₂ precursors. Their pyrolysis was carried out in a quartz reactor with the inner and outer diameters of 6 and 4 mm, respectively, and the length of the heated zone of 100 mm. The reactor was heated by a nichrome heating coil to 915–940 °C (Si₂Cl₆) or 990–1000 °C (SCP). Taking into account equimolar formation of SiCl₂ and SiCl₄ from Si₂Cl₆,²⁴ the SiCl₂ : Ar molar ratio was taken equal to the SiCl₄ : Ar ratio when Si₂Cl₆ was used as a precursor, and was determined on the basis of the SiCl₄ band intensities. When SCP was used as a precursor, it was estimated based on the intensities of bands of SiCl₂ itself. The SiCl₂ : Ar molar ratio was varied within (1–3) : 1000. Annealing of matri-

ces was carried out by their warming to the predetermined temperature within 25–40 K, their keeping at this temperature for several minutes, and by their following cooling to 10–12 K. Photolysis of matrices was carried out using a DRSh-500 high-pressure Hg lamp (500 W) equipped with a water filter. Suitable cut-off filters (with 50% transmission at the wavelengths specified in the text) were used to obtain the light in required wavelength interval. IR spectra of matrices were recorded at 10–12 K using a Bruker IFS 113v FTIR spectrometer in the range of 4000–400 cm^{-1} with a resolution of 0.5 cm^{-1} . Theoretical analysis of the potential energy surface (PES) of the SiCl₂ + CO system was carried out at the G4(MP2) level of theory²⁹ with the use of the Gaussian 09 software package.³⁰ The NBO analysis³¹ implemented in this program package was used to analyze the wave functions of complexes, which were obtained at the B3LYP/GTbas3 level of theory in the framework of the G4(MP2) calculations.

Results and Discussion

In IR spectra of matrices obtained by co-condensation of products of pyrolysis of Si₂Cl₆ (decomposition to SiCl₂ and SiCl₄)²⁴ or SCP (decomposition to SiCl₂ and buta-1,3-diene)²⁶ with mixtures of CO with Ar, a number of new bands were detected, which differed from the bands observed in matrices containing only products of pyrolysis of these precursors or only CO (Fig. 1). Those were a band split into a doublet with poorly resolved maxima at 2161.5 and 2160.5 cm^{-1} on the high-frequency side of the CO band at 2138.5 cm^{-1} (see Refs. 21 and 32) and broadened bands at 486, 483 (with a shoulder at 484 cm^{-1}), and 481 cm^{-1} on the low-frequency side of isotopically split bands of matrix-isolated SiCl₂ (see Fig. 1, bands *I* and *I'* in spectra *b* and *c*). These bands were detectable at SiCl₂ : CO : Ar = 1 : 10 : 1000 or 3 : 5 : 1000 already. Absolute intensities of these bands increased with increasing the concentrations of SiCl₂ or CO in matrices, while their relative intensities were unchanged. The dependence of the intensities of these new bands on the SiCl₂ and CO concentrations and observation of these bands independently on the used precursor unequivocally indicate that they belong to a product of interaction of SiCl₂ with CO. Nevertheless, we additionally checked these bands for their possible belonging to a product of interaction of CO with SiCl₄, which is formed in equimolar amounts together with SiCl₂ in the Si₂Cl₆ pyrolysis. It was found that these bands are absent in IR spectra of matrices obtained by co-condensation of SiCl₄ with mixtures of CO and Ar.

Short-time annealing of matrices at different temperatures (see Fig. 1, spectra *d* and *e*) up to 40 K resulted in a proportional growth of bands *I* and *I'* and their some narrowing. Simultaneously, because of the weakening of the bands of uncomplexed SiCl₂, a less intense component at 487 cm^{-1} (a band of type *I'*) became observable near the band at 486 cm^{-1} (a band of type *I*). This component is analogous to the components at 484 and 2160.6 cm^{-1}

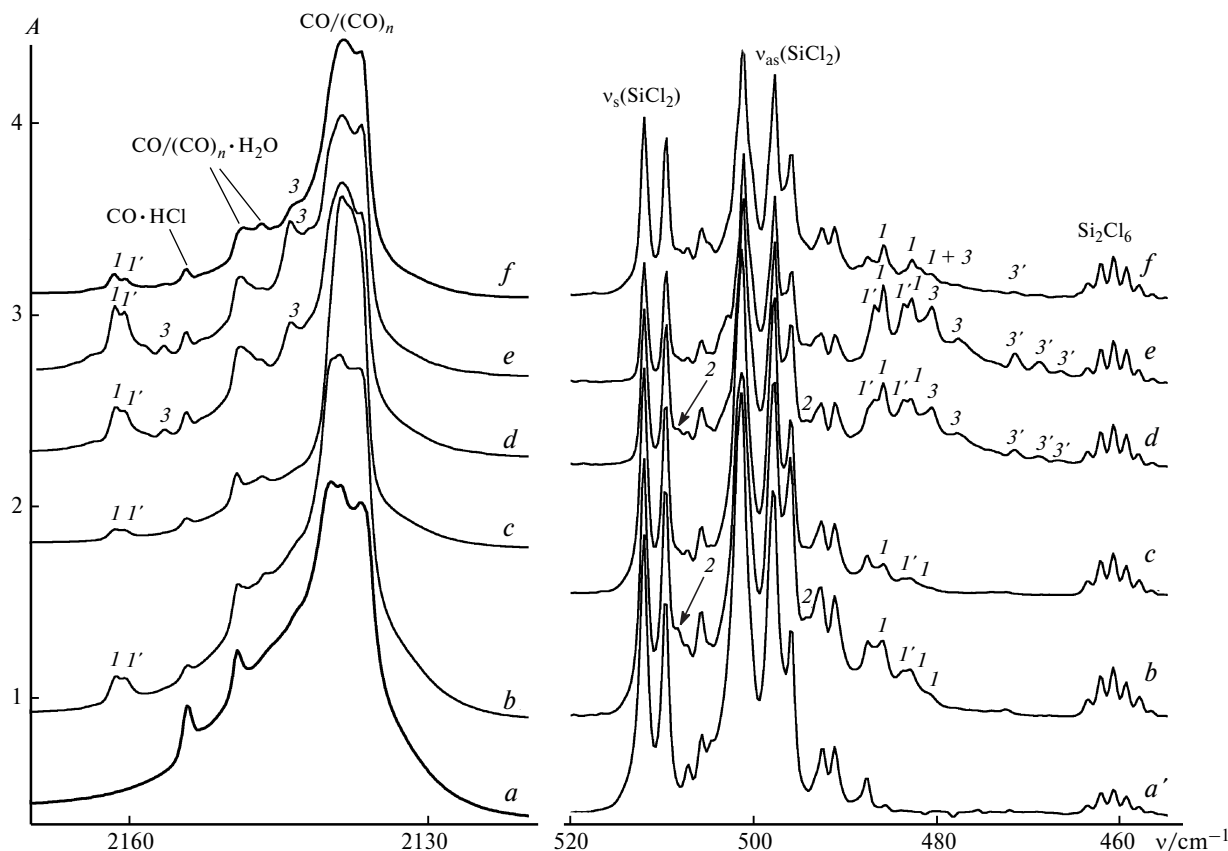


Fig. 1. IR spectra in the regions of the $\nu(\text{CO})$ vibrations and dichlorosilylene $\nu(\text{Si}-\text{Cl})$ vibrations for matrices with ratios $\text{SiCl}_2 : \text{CO} : \text{Ar} = 1.5 : 15 : 1000$ (a), $\text{SiCl}_2 : \text{CO} : \text{Ar} = 3 : 0 : 1000$ (a'), $\text{SiCl}_2 : \text{CO} : \text{Ar} = 2.5 : 8 : 1000$ (b), and $\text{SiCl}_2 : \text{CO} : \text{Ar} = 3 : 5 : 1000$ (c) after their deposition and for the latter matrix after a short-time annealing at 32 K (d), after a subsequent annealing at 37 K (e), and after a following photolysis with the unfiltered light of a high-pressure Hg lamp for 200 min (f). Assignments of bands 1–3 and 1'–3' are given in the text.

(bands 1') in the vicinity of the bands at 483 and 2161.6 cm^{-1} (bands 1). It was hidden before annealing by the $\nu_{\text{as}}(\text{Si}-\text{Cl})$ band at 487.7 cm^{-1} belonging to the $^{30}\text{Si}^{35}\text{Cl}^{37}\text{Cl}$ isotopomer of uncomplexed SiCl_2 . The bands in the $\nu(\text{Si}-\text{Cl})$ vibration region that are marked with numbers 1 and 1' differ from the $\nu_{\text{as}}(\text{Si}-\text{Cl})$ bands of the main isotopomers of SiCl_2 by ~ 14 and ~ 15 cm^{-1} (Table 1), respectively, whereas their relative intensities correspond to the relative intensities of the bands of the main SiCl_2 isotopomers. This makes it possible to identify the bands marked with numbers 1 and 1' as isotopic (due to the Cl isotopes) splitting components of one band of the $\nu_{\text{as}}(\text{Si}-\text{Cl})$ vibrations of a product located in two matrix sites with equal stabilities of these locations, which results in splitting of its bands into two components 1 and 1'.

The observation of bands 1 and 1' at rather low concentrations of SiCl_2 and CO and the absence of any other new bands at lower concentrations of the reactants imply that these bands belong to a product of interaction of one SiCl_2 molecule with one CO molecule. The proximity of the product bands to the bands of the starting reactants

indicates that the identities of the SiCl_2 and CO moieties are mainly retained in this product. Therefore, this product represents a complex of the 1 : 1 composition between SiCl_2 and CO and hereinafter will be referred to as complex 1. The intense matrix and isotopically split $\nu_{\text{as}}(\text{Si}-\text{Cl})$ band expected for this complex should lie in the region of more intense bands of uncomplexed SiCl_2 and, therefore, cannot be revealed (*cf.* data for other SiCl_2 complexes^{24–28}).

In addition to the bands discussed above, two other weak bands at 508.2 and 494.3 cm^{-1} in the region of the $\nu(\text{Si}-\text{Cl})$ vibrations of SiCl_2 were observed in IR spectra of matrices at somewhat higher reactant concentrations ($\text{SiCl}_2 : \text{CO} : \text{Ar} = 2 : 10 : 1000$) before annealing (see Fig. 1, bands 2 in spectra b and d). Intensities of these bands also increased with increasing the SiCl_2 and CO concentrations. Because these bands were not observed in IR spectra of matrices, which did not contain either SiCl_2 or CO, it can be concluded that they also belong to a complex of the 1 : 1 composition between SiCl_2 and CO. However, rather small shifts of these bands relative to the bands of SiCl_2 indicates that they may also be components of

Table 1. Bands (ν/cm^{-1}) of complexes between SiCl_2 and CO detected in the experiment

Band ^a	Conditions of matrix preparation		Complex	Vibrational mode	SiCl_2 isotopomer as a part of the complex	$\Delta\nu$
	deposition	annealing				
1	2161.5	2161.6	$\text{Cl}_2\text{Si} \cdot \text{CO}$	$\nu(\text{CO})$	—	23.1
1'	2160.5	2160.6	$\text{Cl}_2\text{Si} \cdot \text{CO}$	$\nu(\text{CO})$	—	22.1
3	—	2156.6	$\text{Cl}_2\text{Si} \cdot (\text{CO})_x$	$\nu(\text{CO})$	—	18.1
3	—	2143.9	$\text{Cl}_2\text{Si} \cdot (\text{CO})_x$	$\nu(\text{CO})$	—	5.4
2	508	508.2 ^b	$\text{Cl}_2\text{Si} \cdot \text{OC}$	$\nu_s(\text{Si}-\text{Cl})$	$^{28}\text{Si}^{35}\text{Cl}_2$ or $^{28}\text{Si}^{35}\text{Cl}^{37}\text{Cl}$	-4.0 or -1.6 ^c
2	494	494.3 ^b	$\text{Cl}_2\text{Si} \cdot \text{OC}$	$\nu_{\text{as}}(\text{Si}-\text{Cl})$	$^{28}\text{Si}^{35}\text{Cl}_2$ or $^{28}\text{Si}^{35}\text{Cl}^{37}\text{Cl}$	-7.0 or -3.5 ^c
1'	487 ^d	486.9	$\text{Cl}_2\text{Si} \cdot \text{CO}$	$\nu_{\text{as}}(\text{Si}-\text{Cl})$	$^{28}\text{Si}^{35}\text{Cl}_2$	-14.4
1	486	485.9	$\text{Cl}_2\text{Si} \cdot \text{CO}$	$\nu_{\text{as}}(\text{Si}-\text{Cl})$	$^{28}\text{Si}^{35}\text{Cl}_2$	-15.4
1'	484	483.7	$\text{Cl}_2\text{Si} \cdot \text{CO}$	$\nu_{\text{as}}(\text{Si}-\text{Cl})$	$^{28}\text{Si}^{35}\text{Cl}^{37}\text{Cl}$	-14.1
1	483	482.9	$\text{Cl}_2\text{Si} \cdot \text{CO}$	$\nu_{\text{as}}(\text{Si}-\text{Cl})$	$^{28}\text{Si}^{35}\text{Cl}^{37}\text{Cl}$	-14.9
1	481	— ^e	$\text{Cl}_2\text{Si} \cdot \text{CO}$	$\nu_{\text{as}}(\text{Si}-\text{Cl})$	$^{28}\text{Si}^{37}\text{Cl}_2$	-15
3	—	480.7	$\text{Cl}_2\text{Si} \cdot (\text{CO})_x$	$\nu_{\text{as}}(\text{Si}-\text{Cl})$	$^{28}\text{Si}^{35}\text{Cl}_2$	-20.6
3	—	477.8	$\text{Cl}_2\text{Si} \cdot (\text{CO})_x$	$\nu_{\text{as}}(\text{Si}-\text{Cl})$	$^{28}\text{Si}^{35}\text{Cl}^{37}\text{Cl}$	-20.0
3'	—	471.6	$\text{Cl}_2\text{Si} \cdot (\text{CO})_x$	$\nu_{\text{as}}(\text{Si}-\text{Cl})$	$^{28}\text{Si}^{35}\text{Cl}_2$	-29.7
3'	—	469	$\text{Cl}_2\text{Si} \cdot (\text{CO})_x$	$\nu_{\text{as}}(\text{Si}-\text{Cl})$	$^{28}\text{Si}^{35}\text{Cl}^{37}\text{Cl}$	-28.8
3'	—	466.6	$\text{Cl}_2\text{Si} \cdot (\text{CO})_x$	$\nu_{\text{as}}(\text{Si}-\text{Cl})$	$^{28}\text{Si}^{37}\text{Cl}_2$ (contribution)	-29.3

Note. $\Delta\nu$ is the shift of a stretching vibration frequency upon the formation of a complex; $\Delta\nu = \nu(\text{complex}) - \nu(\text{reactant})$.

^a The band numbers correspond to those given in Fig. 1; ^b the band begins to weaken at ~ 34 K; ^c depending on the assignment of this band to vibrations of one or another isotopomer of the SiCl_2 moiety (see text); ^d a contribution into a band of the $\nu_{\text{as}}(\text{Si}-\text{Cl})$ vibrations of the $^{30}\text{Si}^{35}\text{Cl}^{37}\text{Cl}$ isotopomer at 487.7 cm^{-1} ; ^e hidden by band 3 at 480.7 cm^{-1} .

a matrix splitting of SiCl_2 bands due to the presence of high concentrations of CO in matrices. Annealing of matrices at 26–34 K resulted in some increase in the intensity of bands 2. However, at higher temperatures, these bands weakened. The latter fact contradicts their identification as components of matrix splitting of the SiCl_2 bands since the effects of dopants should be enhanced upon annealing. At the same time, this behavior of bands 2 in the course of annealing conforms to their belonging to an additional complex between SiCl_2 and CO, which is less stable than complex 1. Therefore, we tentatively assigned these bands to another complex of the 1 : 1 composition between SiCl_2 and CO, to complex 2.

In addition to the bands of complexes 1 and 2, a series of other new bands were observed in the regions of the $\nu(\text{CO})$ and $\nu(\text{Si}-\text{Cl})$ vibrations upon annealing of matrices (see Table 1 and Fig. 1, bands 3 and 3' in spectra d and e). None of these bands was present in IR spectra after annealing of matrices containing only Si_2Cl_6 or SCP pyrolysis products, or matrices obtained by deposition of mixtures of CO with Ar or co-deposition of SiCl_4 with mixtures of CO and Ar. Therefore, these bands also belong to complexes between SiCl_2 and CO, which, apparently, have more complex composition. To avoid interactions between highly reactive SiCl_2 molecules and, simultaneously, to increase the possibility of interactions between the SiCl_2 and CO molecules, the used CO concentrations were always higher than the SiCl_2 concentrations in our experiments. Therefore, it is reasonable to expect, that the complexes responsible for the appearance of bands 3 and

3' contain one SiCl_2 molecule coordinated to several CO molecules, *i.e.*, represent complexes of the 1 : n composition, $n \geq 2$. It should be noted that bands 3 and 3' in the $\nu(\text{Si}-\text{Cl})$ vibrational region are shifted to low frequencies relative to the main components of the isotopically split $\nu_{\text{as}}(\text{Si}-\text{Cl})$ band of SiCl_2 by the same values equal to $\sim 20 \text{ cm}^{-1}$ for bands 3 and $\sim 29 \text{ cm}^{-1}$ for bands 3' (see Table 1), whereas the ratio of intensities of bands 3' approximately corresponds to the ratio of intensities of the bands of the main isotopomers of matrix isolated SiCl_2 (see Fig. 1, spectra d and e). This indicates that bands 3' are mainly contributed by components of an isotopic splitting (due to the Cl isotopes) of a band of one complex. At the same time, we were unable to establish which of the bands observed for the 1 : n complexes in the region of the $\nu(\text{CO})$ vibrations correspond to each of complexes 3 and 3' since the intensity of all bands 3 and 3' increased upon annealing approximately proportionally. Therefore, all bands of complexes of the 1 : n composition in the $\nu(\text{CO})$ vibrational region are marked as bands 3 in Fig. 1.

The matrices always contain water and CO_2 condensing from the inner surfaces of the cryostat. In addition, little amounts of HCl, a product of hydrolysis of precursors by desorbed water, were always present in matrices in our experiments. Concentrations of these impurities were lower than the SiCl_2 concentrations by an order, at least, and changed randomly from experiment to experiment, being not sufficient for formation of detectable concentrations of the corresponding complexes of SiCl_2 .^{24,27,28} However, because of the use of high CO concentrations,

bands of complexes of water^{16,33} and HCl¹⁹ with CO were always observed in the recorded spectra (see Fig. 1). It is instructive that the observed degree of association of these compounds with CO after deposition of matrices varied from 30 to 85% for water and to 95% for HCl, depending on the CO concentration and increasing with the increase of the latter. At the same time, the degree of association of SiCl₂ with CO after deposition of matrices did not exceed 30%. This fact shows that SiCl₂ has a rather low mobility on the surface of the forming matrix, and indicates the weakness of the complexes of SiCl₂ with CO.

Dichlorosilylene isolated in an Ar matrix has an UV band corresponding to the n–p transition with a maximum at 317 nm.³⁴ Since complexation of silylenes with Lewis bases results in hypsochromic shifts of bands of this type,³⁵ one may expect that complexes of SiCl₂ with CO of different composition absorb in the region of 250–300 nm. Indeed, the observed complexes were stable against irradiation with $\lambda > 400$ nm and with $\lambda > 300$ nm for ~2 h. However, their bands became considerably weaker upon irradiation with unfiltered output light of a high-pressure Hg lamp (~230–1000 nm) in 1 h already. The weakening of bands 1', 3 and 3' was faster than that of bands 1 and 2, and the bands of the first three types almost completely disappeared in the spectra in 3–4 h of irradiation (see Fig. 1, spectrum *f*). The only bands the intensity of that increased upon photolysis were the SiCl₂ bands (see spectrum *f*). The corresponding increase in the CO band intensity could not be detected because of much higher concentrations of CO in matrices in comparison with the concentrations of complexes. Simultaneously, the appearance of a number of very weak bands in different regions of the spectrum was observed. In particular, a weak band at 1898 cm⁻¹ with a wide shoulder on the high-frequency side extending to ~1905 cm⁻¹ was detected. Perhaps, this band and its shoulder belong to carbonylsilylene SiCO^{9,36} and its complexes with Cl₂ and CO. Complexes with CO could be formed upon decomposition of complexes of SiCl₂ with CO of the 1 : *n* composition. Thus, the principal direction of photoinduced transformations of complexes of SiCl₂ with CO is their decomposition into the starting reactants, although minor directions also exist. Partial photoinduced decomposition of the PhMeSi • CO complex isolated in Ar matrices into the starting reactants was reported previously,¹³ whereas the matrix isolated H₂Si • CO complex underwent slow decomposition to SiCO and H₂ upon photolysis.^{9,10}

With the purpose of a deeper understanding of the reaction system under consideration, quantum chemical calculations of this system were carried out. The calculations showed that two complexes of the 1 : 1 composition between SiCl₂ and CO can be formed. Those are complexes with SiCl₂ coordination to either carbon or oxygen atom of CO (complexes **C1** and **C2**, respectively) with practically equal and rather small energies ($\Delta E_0 = \Delta E + \text{ZPE}$) of

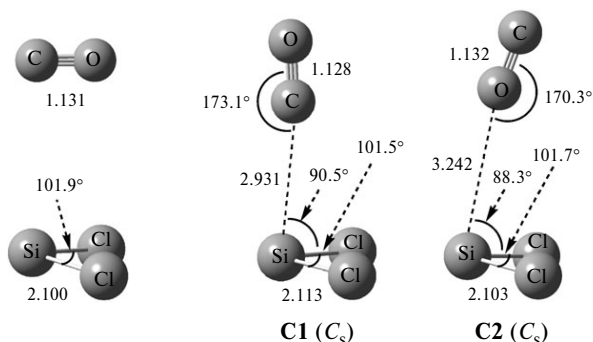


Fig. 2. Structures of starting SiCl₂ and CO and complexes **C1** and **C2** obtained in the B3LYP/GTbas3 calculations; bond lengths (Å) and angles (degree) are shown.

stabilization relative to the free starting reactants equal to -0.85 and -0.87 kcal mol⁻¹, respectively. Formation of both complexes occurs without an activation barrier. The calculated structures of complexes **C1** and **C2** are shown in Fig. 2. As can be seen, the geometric parameters of the reactants change little upon the formation of the complexes, and the lengths of the donor-acceptor bonds in the complexes are closer to the sum of the van der Waals radii of the atoms forming them,³⁷ rather than to the sum of their covalent radii,³⁸ especially, in the case of complex **C2**.

According to the calculations, the complexation results in insignificant changes in the IR intensities of vibrations of the starting reactants (Table 2). Therefore, the ratios of the concentrations of complexes and reactants in matrices are approximately equal to the ratios of the integrated intensities of their respective bands. The calculations predict that the $\nu_s(\text{Si}-\text{Cl})$ and $\nu_{\text{as}}(\text{Si}-\text{Cl})$ frequencies decrease by 7 and 14 cm⁻¹ upon formation of complex **C1** and by 1 and 4 cm⁻¹ upon formation of complex **C2**, whereas $\nu(\text{CO})$ frequency considerably increases by 30 cm⁻¹ in the case of complex **C1**, but decreases by 6 cm⁻¹ only in the case of complex **C2** (see Table 2). The calculated reactant frequency shifts upon formation of complex **C1** are in good agreement with the experimentally measured shifts of the bands of complex **1** relative to the bands of starting SiCl₂ and CO (see Table 1), which makes it possible to identify the latter complex as complex **C1**. A good agreement between the B3LYP/GTbas3 calculated and experimentally observed frequency shifts of SiCl₂ complexes with different Lewis bases relative to the corresponding frequencies of the starting reactants was noted previously.^{25,27,28} The calculated shifts of the reactant frequencies upon formation of complex **C2** do not contradict the assignment of bands 2 to this complex. Moreover, the assignment of these bands to the vibrations of the complex containing the ²⁸Si³⁵Cl³⁷Cl isotopomer leads to practically exact coincidence of the experimentally obtained and calculated shifts (see Table 1). In accordance with the calculations, the $\nu_s(\text{Si}-\text{Cl})$ band of complex **C1** indeed

Table 2. Calculated energies and spectroscopic characteristics of SiCl₂, CO, and complexes between them

Reactant /complex	ΔE_0	CO		Si—Cl				λ/nm (<i>f</i>)
		ν (<i>I</i>)	$\Delta\nu$	ν_s (<i>I</i>)	$\Delta\nu$	ν_{as} (<i>I</i>)	$\Delta\nu$	
SiCl ₂	—	—	—	503 (83)	—	498 (194)	—	327 (0.029)
CO	—	2205 (63)	—	—	—	—	—	—
C1	−0.8	2235 (81)	30	495 (80)	−7	483 (183)	−14	305 (0.055)
C2	−0.9	2199 (104)	−6	501 (81)	−1	493 (189)	−4	319 (0.036)
C3	−2.1	2231 (1) ^a	26	489 (76)	−13	471 (172)	−26	286 (0.081)
		2230 (171) ^b	25					
C4	−1.9	2233 (81) ^c	28	494 (77)	−9	480 (177)	−18	298 (0.063)
		2201 (106) ^d	−4					
C5	−1.8	2200 (6) ^a	−5	500 (79)	−3	489 (184)	−8	311 (0.043)
		2199 (204) ^b	−6					
C6	−1.5	2200 (104) ^e	−5	501 (88)	−2	492 (189)	−5	319 (0.036)
		2199 (80) ^f	−6					

Note. The following quantities are included: the G4(MP2) calculated energies ($\Delta E_0 = \Delta E + \text{ZPE}/\text{kcal mol}^{-1}$) of complexes relative to the energy level of the starting reactants, the B3LYP/GTbas3 calculated frequencies (ν/cm^{-1}) of the $\nu(\text{Si—Cl})$ and $\nu(\text{CO})$ vibrations, their IR intensities ($I/\text{km mol}^{-1}$), and the shifts of the frequencies of complexes relative to the corresponding frequencies of SiCl₂ and CO ($\Delta\nu = \nu(\text{complex}) - \nu(\text{reactant})/\text{cm}^{-1}$), the TD B3LYP/GTbas3 calculated wavelengths (λ/nm) and oscillator strengths (*f*) of the n→p transitions in the SiCl₂ moieties.

^a The symmetric stretching vibration of the CO moieties; ^b the antisymmetric stretching vibration of the CO moieties; ^c the stretching vibration of the CO moiety coordinated due to its carbon atom; ^d the stretching vibration of the CO moiety coordinated due to its oxygen atom; ^e the syn-phase vibration of the CO moieties; ^f the anti-phase vibration of the CO moieties.

lies in the region of the isotopically split $\nu(\text{Si—Cl})$ bands of uncomplexed SiCl₂, while the $\nu(\text{CO})$ band of complex **C2** cannot be detected in the experimental spectra since it is hidden by the much more intense band of uncomplexed CO, the frequency of which is very close to the corresponding frequency of the complex. In accordance with the calculation data, the $\nu_s(\text{Si—Cl})$ and $\nu_{as}(\text{Si—Cl})$ bands of complex **C2** also lie in the region of the $\nu(\text{Si—Cl})$ bands of uncomplexed SiCl₂, and the observation of two of them at 508 and 494 cm^{-1} is rather fortunate.

The calculated negative shift of the $\nu(\text{CO})$ frequency of complex **C2** with coordination of the CO molecule due to its oxygen atom agrees with the general view that a weakening of the bond in the CO molecule occurs upon formation of the complexes of this type.³⁹ In accordance with the same conception, the positive shift of the $\nu(\text{CO})$ frequency of complex **C1** indicates its weakness or that the π back-donation does not play any important role in its formation. It was shown that the π back-donation takes place only at rather short distances between the metal and carbon atoms.³⁹ Clearly the structure of complex **C1** with its very long Si—C bond (see Fig. 2) does not satisfy the above requirement necessary for the occurrence of the π back-donation. For the further theoretical confirmation of this assumption, the NBO analysis of the B3LYP/GTbas3 wave functions of complex **C1** and the analogous H₂Si•CO complex, which is much more stable ($\Delta E_0 = -20.7 \text{ kcal mol}^{-1}$ according to the G4(MP2)

calculations) and characterized by a substantial negative shift (-95 cm^{-1}) of the $\nu(\text{CO})$ frequency,⁹ was carried out. The geometric parameters of the H₂Si•CO complex and its relative energy obtained here are close the corresponding values obtained in the G2 calculations.⁶ The performed NBO analysis showed that the energy of electron density donation from the lone electron pair of the Si atom to the antibonding π^*_{CO} orbital in the case of the H₂Si•CO complex ($18.8 \text{ kcal mol}^{-1}$) considerably exceeds the corresponding energy found for complex **C1** ($0.7 \text{ kcal mol}^{-1}$). This corroborates the identification of complex **C1** as a nonclassical complex in contrast to the H₂Si•CO complex, which is classical.

Though the calculations predicts an equal stability of complexes **C1** and **C2**, bands 2 in the $\nu(\text{Si—Cl})$ vibration region, which, presumably, belong to complex **C2**, were weaker than the bands of complex **C1** in IR spectra of matrices both before and after annealing. This implies that complex **C1** was formed in higher concentrations and, therefore, it is characterized by a higher stability in matrices. This discrepancy can be related to the effect of matrix surroundings on the stability of the complexes or to calculation errors. The latter reason seems to be especially likely taking into account that the obtained energies of complex stabilities are comparable with the expected precision of the calculations.

Several complexes of the 1 : 2 composition were calculated at the G4(MP2) level of theory (see Table. 2),

including complexes with the SiCl_2 coordination to two CO molecules (**C3**–**C5**, Fig. 3) and complex $\text{Cl}_2\text{Si} \cdot (\text{CO})_2$ (**C6**), which contains SiCl_2 coordinated to the oxygen atom of the T-shaped CO dimer. The latter complex should be one of the least stable complexes of this type since the CO dimer in its structure is the least stable among a large number of possible dimers.⁴⁰ The calculated stabilities of complexes **C3**–**C5** are approximately equal ($\Delta E_0 \sim -2 \text{ kcal mol}^{-1}$) and exceed the stabilities of the 1 : 1 complexes by approximately two times. Complex **C6** is slightly less stable with $\Delta E_0 = -1.5 \text{ kcal mol}^{-1}$. According to the calculations, the effect of the CO molecules on the $\nu(\text{Si}-\text{Cl})$ frequencies of complexes **C3**–**C5** is additive (see table 2). The $\nu(\text{Si}-\text{Cl})$ frequency shifts for complexes **C3** and **C5** relative to the starting reactant frequencies are approximately twice as large as the corresponding shifts for complexes **C1** and **C2**, respectively, whereas the shifts of these frequencies in the case of complex **C4** are approximately equal to the sum of the shifts for complexes **C1** and **C2**. Coordination of the second CO molecule to the silylene center has no significant effect on the $\nu(\text{CO})$ frequency of the first coordinated molecule, and the $\nu(\text{CO})$ frequency shifts for complexes **C3**–**C5** are comparable with the corresponding shifts for the 1 : 1 complexes with the analogous coordination of the CO molecule. Coordination of the second CO molecule to the CO moiety of complex **C2** with formation of complex **C6** practically does not affect the $\nu(\text{Si}-\text{Cl})$ and $\nu(\text{CO})$ frequencies: these frequencies are approximately equal for both complexes. The above data make it possible to suppose that the main contribution to the bands 3 and 3' in the $\nu(\text{Si}-\text{Cl})$ vibration region is due to complexes **C4** and **C3**, respectively,

whereas the band at 2156.6 cm^{-1} can include contributions from the corresponding bands of both of these complexes. However, this assumption requires an additional verification.

According to the TD B3LYP/GTBas3 calculations, all complexes **C1**–**C6** have absorption bands at around 300 nm (see Table 2), these bands correspond to the $n \rightarrow p$ transition in the SiCl_2 moiety. This is in agreement with the photolability of the experimentally detected complexes.

We made an attempt to achieve a deeper transformation of the reactants. With this purpose, SiCl_2 was generated from Si_2Cl_6 in the presence of ~ 10 -fold excess of CO at $940 \text{ }^\circ\text{C}$. However, no new product was revealed in the obtained matrices. Therefore, to assess the possibility of the formation of any product differing from complexes from the initial SiCl_2 and CO, the potential energy surface (PES) of the $\text{SiCl}_2 + \text{CO}$ system was explored theoretically. The stationary points **3**–**9**, which were found in the G4(MP2) calculations and correspond to minima on PESs of the singlet and triplet state of the system, are shown in Fig. 4. On the whole, the obtained set of minima in the $\text{SiCl}_2 + \text{CO}$ system is similar to that found for the $\text{SiH}_2 + \text{CO}$ system in the B3LYP/6-31G(d,p) calculations.⁹ However, structures corresponding to silaketene $\text{Cl}_2\text{C}=\text{Si}=\text{O}$, the $\text{SiO} \cdot \text{CCl}_2$ complex, and (chlorocarbonyl)-chlorosilylene $\text{O}=\text{C}(\text{Cl})\text{SiCl}$ were not revealed on the PES of the system under consideration. The latter compound is especially important since it can be an intermediate product on the pathway from the starting complexes to cyclic silylene **3** (see Fig. 4) as it was found for the $\text{SiH}_2 + \text{CO}$ system,⁶ in which the analog of silylene **3** is a global minimum in accordance with the data of the G2 calculations. At the same time, all found minima, includ-

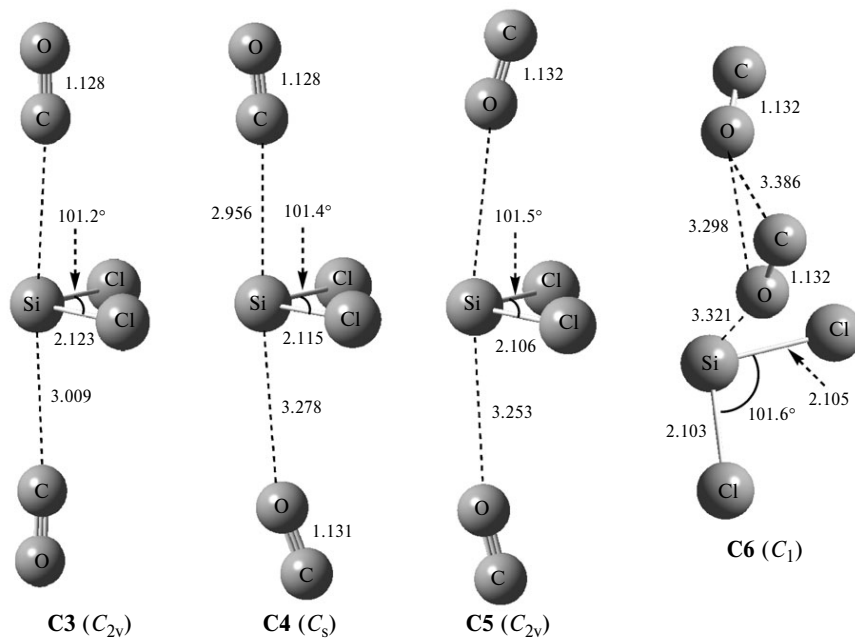


Fig. 3. Structures of complexes **C3**–**C6** obtained in the B3LYP/GTBas3 calculations; bond lengths (Å) and angles (degree) are shown.

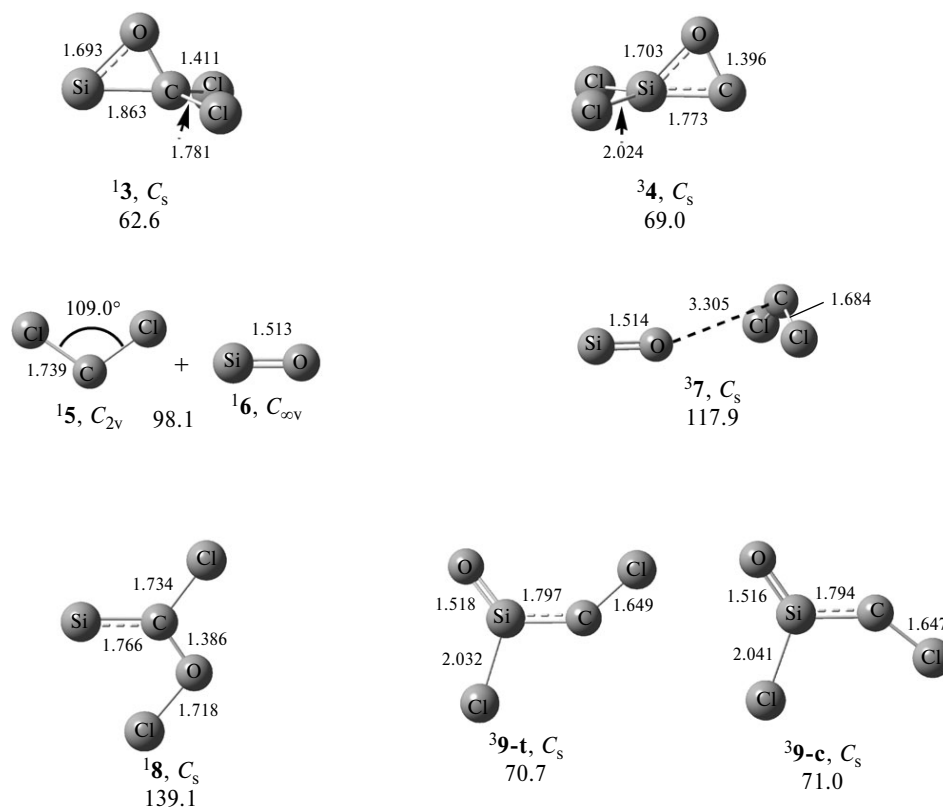


Fig. 4. Minima on PESs of the singlet and triplet states of the $\text{SiCl}_2 + \text{CO}$ system found in the G4(MP2) calculations, their multiplicities, symmetries, and energies ($\Delta E_0 = \Delta E + \text{ZPE}/\text{kcal mol}^{-1}$) relative to free starting SiCl_2 and CO in the singlet states; bond lengths are in Å.

ing silylene **3**, lie considerably higher in energy relative to the starting reactants in the $\text{SiCl}_2 + \text{CO}$ system than in the $\text{SiH}_2 + \text{CO}$ system.^{6,9} Therefore, the introduction of the Cl substituents into silylene not only substantially destabilizes its primary complex with coordination to the carbon atom of the CO molecule, but also results in the energetic unfavorableness of subsequent reactions between the reactants.

Thus, formation of a complex between SiCl_2 and CO of the 1 : 1 composition with silylene coordinated to the carbon atom of the CO molecule was detected in Ar matrices using IR spectroscopy. Complex was characterized by a matrix split band of the $\nu(\text{CO})$ vibration and a matrix and isotopically split band of the $\nu_{\text{as}}(\text{Si}-\text{Cl})$ vibrations. A positive shift of the $\nu(\text{CO})$ band of the complex relative to the corresponding band of starting CO and theoretical analysis of its geometric and electronic structures indicate that the complex represents a nonclassical carbonyl complex. It is the first detected nonclassical carbonyl complex of silylenes. Two additional experimentally observed bands of the $\nu_{\text{s}}(\text{Si}-\text{Cl})$ and $\nu_{\text{as}}(\text{Si}-\text{Cl})$ vibrations were tentatively assigned to a complex between SiCl_2 and CO of the 1 : 1 composition, in which SiCl_2 is coordinated to the oxygen atom of carbon monoxide. The main direction of transformations of the complexes in matrices under UV irra-

diation consists in their decomposition into the starting reactants. Theoretical analysis of the potential energy surface of the $\text{SiCl}_2 + \text{CO}$ system showed that the presence of the Cl substituents in silylene results in the energetic unfavorableness of subsequent transformations of the initially formed complexes.

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