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Planar Tetracoordinated Silicon in Silicon Carbonyl Complexes: A DFT Approach

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Recently, some works have focused attention on the reactivity of the silicon atom with closed-shell molecules. With CO, silicon may form a few relatively stable compounds, i.e., Si(CO), $Si(CO)_2$, and $Si[C_2O_2]$, 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 moieties are datively bonded to Si, and $Si[C_2O_2]$, *c*-silicodiketone, is similar to the compounds formed by silicon and ethylene; $Si(CO)_4$, silicon tetracarbonyl, may be viewed as a resonance between the extreme configurations $(CO)_2Si + 2CO$ and $2CO + Si(CO)_2$. A detailed orbital analysis has shown that 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.

1. Introduction

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

In recent years, motivated by the fact that the thermal oxidation of single crystalline silicon in ambient O_2 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 such as 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 CO would suggest for them the formation of $CO \rightarrow Si \leftarrow CO$ adducts.

Silicon carbonyl complexes $Si(CO)_n$ ($n = 1, 2$) have been detected experimentally,[6,7] and several earlier papers have appeared in the literature on these complexes, where the structures, properties, and bonding character for such silicon carbonyls have been investigated using different theoretical methods.[8−11] The existence of larger polycarbonyl ($n > 2$) complexes was discarded on the basis of the weakness of the bond of the third CO to the complex and the absence of any reported experimental evidence for these species.[8]

In this work, however, we predict the thermodynamic stability of a planar $Si(CO)_4$ complex. Stabilization of planar tetracoordinated silicon is a fascinating experimental and theoretical challenge.[12−15] We will show that its stability is a consequence of the delocalization of the electrons in the silicon p orbital into the ligand framework and of the participation of the silicon d orbital in the σ bonding. Although no experimental evidence for $Si(CO)_4$ has been reported so far, the existence of planar tetracoordinated silicon has been recognized, for instance, from the X-ray crystallographic investigation on the orthosilicic ester.[12]

2. Computational and Methodological Details

The calculations reported in this paper have been performed by employing the Amsterdam Density Functional (ADF) program package.[16−19] 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[20] of the effective one-electron Hamiltonian matrix elements and by the possibility to freeze 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 parametrization of electron gas data[21] by Vosko, Wilk, and Nusair[22] was employed in the local density approximation. Full geometry optimizations were performed within both the spin-unrestricted (open-shell) and spin-restricted (closed-shell) approaches, including Becke's gradient corrections[23] to the exchange part of the potential and Perdew's gradient correction[24,25] to the correlation. For our systems, we considered different symmetries, i.e., $C_{\infty v}$ for Si(CO), C_{2v} for $Si(CO)_2$, and T_d, D_2, D_{4h}, and D_{2h} for $Si(CO)_4$ in an attempt to find the most stable geometry in the latter complex. 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

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frozen. To analyze the silicon−carbonyl interaction energies, we used a method that is an extension of the well-known decomposition scheme of Morokuma.[26] The bonding energy is decomposed into a number of terms. The first term, ΔE^0, is obtained from the energy of the wave function Ψ^o, which is constructed as the antisymmetrized and renormalized product of the wave functions 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, with 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 wave function. In addition to the steric repulsion term ΔE^0, there are the attractive orbital interactions which enter when the wave function Ψ^o is allowed to relax to the fully converged ground-state wave function 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, ΔE_{oi}, that includes both the charge transfer and polarization interactions. This term, according to the decomposition scheme proposed by Ziegler,[27] 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 ($\Delta E = \Delta E^0 + \Delta E_{\mathrm{oi}}$) in the frequent cases where the ground-state wave functions 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

$$\Delta E = \Delta E_{\mathrm{prep}} + \Delta E^0 + \Delta E_{\mathrm{oi}} \qquad (1)$$

3. Results and Discussion

The reaction of silicon with carbonyl has been reinvestigated. Si(CO) and $Si(CO)_2$ species, in singlet and triplet states, have been studied using different theoretical approaches in ref 8. For these species, we considered $C_{\infty v}$ and C_{2v} symmetries, respectively, while for the search of a stable molecule involving 4 CO groups, we assigned a priori reasonable symmetries: T_d, D_2, D_{4h}, and D_{2h}. For all of them, we found structures which are more stable than the corresponding reactants. However, we found D_{2h} symmetry $Si(CO)_4$ as the most stable species.

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 Figure 1 shows the corresponding geometries (with internuclear distances in ångstroms and angles in degrees) of the most stable silicon carbonyls $Si(CO)_n$ ($n = 1, 2, 4$).

To be considered 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, besides Si(CO) and $Si(CO)_2$ in C_{2v} symmetry (both singlet and triplet state structures), only $Si(CO)_4$ in D_{2h} symmetry (singlet state) was found to have all normal modes with real frequencies. We have thus focused our attention only on the minimum structure.

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[c]

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
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

[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.[30] Unless otherwise specified, product is in singlet state.

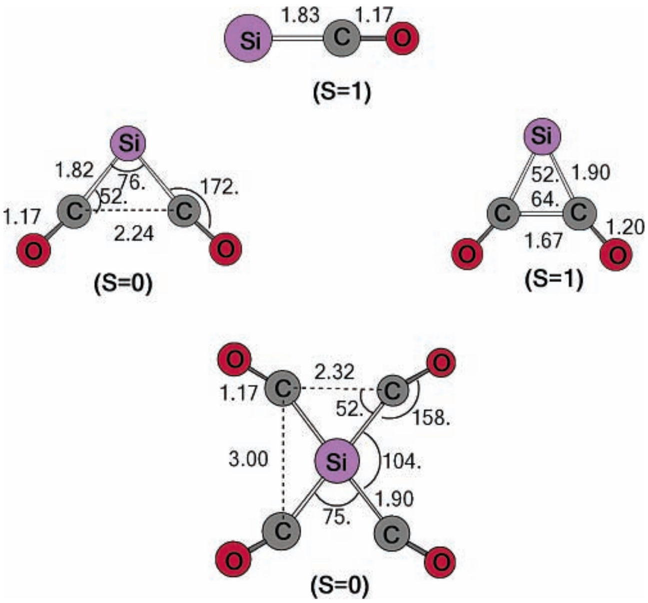


Figure 1. The optimized structures of the most stable complexes resulting from the reaction of silicon with 1, 2, and 4 CO ligands. The spin multiplicity of the electronic state is also reported.

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 (i.e., B3LYP, B3P86, B3PW91, MP2) in ref 8. The ∠CSiC (76°) and ∠SiCO (172°) angles fall within 75.39−79.43° and 170.68−171.83°, respectively, calculated at four theoretical levels in ref 8. The narrow ∠CSiC angle has been studied in ref 11.

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 ∠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 and 2.32 Å, respectively) than in $Si(CO)_2$ in C_{2v} symmetry ($S = 0$), while the C−O

TABLE 2: One-Electron Energies and Percentage Composition (based on Mulliken population analysis per MO) of the Complex $\mathbf{Si(CO)_2}$ ($S = 0$) in C_{2v} Symmetry[a]

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	$5\%\ 3d_{yz} + 54\%\ 3p_y$	$37\%\ 2b_2(2\pi_y^*)$

[a] 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.

distance, 1.17 Å, is unchanged. The ∠CSiC angle is 75°, and the ∠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, is 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 the CCSD(T) value (26.1 kcal mol^{-1}).[8] However, this value indicates that the Si−CO bond 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 3 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, with 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 2.00 e to 1.45 e) and a corresponding increase of the Si $3p_z$ (from 0.00 e to 0.60 e) Mulliken population. The π interaction is a π back-donation from Si $3p_x$ and $3p_y$, whose Mulliken populations decrease from 1.00 αe to 0.63 αe, to CO $2\pi^*$, whose population correspondingly increases from 0.00 αe to 0.36 + 0.36 αe. The resulting Mulliken total charge on silicon is slightly positive, 0.14 e, on C is 0.18 e, and on O atom is −0.32 e. The spin density analysis reveals that roughly one unpaired electron is localized on a Si atom (1.28 e) and the other is shared by the CO group (C 0.45 e, O 0.28 e).

$Si(CO)_2$. 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 the advantage that the Si 3s acts as an 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 a 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 HOMO ($2b_2$) orbital represents a π-bonding interaction between silicon $3p_y$ (46%) and $(CO)_2{}^-$ $2b_2$ (CO $2\pi_y^*$) orbital. Below the HOMO, the $5a_1$ MO depicts the Si−C σ-bonding interaction, together with the low-lying $2a_1$ and the $4b_1$ MOs.

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

From Table 3, we see that the σ and π_{ip} orbital interactions between Si 3s and $3p_z$ and $(CO)_2{}^-$ (CO $2\pi_{ip}^*$) 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 2 e to 1.54 e, and $5a_1$ (CO $2\pi_{ip}^*$) Mulliken population, which reduces from 1 e to 0.22 e, and an increase of the Si 3s (from 1 e to 1.65 e) and $3p_z$ (from 0 e to 0.62 e) Mulliken populations. The Si $3d_{z^2}$ and $3d_{x^2-y^2}$ get slightly populated by 0.02 e and 0.03 e, respectively. In B_1 symmetry, the σ orbital interaction between

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	

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 2 *e* to 1.48 *e*, and a corresponding increase of the Si $3p_x$ (0.43 *e*) and $3d_{xz}$ (0.09 *e*) 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 2 *e* to 0.96 *e*) and a corresponding increase in the $2b_2$ population (from 0 *e* to 1.03 *e*). The Si $3d_{yz}$ also acquires a small population (0.03 *e*).

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

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

$Si(CO)_2$. *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 π-bonding interaction between silicon $3p_y$ (44%) and $(CO)_2$ $2b_2$ ($2\pi^*_y$). The singly occupied $6a_1$ molecular orbital describes the σ^*-type antibonding interaction between silicon $3p_z$ and $(CO)_2$ $5a_1$ (CO $2\pi^*_{ip}$). The Si−C σ-bonding interaction is depicted by $4b_1$ HOMO and $5a_1$ and $2a_1$ MOs.

Table 5 shows the Mulliken gross population of Si and $(CO)_2$ fragment orbitals in the $Si(CO)_2$ ($S = 1$) 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 2 *e* to 1.80 *e*, and in both Si 3s (from 2 *e* to 1.81 *e*) and $3p_z$ (from 1 *e* to 0.67 *e*) Mulliken populations. The $(CO)_2$ $5a_1$ (CO $2\pi^*_{ip}$) gets populated by 0.77 *e*, 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 a donation from CO(2) 3σ orbital, and vice versa, 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 2 *e* to 1.38 *e* and a corresponding increase of the Si $3p_x$ (0.54 *e*) and $3d_{xz}$ (0.08 *e*) 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 1 *e* to 0.50 *e*) and a corresponding increase in the $2b_2$ population (from 0 *e* to 0.51 *e*).

For the $Si(CO)_2$ complex ($S = 1$), the resulting Mulliken total charge on Si is more positive, 0.29 *e*, on C is 0.23 *e*, and on the O atom is −0.37 *e*. The spin density is distributed over Si (0.76 *e*), C (0.26 *e*), and O (0.36 *e*) 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 $2b_2$ MO is doubly occupied, and a π back-donation of about one electron from the p orbital at the Si atom to the vacant $2\pi^*$ CO orbitals occurs. In the *c*-silicodiketone complex ($S = 1$), the $2b_2$ MO is singly occupied, and a π back-donation of about 0.50 electrons from the p orbital at the Si into the vacant $2\pi^*$ CO orbitals takes place. Moreover, the Si−C σ^*-antibonding $6a_1$ MO is singly occupied, and a larger population (0.77 *e* vs 0.22 *e*) of the empty $2\pi^*$ in-plane CO orbitals is calculated. On comparison with the silicon dicarbonyl complex, in the *c*-silicodiketone complex the excitation of one electron from the $2b_2$ to $6a_1$ MO has a net effect: It weakens the Si−C and C−O π-bonding interactions and increases the Si−C σ^*-antibonding interaction. Thus, the overall effect is the elongation of both the Si−C and C−O bonds.

$Si(CO)_4$. 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 are 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 an acceptor orbital for electrons from $(CO)_4^{2-}$ $5a_{1g}$ (CO $2\pi^*$), and the Si $3p_y$ orbital can act as a 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 key molecular orbitals describing mainly the σ-bonding interaction between Si and CO moieties are $5a_{1g}$ (HOMO), $2a_{1g}$, $2b_{3u}$, $4b_{3u}$, $2b_{1u}$, $3b_{1u}$, and $4b_{2g}$. In particular, the $4b_{2g}$ depicts a σ-bonding interaction between $(CO)_4^{2-}$ $4b_{2g}$ (CO 3σ) orbital (79%) and silicon $3d_{xz}$ (9%). Below the HOMO, the $2b_{2u}$ MO represents a π-bonding interaction between silicon $3p_y$ (49%) and $(CO)_4^{2-}$ $2b_{2u}$ (CO $2\pi^*$) orbitals.

Figure 2 constructs the molecular orbitals of $Si(CO)_4$ from the interaction of four CO ($(CO)_4^{2-}$) with the central Si (Si^{2+}). The colors distinguish the MO symmetries. The combination of the 2σ nonbonding (localized on O) MOs of the four CO moieties gives rise to $2a_{1g}$, $2b_{1u}$, $2b_{3u}$, and $2b_{2g}$ MOs, and the combination of the 3σ nonbonding (localized on C) MOs gives rise to $4a_{1g}$, $4b_{1u}$, $4b_{3u}$, and $4b_{2g}$ MOs. Analogously, the 1π MOs combine to form eight MOs, which are assigned black in Figure 2, and the $2\pi^*$ MOs combine to form eight MOs (three of them are omitted in the diagram), one of which ($5a_{1g}$) has been doubly occupied. The 1π MO set is stabilized by interaction with Si (see Table 6). The p and $2\pi^*$ orbitals perpendicular to the plane, which are involved in the formation of π MOs, are shown as circles, symbolizing their "top" (above the plane) phase. The two π MOs are identified as $2b_{3g}$ (LUMO) and $2b_{2u}$ in Figure 2.

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 the D_{2h} point group.

From Table 7, we see that the π_{ip} orbital interaction in the HOMO $5a_{1g}$ causes a decrease in the $(CO)_4^{2-}$ $5a_{1g}$ Mulliken population, which reduces from 2 *e* to 1.13 *e*, and an increase of the Si $3d_{z^2}$ and $3d_{x^2-y^2}$ populations (0.09 *e* and 0.07 *e*, respectively). The remaining $(CO)_4^{2-}$ $5a_{1g}$ decrease of the Mulliken population is due to a σ donation into the Si 3s, which

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[a]

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% $2a_2(2\pi^*_y)$

[a] 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.

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	

populates by 1.18 *e*, partly coming also from $(CO)_4^{2-}$ $4a_{1g}$, whose population changes from 2 *e* to 1.62 *e*.

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

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

In B_{3u} symmetry, a similar Si $3p_x$−CO 3σ orbital interaction populates the Si $3p_x$ by 0.63 *e*, coming from $(CO)_4^{2-}$ $3b_{3u}$ (1.93 *e*) and $4b_{3u}$ (from 2 *e* to 1.37 *e*) 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 2 *e* to 1.06 *e*) and a corresponding increase in the $2b_{2u}$ population (from 0 *e* to 0.91 *e*).

In this complex, the silicon $3d_{xz}$ orbital participates quite largely to the σ bonding with the four carbonyl set. The resulting Mulliken total charge on the Si atom is close to zero (0.05 *e*), on C is 0.32 *e*, and on the O atom is −0.33 *e*.

Both the 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 σ donation of electrons from CO into the vacant 3d orbitals of silicon and the π back-donation of electrons from Si p into the empty $2\pi^*$ orbitals of CO are responsible for the sp^2d hybridization preference over the usual sp^3 one.

3.2.2. Bonding Energy Analysis. The charge rearrangements are a qualitative indication for the bonding interactions, but not a quantitative measure of the corresponding energies. Those are explicitly calculated by the energy decomposition scheme discussed in section 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 $3s^1 3p_\sigma^0 3p_{\pi_{ip}}^0 3p_\pi^2$, as found in the $Si(CO)_2$ situation, and an ionic Si^{2+} fragment in the valence state $3s^0 3p_\sigma^0$-$3p_{\pi_{ip}}^0 3p_\pi^2$ as found in the $Si(CO)_4$ molecule. For ligands, we use $(CO)_2^-$ as a fragment, singly occupying the $5a_1$ molecular orbital, and $(CO)_4^{2-}$ as a fragment, doubly occupying the $5a_{1g}$ 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 the $Si(CO)_4$ complex, because 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} donations into silicon orbitals. For the $Si(CO)_2$ complex, the donation into the 3s (0.65 *e*), $3p_z$ (0.62 *e*), $3d_{z^2}$ (0.02 *e*), and $3d_{x^2-y^2}$ (0.03 *e*) orbitals gives rise to a large ΔE_{A_1} energy contribution (−13.76 eV). For the $Si(CO)_4$ complex, the donation into the silicon $3p_z$ (0.55 *e*) is responsible for a $\Delta E_{B_{1u}}$ term of −4.40 eV, while the donation into the 3s (1.18 *e*), $3d_{z^2}$ (0.09 *e*), and $3d_{x^2-y^2}$ (0.07 *e*) orbitals gives a −8.99 eV contribution ($\Delta E_{A_{1g}}$). The energy contributions due to the σ and π_{ip} donations into 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 a quite 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 $3p_x$ (0.43 *e* for $Si(CO)_2$ and 0.63 *e* for $Si(CO)_4$) by carbonyl orbitals. For the silicon tetracarbonyl complex, more relevant charge transfer occurs into $3d_{xz}$ (0.24 *e*), 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 (1.03 *e* into $2b_2$ for $Si(CO)_2$ and 0.91 *e* 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 a contribution due to a small donation into $3d_{yz}$, which is measured by the $\Delta E_{B_{3g}}$ term (−0.57 eV) in the $Si(CO)_4$ complex.

TABLE 6: One-Electron Energies and Percentage Composition (based on Mulliken population analysis per MO) of the $Si(CO)_4$ ($S = 0$) Complex[a]

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	$6\%\ 3d_{xy}$	$93\%\ 2b_{1g}(2\pi^*)$

[a] 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.

The ΔE_{A_2} term for $Si(CO)_2$ and the corresponding $\Delta E_{B_{1g}}$ term for $Si(CO)_4$ are small, because 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 (0.01 e for $Si(CO)_2$ and 0.02 e for $Si(CO)_4$).

As a result of all these contributions, the orbital interaction term ΔE_{oi} 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 ΔE_{oi} for $Si(CO)_4$ is larger than ΔE_{oi} for $Si(CO)_2$ by 4.79 eV, mainly due to the larger charge transfer into Si $3d_{xz}$ (0.24 e) and $3p_x$ (0.63 e) orbitals in the $Si(CO)_4$ rather than the $Si(CO)_2$ complex. Moreover, if we consider the steric term ΔE^0 as a measure of the "ionic" contribution to the bonding, our results show that in $Si(CO)_4$ ionic and covalent contributions to the bond are roughly the same and, thus, indicate an increased importance of ionic silicon to CO bonding.

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 ΔE_{oi} points out that in the two complexes (i) 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, and (ii) 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 the $Si(CO)_4$ complex the Mulliken charge on Si is close to zero, due to a net charge donation from $(CO)_4^{2-}$ to Si^{2+}, a nonnegligible positive charge can be calculated on Si in the $Si(CO)_2$ complex, i.e., 0.15.

3.3. A Lewis Description of the Silicon−Carbonyl Bond. Even though to a certain extent the comments on the results given in the previous part may be considered an adequate interpretation of the outcomes of calculations, we however believe that the ultimate understanding is achieved when calculations are interpreted in terms of characteristics 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 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.

3.4. Si(CO) ($S = 1$)—Silicon Carbonyl. The Si−C distance in Si(CO) clearly denotes that a Si−C bond is actually formed. Since the species is in the triplet state, it contains two unpaired electrons. Two extreme situations may be hypothesized: Either both electrons are on silicon (in species ${}^{(2\bullet)-}\mathrm{Si{-}C{\equiv}O^{+}}$) or are distributed on carbon and silicon (in species ${}^{\bullet}\mathrm{Si{-}{}^{\bullet}C{=}O}$ or possibly ${}^{\bullet}\mathrm{Si{-}[C{=}O]^{\bullet}}$). Mulliken charge analysis, giving spin densities 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

$$[{}^{(2\bullet)-}\mathrm{Si{-}C{\equiv}C^{+}} \leftrightarrow {}^{\bullet}\mathrm{Si{-}{}^{\bullet}C{=}O} \leftrightarrow {}^{\bullet}\mathrm{Si{-}[C{=}O]^{\bullet}}]$$

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

3.5. $Si(CO)_2$ ($S = 0$)—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 ${}^{-}\mathrm{C{\equiv}O^{+}}$, remains however shorter than that characteristic of the carbonyl group (1.20 Å in aldehydes). This might be explained by assuming that the C=O distance is relaxed with respect to that in ${}^{-}\mathrm{C{\equiv}O^{+}}$, because the electrostatic reinforcement to 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

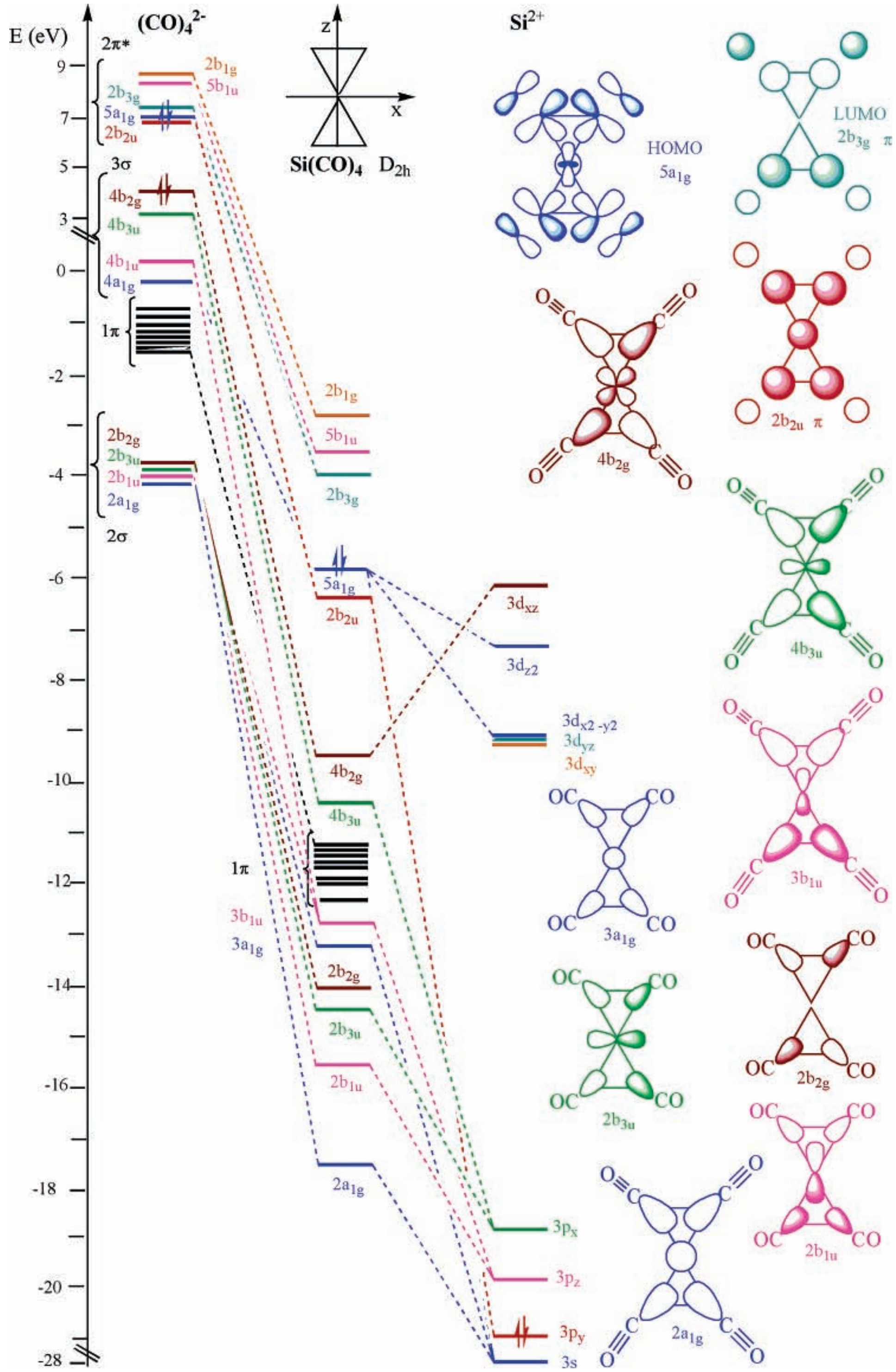


Figure 2. Correlation diagram between the four CO and the central Si generating the MOs of Si(CO)$_4$.

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$_{1g}$(3σ)1.62 5a$_{1g}$($2\pi^*$)1.13	4b$_{2g}$(3σ)1.72	4b$_{1u}$(3σ)1.41	2b$_{2u}$($2\pi^*$)0.91	3b$_{3u}$(1π)1.93 4b$_{3u}$(3σ)1.37
gross charge	Si 0.05	C 0.32	O −0.33		

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≡O$^+$, has shifted to silicon, thus reducing the electrostatic reinforcement to the C≡O bonds. In this way, compound

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[a]

	$Si(CO)_2$		$Si(CO)_4$
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
ΔE_{oi}	−19.84	ΔE_{oi}	−24.63
ΔE_{total}	−20.85	ΔE_{total}	−49.60
ΔE_{prep}	17.58	ΔE_{prep}	46.38
ΔE	−3.27	ΔE	−3.22

[a] ΔE^0 is the steric repulsion, ΔE (Γ) is the contribution due to orbital interaction in different irreducible representations, ΔE_{oi} is the total orbital interaction contribution, and ΔE_{total} is the sum of ΔE^0 and ΔE_{oi}. Preparation energies (ΔE_{prep}) of the fragments and bonding energies (ΔE) of the adducts are also given.

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 Bond Lengths

bond	E_b [eV]		bond length [Å]
C−C	3.59		1.54
$C\overset{\cdots}{-}C$	5.25	in benzene	1.40
C=C	6.36		1.34
C≡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

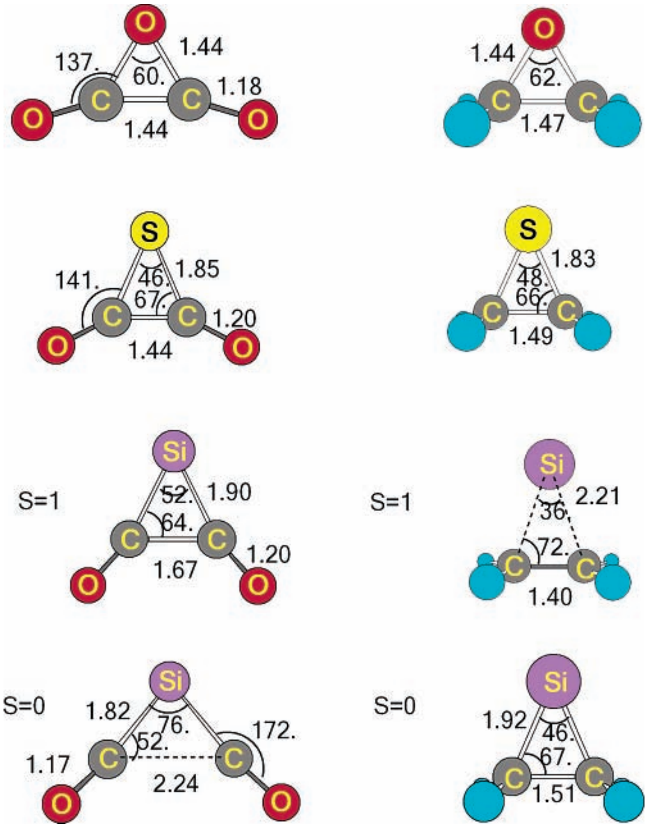
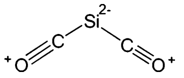
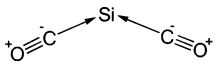


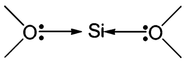
Figure 3. The optimized structures of the C_2H_4X (X = O, Si, S) and $(CO)_2X$ (X = O, Si, S) molecules. The spin multiplicity of the electronic state is also reported for silicon-based molecules.



$Si(CO)_2$ ($S = 0$) 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

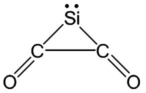


This picture is substantially the same as that advocated for the formation of oxo-oxygen−silicon adducts in siloxanic networks[3−5]



The stability of silicon dicarbonyl with respect to the dissociation $Si(CO)_2 \rightarrow Si + 2CO$ 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.

3.6. $Si(CO)_2$ ($S = 1$)—*c*-Silicodiketone. Totally different is the internuclear distance distribution in $Si(CO)_2$ ($S = 1$). With $Si(CO)_2$ ($S = 0$) 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 distances 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 ∠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 28 and 29. Figure 3 shows the structure of $X[C_2H_4]$ molecules (X = O, oxirane; X = S, thiirane; X = Si, “silirane” or silacyclopropylidene of ref 28), and Table 11 gives their dissociation energies with respect to X + C_2H_4 (the calculations having being carried out at the same level as that adopted in this work).

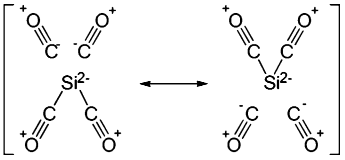
Interestingly enough, the corresponding molecules $X[C_2O_2]$ (“*c*-X-diketones”) have well-defined minima that allow them

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 Δ*E* of the Molecules with Respect to Reactants

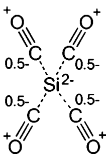
reactants	*E* [eV]	product	*E* [eV]	Δ*E* [eV]
$C_2H_4 + O$	−33.43	$O(CH_2)_2$	−37.54	−4.11
$C_2H_4 + S$	−32.49	$S(CH_2)_2$	−35.24	−2.75
$C_2H_4 + Si$	−32.25	$Si(CH_2)_2$ ($S = 0$)	−34.45	−2.10
$C_2H_4 + Si$	−32.25	$Si(CH_2)_2$ ($S = 1$)	−33.40	−1.15
$2CO + O$	−31.31	$O(CO)_2$	−35.85	−4.54
$2\ CO + S$	−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

to be considered as chemical species. Of course, $X[C_2O_2]$ (X = O, S) are unstable and dissociate spontaneously to CO + XCO; however, $Si[C_2O_2]$ is stable with respect to this dissociation, thus suggesting the hypothesis of its possible preparation.

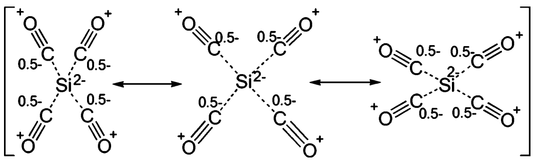
3.7. $Si(CO)_4$ ($S = 0$)—Silicon Tetracarbonyl. The C−O distance in $Si(CO)_4$ indicates that carbon and oxygen are bonded in a carbonyl configuration. The distribution of the C−C and Si−C interatomic distances (closer to, but somewhat larger than, the corresponding distances in $Si(CO)_2$), the binding 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



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[12] to establish it as the first compound with planar tetracoordinated silicon. Later, Schomburg[13] 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.[15]

4. 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 $Si[C_2O_2]$. For $Si(CO)_n$ ($n = 1, 2$), our results are in good agreement with the ones of 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 on semiphenomenological bases, such as the prediction (as an extrapolation from Si(CO) and $Si(CO)_2$ results) of a smaller fourth CO binding energy of Si and the lack of experimental observations for these polycarbonyl species. In $Si(CO)_2$, silicon dicarbonyl, the CO are datively bonded to silicon, and $Si[C_2O_2]$, *c*-silicodiketone, is somewhat similar to the compounds formed by silicon and ethylene; $Si(CO)_4$, silicon tetracarbonyl, may be viewed as a resonance between the extreme configurations $(CO)_2Si + 2CO$ and $2CO + Si(CO)_2$. A detailed orbital analysis has pointed out 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 the Si and $(CO)_2$ framework due to electron donation from carbonyl to silicon accounts for most of the bond strength, and π back-donation 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 back-donation from silicon to $2\pi^*$ CO orbitals occurs. The bonding mechanism is similar to that in transition-metal carbonyl complexes, with the major difference that Si uses its p orbitals for π back-donation instead of the d orbitals of transition metals. As a consequence, the weakening of the C−O bond in the silicon carbonyls is greater than that in transition-metal carbonyls.

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 planar tetracoordinated silicon where the delocalization of the electrons in the silicon p orbital into the CO framework and the participation of silicon d orbital in the σ bonding are responsible for its thermodynamic stability.

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