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Interaction of $SiCl_2$ with CO_2 in Ar matrices

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A 1 : 1 photostable complex between dichlorosilylene and CO_2 was detected using matrix-isolation FTIR spectroscopy. The photostability can be attributed to the existence of photochemical equilibria between this complex and products of its isomerization, first of all, a complex of dichlorosilanone with CO, which are strongly shifted to the complex. A detailed computational study of the potential energy surface of the $SiCl_2$ + CO_2 system was carried out.

Ar matrix, 10 K

$$Cl_2Si\cdot CO_2 \overset{h\nu}{\rightleftarrows} Cl_2Si{=}O\cdot CO$$

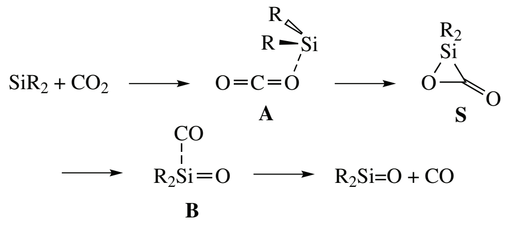
Keywords: dichlorosilylene, dichlorosilanone, carbon dioxide, carbon monoxide, donor–acceptor complexes, matrix isolation, FTIR spectroscopy, quantum chemical calculations.

Activation of small molecules using derivatives of low-valent p-block elements and, in particular, carbene analogs of the Group 14 elements, is an actively developing area of modern organoelement chemistry[1–4] since the potential possibility of using relatively inexpensive and low-toxic compounds for the preparation of chemically valuable products from simple molecules is very attractive. Carbon dioxide is one of the greenhouse gases. Its reserves are practically unlimited, and the problem of converting this highly thermodynamically stable compound into useful organic products is very acute.[5] It readily reacts with various stable silylenes,[6–15] with the initial stage of the interaction, apparently, being a silylene abstraction of the oxygen atom from CO_2 to form the corresponding silanone:

$$R_2Si\!: + CO_2 \rightarrow R_2Si{=}O + CO.$$

The formation of all observed final products, which differ for different silylenes, can be explained by subsequent transformations of silanones, including their reactions with additional CO_2 molecules.[6–15]

Theoretical consideration of the interactions of prototype SiH_2[16] and 2,2,5,5-tetrasilyl-1-silacyclopentan-1-ylidene (SCPY),[9] a silylene structurally close to stable 2,2,5,5-tetrakis(trimethylsilyl)-1-silacyclopentan-1-ylidene, with CO_2 showed that this initial stage is not an elementary, but multistep reaction proceeding *via* intermediate formation of two complexes (**A** and **B**) and siloxiranone **S**:



The energy profiles of this transformation in both reaction systems are very similar,[9,16] which means that interactions between both stable and labile silylenes and CO_2 follow the same general pathway. The obtained theoretical data are in general agreement with the results of a kinetic investigation of the interaction between SiH_2 and CO_2,[16] which represents the only experimental study of this reaction for labile silylenes. The scarcity of experimental data on interactions of labile silylenes with CO_2 prompted us to investigate this reaction for another labile silylene, *viz*., dichlorosilylene, $SiCl_2$, using matrix IR spectroscopy.

A detailed description of the used experimental setup is given in the Online Supplementary Materials. Matrices were formed by co-deposition of mixtures of CO_2 (99.995%) and Ar (99.998%) of known compositions (the CO_2/Ar molar ratios were varied from 1 : 20 to 1 : 500) with products of the Si_2Cl_6 or 1,1-dichloro-1-silacyclopent-3-ene (SCP) pyrolysis ($SiCl_2$ and $SiCl_4$[17] or 1,3-butadiene;[18] a quartz reactor, $T_{pyr} \sim 900$ or 1000 °C, respectively) on a mirror copper plate located inside a cryostat and cooled to ~10 K. The resulting $SiCl_2$/Ar molar ratio in matrices was varied from 1 : 400 to 1 : 1000. A DRSh-500 high pressure Hg arc lamp (500 W) equipped with a water and suitable cut-off filters was used to irradiate matrices. IR spectra were recorded using a Bruker IFS 113v FTIR spectrometer in the range of 4000–400 cm^{-1} with a resolution of 0.5 cm^{-1}.

Two new bands differing from those of the reactants were observed in the IR spectra of formed matrices. Those were slightly broadened bands at 492.9 and 488.3 cm^{-1} with the integral intensity ratio of *ca*. 3 : 2, which lay on the low frequency side of the isotopically split ν_{as}(SiCl) band, overlapping with its weak components at 492.7 ($^{29}Si^{35}Cl^{37}Cl$), 491.3 ($^{30}Si^{35}Cl_2$), and 487.7 ($^{30}Si^{35}Cl^{37}Cl$).[19] They could be discerned in the matrix spectra already at the $SiCl_2$/CO_2/Ar ratios of 2 : 5 : 1000 or 1 : 10 : 1000, and their intensities increased with an increase in the concentration of CO_2 or $SiCl_2$ (Figure 1). None of these bands appeared when $SiCl_4$, the only co-product of the Si_2Cl_6

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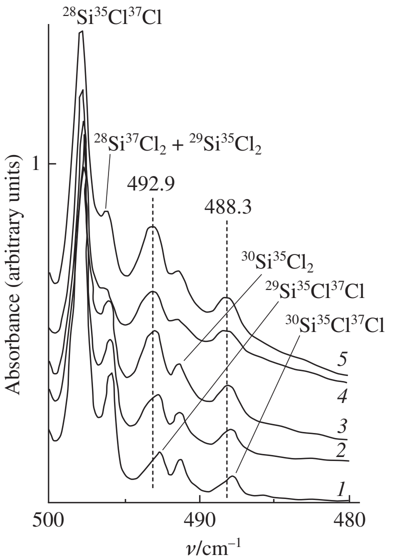

Figure 1 IR bands of $Cl_2Si \cdot CO_2$ at different $SiCl_2/CO_2/Ar$ ratios: (*1*) 2 : 2 : 1000, (*2*) 2 : 5 : 1000, (*3*) 2 : 10 : 1000, (*4*) 1.5 : 20 : 1000, and (*5*) 2 : 20 : 1000.

pyrolysis, was co-deposited with CO_2/Ar mixtures. The listed observations show that these bands represent the most intense components of the isotopically split ν_{as}(SiCl) band of $SiCl_2$ involved into a complexation with CO_2. Their distinct appearance at rather low concentrations of the reactants implies that the complex has the simplest 1 : 1 composition. Thus, the theoretically predicted[9,16] formation of complexes in the reaction between silylenes and CO_2 has found its experimental confirmation.

The expected intense ν_s(SiCl) band of this complex could not be observed because of its overlap with much more intense ν_s(SiCl) and ν_{as}(SiCl) bands of free $SiCl_2$[19] (see the Online Supplementary Materials). Surprisingly, no band of the complex was revealed in the CO_2 vibration regions, which indicated rather small displacement of these vibrational bands upon complexation.

Short-time annealing of matrices, naturally, resulted in growth of the bands of the complex. However, starting from *ca.* 33 K already, their growth almost ceased, while a broad band extending from 466 cm^{-1} to the region of the $SiCl_2$ bands and having several poorly resolved maxima at its low-frequency side appeared, apparently, due to the formation of larger associates involving two or more CO_2 molecules. No formation of other products was detected upon annealing of matrices, showing that deeper transformations in this reaction system require overcoming perceptible activation barriers.

In an attempt to achieve deeper transformations of the reactants, the Si_2Cl_6 pyrolysis was carried out in the presence of CO_2 (the pressure in the reactor was increased due to added CO_2 from typical 0.01 up to *ca.* 0.1 Torr, and it could not be raised anymore without deteriorating the optical quality of the formed matrices). However, no new product was observed in the matrices in this case also, showing that the rate constant of the reaction between $SiCl_2$ and CO_2 at *ca.* 1200 K and the used pressure was below 10^{-17}–10^{-15} cm^3 molec^{-1} s^{-1}, which corresponded to $\Delta G^{\ddagger} \geqslant 50$–60 kcal mol^{-1} if the collisional stabilization of the products was not too critical, or the reaction was reversible.

Interactions of silylenes with various substrates often stop at the stage of complexation in low-temperature matrices. However, irradiation of stabilized complexes with UV light can induce their further transformations,[18,20–27] which makes it possible to explore the photochemical versions of the reactions. Complexation of silylenes with Lewis bases typically results in hypsochromic shifts of their n–p$_\pi$ bands.[28] Therefore, the absorption maximum of $Cl_2Si \cdot CO_2$ is expected to lie around or below 300 nm since the absorption maximum of matrix isolated $SiCl_2$ lies at 317 nm.[29] Therefore, it was not surprising that the light with $\lambda > 300$ nm had no effect on the complex. However, in contrast to the previously studied complexes of $SiCl_2$with allyl chloride, allyl bromide, 1,3-butadiene, and HCl,[18,20,21] $Cl_2Si \cdot CO_2$ turned out to be utterly stable against irradiation with unfiltered light of a Hg arc lamp ($\lambda \approx 230$–1000 nm). Even its prolonged (up to 5 h) irradiation resulted only in its hardly detectable decomposition and the appearance of a number of very weak bands in different regions. Two of these new bands exhibited characteristic splitting (Figure 2) due to the Cl isotopes and were the only bands that disappeared upon annealing, indicating high lability of their carrier identified based on these observations as dichlorosilanone, $Cl_2Si{=}O$.[30,31] A band of CO at 2138 cm^{-1} with an intensity comparable to the intensities of the $Cl_2Si{=}O$ bands also appeared upon photolysis. However, no band of $Cl_2Si{=}O \cdot CO$, an expected product of the light induced rearrangement of $Cl_2Si \cdot CO_2$, was observed in the vicinity of the dichlorosilanone bands. The escape of one of the photolysis co-products from a matrix cage is a known, but rather non-efficient process.[25] Therefore, it can be concluded that the transformation of $Cl_2Si \cdot CO_2$ into $Cl_2Si{=}O \cdot CO$ represents one of the main pathways of the $Cl_2Si \cdot CO_2$ rearrangements during irradiation. At the same time, the absence of detectable amounts of $Cl_2Si{=}O \cdot CO$ in matrices upon irradiation together with the almost invariable concentration of $Cl_2Si \cdot CO_2$ means that these complexes are in a photochemical equilibrium strongly shifted to $Cl_2Si \cdot CO_2$. Thus, like the thermal reactions of silylenes with CO_2, the photochemical reaction of $SiCl_2$ with CO_2 leads to the corresponding silanone, although can produce other products as well.

Photolysis of annealed matrices containing both the $Cl_2Si \cdot CO_2$ complex and larger associates did not increase the yields of products observed upon photolysis of non-annealed matrices and did not lead to formation of additional products, although the decrease in the intensities of the band of the associates was considerably stronger than that of the bands of the complex. The rather high efficiency of the decomposition of the associates under irradiation can be due to their looseness, which results in their easy deformations, including those accompanied by the loss of the association. The band of the associates was restored after subsequent annealing.

The performed G4(MP2) calculations[32] (which include the B3LYP/6-31G(2df) geometry optimization and frequency calculations;[32] the Gaussian 09 software package[33] was used) revealed a complex between $SiCl_2$ and CO_2 of the C_s symmetry with *syn*-oriented moieties of the reactants (Figure 3), which was

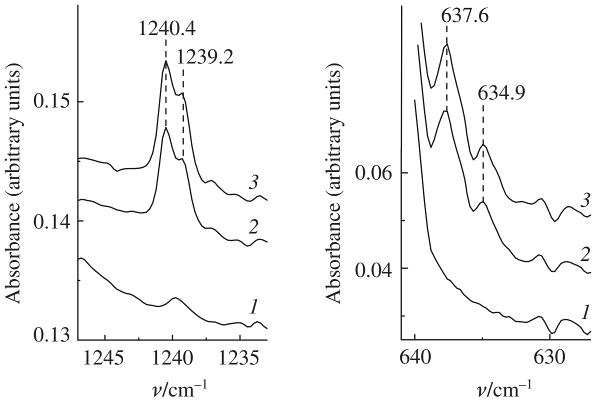

Figure 2 Fragments of IR spectra of an Ar matrix containing $Cl_2Si \cdot CO_2$ ($SiCl_2/CO_2/Ar$ = 1.5 : 20 : 1000, SCP is a precursor) (*1*) after deposition, (*2*) after subsequent photolysis with unfiltered light of a Hg arc lamp for 80 min, and (*3*) after an additional photolysis for 90 min; the frequencies of the $Cl_2Si{=}O$ bands are shown.

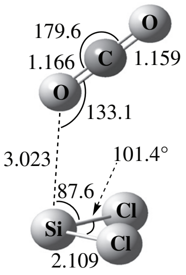

Figure 3 The B3LYP/6-31G(2df) optimized structure of $Cl_2Si \cdot CO_2$.

stabilized relative to free $SiCl_2$ and CO_2 by *ca.* 2 kcal mol^{-1} only ($\Delta E_0 = \Delta E + ZPE = -2.0$ kcal mol^{-1}, $\Delta H^0_{298} = -1.4$ kcal mol^{-1}). Its stabilization energy is slightly smaller than those found in the G2 calculations for *syn*- ($\Delta H^0_{298} = -3.7$ kcal mol^{-1}) and *anti*-complexes ($\Delta H^0_{298} = -2.9$ kcal mol^{-1}) of SiH_2 with CO_2.[16] It can be due to somewhat lowered ability of $SiCl_2$ to coordinate Lewis bases in comparison with SiH_2 due to the interaction of its p_π-orbital, which is responsible for its Lewis acidity, with lone electron pairs of the chlorine substituents. The decreased acidity of $SiCl_2$ can also be the reason for the absence of the complex with *anti*-oriented reactant moieties since in contrast to the *syn*-complex additionally stabilized by the dipole–dipole interaction between the $SiCl_2$ moiety and the C=O bond with the coordinated O atom, the *anti*-complex should be destabilized by this interaction, and its stabilization energy should be even lower than that of the *syn*-complex as in the case of the $SiH_2 + CO_2$ system.[16] At the same time, some broadening of the observed bands of the complex indicates that the matrix surroundings noticeably affect its structure, which is rather flexible, and the real conformation of the complex in the matrix can somewhat differ from the calculated one. According to the calculations, structural parameters of $SiCl_2$ and CO_2 remain practically unchanged upon complexation [Δd(Si–Cl) = 0.008 Å, Δ(Cl–Si–Cl) = –0.5°, $\Delta d(C{=}O)_{coordinated} = 0.003$ Å, $\Delta d(C{=}O)_{free} = -0.004$ Å], which reflects the weakness of the interaction of the reactant moieties within the complex.

The calculations show that the complexation does not result in significant changes in the intensities of IR bands of $SiCl_2$ or CO_2 (see Online Supplementary Materials). The ν_{as}(C=O) and δ(O=C=O) bands of CO_2 undergo only small shifts to low frequencies [by –4 for ν_{as}(C=O) and –2 and –5 cm^{-1} for δ(O=C=O)] upon complexation, which is not sufficient for their observation in the experiment against intense bands of CO_2 always being taken in an excess. The calculated shifts of the ν_s(Si–Cl) and ν_{as}(Si–Cl) bands of $SiCl_2$ are equal to –5 and –11 cm^{-1}. The first number shows that the ν_s(Si–Cl) band of the complex falls into the region of the intense ν_s(Si–Cl) and ν_{as}(Si–Cl) bands of $SiCl_2$.[19] The second number is comparable with the experimentally observed shift of the ν_{as}(Si–Cl) upon complexation (of *ca.* 9 cm^{-1}), slightly exceeding the latter as it was already noted for other $SiCl_2$ complexes studied using matrix IR spectroscopy and the G4(MP2) calculations.[18,20,21]

A number of complexes containing one $SiCl_2$ and two CO_2 molecules (the 1 : 2 complexes) were also calculated (see Online Supplementary Materials). Those were complexes, in which silylene is coordinated to each of the CO_2 molecules, and those, in which $SiCl_2$ is coordinated to one of the CO_2 molecule of the CO_2 dimer.[34] All of the found 1 : 2 complexes are stabilized relative to the starting reactants by *ca.* 4 kcal mol^{-1}, *i.e.*, are twice as stable as the $Cl_2Si \cdot CO_2$ complex. As in the case of the 1 : 1 complex, the only bands observable in our experiment for these 1 : 2 complexes should be the ν_{as}(Si–Cl) bands, which are more strongly shifted to low frequencies (by –13 to –23 cm^{-1}) than the ν_{as}(Si–Cl) band of the $Cl_2Si \cdot CO_2$ complex. This qualitatively agrees with the observation of a broad band in the vicinity of the ν_{as}(Si–Cl) bands of $SiCl_2$ and $Cl_2Si \cdot CO_2$ in the lower frequency region in annealed matrices and their assignment to a mixture of associates of $SiCl_2$ with more than one CO_2 molecule, which should easily be formed because of a considerable mobility of CO_2 during annealing of matrices.[35] Therefore, we did not carried out a further theoretical search for possible 1 : 2 or larger complexes.

A search for possible minima on singlet PES revealed existence of a large number of species (see Online Supplementary Materials). However, most of them lie in energy substantially higher than the starting reactants (usually, $\Delta E_0 \gg 20$ kcal mol^{-1}), which excludes their formation in a thermal reaction of $SiCl_2$ with CO_2. Only 1,1-dichloro-1-siloxiranone **1**, 3,3-dichloro-3-sila-2,4-dioxetan-1-ylidene **2**, $Cl_2Si{=}O + CO$, and the complex between the latter pair of species have energies comparable or lower than that of $SiCl_2 + CO_2$. The search for transition states (TSs) connecting these low-energy minima with $SiCl_2$ and CO_2 gave the only stationary point **TS1** corresponding to the transformation of the starting reactants in the form of their complex into **1**, which in turn readily isomerizes (*via* **TS2**) into the $Cl_2Si{=}O \cdot CO$ complex (Figure 4). This finding agrees with the theoretical data obtained for other silylene systems.[9,16] No direct pathway to **2** from starting $SiCl_2 + CO_2$, their complex, or **1** was revealed. However, as in the case of the $SiH_2 + CO_2$ system,[16] another TS (**TS3**) comparable in energy with **TS1** was found, which connected the $Cl_2Si \cdot CO_2$ complex with higher-lying silylene **3** (see Figure 4).

The transition state **TS1** has a substantially higher energy ($\Delta E_0 = 18.0$, $\Delta H^0_{298} = 17.5$, $\Delta G^0_{298} = 27.4$ kcal mol^{-1} relative to free $SiCl_2 + CO_2$) than the corresponding transition states found in the $SiH_2 + CO_2$ ($\Delta H^0_{298} = 2.8$ kcal mol^{-1})[16] and SCPY + CO_2 ($\Delta E_0 = 7.2$, $\Delta H^0_{298} = 6.5$, $\Delta G^0_{298} = 18.8$ kcal mol^{-1})[9] systems in the G2 and BMK/6-31G(d,p) calculations, respectively. The

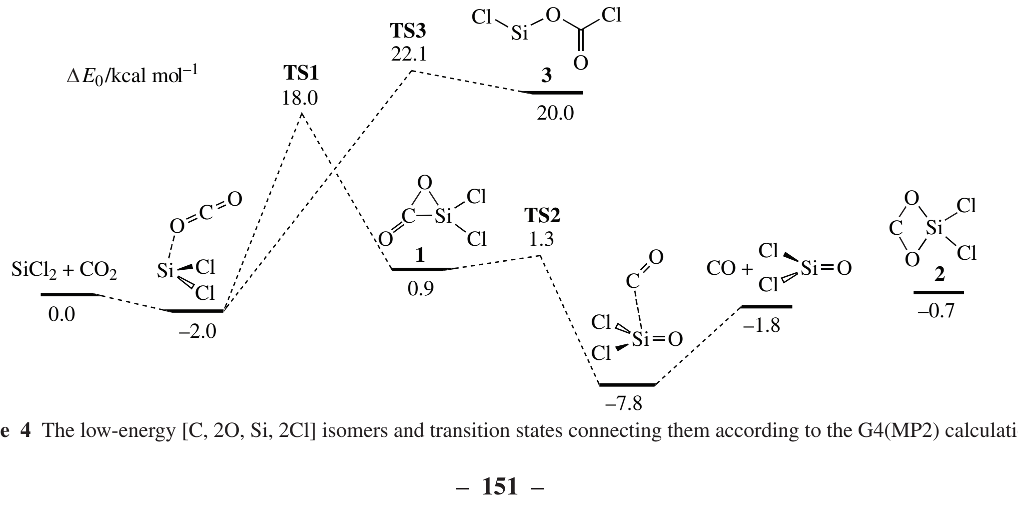

Figure 4 The low-energy [C, 2O, Si, 2Cl] isomers and transition states connecting them according to the G4(MP2) calculations.

formation of final silanone and CO is also less favorable in the case of the $SiCl_2 + CO_2$ system ($\Delta E_0 = -1.8$, $\Delta H^0_{298} = -1.4$, $\Delta G^0_{298} = -1.7$ kcal mol^{-1}) than in the case of the $SiH_2 + CO_2$ ($\Delta H^0_{298} = -17.7$ kcal mol^{-1})[16] and SCPY + CO_2 ($\Delta E_0 = -11.3$, $\Delta H^0_{298} = -10.5$, $\Delta G^0_{298} = -12.7$ kcal mol^{-1})[9] systems. This reflects a strong stabilization effect of the Cl substituents on silylenes,[36] and their destabilizing effect on silanones due to additional polarization of the Si=O bond.[37] The $\Delta G^{\ddagger}$ value for the addition of $SiCl_2$ to CO_2 with formation of **1** increases with increasing temperature and becomes equal to 56.5 kcal mol^{-1} at 1200 K (see Online Supplementary Materials), which agrees with the rough estimation made above on the basis of the co-pyrolysis experiments. The $\Delta G^{\ddagger}$ values for reactions *via* **TS2** and **TS3** also increase with increasing temperature. However, at all temperatures, the ΔG^0 value of **TS2** is lower, while the ΔG^0 value of **TS3** is higher than that of **TS1**, becoming equal to 43.4 and 63.6 kcal mol^{-1} at 1200 K, respectively. Thus, formation of $Cl_2Si{=}O\cdot CO$ is kinetically preferable at all temperatures, and the rate determining step of this reaction is always formation of **1**.

The TD B3LYP/6-31G(2df) calculated absorption wavelength for the n–p transition in $SiCl_2$ equal to 327 nm (3.79 eV, $f = 0.029$) is close to the experimentally observed value of 317 nm.[29] The energy and oscillator strength of this transition increases on going to the $Cl_2Si\cdot CO_2$ complex (3.94 eV, 315 nm, $f = 0.040$) and $SiCl_2$ complexes with the CO_2 dimer (3.91–3.95 eV, 314–317 nm, $f = 0.039$–0.042) and then to $SiCl_2$ complexes with two CO_2 molecules (4.07 eV, 304 nm, $f = 0.052$–0.053). According to the TD B3LYP calculations, $Cl_2Si{=}O$ has two electronic transitions in the UV region with a significant oscillator strength: n–π* (5.03 eV, 247 nm, $f = 0.022$) and π–π* (5.46 eV, 227 nm, $f = 0.012$), whereas $Cl_2Si{=}O{*}CO$ has only one with considerably higher oscillator strength: π–π* (4.99 eV, 249 nm, $f = 0.079$). These data support the possibility of a photochemical equilibrium between the $Cl_2Si\cdot CO_2$ and $Cl_2Si{=}O\cdot CO$ complexes under a broad band irradiation. The calculations also show that compounds **1** and **2**, which belong to the low-energy species on PES of the $SiCl_2 + CO_2$ system, absorb in the UV region too (see Online Supplementary Materials). Since almost all high-energy minima found on PES of the $SiCl_2 + CO_2$ systems are either silylenes or species with double bonded Si atoms, they should absorb in the UV region as well. This suggests that the reluctance of the $Cl_2Si\cdot CO_2$ complex to undergo rearrangements under irradiation can be related to the photolability of possible end products rather than to the absence of suitable pathways on excited-state PES.

According to the calculated IR spectra of products found on PES of the $SiCl_2 + CO_2$ system, none of them can be responsible for the entire set of weak unassigned bands observed after photolysis of matrices, although several product combinations can be selected to assign all the bands.

Like other silanones,[9,38] $Cl_2Si{=}O$ is very active in the reaction with CO_2 leading to 1,1-dichloro-1-sila-2,4-dioxetan-3-one **4** (Figure 5), which, in accordance with the TD B3LYP calculations, has no UV absorptions and, therefore, is a photostable species. However, the initial formation of the $Cl_2Si{=}O\cdot CO_2$ complex makes this reaction difficult in matrices since the calculated barrier of the rearrangement of the complex is 1.8 kcal mol^{-1}, which is too high at 10 K. Formation of the triple $Cl_2Si{=}O\cdot CO_2\cdot CO$ complex increases the barrier of the corresponding rearrangement to 6.5 kcal mol^{-1} (see Figure 5), making it prohibitively high. Apparently, rather high barriers of this rearrangement for mixed associates $Cl_2Si{=}O\cdot (CO_2)_n\cdot CO$, $n \geqslant 1$, is a reason why no siladioxetanone **4** (or its associates with CO or/and CO_2) was observed when annealed matrices containing associates $Cl_2Si\cdot (CO_2)_n$, $n > 1$, were photolysed, in spite of the fact that these mixed associates could be formed in vibrationally excited states.

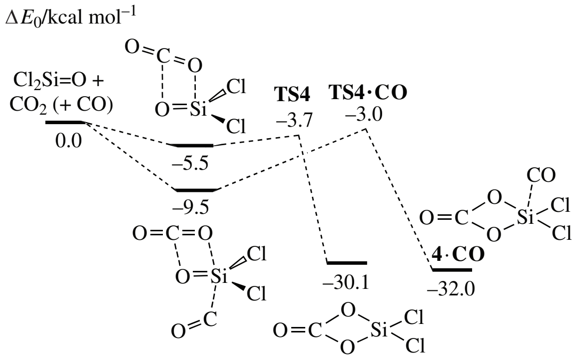

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Figure 5 Interaction of $Cl_2Si{=}O$ with CO_2 according to the G4(MP2) calculations.

In conclusion, a complex of dichlorosilylene and CO_2 of the 1 : 1 composition, $Cl_2Si\cdot CO_2$, was stabilized in low-temperature Ar matrices and characterized using IR spectroscopy. It is the first direct observation of a complex between any silylene and CO_2, although the existence of such complexes was predicted theoretically. In contrast to previously observed complexes of $SiCl_2$ with various Lewis bases, this complex is photostable. Performed quantum chemical calculations showed that the occurrence of further thermal transformations in the $SiCl_2 + CO_2$ system required overcoming rather high activation barriers, and they could not be observed under the used conditions. The calculations also suggest that the reluctance of the complex to undergo photoinduced rearrangements is most probably related to the photolability of possible end products. In particular, on the basis of experimental observations and theoretical consideration, it has been argued that there is a photochemical equilibrium between this complex and a complex of dichlorosilanone with CO, which is strongly shifted to the $Cl_2Si\cdot CO_2$ complex.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.03.002.

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