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REGULAR ARTICLE

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The silicon carbonyls revisited: on the existence of a planar $Si(CO)_4$

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Abstract Recently, some works have focused attention on the reactivity of silicon atom with closed-shell molecules. Silicon may form a few relatively stable compounds with CO, i.e. Si(CO), $Si(CO)_2$, $Si[C_2O_2]$, while the existence of polycarbonyl ($n > 2$) silicon complexes has been rejected by current literature. In this paper, the reaction of silicon with carbonyl has been reinvestigated by density functional calculations. It has been found that the tetracoordinated planar $Si(CO)_4$ complex is thermodynamically stable. In Si(CO), silicon carbonyl, and $Si(CO)_2$, silicon dicarbonyl, the CO are datively bonded to Si; $Si(CO)_4$, silicon tetracarbonyl, may be viewed as a resonance between the extreme configurations $(CO)_2Si + 2CO$ and $2CO + Si(CO)_2$; while $Si[C_2O_2]$, *c*-silicodiketone, is similar to the compounds formed by silicon and ethylene. A detailed orbital analysis has shown that the Si bonding with two CO is consistent with the use of sp^2-hybridized orbitals on silicon, while the Si bonding with four CO is consistent with the use of sp^2d-hybridized orbitals on silicon, giving rise to a planar structure about Si.

Keywords Silicon carbonyl complexes · Planar tetracoordinated silicon · Density functional calculations

1 Introduction

In view of its numerous applications in the chemical (silicones) and electronic (single crystalline silicon) industries, silicon has been the subject of extended experimental and theoretical investigations. Despite of that, many remarkable specific chemical behaviors (like the exceptional strength of its bond to fluorine and the formation of planar silyl amines) have remained partially unexplained and are still a matter for discussion.

In recent years, motivated by the fact that the thermal oxidation of single crystalline silicon in O_2 ambient injects atomic silicon into the growing SiO_2 [1,2], we have been attracted by the chemical behavior of atomic-like silicon in siloxanic networks. The major conclusion of our investigation was that silicon may behave as a weak bifunctional Lewis acid forming $((-O)_3Si)_2O{:}\rightarrow Si \leftarrow{:}O(Si(O-)_3)_2$ adducts [3–5].

Atomic silicon may also be produced in such a state with relatively simple methods like sputtering or evaporation. These methods allow in principle an experimental study of the reaction of silicon with closed-shell molecules (for instance, as condensed film physisorbed at the surface of a substrate where the silicon atoms are being deposited) which are expected to behave to some extent as the siloxanic species mentioned above. In particular, the base nature of NH_3, H_2O and CO (ordered for decreasing basic strength) would suggest for them the formation of $R \rightarrow Si \leftarrow R$ adducts ($R = NH_3, H_2O, CO$).

Recently, some works have focused attention on the reactivity of Si atom with unsaturated molecules (i.e. C_2H_2 and C_2H_4) [6,7].

This background has suggested to us a theoretical study of the expected species which may be formed in such conditions. Such analysis would be certainly useful while assesing the experiments and eventually rationalizing the results. We anticipate that while for NH_3 and H_2O the calculations confirmed the expectations (P. Belanzoni, G. Giorgi, G.F. Cerofolini and A. Sgamellotti, unpublished), calculations provided surprising results for CO. Several papers have appeared in literature on $Si(CO)_n$ ($n = 1, 2$) complexes, where the structures, properties and the bonding character for such silicon carbonyls have been investigated using different theoretical methods [8–10]. The existence of larger complexes was discarded on the basis of the weakness of the bond of

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the third CO to the complex and the absence of any reported experimental evidence for these species [8], while Si(CO) and $Si(CO)_2$ have been experimentally observed [11,12].

In this work, we, however, predict the thermodynamic stability of a planar tetracoordinated $Si(CO)_4$ complex.

2 Computational and methodological details

The calculations reported in this paper have been performed employing the Amsterdam Density Functional (ADF) program package [13–16]. The ADF code is characterized by the use of a density fitting procedure to obtain accurate Coulomb and exchange potentials in each self-consistent-field cycle in the solution of the one-electron Kohn–Sham equations, by accurate and efficient numerical integration [17] of the effective one-electron Hamiltonian matrix elements and by the possibility of freezing core orbitals. The molecular orbitals were expanded in a basis set of Slater-type orbitals (STOs) and the frozen core approximation was used for the evaluation of valence orbitals. The parameterization of electron gas data [18] by Vosko et al. [19] was employed in the local density approximation. Full geometry optimizations were performed within both spin unrestricted (open shell) and spin restricted (closed shell) approach including Becke's gradient corrections [20] to the exchange part of the potential and Perdew's gradient correction [21,22] to the correlation. For our systems, we considered different symmetries, i.e., $C_{\infty v}$, C_{2v}, $D_{\infty h}$, D_{4h}, D_{2h}, T_d and D_2, in an attempt to find the "most" stable geometry in each series. For the model molecules, the Si, C, H, and O molecular orbitals were expanded in a triple-ζ STO basis set, adding as polarization functions one $3d$ STO for C and O, and one $3d$ plus one $4f$ STO for Si. The core orbitals (from $1s$ to $2p$ for Si, and $1s$ for O and C) were kept frozen. In order to analyze the silicon–carbonyl interaction energies, we used a method that is an extension of the well-known decomposition scheme of Morokuma [23,24]. The bonding energy is decomposed into a number of terms. The first term, ΔE^0, is obtained from the energy of the wavefunction Ψ^0 which is constructed as the antisymmetrized and renormalized product of the wavefunctions Ψ^A and Ψ^B of the fragments A and B from which the molecule is built up. ΔE^0, which is called *steric repulsion*, consists of two components. The first is the *electrostatic interaction*, $\Delta E_{\mathrm{elstat}}$, of the nuclear charges and unmodified electronic charge density of one fragment with those of the other fragment, both fragments being at their final positions. The second component is the so-called *exchange repulsion* or *Pauli repulsion*, $\Delta E_{\mathrm{Pauli}}$, which is essentially due to the antisymmetry requirement of the total wavefunction. In addition to the steric repulsion term ΔE^0 there are attractive orbital interactions which enter when the wavefunction Ψ^0 is allowed to relax to the fully converged ground state wavefunction of the total molecule, Ψ^{AB}. The energy lowering due to mixing of virtual orbitals of the fragments into the occupied orbitals is called *orbital interaction energy*, $\Delta E_{\mathrm{o.i.}}$, that includes both the charge transfer and polarization interactions. This term, according to the decomposition scheme proposed by Ziegler [25], may be broken up into contributions from the orbital interactions within the various irreducible representations of the overall symmetry group of the system. There is a third contribution to the total bonding energy ($\Delta E = \Delta E^0 + \Delta E_{\mathrm{o.i.}}$) in the frequent cases where the ground state wavefunctions Ψ^A and Ψ^B, at the equilibrium geometries of the free fragments, cannot be used to calculate ΔE^0. The geometry of the free fragment is often different from the geometry of the fragments as it occurs in the overall molecule. Also, the ground electronic configuration of the free fragment may not be suitable for interaction with the other fragment. The energy required to prepare the fragments for interaction by changing the geometry and the electronic configuration is called *preparation energy*, ΔE_{prep}. Thus the total bonding energy will be:

$$\Delta E = \Delta E_{\mathrm{prep}} + \Delta E^0 + \Delta E_{\mathrm{o.\,i.}} \tag{1}$$

3 Results

For the search of stable molecules, we considered species involving 1, 2 and 4 CO groups, assigning a priori for each candidate species reasonable symmetries: $C_{\infty v}$ for Si(CO), C_{2v} and $D_{\infty h}$ for $Si(CO)_2$; D_{2h}, D_{4h}, D_2 and T_d for $Si(CO)_4$. For all of them, we found structures which are more stable than the corresponding reactants.

3.1 Geometry and energetics

Table 1 compares the energies E of the considered geometries with those of the corresponding reactants (E is measured with respect to the constituting atoms; ΔE are the reaction enthalpies of the compounds with respect to reactants), while Fig. 1 shows the corresponding geometries (with internuclear distances in ångstroms and angles in degrees) of the most stable silicon carbonyls $Si(CO)_n$ ($n = 1, 2, 4$).

In order to be considered as molecules, these structures must, however, be stable with respect to small nuclear displacements. We have thus performed a normal mode analysis of the vibrational spectra of all considered molecules. Of them, only Si(CO), $Si(CO)_2$ in C_{2v} symmetry (both singlet and triplet state structures) and $Si(CO)_4$ in D_{2h} symmetry (only singlet state structure) were found to have all normal modes with real frequencies. We have thus focused our attention only on the minimum structures. In Si(CO) the Si–C distance is 1.83 Å, and the C–O bond is 1.17 Å. These bond length values are in good agreement with the optimized Si–C (1.810–1.835 Å) and C–O (1.157–1.161 Å) bond lengths at five theoretical levels (i.e. CASSCF, B3LYP, B3P86, B3PW91, MP2) [8].

In $Si(CO)_2$ in C_{2v} symmetry ($S = 0$) the internuclear distances are the following: 1.82 Å for the Si–C distance, 2.24 Å for the C–C distance, and 1.17 Å for the C–O bond. All these values are in good agreement with those calculated (Si–C: 1.8133 Å; C–O: 1.1500–1.1638 Å) at four theoretical levels

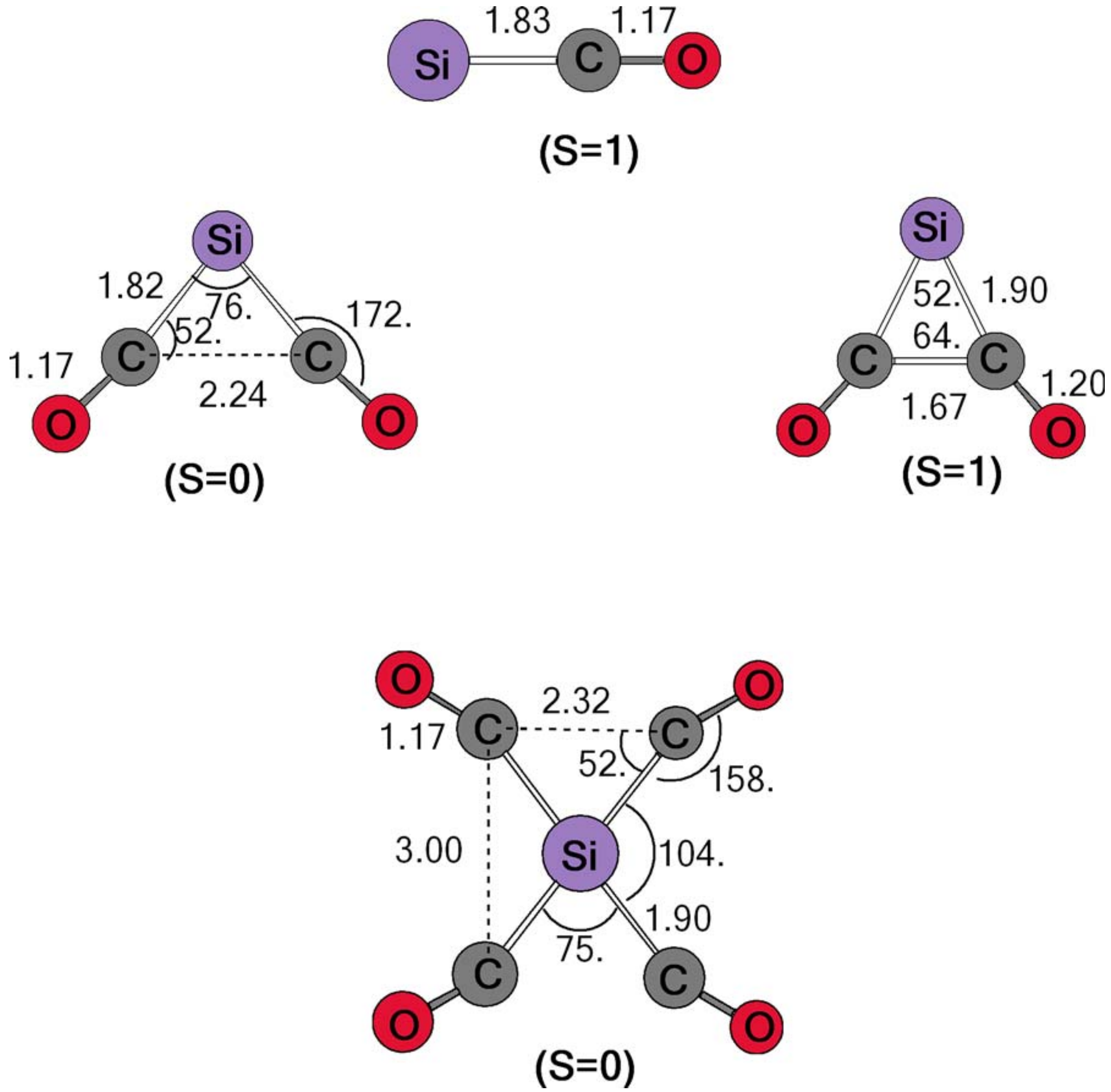


Fig. 1 The optimized structures of the most stable complexes resulting from the reaction of silicon with 1, 2, and 4 CO ligands. The spin multiplicity of the electronic state is also reported

(i.e. B3LYP, B3P86, B3PW91, MP2) in Ref. [8]. The $\widehat{\mathrm{CSiC}}$ (76°) and $\widehat{\mathrm{SiCO}}$ (172°) angles fall within 75.39°–79.43° and 170.68°–171.83°, respectively, calculated at four theoretical levels in Ref. [8].

In $Si(CO)_2$ ($S = 1$) the Si–C bond lengthens to 1.90 Å, while the C–C distance shortens to 1.67 Å; CO bond length is 1.20 Å. As a consequence, the $\widehat{\mathrm{CSiC}}$ angle decreases to 52°. Analogously, a good comparison can be found with the corresponding calculated data in Ref. [8].

In $Si(CO)_4$ in D_{2h} symmetry ($S = 0$) the Si–C and C–C distances are somewhat larger (1.90 Å and 2.32 Å, respectively) than in $Si(CO)_2$ in C_{2v} symmetry ($S = 0$), while the C–O distance, 1.17 Å, is unchanged. The $\widehat{\mathrm{CSiC}}$ angle is 75° and the $\widehat{\mathrm{SiCO}}$ angle is 158°. No theoretical and experimental values for $Si(CO)_4$ geometrical parameters have been reported so far. However, the DFT method, with the Becke88 and Perdew86 functional, and the basis sets used in this work, are reliable and sufficiently accurate, as shown by Si(CO) and $Si(CO)_2$ results, which are in good agreement with those calculated with different methods [8].

$Si(CO)_2$ $S = 1$ is less stable than the corresponding $S = 0$ by 1.50 eV (about 35 kcal mol^{-1}), as shown in Table 1, and in agreement with Ref. [8] (34–42 kcal mol^{-1} with different theoretical methods). Within calculation accuracy $Si(CO)_4$ in D_{2h} symmetry has the same binding energy as $Si(CO)_2$ in C_{2v} symmetry ($S = 0$) plus 2 CO. From Table 1, the dissociation energy of the Si(CO) species in Si plus CO is about 44 kcal mol^{-1}, and it is very close to the values from Ref. [8] (36.5–41.5 kcal mol^{-1} from DFT methods, 42.5 kcal mol^{-1} from CASSCF-MP2 methods), and slightly overestimated with respect to CCSD(T) value (26.1 kcal mol^{-1})

Table 1 Binding energy E with respect to atoms of the reacting molecules and of the corresponding compounds, and reaction enthalpy ΔE of the compounds with respect to reactants

Reactants	E (eV)	Product	Symmetry	E (eV)	ΔE (eV)	ΔE (kcal mol^{-1})
1 CO + Si	−15.54	$Si(CO)^a$	$C_{\infty v}$	−17.45	−1.91	−44.0
2 CO + Si	−30.23	$Si(CO)_2$	C_{2v}	−33.49	−3.26	−75.2
2 CO + Si	−30.23	$Si(CO)_2{}^a$	C_{2v}	−31.99	−1.76	−40.6
2 CO + Si	−30.23	$Si(CO)_2{}^a$	$D_{\infty h}$	−31.30	−1.07	−24.7
2 CO + Si	−30.23	$Si(CO)_2$	$D_{\infty h}$	−31.05	−0.82	−18.9
4 CO + Si	−59.62	$Si(CO)_4$	D_{2h}	−62.85	−3.23	−74.5
4 CO + Si	−59.62	$Si(CO)_4$	D_{4h}	−62.34	−2.72	−62.7
4 CO + Si	−59.62	$Si(CO)_4^b$	D_2	−60.29	−0.67	−15.5
4 CO + Si	−59.62	$Si(CO)_4^b$	T_d	−60.04	−0.42	−9.7

Unless otherwise specified, the product is in singlet state

[a] Triplet state

[b] Quintet state

[c] For the silicon atom in electronic state ^3P, a ground state energy of -0.84 eV has been assumed, as recommended by Baerends et al. [26]

[8]. However, this value indicates that the Si–CO bonding should not be considered a weak interaction.

The first dissociation energy for $Si(CO)_2$ ($S = 1$) is about 31 kcal mol^{-1}, comparable to the values from Ref. [8] (23.6–28.3 kcal mol^{-1} from DFT methods, 24.8 from MP2), and smaller than the second CO dissociation energy by about 13 kcal mol^{-1}, as in Ref. [8], i.e. the first CO binding energy of an Si atom is greater than the second CO one. At variance with Ref. [8], it is very important to note that the third or fourth CO binding energy of Si is NOT smaller than the second one. In particular, the dissociation energy of $Si(CO)_4$ into Si(CO) plus three CO is about 30 kcal mol^{-1}, i.e. the second CO binding energy of an Si atom is as large as the fourth CO one. From the viewpoint of the average single CO binding energy, the average value (19 kcal mol^{-1}) for the $Si(CO)_4$ species is smaller than that (38 kcal mol^{-1}) for the $Si(CO)_2$ species, the latter being smaller than that (44 kcal mol^{-1}) for the Si(CO) species.

3.2 Orbital analysis and the nature of the silicon-carbonyl bond

3.2.1 Electronic structure

Si(CO) : Silicon carbonyl ($S = 1$)

This system has a triplet ($S = 1$) ground state ($^3A_2$). The linear molecule has been chosen to lie along the z axis and descent to C_{2v} symmetry has been used to analyze the one-electron molecular orbitals obtained by spin unrestricted calculations in terms of percentage composition based on Mulliken population. The $4a_1$ HOMO orbital represents a bonding combination of the doubly occupied 3σ orbital on CO (20%) with $3s$ (57%) and $3p_z$ (20%) orbitals on Si. Above the HOMO, the singly occupied $2b_1$ and $2b_2$ α molecular orbitals can be described as Si $3p_x$ (61%) and $3p_y$ (61%), respectively, interacting with CO $2\pi^*$ orbitals ($36\% 2\pi_x$, $36\% 2\pi_y$). From the Mulliken gross population analysis, the σ orbital interaction between Si $3s$ and $3p_z$ and CO 3σ causes a decrease in the 3σ population (from $2.00e$ to $1.45e$) and a corresponding increase in the Si $3p_z$ (from $0.00e$ to $0.60e$) Mulliken population. The π interaction is a π-backdonation from Si $3p_x, 3p_y$, whose Mulliken populations decrease from $1.00\alpha e$ to $0.63\alpha e$, to CO $2\pi^*$, whose population correspondingly increases from $0.00\alpha e$ to $0.36 + 0.36\alpha e$. The resulting Mulliken total charge on silicon is slightly positive, $0.14e$, on C is $0.18e$ and on O atom is $-0.32e$. The spin density analysis reveals that roughly one unpaired electron is localized on Si atom ($1.28e$) and the other is shared by the CO group (C $0.45e$, O $0.28e$).

$Si(CO)_2$: Silicon dicarbonyl ($S = 0$)

Table 2 shows selected one-electron orbitals obtained by spin restricted calculations for the $Si(CO)_2$ complex in C_{2v} symmetry ($S = 0$) ($^1A_1$). The energies and the percentage composition based on Mulliken population analysis is given in terms of atomic Si^+ ion orbitals and $(CO)_2^-$ orbitals, with the nature of the single "CO" orbitals reported in parentheses. We promoted the fragments to the ionic configurations Si^+ $[(3s)^1(3p_z)^0(3p_x)^0(3p_y)^2]$ and $(CO)_2^-$ with one, namely $5a_1$ ($2\pi^*_{ip}$), of the $2\pi^*$ set of orbitals singly occupied. This change of configuration has an advantage in that the Si $3s$ acts as acceptor orbital for electrons from $(CO)_2^-$ singly occupied $5a_1$ ("CO" $2\pi^*$) and $4a_1$ ("CO" 3σ), and the Si $3p_y$ orbital can act as donor orbital to the empty $(CO)_2^-$ $2b_2$ ("CO" $2\pi^*_y$) orbital. The planar molecule has been chosen to lie on the xz plane.

The $2b_2$ HOMO orbital represents a bonding interaction between silicon $3p_y$ (46%) and $(CO)_2^-$ $2b_2$ ("CO" $2\pi^*$) orbital, with a small mixing of Si $3d_{yz}$ orbital. Below the HOMO, the $5a_1$ MO can be described as silicon $3s$ (50%) and $3p_z$ (25%) interacting with $5a_1$ $(CO)_2^-$ ("CO" $2\pi^*$) and $4a_1$ $(CO)_2^-$ ("CO" 3σ) orbitals. The low-lying $2a_1$ orbital is characterized by a Si $3s$ (22%) and $(CO)_2^-$ $4a_1$ ("CO" 3σ) and $2a_1$ ("CO" 2σ), with small contribution from Si $3p_z$ (5%). Silicon $3p_x$– "CO" 3σ ($4b_1$)-1π ($3b_1$) bonding interactions are described by $4b_1$ and $3b_1$ MOs.

Table 2 One-electron energies and percentage composition (based on Mulliken population analysis per MO) of the complex $Si(CO)_2$ ($S = 0$) in C_{2v} symmetry

Orbital	ϵ (eV)	Si^{+1}	$(CO)_2^{-1}$
$2a_1$	-17.23	$22\%\,3s + 5\%\,3p_z$	$37\%\,2a_1(2\sigma) + 23\%\,4a_1(3\sigma)$
$2b_1$	-14.20	$4\%\,3p_x$	$85\%\,2b_1(2\sigma) + 7\%\,4b_1(3\sigma)$
$3a_1$	-13.12	$8\%\,3s$	$62\%\,2a_1(2\sigma) + 23\%\,4a_1(3\sigma)$
$4a_1$	-12.01	$3\%\,3s$	$86\%\,3a_1(1\pi_{ip}) + 9\%\,4a_1(3\sigma)$
$3b_1$	-11.83	$9\%\,3p_x$	$11\%\,2b_1(2\sigma) + 60\%\,3b_1(1\pi_{ip}) + 18\%\,4b_1(3\sigma)$
$1b_2$	-11.62	$2\%\,3d_{yz}$	$96\%\,1b_2(1\pi_y) + 1\%\,2b_2(2\pi_y^*)$
$1a_2$	-11.29		$99\%\,1a_2(1\pi_y)$
$4b_1$	-10.47	$2\%\,3d_{xz} + 8\%\,3p_x$	$4\%\,2b_1(2\sigma) + 37\%\,3b_1\,(1\pi_{ip}) + 49\%\,4b_1(3\sigma)$
$5a_1$	-7.88	$50\%\,3s + 25\%\,3p_z$	$15\%\,4a_1(3\sigma) + 10\%\,5a_1(2\pi_{ip}^*)$
$2b_2$ HOMO	-5.65	$1\%\,3d_{yz} + 46\%\,3p_y$	$3\%\,1b_2(1\pi_y) + 51\%\,2b_2(2\pi_y^*)$
$6a_1$ LUMO	-3.78	$4\%\,3s + 10\%\,3p_z$	$74\%\,5a_1(2\pi_{ip}^*)$
$2a_2$	-2.49	$4\%\,3d_{xy}$	$94\%\,2a_2(2\pi_y^*)$
$5b_1$	-2.17	$4\%\,3d_{xz} + 36\%\,3p_x$	$53\%\,5b_1(2\pi_{ip}^*)$
$3b_2$	-1.33	$5\%\,3d_{yz} + 54\,\%3p_y$	$37\,\%2b_2(2\pi_y^*)$

Selected orbitals involving Si atom in terms of Si^{+1} and $(CO)_2^{-1}$ fragments are reported. The "CO" orbital character is shown in parentheses

Table 3 Mulliken gross population of valence MO of Si^{+1} and $(CO)_2^{-1}$ fragments in $Si(CO)_2$ ($S = 0$) in different irreducible representations in C_{2v} point group

	A_1	A_2	B_1	B_2
Si^{+1}	$3s$ 1.65 $3d_{z^2}$ 0.02 $3d_{x^2-y^2}$ 0.03 $3p_z$ 0.62	$3d_{xy}$ 0.01	$3d_{xz}$ 0.09 $3p_x$ 0.43	$3d_{yz}$ 0.03 $3p_y$ 0.96
$(CO)_2^{-1}$	$4a_1(3\sigma)1.54$ $3a_1(1\pi_{ip})1.94$ $5a_1(2\pi_{ip}^*)0.22$	$1a_2(1\pi_y)1.98$	$4b_1(3\sigma)1.48$ $3b_1(1\pi_{ip})1.96$	$2b_2(2\pi_y^*)1.03$
Gross charge	Si 0.15	C 0.26	O -0.33	

Table 3 shows the Mulliken gross population of Si^+ and $(CO)_2^-$ fragment orbitals in the complex, in different irreducible representations in C_{2v} point group.

From Table 3, we see that the σ and $\pi_{i.p.}$ orbital interactions between Si $3s$ and $3p_z$ and $(CO)_2^-$ ("CO" $2\pi^*$) and ("CO" 3σ) orbitals in the $5a_1 - 2a_1$ MOs causes a decrease in the $(CO)_2^- 4a_1$ (3σ) Mulliken population, which reduces from $2e$ to $1.54e$, and $5a_1$ ("CO" $2\pi^*$) Mulliken population, which reduces from $1e$ to $0.22e$, and an increase in the Si $3s$ (from $1e$ to $1.65e$) and $3p_z$ (from $0e$ to $0.62e$) Mulliken populations. The Si $3d_{z^2}$ and $3d_{x^2-y^2}$ get slightly populated by $0.02e$ and $0.03e$, respectively. In B_1 symmetry, the σ orbital interaction between Si $3p_x$, $3d_{xz}$ and $(CO)_2^- 4b_1$ ("CO" 3σ character) causes a decrease in the $(CO)_2^- 4b_1$ Mulliken population which reduces from $2e$ to $1.48e$, and a corresponding increase in the Si $3p_x$ ($0.43e$) and $3d_{xz}$ ($0.09e$) populations.

Finally, in B_2 symmetry, the π out-of-plane interaction between the doubly occupied Si $3p_y$ and $(CO)_2^- 2b_2$ empty orbital ("CO" $2\pi^*$ character), causes a decrease in the Si $3p_y$ population (from $2e$ to $0.96e$) and a corresponding increase in the $2b_2$ population (from $0e$ to $1.03e$). The Si $3d_{yz}$ also acquires a small population ($0.03e$).

In A_2 symmetry very weak interaction between Si $3d_{xy}$ ($0.01e$) and $(CO)_2^- 1a_2$ ($1.98e$) can be observed.

We note that silicon $3d_{xz}$ orbital participates in the σ bonding with the two carbonyl set.

The resulting Mulliken total charge on Si atom is slightly positive, $0.15e$, on C is $0.26e$, and on O atom is $-0.33e$.

$Si(CO)_2$: *c*-silicodiketone ($S = 1$)

In Table 4 selected one-electron orbitals (only α-spin) obtained by spin unrestricted calculations of the $Si(CO)_2$ complex ($S = 1$) ($^3B_2$) are shown. The energies and the percentage composition based on Mulliken population analysis is given in terms of atomic Si $[(3s)^2(3p_x)^0(3p_y)^1(3p_z)^1]$ and $(CO)_2$ orbitals.

The $2b_2$ molecular orbital is singly occupied and represents a bonding interaction between silicon $3p_y$ (44%) and $(CO)_2 2b_2$ ($2\pi_y^*$). The singly occupied $6a_1$ molecular orbital can be described as silicon $3p_z$ (27%) interacting with $(CO)_2 5a_1$ ("CO" $2\pi_{ip}^*$). Silicon $3p_x$– "CO"3σ ($4b_1$) bonding interaction is described by $4b_1$ HOMO orbital, while $5a_1$ represents a bonding interaction between silicon $3s$ (52%),

Table 4 One-electron energies and percentage composition (based on Mulliken population analysis per MO) of the $Si(CO)_2$ ($S = 1$) complex in C_{2v} symmetry

Orbital	ϵ (eV)	Si	$(CO)_2$
$2a_1$	−18.99	$14\%\, 3s + 5\%\, 3p_z$	$70\%\, 2a_1(2\sigma) + 6\%\, 4a_1(3\sigma)$
$2b_1$	−13.33	$2\%\, 3p_x$	$93\%\, 2b_1(2\sigma) + 2\%\, 4b_1(3\sigma)$
$3a_1$	−12.93	$20\%\, 3s$	$25\%\, 2a_1(2\sigma) + 18\%\, 3a_1(1\pi_{ip}) + 36\%\, 4a_1(3\sigma)$
$4a_1$	−12.12	$4\%\, 3s$	$78\%\, 3a_1(1\pi_{ip}) + 16\%\, 4a_1(3\sigma)$
$1b_2$	−11.67	$3\%\, 3p_y$	$95\%\, 1b_2(1\pi_y)$
$3b_1$	−10.78	$8\%\, 3p_x$	$75\%\, 3b_1(1\pi_{ip}) + 10\%\, 4b_1(3\sigma)$
$1a_2$	−10.65		$100\%\, 1a_2(1\pi_y)$
$5a_1$	−9.21	$52\%\, 3s + 14\%\, 3p_z$	$29\%\, 4a_1(3\sigma) + 4\%\, 5a_1(2\pi^*_{ip})$
$4b_1$ HOMO	−8.31	$2\%\, 3d_{xz} + 16\%\, 3p_x$	$22\%\, 3b_1(1\pi_{ip}) + 57\%\, 4b_1(3\sigma)$
$2b_2$ SOMO	−6.47	$44\%\, 3p_y$	$49\%\, 2b_2(2\pi^*_y)$
$6a_1$ SOMO	−4.86	$27\%\, 3p_z$	$61\%\, 5a_1(2\pi_{ip})$
$3b_2$ LUMO	−2.87	$3\%\, 3d_{yz} + 56\%\, 3p_y$	$45\%\, 2b_2(2\pi^*_y)$
$5b_1$	−1.86	$7\%\, 3d_{xz} + 82\%\, 3p_x$	$18\%\, 4b_1(3\sigma)$
$2a_2$	−1.61	$4\%\, 3d_{xy}$	$95\%\, 2a_2(2\pi^*_y)$

Selected orbitals (only α-spin) involving Si atom in terms of Si ($3s^2 3p_x^0 3p_y^1 3p_z^1$) and $(CO)_2$ fragments are reported. The "CO" orbital character is shown in parentheses

$3p_z$ (14%), and $(CO)_2 4a_1$ ("CO" 3σ) and $5a_1$ ($2\pi^*_{ip}$). Table 5 shows the Mulliken gross population of Si and $(CO)_2$ fragment orbitals in $Si(CO)_2$ ($S = 1$) complex.

In A_1 symmetry we see that the σ and π_{ip} orbital interactions between Si $3s$ and $3p_z$ and $(CO)_2$ 3σ and $2\pi^*_{ip}$ orbitals cause a decrease in the $(CO)_2$ $4a_1$ (3σ) Mulliken population, which reduces from $2e$ to $1.80e$, and in both Si $3s$ (from $2e$ to $1.81e$) and $3p_z$ (from $1e$ to $0.67e$) Mulliken populations. The $(CO)_2$ $5a_1$ ("CO" $2\pi^*_{ip}$) gets populated by $0.77e$, due to Si $3s$ and $3p_z$ donation. Moreover, a single point calculation performed on the two CO at the same geometry as in the complex has shown that CO (1) $2\pi^*_{ip}$ orbital is populated by donation from CO (2) 3σ orbital, and viceversa, thus indicating a bonding interaction between the two CO already without the presence of Si. In B_1 symmetry, the σ orbital interaction between Si $3p_x$, $3d_{xz}$ and $(CO)_2$ $4b_1$ ("CO" 3σ) causes a decrease in the $(CO)_2$ $4b_1$ Mulliken population from $2e$ to $1.38e$ and a corresponding increase in the Si $3p_x$ ($0.54e$) and $3d_{xz}$ ($0.08e$) populations. In B_2 symmetry, the π out-of-plane interaction between the singly occupied Si $3p_y$ and $(CO)_2$ $2b_2$ empty orbital ("CO" $2\pi^*_y$) causes a decrease in the Si $3p_y$ population (from $1e$ to $0.50e$) and a corresponding increase in the $2b_2$ population (from $0e$ to $0.51e$). For the $Si(CO)_2$ complex ($S = 1$), the resulting Mulliken total charge on Si is more positive, $0.29e$, on C is $0.23e$ and on O atom is $-0.37e$. The spin density is distributed over Si ($0.76e$), C ($0.26e$) and O ($0.36e$) atoms.

In the $Si(CO)_2$ complex, the nature of the Si bonding is consistent with the use of sp^2-hybridized orbitals on silicon. For the silicon dicarbonyl complex ($S = 0$) the p orbital at the Si atom is doubly occupied and a π back-donation of lone-pair electrons from this p orbital to the vacant $2\pi^*$ CO orbitals occurs. In the c-silicodiketone complex ($S = 1$) complex both the p orbital and one of the sp^2 orbital at the Si atom are singly occupied and a π back-donation of the two electrons from Si into the vacant $2\pi^*$ (in-plane and out-of-plane) CO orbitals takes place.

$Si(CO)_4$: Silicon tetracarbonyl ($S = 0$)

Table 6 shows selected one-electron orbitals obtained by spin restricted calculations for the $Si(CO)_4$ complex in D_{2h} symmetry ($^1A_{1g}$). The energies and the percentage composition based on Mulliken population analysis is given in terms of atomic Si^{2+} ion orbitals and $(CO)_4^{2-}$ orbitals, with the nature of the single "CO" orbitals reported in parentheses. We promoted the fragments to the ionic configurations Si^{2+} $[(3s)^0(3p_z)^0(3p_x)^0(3p_y)^2]$ and $(CO)_4^{2-}$ (with one, namely $5a_{1g}$, of the $2\pi^*$ set of orbitals doubly occupied). This change of configuration has the advantage that the Si $3s$ is emptied and acts as acceptor orbital for electrons from $(CO)_4^{2-}$ $5a_{1g}$ ("CO" $2\pi^*$), and the Si $3p_y$ orbital can act as donor orbital to the empty $(CO)_4^{2-}$ $2b_{2u}$ ("CO" $2\pi^*$) orbital.

The planar molecule has been chosen to lie on the xz plane.

The $5a_{1g}$ HOMO orbital can be described as silicon $3s$ (22%), with small mixing of Si $3d_{z^2}$ and $3d_{x^2-y^2}$, interacting with $5a_{1g}$ $(CO)_4^{2-}$ ("CO" $2\pi^*$) and $4a_{1g}$ $(CO)_4^{2-}$ ("CO" 3σ) orbitals. The low-lying $2a_{1g}$ orbital is characterized by a Si $3s$ and $(CO)_4^{2-}$ $4a_{1g}$ ("CO" 3σ) and $5a_{1g}$ ("CO" $2\pi^*$) orbital combination. Below the HOMO, the $2b_{2u}$ MO represents a bonding interaction between silicon $3p_y$ (49%) and $(CO)_4^{2-}$ $2b_{2u}$ ("CO" $2\pi^*$) orbital, while the $4b_{2g}$ is mainly $(CO)_4^{2-}$ $4b_{2g}$ ("CO" 3σ) orbital (79%) mixing with silicon $3d_{xz}$ (9%). Silicon $3p_x$ – "CO" 3σ–2σ bonding interactions are described by orbitals $3b_{3u}$ and $2b_{3u}$, while the corresponding silicon $3p_z$ – "CO" $3\sigma - 2\sigma$ bonding interactions are represented by $3b_{1u}$ and $2b_{1u}$ MOs.

Table 7 shows the Mulliken gross population of Si^{2+} and $(CO)_4^{2-}$ fragment orbitals in the silicon tetracarbonyl complex, in different irreducible representations in D_{2h} point group.

From Table 7 we see that the $\pi_{i.p.}$ orbital interaction in the HOMO $5a_{1g}$ causes a decrease in the $(CO)_4^{2-} 5a_{1g}$ Mulliken

Table 5 Mulliken gross population of valence MO of Si and $(CO)_2$ fragments in $Si(CO)_2$ ($S = 1$) in different irreducible representations in C_{2v} point group

	A_1	A_2	B_1	B_2
Si	$3s$ 1.81 $3d_{z^2}$0.04 $3d_{x^2-y^2}$0.02 $3p_z$0.67	$3d_{xy}$ 0.00	$3d_{xz}$ 0.08 $3p_x$0.54	$3d_{yz}$ 0.03 $3p_y$0.50
$(CO)_2$	$4a_1(3\sigma)1.80$ $3a_1(1\pi_{ip})1.99$ $5a_1(2\pi^*_{ip})0.77$	$1a_2(1\pi_y)1.99$	$4b_1(3\sigma)1.38$ $3b_1(1\pi_{ip})1.96$	$2b_2(2\pi^*_y)0.51$
Gross charge	Si 0.29	C 0.23	O −0.37	
Spin density	Si 0.76	C 0.26	O 0.36	

Table 6 One-electron energies and percentage composition (based on Mulliken population analysis per MO) of the $Si(CO)_4$ ($S = 0$) complex

Orbital	ϵ (eV)	Si^{2+}	$(CO)_4^{2-}$
$2a_{1g}$	−17.64	30% $3s$	$28\%2a_{1g}(2\sigma) + 38\%4a_{1g}(3\sigma) + 1\%5a_{1g}(2\pi^*)$
$2b_{1u}$	−15.72	18% $3p_z$	$51\%2b_{1u}(2\sigma) + 26\%4b_{1u}(3\sigma) + 3\%3b_{1u}(1\pi)$
$2b_{3u}$	−14.54	10% $3p_x$	$76\%2b_{3u}(2\sigma) + 9\%4b_{3u}(3\sigma) + 4\%3b_{3u}(1\pi)$
$2b_{2g}$	−14.07	1% $3d_{xz}$	$95\%2b_{2g}(2\sigma) + 3\%4b_{2g}(3\sigma)$
$3a_{1g}$	−13.32	7% $3s$	$72\%2a_{1g}(2\sigma) + 20\%4a_{1g}(3\sigma)$
$3b_{1u}$	−12.81	9% $3p_z$	$34\%4b_{1u}(3\sigma) + 47\%2b_{1u}(2\sigma) + 9\%3b_{1u}(1\pi)$
$3b_{3u}$	−12.34	13% $3p_x$	$52\%3b_{3u}(1\pi) + 19\%2b_{3u}(2\sigma) + 15\%4b_{3u}(3\sigma)$
$4a_{1g}$	−11.99	1% $3d_{x^2-y^2}$	$97\%3a_{1g}(1\pi)$
$1b_{2u}$	−11.86	4% $3p_y$	$94\%1b_{2u}(1\pi) + 1\%2b_{2u}(2\pi^*)$
$1b_{3g}$	−11.69	1% $3d_{yz}$	$99\%1b_{3g}(1\pi)$
$4b_{1u}$	−11.60	1% $3p_z$	$87\%3b_{1u}(1\pi) + 10\%4b_{1u}(3\sigma) + 1\%2b_{1u}(2\sigma)$
$1b_{1g}$	−11.56	1% $3d_{xy}$	$99\%1b_{1g}(1\pi)$
$1a_{1u}$	−11.49		$99\%1a_{1u}(1\pi)$
$3b_{2g}$	−11.42	1% $3d_{xz}$	$93\%3b_{2g}(1\pi) + 4\%4b_{2g}(3\sigma) + 1\%2b_{2g}(2\sigma)$
$4b_{3u}$	−10.51	8% $3p_x$	$45\%4b_{3u}(3\sigma) + 41\%3b_{3u}(1\pi) + 4\%2b_{3u}(2\sigma)$
$4b_{2g}$	−9.53	9% $3d_{xz}$	$79\%4b_{2g}(3\sigma) + 6\%3b_{2g}(1\pi) + 3\%2b_{2g}(2\sigma)$
$2b_{2u}$	−6.35	49% $3p_y$	$45\%2b_{2u}(2\pi^*) + 5\%1b_{2u}(1\pi)$
$5a_{1g}$ HOMO	−5.94	22% $3s + 3\%3d_{z^2} + 2\%3d_{x^2-y^2}$	$54\%5a_{1g}(2\pi^*) + 22\%4a_{1g}(3\sigma)$
$2b_{3g}$ LUMO	−4.00	7% $3d_{yz}$	$92\%2b_{3g}(2\pi^*)$
$5b_{1u}$	−3.45	4% $3p_z$	$83\%5b_{1u}(2\pi^*) + 9\%4b_{1u}(3\sigma)$
$2b_{1g}$	−2.93	6% $3d_{xy}$	$93\%2b_{1g}(2\pi^*)$

Selected orbitals involving Si atom in terms of Si^{2+} and $(CO)_4^{2-}$ fragments are reported. The "CO" orbital character is shown in parentheses

Table 7 Mulliken gross population of the most important valence MO of Si^{2+} and $(CO)_4^{2-}$ fragments in $Si(CO)_4$ ($S = 0$) in the irreducible representations in D_{2h} point group

	A_{1g}	B_{2g}	B_{1u}	B_{2u}	B_{3u}
Si^{2+}	$3s$ 1.18 $3d_{x^2-y^2}$ 0.07 $3d_{z^2}$ 0.09	$3d_{xz}$ 0.24	$3p_z$ 0.55	$3p_y$ 1.06	$3p_x$ 0.63
$(CO)_4^{2-}$	$4a_{1g}(3\sigma)1.62$ $5a_{1g}(2\pi^*)1.13$	$4b_{2g}(3\sigma)1.72$	$4b_{1u}(3\sigma)1.41$	$2b_{2u}(2\pi^*)0.91$	$3b_{3u}(1\pi)1.93$ $4b_{3u}(3\sigma)1.37$
Gross charge	Si 0.05	C 0.32	O −0.33		

population which reduces from $2e$ to $1.13e$, and an increase in the Si $3d_{z^2}$ and $3d_{x^2-y^2}$ population ($0.09e$ and $0.07e$, respectively). The remaining $(CO)_4^{2-}$ $5a_{1g}$ decrease in Mulliken population is due to a σ donation to Si $3s$, which populates as $1.18e$, donations partly coming from $(CO)_4^{2-}4a_{1g}$ also, whose population changes from $2e$ to $1.62e$.

In B_{2g} symmetry, the σ orbital interaction in $4b_{2g}$ MO causes a decrease in the $(CO)_4^{2-}$ $4b_{2g}$ ("CO" 3σ character) Mulliken population which reduces from $2e$ to $1.72e$, and a corresponding increase in the Si $3d_{xz}$ population ($0.24e$).

In B_{1u} symmetry, the Si $3p_z$ – "CO" 3σ orbital interaction populates the Si $3p_z$ by $0.55e$, coming from $(CO)_4^{2-}$ $4b_{1u}$ ($1.41e$) orbital.

In B_{3u} symmetry, a similar Si $3p_x$ – "CO" 3σ orbital interaction populates the Si $3p_x$ by $0.63e$, coming from $(CO)_4^{2-}$ $3b_{3u}$ ($1.93e$) and $4b_{3u}$ (from $2e$ to $1.37e$) orbitals.

Finally, the π out-of-plane interaction between the doubly occupied Si $3p_y$ and $(CO)_4^{2-}$ $2b_{2u}$ empty orbital ("CO" $2\pi^*$ character), causes a decrease in the Si $3p_y$ population (from $2e$ to $1.06e$) and a corresponding increase in the $2b_{2u}$ population (from $0e$ to $0.91e$).

In this complex silicon, $3d_{xz}$ orbital participates quite largely to the σ bonding with the four carbonyl set.

The resulting Mulliken total charge on Si atom is close to zero ($0.05e$), on C is $0.32e$, and on O atom is $-0.33e$.

Both the pseudo-square planar structure about Si and the Si bonding in $Si(CO)_4$ are consistent with the use of sp^2d-hybridized orbitals on silicon. The donation of lone-pair electrons from CO into the vacant $3d$ orbitals of silicon is responsible for the sp^2d hybridization preference over the usual sp^3 one. This complex represents a clear example of d orbital involvement in the formation of a four-coordinated silicon.

Table 8 Decomposition of the bonding energy for the formation of the silicon dicarbonyl ($S = 0$) complex in C_{2v} symmetry in terms of Si^{1+} and $(CO)_2^{1-}$ fragments and of the silicon tetracarbonyl ($S = 0$) complex in D_{2h} symmetry in terms of Si^{2+} and $(CO)_4^{2-}$ fragments

	$Si(CO)_2$		$Si(CO)_4$
ΔE_{Pauli}	12.13	ΔE_{Pauli}	5.46
ΔE_{elstat}	−13.16	ΔE_{elstat}	−30.08
ΔE^0	−1.01	ΔE^0	−24.97
ΔE_{A_1}	−13.76	$\Delta E_{A_{1g}}$	−8.99
ΔE_{A_2}	−0.27	$\Delta E_{B_{1g}}$	−0.45
ΔE_{B_1}	−3.23	$\Delta E_{B_{2g}}$	−3.03
ΔE_{B_2}	−2.58	$\Delta E_{B_{3g}}$	−0.57
		$\Delta E_{A_{1u}}$	−0.37
		$\Delta E_{B_{1u}}$	−4.40
		$\Delta E_{B_{2u}}$	−2.56
		$\Delta E_{B_{3u}}$	−4.27
$\Delta E_{o.i.}$	−19.84	$\Delta E_{o.i.}$	−24.63
ΔE_{total}	−20.85	ΔE_{total}	−49.60
ΔE_{prep}	17.58	ΔE_{prep}	46.38
ΔE	−3.27	ΔE	−3.22

ΔE^0 is the steric repulsion, the $\Delta E(\Gamma)$ is the contribution due to orbital interaction in different irreducible representations, $\Delta E_{o.i.}$ is the total orbital interaction contribution, ΔE_{total} is the sum of ΔE^0 and $\Delta E_{o.i.}$. Preparation energies (ΔE_{prep}) of the fragments and bonding energies (ΔE) of the adducts are also given

3.2.2 Bonding energy analysis

The charge rearrangements are a qualitative indication of the bonding interactions, but not a quantitative measure of the corresponding energies. Those are explicitly calculated by the energy decomposition scheme discussed in Sect. 2 and displayed in Table 8 for silicon dicarbonyl and silicon tetracarbonyl complexes.

As already noted above, we use an ionic Si^+ fragment in the valence state $3s^1\ 3p_\sigma^0\ 3p_{\pi_{i.p}}^0\ 3p_\pi^2$ as found in the $Si(CO)_2$ situation, and an ionic Si^{2+} fragment in the valence state $3s^0\ 3p_\sigma^0\ 3p_{\pi_{i.p}}^0\ 3p_\pi^2$ as found in the $Si(CO)_4$ molecule. For ligands, we use $(CO)_2^-$ as fragment, singly occupying the $5a_1$ molecular orbital, and $(CO)_4^{2-}$ as fragment, doubly occupying $5a_{1g}$ molecular orbital, and the geometry of the fragments as it occurs in the complexes.

As shown in Table 8, the steric interaction energy ΔE^0 is strongly attractive for $Si(CO)_4$ complex, due to the fact that the stabilizing contribution arising from the large attractive interaction between the charged fragments, ΔE_{elstat}, overcomes the positive (destabilizing) Pauli repulsion term, ΔE_{Pauli}. The electrostatic interaction in $Si(CO)_2$ is much less attractive than in $Si(CO)_4$, due to the less charged interacting fragments, and slightly overcomes the positive (destabilizing) Pauli repulsion term, thus causing a slightly attractive steric interaction energy ΔE^0.

From the data reported in Table 8, we note that the ΔE_{A_1} term for $Si(CO)_2$ and the $\Delta E_{A_{1g}}$ and $\Delta E_{B_{1u}}$ terms for $Si(CO)_4$ account for σ- and π_{ip}-donation to silicon orbitals. For $Si(CO)_2$ complex, the donation to the $3s$ ($0.65e$), $3p_z$ ($0.62e$), $3d_{z^2}$ ($0.02e$) and $3d_{x^2-y^2}$ ($0.03e$) orbitals gives rise to a large ΔE_{A_1} energy contribution (−13.76eV). For $Si(CO)_4$ complex, the donation to the silicon $3p_z$ ($0.55e$) is responsible for a $\Delta E_{B_{1u}}$ term of −4.40 eV, while the donation to the $3s$ ($1.18e$), $3d_{z^2}$ ($0.09e$) and $3d_{x^2-y^2}$ ($0.07e$) orbitals gives a −8.99 eV contribution ($\Delta E_{A_{1g}}$). The energy contributions due to the $\sigma-$ and π_{ip}-donation to silicon orbitals are, therefore, comparable for the two complexes.

The ΔE_{B_1} term for $Si(CO)_2$ and the $\Delta E_{B_{3u}}$ and $\Delta E_{B_{2g}}$ terms for $Si(CO)_4$ are also found to give quite a relevant contribution to the σ bond (−3.23 eV for silicon dicarbonyl and −4.27 and −3.03 eV, respectively, for silicon tetracarbonyl), reflecting the large charge transfers into $3p_x$ ($0.43e$ for $Si(CO)_2$ and $0.63e$ for $Si(CO)_4$), by carbonyl orbitals. For silicon tetracarbonyl complex, more relevant charge transfer occurs into $3d_{xz}$ ($0.24e$), which accounts for −3.03 eV ($\Delta E_{B_{2g}}$) energy contribution.

As for the energy terms which account for the π out of plane bond, the ΔE_{B_2} for $Si(CO)_2$ and $\Delta E_{B_{2u}}$ plus $\Delta E_{B_{3g}}$ for $Si(CO)_4$ terms are large. As inferred by the charge transfers that occur in these symmetries ($1.03e$ into $2b_2$ for $Si(CO)_2$ and $0.91e$ into $2b_{2u}$ for $Si(CO)_4$), the ΔE_{B_2} (−2.58 eV) is comparable to $\Delta E_{B_{2u}}$ (−2.56 eV). However, ΔE_{B_2} also contains contributions due to small donations to $3d_{yz}$, while this is measured by $\Delta E_{B_{3g}}$ term (−0.57 eV) in $Si(CO)_4$ complex.

The ΔE_{A_2} term for $Si(CO)_2$ and the corresponding $\Delta E_{B_{1g}}$ term for $Si(CO)_4$ are small, due to the fact that these terms contain the contribution due to interaction of $3d_{xy}$ orbitals of Si with "CO" 1π orbitals of the carbonyl frameworks. Only a very small charge transfer into $3d_{xy}$ is calculated ($0.01e$ for $Si(CO)_2$ and $0.02e$ for $Si(CO)_4$).

As a result of all these contributions, the orbital interaction term $\Delta E_{\mathrm{o.i.}}$ is larger than the steric interaction term ΔE^0 for $Si(CO)_2$ (-19.84 vs. -1.01 eV), while the orbital interaction term is smaller than the steric interaction term for $Si(CO)_4$ (-24.63 vs. -24.97 eV). However, it is interesting to note that $\Delta E_{\mathrm{o.i.}}$ for $Si(CO)_4$ is larger than $\Delta E_{o.i.}$ for $Si(CO)_2$ by 4.79 eV, mainly due to the larger charge transfer into Si $3d_{xz}$ ($0.24e$) and $3p_x$ ($0.63e$) orbitals in $Si(CO)_4$ than in $Si(CO)_2$ complex.

In order to calculate the reaction enthalpy ΔE for the formation of the complexes, the preparation energy of the fragments has to be taken into account. The preparation energy, ΔE_{prep}, is largely dominated by the energy necessary to excite the silicon atom from the ground electronic configuration to empty or singly occupy the $3s$ orbital and to doubly populate the $3p_\pi$ orbital as we calculate in the converged complexes. The remaining value represents the geometry and valence changes of $(CO)_2^-/(CO)_4^{2-}$, with one of the $2\pi^*$ singly or doubly occupied, bonding to Si in the complex. The above detailed analysis of the different contributions to $\Delta E_{\mathrm{o.i.}}$ points out that in the two complexes: (1) the σ interactions between the Si^+/Si^{2+} and the $(CO)_2^-/(CO)_4^{2-}$ framework, due to electron donation from carbonyl to silicon are by far dominant and account for most of the bond strength; (2) π out of plane back-donation from silicon $3p_\pi$ to empty π^* antibonding $(CO)_4^{2-}$ and $(CO)_2^-$ orbitals gives a 13% contribution for $Si(CO)_2$ and 10% contribution for $Si(CO)_4$ to the silicon-carbonyl bond.

Finally, although in $Si(CO)_4$ complex, the Mulliken charge on Si is close to zero, due to a net charge donation from $(CO)_4^{2-}$ to Si^{2+}, a not negligible positive charge can be calculated on Si in $Si(CO)_2$ complex, i.e. 0.15.

4 Discussion

Even though to a certain extent the comments on the results given in the previous part may be considered as an adequate interpretation of the outcomes of calculations, we, however, believe that the ultimate understanding is achieved when calculations are interpreted in terms of characters of general chemistry like nature (covalent, dative or ionic) and multiplicity of bond, and charge distribution on atoms. To this purpose, we focus our attention on geometry, interatomic-distance distribution, and stability.

We shall consider the four candidate species Si(CO) ($S = 1$), $Si(CO)_2$ ($S = 0$), $Si(CO)_2$ ($S = 1$) and $Si(CO)_4$.

The calculated bond distances are summarized in Table 9, while reference bonding enthalpies (in eV) are reported in Table 10.

Table 9 Calculated bond distances in the considered silicon carbonyls

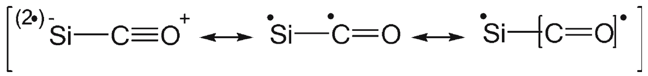
Interatomic pair	Species			
	Si(CO)	$Si(CO)_2$		$Si(CO)_4$
		$S = 0$	$S = 1$	
Si-C	1.83	1.82	1.90	1.90
C-O	1.17	1.17	1.20	1.17
C-C		2.24	1.67	2.32

Table 10 Some relevant reference bonding enthalpies and bondlengths

Bond	E_b (eV)	Bond length (Å)
C–C	3.59	1.54
$C\underline{\cdots}C$	5.25 (in benzene)	1.40
$C=C$	6.36	1.34
$C\equiv C$	8.70	1.20
C–O	3.71	1.43
$C=O$	8.33	1.20
$^-C\equiv O^+$	11.15	1.13
Si–C	3.18	1.87
S–C	2.82	1.82
O=O	5.16	1.21

4.1 Si(CO) ($S = 1$): silicon carbonyl

The Si–C distance in Si(CO) clearly denotes that an Si–C bond is actually formed. Since the species is in triplet state, it contains two unpaired electrons. Two extreme situations may be hypothesized: either both electrons are on silicon (in species $^{(2\bullet)-}Si–C\equiv O^+$) or are distributed on carbon and silicon (in species $^\bullet Si–^\bullet C=O$ or possibly $^\bullet Si–[C=O]^\bullet$). Mulliken charge analysis, giving a spin density of 1.28 on Si, 0.45 on C and 0.28 on O, suggests that Si(CO) may be viewed as a kind of resonant structure



The C–O distance, intermediate between that in $^-C\equiv O^+$ (1.13 Å) and that in aldehydes (1.20 Å), suggests the correctness of this attribution.

4.2 $Si(CO)_2$: ($S = 0$) silicon dicarbonyl

The first structure with two CO upon which we focus our attention is $Si(CO)_2$ ($S = 0$). The clue for attributing a Lewis formula to this species is the observation that the C–O distance therein (1.17 Å), though larger than in $^-C\equiv O^+$, remains, however, shorter than that characteristic of the carbonyl group (1.20 Å in aldehydes). This might be explained assuming that the C–O distance is relaxed with respect to that in $^-C\equiv O^+$ because the electrostatic reinforcement to

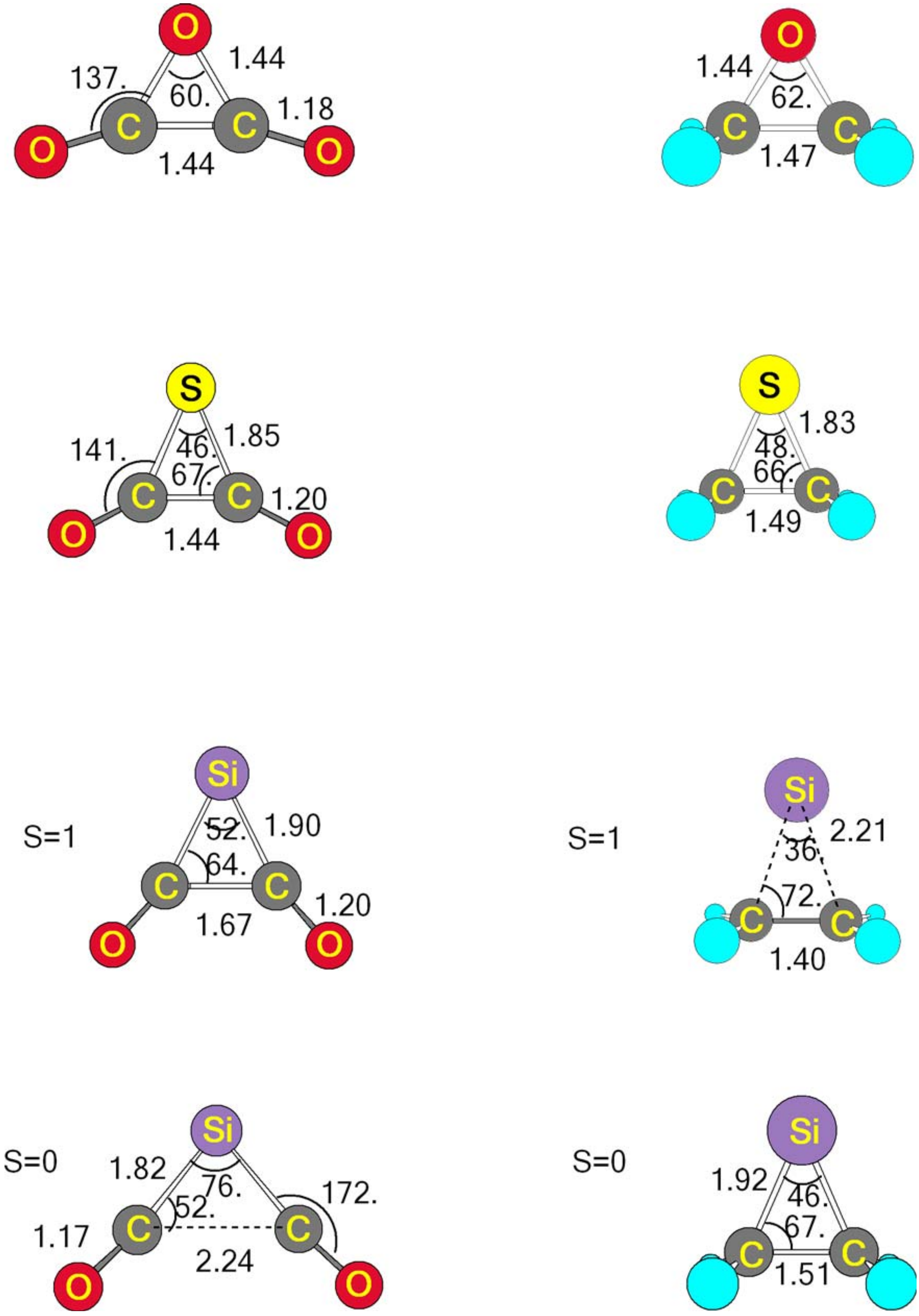
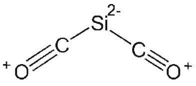
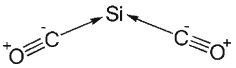


Fig. 2 The optimized structures of the C_2H_4X (X = O, Si, S) and $(CO)_2X$ (X = O, Si, S) molecules. The spin multiplicity of the electronic state is also reported for silicon based molecules

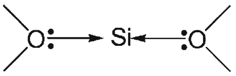
this bond (due to the slight negative net charge on carbon and positive on oxygen) is suppressed because of electronic shift to the silicon atom and the formation of a bond between silicon and carbon because of the unpaired electron on them. The resulting Si–C bond has no strain and is thus characterized by the same internuclear separation characteristic as for the Si–C bond. This compound admits a Lewis formula



which clarifies that the negative charge, originally on carbon in $^{-}C \equiv O^{+}$, has shifted to silicon thus reducing the electrostatic reinforcement to the $C \equiv O$ bonds. In this way, compound $Si(CO)_2$ ($S = 0$) may be regarded as *silicon dicarbonyl*. An alternative, but substantially equivalent, description of $Si(CO)_2$ ($S = 0$) is in terms of formation of dative bonds via lone pair donation from carbon to silicon:



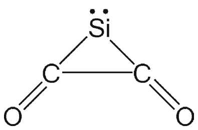
This picture is substantially the same as that advocated for the formation of oxo–oxygen–silicon adducts in siloxanic networks [3–5]:



The stability of silicon dicarbonyl with respect to dissociation $Si(CO)_2 \longrightarrow Si + 2CO$ is essentially conferred by the dative bond. This implies that the bond dissociation energy of the $^{+}O \equiv C^{-} \rightarrow Si$ dative bond is 1.63 eV.

4.3 $Si(CO)_2$ ($S = 1$): *c*-silicodiketone

Totally different is the internuclear distance distribution in $Si(CO)_2$ ($S = 1$). Taking $Si(CO)_2$ ($S = 0$) as reference, in the triplet compound the C–O distance coincides with the carbonyl bond length, the C–C distance is appreciably shortened (actually, it is so short as to make not unreasonable the formation of a C–C bond), and the Si–C distance is slightly larger than the Si–C bond length. This situation suggests the following structural formula



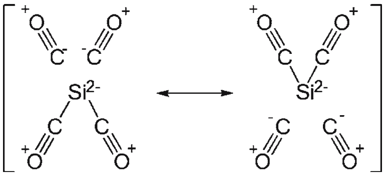
which attributes the increase of the Si–C and C–C distance with respect to the corresponding bond lengths to the strain of the C–Si–C ring. An additional indication of the correctness of this formula is given by the direction of the C–O bond, which points approximately along the bisector of the $\widehat{\text{Si–C–C}}$ angle, thus suggesting sp^2 hybridization for carbon. This species, whose bare formula might be more properly written as $Si[C_2O_2]$, might be called c-*silicodiketone*.

Mutatis mutandis, *c*-silicodiketone is indeed the structural analogue of the silacyclopropylidene species studied in refs. [6,7]. Figure 2 shows the structure of $X[C_2H_4]$ molecules ($X = O$, oxirane; $X = S$, thiirane; $X = Si$, 'silirane' or silacyclopropylidene of Ref. [6]), and Table 11 gives their dissociation energies with respect to $X + C_2H_4$ (the calculations having been carried out at the same level as that adopted in this work).

Interestingly enough, the corresponding molecules $X[C_2O_2]$ ('*c*Xdiketones') have well defined minima, that allows them to be considered as chemical species. Of course $X[C_2O_2]$ ($X = O, S$) are unstable and dissociate spontaneously with $CO + XCO$; however, $Si[C_2O_2]$ is stable with respect to this dissociation, thus suggesting the hypothesis of its possible preparation.

4.4 $Si(CO)_4$ ($S = 0$): silicon tetracarbonyl

The C–O distance in $Si(CO)_4$ indicates that carbon and oxygen are bonded in carbonyl configuration. The distribution of the C–C and Si–C interatomic distances [closer to, but somewhat larger than, the corresponding distances in $Si(CO)_2$], the binding energy [very close to that of $Si(CO)_2 + 2CO$], and the Mulliken charge on silicon [near that on silicon in $Si(CO)_2$], all together suggest that $Si(CO)_4$, *silicon tetracarbonyl*, may be seen as a resonance structure between the limiting configurations



so that it can be described with the following half-bond formula

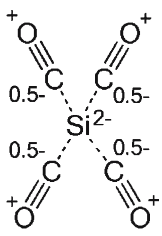
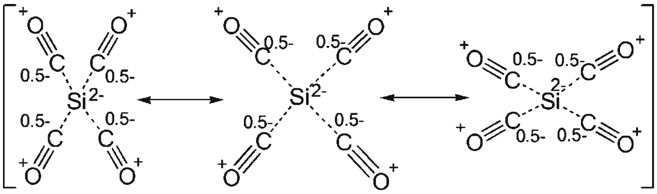


Table 11 Binding energy E with respect to atoms of the reacting molecules and of the corresponding complexes (in C_{2v} symmetry), and reaction enthalpy ΔE of the molecules with respect to reactants

Reactants	E (eV)	Product	E (eV)	ΔE (eV)
$C_2H_4 + O$	−33.43	$O(CH_2)_2$	−37.54	−4.11
$C_2H_4 + S$	−32.49	$S(CH_2)_2$	−35.24	−2.75
$C_2H_4 + Si$	−32.25	$Si(CH_2)_2$ ($S = 0$)	−34.45	−2.10
$C_2H_4 + Si$	−32.25	$Si(CH_2)_2$ ($S = 1$)	−33.40	−1.15
2 CO + O	−31.31	$O(CO)_2$	−35.85	−4.54
2 CO + S	−30.37	$S(CO)_2$	−32.87	−2.50
2 CO + Si	−30.23	$Si(CO)_2$ ($S = 0$)	−33.49	−3.26
2 CO + Si	−30.23	$Si(CO)_2$ ($S = 1$)	−31.99	−1.76

Even though the square planar Si(CO)$_4$ complex may actually be viewed as the activated complex allowing the transition from resonance I to resonance II,



actually the same transition is also achieved via a path involving appreciably lower energy-rotation.

The existence of planar tetracoordinated silicon is not so absurd. In fact, X-ray crystallographic investigation on the orthosilicic acid ester led Meyer and Nagorsen [27] to establish it as the first compound with planar tetracoordinated silicon. Later, Schomburg [28] reported evidence of strong distortion of the tetrahedral geometry in a spirosilicate, bis(tetramethylethylenedioxy)silane. At last, silicon has recently been reported to be a better candidate than carbon for the detection and observation of planar tetracoordinated structures [29].

5 Conclusions

Density functional calculations have been performed on a few relatively stable compounds of silicon with CO: Si(CO), Si(CO)$_2$, Si(CO)$_4$ and Si[C$_2$O$_2$]. For Si(CO)$_n$ ($n = 1, 2$), our results are in good agreement with the ones in literature, confirming the accuracy of our approach. The thermodynamic stability of a planar tetracoordinated Si(CO)$_4$ complex has been shown. To the best of our knowledge, the existence of this polycarbonyl species has been explicitly rejected by literature. In Si(CO)$_2$, silicon dicarbonyl, the CO are datively bonded to silicon; Si(CO)$_4$, silicon tetracarbonyl, may be viewed as a resonance between the extreme configurations (CO)$_2$Si + 2CO and 2CO + Si(CO)$_2$; while Si[C$_2$O$_2$], *c*-silicodiketone, is somewhat similar to the compounds formed by silicon and ethylene. A detailed orbital analysis has revealed how in the Si(CO)$_2$ complex the nature of the Si bonding is consistent with the use of sp^2-hybridized orbitals on silicon. For the ($S = 0$) silicon dicarbonyl complex the σ interaction between Si and (CO)$_2$ framework due to electron donation from carbonyl to silicon accounts for most of the bond strenght, but π backdonation from silicon $3p_\pi$ to empty $2\pi^*$ CO orbitals takes place. For the ($S = 1$) *c*-silicodiketone complex additional σ interaction occurs between the two C atoms and π backdonation from silicon to $2\pi^*$ CO orbitals occurs.

The Si bonding in Si(CO)$_4$ is consistent with the use of sp^2d-hybridized orbitals on silicon. This complex represents a clear example of d orbital involvement in the formation of a four-coordinated planar silicon.

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