



# **Investigation of the C=L Bond Nature in $CL_2$ Compounds with Valence Bond Theory**

Xintao Feng

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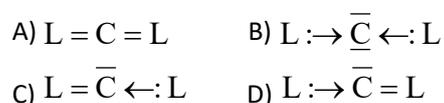
x.feng.1@student.rug.nl

## Abstract

This project aims to use valence bond (VB) theory to study the bond nature of  $CL_2$ , where the  $CL_2$  are  $C(CH_2)_2$ ,  $C(SiH_2)_2$ ,  $C(CCl_2)_2$ ,  $C(SiCl_2)_2$ ,  $C(NH_2)_2$ , as well as the bond nature of  $C(PH_3)_2$ , to show whether the bond is more carbene or covalent. The singlet-triplet gaps of the carbene ligands  $CR_2$  and  $PH_3$  were calculated to predict the carbene character of  $CL_2$ . The configurations  $L=C=L$ ,  $L\rightarrow C\leftarrow L$  and  $L\rightarrow\bar{C}=L$  were built up, and the weights of these structures were determined by the VB calculations. Moreover, the analysis of the composition of the bonding orbitals was used to figure out the reason for the six  $CL_2$  differ in carbene character. The experimental data suggest that the  $C(PH_3)_2$  has relatively strong carbene-type bonding, while  $C(CH_2)_2$ ,  $C(SiH_2)_2$ , and  $C(CCl_2)_2$  have strong covalent-type bonding.

## 1 Introduction

Carbon is one of the richest elements in nature, being present in organic and inorganic compounds. Carbon belongs to the IV A group in the periodic table, so it has four valence electrons in the outer shell. The most common oxidation state of carbon present in carbon compounds is +4. The bonding situation of the carbon compounds usually is tetravalent, which means it engages all the four valence electrons to form the stable single or double bonds. Tetravalent carbon compounds have the potentiality to form four configurations (Figure 1.1), where the carbon atom is in



**Figure 1.1** The four configurations of  $CL_2$  compounds. The structures correspond to: A) carbon compound, B) divalent carbene(0) and C,D) divalent carbon(2).

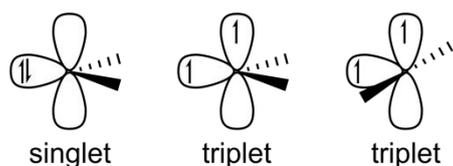
oxidation state +4, 0 and +2. The central carbon is bonded to one ligand by a covalent bond  $C=L$  or a donor-acceptor bond  $C\leftarrow L$ . The  $C=L$  bond consists of a  $\sigma$  bond, which is built by the two  $sp^2$  hybrid orbitals, and a  $\pi$

bond, which is built by the two parallel  $p$  orbitals. The  $C\leftarrow L$  bond refers to the interaction between the  $\sigma$ -donor L and the central carbon, where the carbon atom has two  $\sigma$ - and  $\pi$ - donors. This kind of special bond also has presented in organometallic chemistry [1].

Divalent carbene compounds  $CL_2$  have a central carbon, which has two retained lone pairs with  $\sigma$ - and  $\pi$ - symmetry, and two carbene ligands L, which are bonded to the carbon by donor-acceptor bonds  $C\leftarrow L$ . Frenking and Tonner [1] have studied this compound in detail in terms of energy. They used the charge- and energy- decomposition analysis to study the carbene character of  $C(PR_3)_2$  and  $C(NHC)_2$ . The  $C(PR_3)_2$  called carbodiphosphorane (CDP), and the carbene  $PR_3$  donates an electron pair into the empty orbital on the central carbon. The first stable carbene  $C(PPh_3)_2$ , which has the melting point at 208-210°C, was successfully synthesized by Ramirez et al in 1961 [5]. Other divalent carbene compounds  $CL_2$ , where the ligand was N-heterocyclic carbenes (NHCs), was compared with CDP by Frenking and Tonner [12]. The

carbodicarbene compounds  $C(NHC)_2$ , where the central carbon was bonded to two carbene ligands NHC by  $\sigma$  lone pairs, were synthesised by Bertrand et al. [5].

The carbene ligands  $CR_2$  in  $CL_2$  compounds may have electronic singlet or triplet ground state (Figure 1.2). The singlet carbene has a



**Figure 1.2** The singlet and triplet carbenes [4].

The singlet carbene has paired two electrons in the  $sp^2$  orbital, while the electrons in triplet carbene are located at neighbouring orbital.

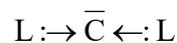
$\sigma$  lone-pair orbital and an empty  $\pi$  orbital, and they are perpendicular to each other. The two donor-acceptor bonds  $C \leftarrow L$  in  $CL_2$  depend on the interaction between the lone-pair orbital on the ligand and the empty valence orbital on the central carbon. Therefore, the compounds  $CL_2$ , where the L is in electronic singlet ground state, have more carbene character.

The carbenes  $CR_2$  and carbenes  $CL_2$  are different from the oxidation state of the carbon. The carbenes  $CR_2$  have a carbon atom in oxidation state two, while the carbenes  $CL_2$  have a carbon atom in oxidation state 0.

Troade et al. [10] suggested that the donor-stabilized silylenes (DSSs) have stronger nucleophilicity than NHCs. They found that the strongly electron-donating DSS ligand causes a rapidly increased electron density on the central carbon.

For the investigation of the influence of different electron-donating ligands L on the central carbon, six ligands were selected:

$CH_2$ ,  $CCl_2$ ,  $SiH_2$ ,  $SiCl_2$ ,  $C(NH_2)_2$ , and  $PH_3$ . The  $CL_2$  were assumed as linear molecules, which means the bond angle  $L-C-L$  was set to  $180^\circ$  (Scheme 1.1). The influence of the ability to donate electrons of carbene ligand L (i.e.  $CR_2$ ) on carbon character can be seen from the comparison between  $C(CH_2)_2$  (**1**) and  $C(SiH_2)_2$  (**2**). For the investigation of the influence of R in  $CR_2$ , the hydrogens in **1** and **2** were substituted by the chlorine, which has much stronger electronegativity. This resulted in the comparison between  $C(CCl_2)_2$  (**3**) and  $C(SiCl_2)_2$  (**4**). The ligand  $NH_2$  was used instead of imidazol-2-ylidene in this research. The obtained  $C(NH_2)_2$  (**5**) probably has the  $C(NHC)_2$ -like properties. The simplest CDP compound  $C(PH_3)_2$  (**6**), where the  $R=H$ , was studied.



| #        | $L_1$    | $L_2$    |
|----------|----------|----------|
| <b>1</b> | $CH_2$   | $CH_2$   |
| <b>2</b> | $SiH_2$  | $SiH_2$  |
| <b>3</b> | $CCl_2$  | $CCl_2$  |
| <b>4</b> | $SiCl_2$ | $SiCl_2$ |
| <b>5</b> | $NH_2$   | $NH_2$   |
| <b>6</b> | $PH_3$   | $PH_3$   |

**Scheme 1.1** The structure of  $CL_2$  and ligands L.

The linear allene **1**, which serves as a reference, is the simplest divalent carbene(0) among the six compounds. The compounds **2** and **4** with DSS ligands are studied to see the influence of better ability of donating electrons. The effect of substituting N-heterocyclic carbenes with  $NH_2$  on  $CL_2$  can be observed from the experimental results of **5**. The divalent carbene **6**, which belongs to CDP, probably has more carbene

character than the others.

For the prediction of the carbon character of  $CL_2$  compound, it is necessary to calculate the energy gap between electronic singlet and triplet states of the ligand. The singlet-triplet gap is given by Eq 1.1. The energy of the state is given by Eq 1.2.

$$\Delta E = E_{Singlet} - E_{Triplet} \quad (1.1)$$

$$E_{state} = E_{total} + E_{ZPVE} \quad (1.2)$$

Where the  $E_{total}$  is the total energy and the  $E_{ZPVE}$  is the zero point vibrational energy. The carbene ligand which has a more stable electronic singlet state is likely to give a more carbene  $CL_2$ . As discussed in the former paragraphs, the divalent carbene(0) has a central carbon, where the four valence electrons retain as two lone pairs, that is bonded to two ligands by donor-acceptor  $C \leftarrow L$  bonds. Therefore, the ligand with a negative singlet-triplet gap, which means the singlet state is lower than triplet state, is likely to contribute to the carbene character of the corresponded compound, and carry out stronger donor-acceptor bond.

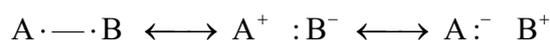
The bond length might correlate to the strength of the donor-acceptor interaction. The electron density of the central carbon is relatively high due to the electron-donating ligands L<sup>[5]</sup>. The view of nucleophilicity could be an explanation of the difference in carbene characters of the compounds. The central carbon and the two ligands can be regarded as three electron-rich species. The interaction probably influenced by the reactivity of the carbene ligands. The ligands differ from the ability to donor electrons due to the atom that used to serve as the electron donor. Theoretically, the  $SiH_2$

should have better nucleophilicity than  $CH_2$  results from the larger atomic orbital as well as weaker electron affinity. To verify this assumption, the bond lengths of compounds **1-4** were calculated.

This project studied the divalent carbon in terms of wavefunction instead of bonding energy, and used mathematical method to describe the carbene character of  $CL_2$ .

#### *Valence bond theory*

The chemical bond has been described by Lewis<sup>[13]</sup> as an electron-pair bond, which has a deep impact on the acknowledge of reaction mechanism. Afterwards, Heitler and London<sup>[14]</sup> found that the bonding energy in  $H_2$  driven from the resonance energy between  $H^\uparrow H^\downarrow$  and  $H^\downarrow H^\uparrow$ , which equalled to the energy required for obtaining a singlet electron pair. Pauling was inspired by Lewis and the Heitler-London papers, and he described the bond as covalent-ionic superposition bond (*Scheme 1.2*).



**Scheme 1.2** *The covalent-ionic superposition bond.*

The resonance energy arised from the bond refers to the charge-shift resonance energy ( $RE_{CS}$ ), and it contribute to the actual bond energy. Other theory, namely molecular orbital (MO) theory, quantifies the  $RE_{CS}$  by the charge distribution of the molecule. In this theory, the delocalized orbitals, which result from the linearly combined atomic orbitals (AOs), are occupied by electrons. Both VB and MO theories give the same description of the interactions between two centers in one-electron, three-electron and four-electron bonds<sup>[14]</sup>.

$$\Psi_{HLVB} = \left| \chi_a \overline{\chi_b} \right| - \left| \overline{\chi_a} \chi_b \right| \quad (1.3)$$

$$\Psi_{VB-full} = \lambda \left( \left| \chi_a \overline{\chi_b} \right| - \left| \overline{\chi_a} \chi_b \right| \right) + \mu \left( \left| \chi_a \overline{\chi_a} \right| + \left| \chi_b \overline{\chi_b} \right| \right), \quad \lambda > \mu \quad (1.4)$$

$$\sigma^2 = \left| \overline{\sigma} \overline{\sigma} \right| = \left| \chi_a \overline{\chi_b} \right| - \left| \overline{\chi_a} \chi_b \right| + \left| \chi_a \overline{\chi_a} \right| + \left| \chi_b \overline{\chi_b} \right| \quad (1.5)$$

$$\sigma^{*2} = \left| \overline{\sigma^*} \overline{\sigma^*} \right| = - \left( \left| \chi_a \overline{\chi_b} \right| - \left| \overline{\chi_a} \chi_b \right| \right) + \left( \left| \chi_a \overline{\chi_a} \right| + \left| \chi_b \overline{\chi_b} \right| \right) \quad (1.6)$$

$$\Psi_{MOCI} = c_1 \left| \overline{\sigma} \overline{\sigma} \right| - c_2 \left| \overline{\sigma^*} \overline{\sigma^*} \right| \quad c_1, c_2 < 0 \quad (1.7)$$

$$\Psi_{MOCI} = (c_1 + c_2) \left( \left| \chi_a \overline{\chi_b} \right| - \left| \overline{\chi_a} \chi_b \right| \right) + (c_1 - c_2) \left( \left| \chi_a \overline{\chi_a} \right| + \left| \chi_b \overline{\chi_b} \right| \right) \quad (1.8)$$

$$\Psi_{CL} = c_{COV} \Phi_{COV} + c_{C(0)} \Phi_{C(0)} + c_{C(2)} \Phi_{C(2)} \quad (1.9)$$

The bonding situation in a molecule AB can be described by wavefunction at the HLVB level (Eq. 1.3), where  $\chi_a$  and  $\chi_b$  represent for the atomic orbitals in the A-B bond. The  $\beta$  spin is indicated with the bar on the top of  $\chi$ . The  $\Psi_{HLVB}$  refers to the wave function of Heitler-London Valence Bond. The HLVB wavefunction, which mainly considers the covalent two-electron bond, describes the bond correctly when the distance between the two center is longer than the equilibrium distance. For the improvement of HLVB wavefunction, the ionic terms  $\left| \chi_a \overline{\chi_a} \right|$  and  $\left| \chi_b \overline{\chi_b} \right|$  are added, and the coefficients are optimized by configuration interaction (CI). The obtained function is  $\Psi_{VB-full}$  (Eq 1.4). When the distance between the two atoms becomes further, the ionic terms would be neglectable.

According to the MO theory, the two bonded atoms result in forming the bonding ( $\sigma = \chi_a + \chi_b$ ) and the anti-bonding ( $\sigma^* = \chi_a - \chi_b$ ) molecular orbitals. The  $\sigma^2$  is used to display the ground state of a molecule. The obtained

function (Eq 1.5) differs from the HLVB wave function but similar to  $\Psi_{VB-full}$ . It suggests that the two-electron bond always regarded as a half-covalent and half-ionic bond in MO theory. But the MO theory fail in describing the stretched bond. The description is resumed by CI, which mixes the ground state  $\sigma^2$  and diexcited state  $\sigma^{*2}$  (Eq 1.6). The optimized function is Eq. 1.7. Where the  $\sigma^2$  refers to the doubly occupied MO, the  $\sigma$  with a bar on the top indicates the  $\beta$  spin orbital. After the extension of MOCI wavefunction, it is clearly that the function has the inequivalent covalent and ionic components (Eq 1.8). The  $\Psi_{VB-full}$  and  $\Psi_{MOCI}$  become equivalent when the relationship  $\lambda = c_1 + c_2$  and  $\mu = c_1 - c_2$  are established. In general, the VB and MO theories converge to the accurate description of two-electron bond with the assist of CI [6].

The bonds in  $CL_2$  are described by VB wavefunctions, which has a general function Eq.1.9. Where the  $c_{COV}$ ,  $c_{(0)}$ , and  $c_{(2)}$  are the coefficients of covalent compound, divalent carbone(0), and divalent carbon(2), respectively. The  $\Phi_{COV}$ ,  $\Phi_{(0)}$ , and  $\Phi_{(2)}$ ,

**Table 1.1** The compositions of basis set 6-31G\* [8].

| Quality | Label | Name   | Element   | Primitives |    |   |   |   |   | Contracted |   |   |   |   |   |  |
|---------|-------|--------|-----------|------------|----|---|---|---|---|------------|---|---|---|---|---|--|
|         |       |        |           | s          | p  | d | f | g | h | s          | p | d | f | g | h |  |
| DZP     | Pople | 6-31G* |           |            |    |   |   |   |   |            |   |   |   |   |   |  |
|         |       |        | H         | 10         | 4  | 1 |   |   |   | 3          | 2 | 1 |   |   |   |  |
|         |       |        | C         | 16         | 10 | 1 |   |   |   | 4          | 3 | 1 |   |   |   |  |
|         |       |        | Si, P, Cl | 22         | 16 | 5 |   |   |   | 5          | 4 | 3 |   |   |   |  |

which are the VB structures that engage the valence electrons, describe the covalent bonding, divalent carbene(0) bonding, and divalent carbon(2) bonding, respectively. The core electrons stay in doubly occupied orbitals. To solve out the function, the method called *valence bond self-consistent filed* (VBSCF) method, which also called the *Hartree-Fock* method, is used. The sum of the coefficients, namely G-N weights, should be 1.0.

For the VB calculation, it is necessary to determine the level of theory, which is the functional, and the basis set, which is used to expand the molecular orbitals. The MOs can also be described by Eq 1.10, where the  $\phi_i(x)$  is called the *basis set* [8]. The basis set compositions for H, C, Si, P and Cl are shown in Table 1.1 [8].

$$\chi_j(x) = \sum_{i=1}^K \alpha_{j,i} \phi_i(x) \quad (1.10)$$

This project used the B3LYP functional, which is widely used as the hybrid functional, and the 6-31G\* basis set, which represents the unknown electronic structures properly [8]. The concept ‘hybrid functional’ refers to the combination of the exact results for the exchange part and the approximation for the correlation part, which is depended on the spatial localization [8].

## 2 Methods

The program GAMESS-UK [15] was adopted to perform the computational calculation.

The MOLDEN program was used to build up the CL<sub>2</sub> compounds and L ligands, where the ligands were CH<sub>2</sub>, CCl<sub>2</sub>, SiH<sub>2</sub>, SiCl<sub>2</sub>, C(NH<sub>2</sub>)<sub>2</sub>, and PH<sub>3</sub>. Geometry optimizations were implemented at the B3LYP/6-31G\* level of theory. The structures of the singlet ligands, the triplet ligands, and the singlet molecules were optimized by the program. The frequency calculation was applied to the singlet ligands, triplet ligands and singlet molecules. The zero point energy was added to the total energy to obtain the relatively accurate state energy. The singlet-triplet gap of ligand was calculated by subtracting the energy of the triplet state from the energy of the singlet state. For the calculation of singlet ligands, the runtime was *hessian*; for the calculation of triplet ligands, the runtime was *force*. The bond lengths between the ligands and central carbon were obtained from the results of the geometry optimizations.

The optimized coordinate was used to run the VB calculation. Before running the VB calculation, the fragment was isolated from the molecule. For the isolation of fragment, number ‘1’ was written after the elements in the fragment, that they have been regarded as ghost. The VB structures have been built up with the valence molecular orbitals, which were possible for constructing the four configurations. Then the VB

calculations, which were not orthogonal, were operated by using the TURTLE program. The covalent configuration has been calculated at first. The four configurations haven been calculated when the calculation of covalent configuration has finished. The bonding orbitals of the central carbon were two  $sp^2$  hybrid orbitals and two perpendicular  $2p$  orbitals. The bonding orbitals of  $\text{CH}_2$ ,  $\text{CCl}_2$  and  $\text{C}(\text{NH}_2)_2$  were two  $sp^2$  hybrid orbitals and two perpendicular  $2p$  orbitals. The bonding orbitals of  $\text{SiH}_2$ ,  $\text{SiCl}_2$  and  $\text{PH}_3$  were two  $sp^2$  hybrid orbitals and two  $3p$  orbitals. The compositions of the molecular orbitals of  $\text{C}(\text{CH}_2)_2$ ,  $\text{C}(\text{Cl}_2)_2$ ,  $\text{C}(\text{SiH}_2)_2$ , and  $\text{C}(\text{PH}_3)_2$  were analysed.

### 3 Results and Discussions

#### *Singlet-triplet gap*

The electronic singlet state would be more stable than the electronic triplet state when the energy of the singlet state is lower than

the triplet state. According to *Eq 1.1*, the ligand with a more stable singlet state would have a negative singlet-triplet gap. The ‘size’ of the gap of the ligand reveals the distance between the singlet and triplet states, which can be used to predict the level of carbone character of the corresponded compound. The smaller gap allows the electron to go to another orbital much easier, and then resulted in forming the triplet state. On the other hand, the ligand which has a relatively stable triplet state would give a positive gap.

As shown in *Figure 3.1*, the  $\text{PH}_3$  ligand has the largest and most negative singlet-triplet gap. Thus, probably, the  $\text{C}(\text{PH}_3)_2$  compound would be the one with the most carbone character among the six  $\text{CL}_2$  compounds. Because the  $\text{CH}_2$  has the shallowest and positive gap, the  $\text{C}(\text{CH}_2)_2$  compound might be the one with the most covalent character. The ligands  $\text{CH}_2$ ,  $\text{SiH}_2$ ,  $\text{CCl}_2$ ,  $\text{SiCl}_2$  and

**Table 3.1** The energy gap between the singlet and triplet states of the ligands

| eV  | $\text{CH}_2$ | $\text{SiH}_2$ | $\text{CCl}_2$ | $\text{SiCl}_2$ | $\text{C}(\text{NH}_2)_2$ | $\text{PH}_3$ |
|-----|---------------|----------------|----------------|-----------------|---------------------------|---------------|
| Gap | +0.40         | -0.87          | -1.07          | -2.25           | -1.88                     | -18.53        |



**Figure 3.1** The energy gaps between the singlet and triplet ligands. The larger energy gap corresponded to more obvious carbon feature, which responded to the ability of electrons to move from singlet state to triplet state.

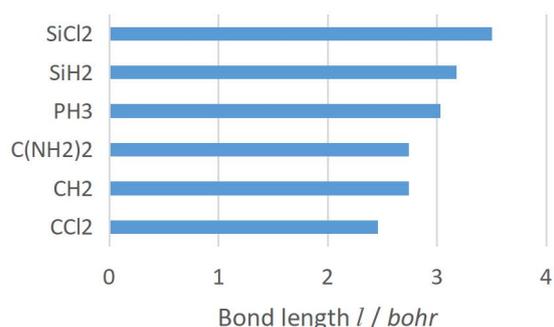
$C(NH_2)_2$  have relatively shallow singlet-triplet gaps, thus the electrons can go to the triplet state much easier than that in the ligand  $PH_3$ .

The atom X that bound to the central carbon in  $XR_2$  ( $X=C, Si$ ) and  $XR_3$  ( $X=P$ ) may have an impact on the size of the gap. The gap of  $SiH_2$  is larger than that of  $CH_2$ ; the gap of  $SiCl_2$  is larger than that of  $CCl_2$ . The C and Si are in the same group in the periodic table, so the number of valence electrons are the same. The influence on the gap may result from the larger molecular orbitals, where the distance between the adjacent energy levels is further.

The sizes of the singlet-triplet gaps of  $CH_2$ ,  $CCl_2$  and  $C(NH_2)_2$  are increased in order. The nucleophilicity of the side group R in the  $XR_2$  probably has a positive effect on the stability of the singlet state. The nucleophilicity of  $NH_2^+$  and  $Cl^-$  are better than  $H^+$ . Thus,  $C(NH_2)_2$  and  $CCl_2$  seem to be good electron-rich species and react with an electron-deficient centre easily [9].

### Bond length

The bond lengths between the ligands and the central carbon are shown in *Figure 3.2* in order from long to short. The tendency of bond length does not accord with that of the size of singlet-triplet gap. The bond length probably only depends on the size of the ligand. The  $C(SiCl_2)_2$  has the longest bond length, which resulted from the largest size of the ligand. However, the singlet-triplet gap of it is not large. The  $C(PH_3)_2$  with the ligand  $PH_3$ , which has the largest singlet-triplet gap, only has a medium bond length. The  $C(CH_2)_2$  with the ligand  $CH_2$ ,



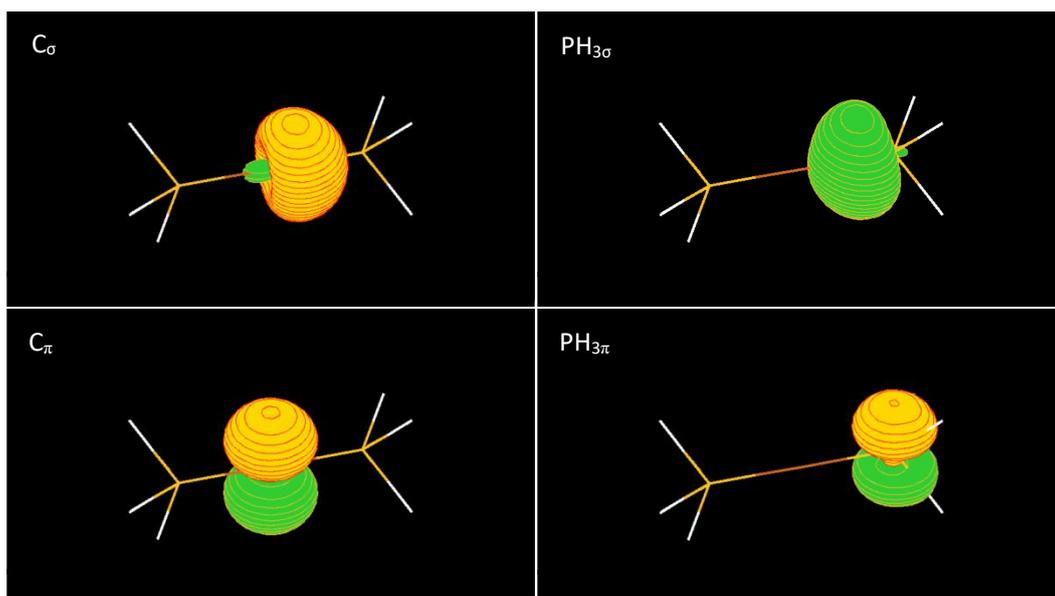
**Figure 3.2** The bond length of  $C-L$ . Generally, the bond length depends on the size of the ligand. The  $l_{CH_2}$  and  $l_{CCl_2}$  might be impacted by the electronegativity of the L group.

which has the shallowest energy gap, has a relatively short bond length. The  $C(Cl_2)_2$  has the shortest bond length. The distance between Si and Cl is much shorter than that between C and Cl, while the difference between the absolute values of the singlet-triplet gaps of  $SiCl_2$  and  $CCl_2$  is not too big. So the bond length dose not have significant effect on the carbone characters.

### G-N weights

The bonding orbitals of four configurations are shown in *Figure 3.3*. The patterns of the four compounds are similar, so only the  $C(PH_3)_2$  is shown.

The G-N weights of four configurations of  $C(CH_2)_2$ ,  $C(CCl_2)_2$ ,  $C(SiH_2)_2$  and  $C(PH_3)_2$  compounds are shown in *Table 3.2*. The G-N weight of configuration  $L=C=L$  refers to the covalent character of the compound. It is obvious that the compounds  $C(CH_2)_2$ ,  $C(SiH_2)_2$  and  $C(CCl_2)_2$  have much more covalent characters than  $C(PH_3)_2$ . This result is consistent with the prediction derived from the tendency of the singlet-triplet gap. The distribution of G-N weights of the three types of configurations of the compounds  $C(CH_2)_2$ ,  $C(CCl_2)_2$  and  $C(SiH_2)_2$  are similar.



**Figure 3.3** The bonding orbitals on the central carbon and one of the  $\text{PH}_3$  ligands. The  $C_\sigma$  and  $\text{PH}_{3\sigma}$  form the  $\sigma$  bond in  $\text{C}=\text{P}$  bond, and the  $C_\pi$  and  $\text{PH}_{3\pi}$  form the  $\pi$  bond in  $\text{C}=\text{P}$  bond. The doubly occupied  $C_\pi$  represents for one of the two retained lone pairs on the central carbon. The doubly occupied  $\text{PH}_{3\sigma}$  represents for the  $\sigma$ -donor in  $\text{C}\leftarrow\text{P}$  bond. The other ligand has the same bonding situation as this one.

**Table 3.2** The G-N weights of four configurations of  $\text{C}(\text{CH}_2)_2$ ,  $\text{C}(\text{CCl}_2)_2$ ,  $\text{C}(\text{SiH}_2)_2$  and  $\text{C}(\text{PH}_3)_2$  compounds. The terms  $\text{L}=\text{C}=\text{L}$ ,  $\text{L}\rightarrow\text{C}\leftarrow\text{L}$ , and  $\text{L}=\text{C}\leftarrow\text{L}$  represent for covalent configuration, divalent carbene(0) configuration, and divalent carbon(2) configuration, respectively.

| Ligands        | $\text{L}=\text{C}=\text{L}$ | $\text{L}\rightarrow\text{C}\leftarrow\text{L}$ | $\text{L}=\text{C}\leftarrow\text{L}$ |
|----------------|------------------------------|---|---------------------------------------|
| $\text{CH}_2$  | 0.89                         | 0.00  | 0.11                                  |
| $\text{CCl}_2$ | 0.87                         | 0.00  | 0.13                                  |
| $\text{SiH}_2$ | 0.88                         | 0.00  | 0.11                                  |
| $\text{PH}_3$  | 0.62                         | 0.04  | 0.34                                  |

The  $\text{C}(\text{CH}_2)_2$  is the most covalent compound among the three, while the  $\text{C}(\text{CCl}_2)_2$  is the least covalent one. It corresponds to the size of the singlet-triplet gap: the size of the singlet-triplet gap of  $\text{CCl}_2$  is larger than that of the  $\text{CH}_2$ , and the gap of  $\text{CCl}_2$  is negative. The  $\text{C}(\text{PH}_3)_2$  has the highest G-N weight in the cases of configurations  $\text{L}\rightarrow\text{C}\leftarrow\text{L}$  and  $\text{L}=\text{C}\leftarrow\text{L}$ . Therefore, the  $\text{C}(\text{PH}_3)_2$  is the most carbene(0) compound among the four. This result aligns with the prediction, and verifies the carbene properties of CDP.

Although the  $\text{C}(\text{PH}_3)_2$  is the most carbene

compound among the four, surprisingly, the G-N weight of configuration  $\text{H}_3\text{P}\rightarrow\text{C}\leftarrow\text{PH}_3$  is much lower than expected. On the other hand, the weights of the other two configurations, covalent  $\text{H}_3\text{P}=\text{C}=\text{PH}_3$  and divalent carbon(2)  $\text{H}_3\text{P}\rightarrow\text{C}=\text{PH}_3$ , are much higher than expected. This unsatisfactory phenomenon may be caused by the linear structure. The interaction of the linearly combination of the central carbon and phosphine probably is weaker than the bent structure.

To investigate the bonding situation in more

**Table 3.3** The composition of bonding orbitals of ligand  $XL_2$ . The  $d$  character of bonding orbitals of  $C(CH_2)_2$ ,  $C(CCl_2)_2$  and  $C(SiH_2)_2$  is much less than that of  $C(PH_3)_2$ .

| Ligand                 | $XL_{2,left}(\sigma)$ |       |       | $XL_{2,left}(\pi)$ |       |       | $XL_{2,right}(\sigma)$ |       |       | $XL_{2,right}(\pi)$ |       |       |
|------------------------|-----------------------|-------|-------|--------------------|-------|-------|------------------------|-------|-------|---------------------|-------|-------|
|                        | $s$                   | $p$   | $d$   | $s$                | $p$   | $d$   | $s$                    | $p$   | $d$   | $s$                 | $p$   | $d$   |
| <b>CH<sub>2</sub></b>  | 0.324                 | 0.675 | 0.005 | 0.000              | 0.994 | 0.002 | 0.324                  | 0.675 | 0.005 | 0.000               | 0.994 | 0.002 |
| <b>CCl<sub>2</sub></b> | 0.368                 | 0.609 | 0.006 | 0.000              | 0.939 | 0.004 | 0.368                  | 0.609 | 0.006 | 0.000               | 0.939 | 0.004 |
| <b>SiH<sub>2</sub></b> | 0.342                 | 0.603 | 0.031 | 0.000              | 0.990 | 0.009 | 0.342                  | 0.603 | 0.031 | 0.000               | 0.990 | 0.009 |
| <b>PH<sub>3</sub></b>  | 0.297                 | 0.654 | 0.026 | 0.000              | 0.674 | 0.122 | 0.300                  | 0.652 | 0.023 | 0.001               | 0.645 | 0.159 |

detail, the compositions of bonding orbitals were analysed. The results are shown in Table 3.3. The bonding orbitals of  $C(PH_3)_2$  have relatively more  $d$  character, which are 2.6%, 2.3%, 12.2% and 15.9%. The  $\sigma$  orbital of  $SiH_2$  has higher  $d$  character than  $PH_3$ , but the  $\pi$  orbital has less  $d$  character than  $PH_3$ . Both of the  $\sigma$  and  $\pi$  orbitals of ligands  $CH_2$  and  $CCl_2$  have a small amount of  $d$  character. Perhaps, the higher weights of  $d$  character of  $\pi$  orbitals would increase the carbon character of the compound. In theory [16], the P atom would use  $3d$  orbital to form a bond, while in the table the  $\pi$  orbital has much more  $p$  character rather than  $d$  character. The  $\sigma$  and  $\pi$  orbitals of  $CH_2$ ,  $CCl_2$  and  $SiH_2$  also have much more  $p$  character rather than  $d$  character. The  $p$  character might be the explanation of the unexpected highly covalent character of  $C(PH_3)_2$ .

The strength of donor-acceptor interactions probably is influenced by the size of bonding orbital. From the analysis of the composition of bonding orbitals, the ligands  $CH_2$  and  $CCl_2$  donate  $2p$  orbitals, while the ligands  $SiH_2$  and  $PH_3$  donate  $3p$  orbitals. The  $3p$  orbital is larger than  $2p$  orbitals. Therefore, the interactions  $C\leftarrow SiH_2$  and  $C\leftarrow PH_3$  are stronger than  $C\leftarrow CH_2$  and  $C\leftarrow CCl_2$ . This can be used to explain the

$C(SiH_2)_2$  has a slightly higher carbon character than  $C(CH_2)_2$ . Because the difference is not large, the influence of the size of bonding orbital on carbon character is limited.

The  $L-C-L$  angle is  $180^\circ$  in every  $CL_2$  compound. The linear structure might have negative effect on the interaction between central carbon and ligand. Frenking and Tonner [5] suggested that the bonding situations in  $C(PH_3)_2$  can be interpreted by using donor-acceptor interactions when the carbon valence orbitals are in  $C_{2v}$  symmetry. Thus, the linear  $C(PH_3)_2$  would have much less carbon character than bent  $C(PH_3)_2$ .

#### 4 Conclusions

The analysis of singlet-triplet gap and the structure weights reveal the level of carbon character of compounds  $C(CH_2)_2$ ,  $C(CCl_2)_2$ ,  $C(SiH_2)_2$ , and  $C(PH_3)_2$ . The  $C=X$  ( $X=C, Si$ ) bonds in compounds  $C(CH_2)_2$ ,  $C(CCl_2)_2$ , and  $C(SiH_2)_2$  have almost 0% carbon character but nearly 90% covalent character. The  $C(PH_3)_2$ , which is a carbodiphosphorane, is the highest carbon compound among the four. The analysis of the singlet-triplet gaps of ligands suggests that the level of carbon characters probably be decided in large part by the size of the gap. The  $CH_2$  ligand has

the shallowst gap, which is +0.40 eV, while the PH<sub>3</sub> ligand has the largest gap, which is -18.53 eV. The results of the calculations of VB structures suggest that the compounds **1-3** have covalent bonds, where the G-N weights of L=C=L are 0.89, 0.87 and 0.88, and compound **6** has less covalent character, where the G-N weight of L=C=L is 0.62. The bonding situations in CDP **6** have relatively high percentage in configuration of divalent carbon(2) rather than divalent carbene(0), where the G-N weights are 0.04 and 0.34, respectively. The analysis of the composition of molecular orbitals provides an explanation to the differences in the G-N weights of compounds **1-3** and **6**: the CL<sub>2</sub> with the ligand, which has a  $\pi$  orbital with relatively high *d* character, likely to have more carbene character. The linear structure probably results in the reduction in carbene character, because the symmetry of carbon valence orbitals cannot fit with the ligand valence orbitals properly.

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## Appendix

1. Total energy, zero point vibrational energy, and singlet-triplet gap of each ligand

|                                      | $E_{\text{total},1}$<br>(hartree) | $E_{\text{ZPVE},1}$<br>(hartree) | $E_{\text{total},3}$<br>(hartree) | $E_{\text{ZPVE},3}$<br>(hartree) | $E_1$<br>(hartree) | $E_3$<br>(hartree) | $\Delta E$<br>(hartree) | $\Delta E$<br>(eV) |
|--------------------------------------|-----------------------------------|----------------------------------|-----------------------------------|----------------------------------|--------------------|--------------------|-------------------------|--------------------|
| <b>CH<sub>2</sub></b>                | -39.129                           | 0.017                            | -39.144                           | 0.018                            | -39.112            | -39.127            | -39.129                 | 0.402              |
| <b>SiH<sub>2</sub></b>               | -290.614                          | 0.012                            | -290.583                          | 0.012                            | -290.603           | -290.571           | -290.614                | -0.865             |
| <b>CCl<sub>2</sub></b>               | -958.383                          | 0.004                            | -958.343                          | 0.004                            | -958.379           | -958.339           | -958.383                | -1.067             |
| <b>SiCl<sub>2</sub></b>              | -1209.94                          | 0.003                            | -1209.86                          | 0.003                            | -1209.94           | -1209.85           | -1209.94                | -2.252             |
|                                      | 3                                 |                                  | 1                                 |                                  | 0                  | 8                  | 3                       |                    |
| <b>C(NH<sub>2</sub>)<sub>2</sub></b> | -149.930                          | 0.055                            | -149.861                          | 0.055                            | -149.875           | -149.806           | -149.930                | -1.879             |
| <b>PH<sub>3</sub></b>                | -343.144                          | 0.024                            | -342.481                          | 0.041                            | -343.120           | -342.439           | -343.144                | -18.534            |