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Chemical Bonding in Silicon−Carbene Complexes

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The bonding situations in the newly synthesized silicon−carbene complexes with formulas L:SiCl4, L:(Cl)Si−Si(Cl):L, and L:Si═Si:L (where L: is an N-heterocyclic carbene), are reported using density functional theory at the BP86/TZ2P level. The bonding analysis clearly shows that the bonding situation in the silicon−carbene complexes cannot be described in terms of donor−acceptor interactions depicted in the Dewar−Chatt−Duncanson model. The energy decomposition analysis (EDA) shows that the electrostatic attraction plays an important or even dominant role for the Si−$C_{carbene}$ binding interactions in the silicon−carbene complexes. That the molecular orbitals of the silicon−carbene complexes are lower in energy than the parent orbitals of carbenes indicates that these complexes are better described as stabilized carbene complexes.

1. Introduction

Chemical bonding can be visualized as an exchange of electrons between the atoms of the different elements. The oxidation number of an element indicates the number of electrons lost, gained, or shared as a result of chemical bonding. When an atom is in the elemental state, the oxidation number is zero. Elements can occur as allotropes, which differ in the manner of bonding between atoms. However, all allotropes are alike in that the atoms are in the zero oxidation state. Aside from allotropes, the zero oxidation state is classically assumed in metals, when stabilized by ligands that donate electron pairs into their empty orbitals. However, the oxidation state of zero is rare for main group elements in their compounds. Lately, Wang et al. report that the reduction of the neutral hypervalent silicon−carbene complex L:$SiCl_4$, **1** (where L: is C[N(2,6-Pr^i_2-C_6H_3)CH]$_2$ and Pr^i is isopropyl) produces L:(Cl)Si−Si(Cl):L, **2**, a carbene-stabilized bis-silylene, and L:Si═Si:L, **3**, a carbene-stabilized diatomic silicon allotrope with the Si atoms in the formal oxidation state of zero.[1] The strategy used by the authors can be thought of as follows. The nucleophilic carbene ligands of the compounds, stabilized by the π-donor substituent, N-heterocyclic ring, with their nonbonding electrons in the same orbital (the spin-paired singlet state) act as nonoxidizing two-electron donors toward Si_2 units.[2] The silicon centers of compounds **2** and **3** possess one electron pair and are in the +1 and zero oxidation states, respectively. The silicon−carbene bonding in the compounds can be discussed by the familiar Dewar−Chatt−Duncanson (DCD) donor−acceptor model,[3,4] which provides a bonding picture that a σ-type donation from the carbene lone-pair orbital with concomitant π-backbonding into the empty π^* orbital. However inspections of metal−carbene interactions showed that electrostatic forces and the Pauli exclusion principle must be considered for a true understanding of the chemical bonding.[5]

In this work, the situation of the Si−$C_{carbene}$ bonding in the silicon−carbene complexes is investigated with the energy decomposition analysis (EDA)[6] method using DFT calculations at the BP86/TZ2P level. The EDA makes it possible to quantitatively estimate how the interplay of electrostatic interaction, orbital interaction, and Pauli repulsion determines the strength of chemical bonding in these complexes. By means of the bond-energy analysis, it is found that the stabilizing orbital interactions of the silicon carbene complexes discussed here do not follow the DCD model, although many other carbene complexes follow the donor−acceptor model.[5,7]

2. Computational Details

The calculations were carried out with the program package ADF 2006.01.[6,8] The nature of the bonding in **1**, **2**, and **3** were investigated on the simplified L:$SiCl_4$, 1-Me, L:(Cl)Si−Si(Cl):L, 2-Me, and L:Si═Si:L, 3-Me models (where L: is C(CHNCH_3)$_2$). For 1-Me, 2-Me, and 3-Me, we used B3LYP/6-311+G(d,p) geometries from ref 1 (see Figure 1). All molecular orbital analyses were based on single point calculations performed with the generalized gradient approximation (GGA) to density functional theory (DFT) by using the exchange functional of Becke[9] in conjunction with the correlation functional of Perdew[10] (BP86). Uncontracted Slater-type triple-z basis sets with two sets of polarization functions were used for all atoms. Core electrons were treated by the frozen-core approximation. This level of theory is denoted as BP86/TZ2P, which has been successfully used in the study of the properties for the chemical bonds of second and third period diatomic molecules.[11] The built-in fragment-oriented approach in ADF makes it possible to analyze the relationship between complex orbitals and orbitals of the fragments that make up the final complexes.

The bonding analysis was carried out by looking at the interactions between one carbene ligand and the silicon center fragment, retaining the symmetry of the complexes. It is possible to identify the energy contributions of the fragment orbitals to the σ-donation and π-back-donation. The interatomic interactions were analyzed by means of EDA scheme. Within this method, the bond dissociation energy ΔE between the fragments is partitioned into two major components (eq 1).

$$\Delta E = \Delta E_{prep} + \Delta E_{int} \tag{1}$$

ΔE_{prep} is the energy necessary to promote the fragments from their equilibrium geometry and electronic ground state to the geometry and electronic state they have in the complex. ΔE_{int} is the instantaneous interaction energy between the fragments

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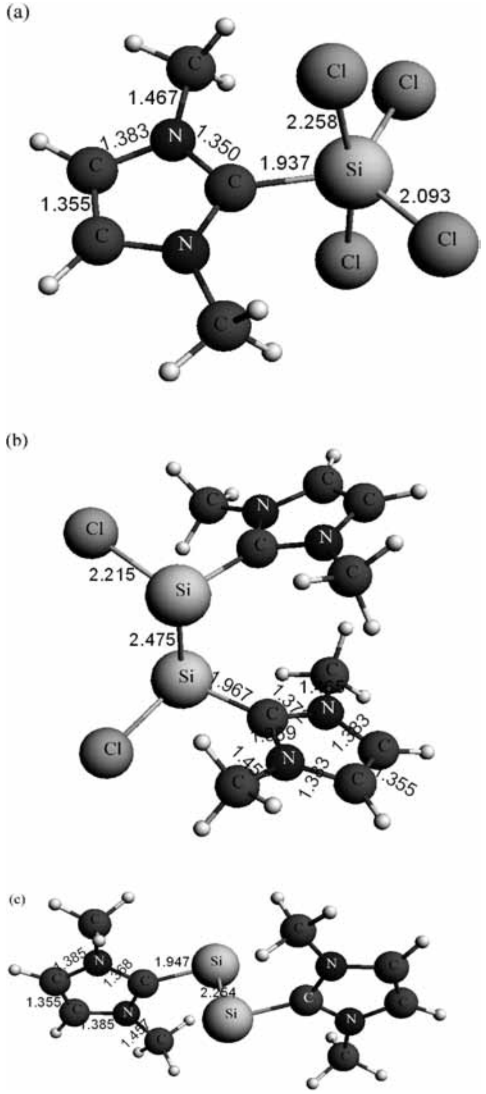

Figure 1. Molecular structures of (a) 1-Me, (b) 2-Me, (c) 3-Me. The numbers represent bond lengths in angstroms. The structural data are present in detail in ref 1.

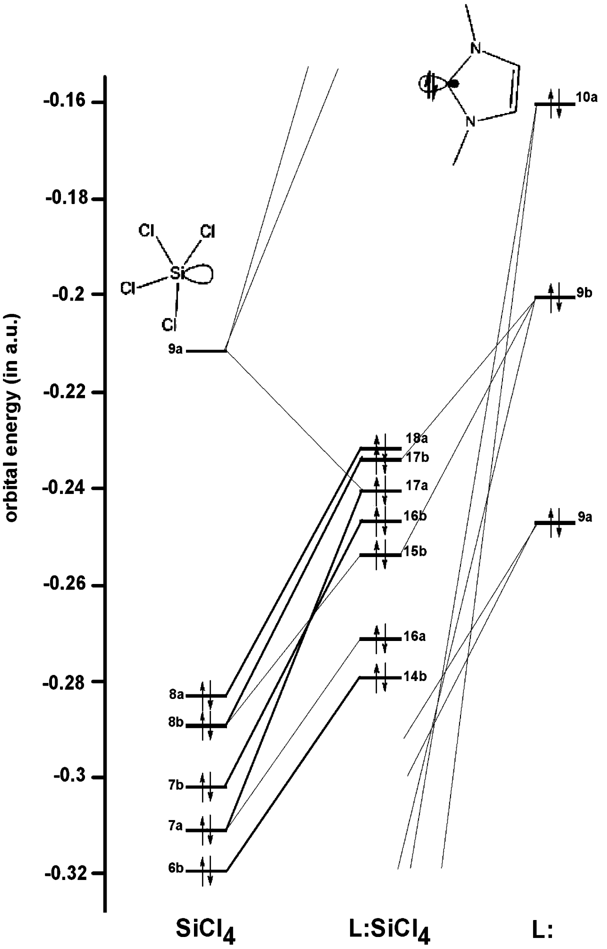

Figure 2. Orbital correlation diagram built from [$SiCl_4$] and [L:]. Only some important outer orbitals are shown. The thickness of the diagonal lines are in direct proportion with the percentage of the fragment orbitals in the [L:$SiCl_4$] orbitals.

in the complex. The latter quantity will be the focus of the present work. The interaction energy, ΔE_{int}, can be divided into three main components (eq 2)

$$\Delta E_{\mathrm{int}} = \Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{Pauli}} + \Delta E_{\mathrm{orb}} \tag{2}$$

$\Delta E_{\mathrm{elstat}}$ gives the electrostatic interaction energy between the fragments, which is calculated with a frozen electron density distribution in the geometry of the complex. $\Delta E_{\mathrm{Pauli}}$ gives the repulsive interaction energy between the fragments, which is caused by the fact that two electrons with the same spin cannot occupy the same region in space. ΔE_{orb} accounts for the stabilizing orbital interaction energy as a result of the interatomic orbital overlapping. Details about the EDA method are described in the literature.[6,8]

3. Results and Discussion

3.1. Fragment Orbital Analysis. ***Fragment Orbital Analysis for 1-Me Built from [$SiCl_4$] and [:$C(CHNCH_3)_2$].*** The orbital interactions between the L: and $SiCl_4$ fragments are displayed in Figure 2. The geometries of the two fragments are from the optimized structure of 1-Me at C_2 symmetry.[1] Figure 2 gives the orbital interactions with *a* and *b* symmetry contribute to the stabilizing orbital interaction term. The occupied 10a (HOMO) of the L: fragment and the virtual 9a (LUMO) of the $SiCl_4$ fragment are mainly the carbene lone-pair orbital and the Si sp hybrid orbital in character, respectively. However, the fragment orbital analysis shows very weak donor−acceptor interactions between the two orbitals, as the orbital 17a, the only orbital of 1-Me coming from the mixing of the two fragment orbitals, 9a of $SiCl_4$ and 10a of L:, is mainly centered on the $SiCl_4$ chlorine atoms; there are only small contributions of 9a (18%) and 10a (4%). Hence it can reasonably be argued that the dominant contributions to the stabilization of complex 1-Me, which arises from the orbital interactions, do not come from closed shell donor−acceptor interactions depicted in the DCD model.

Fragment Orbital Analysis for 2-Me Built from [$C(CHNCH_3)_2(Cl)$:Si−Si(Cl)] and [:$C(CHNCH_3)_2$]. The bonding analysis was carried out for 2-Me to look at the interactions between one L: and the (Cl)Si−Si(Cl):L fragment. The results give insight into the factors related to the bonding situation of the Si−C_{carbene} bond. The orbital interactions between the L: and the (Cl)Si−Si(Cl):L fragments are displayed in Figure 3. The geometries of the two fragments are from the optimized structure of 2-Me at C_2 symmetry.[1] Figure 3 gives the orbital interactions with only *a* symmetry contribute to the stabilizing orbital interaction term. The occupied 19a (HOMO) of the L: fragment and the virtual 31a (LUMO) of the (Cl)Si−Si(Cl):L fragment are mainly the carbene lone-pair orbital and the Si p

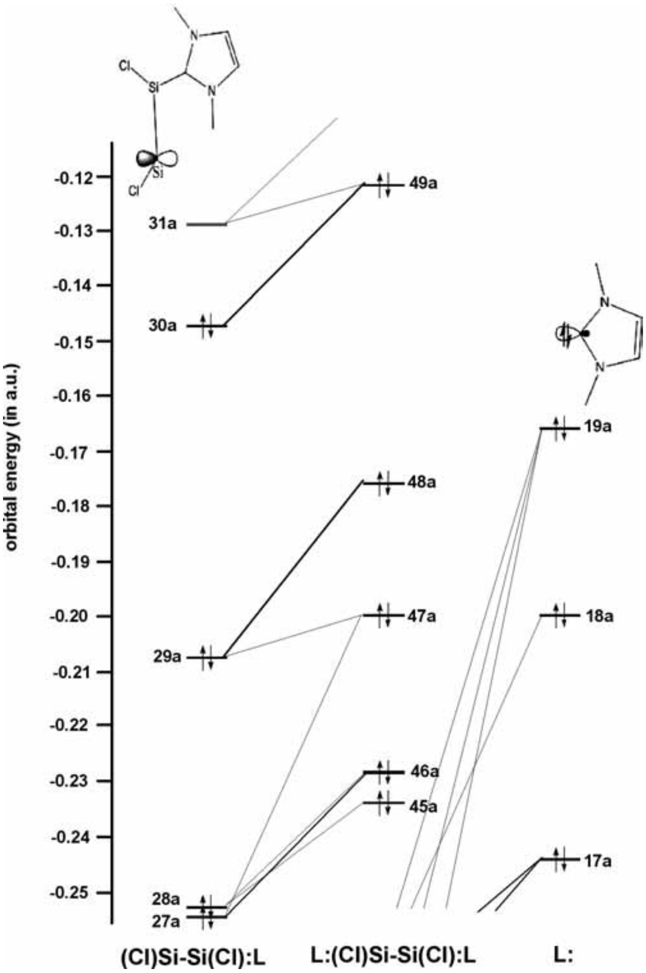

Figure 3. Orbital correlation diagram built from [(Cl)Si−Si(Cl):L] and [L:]. Only some important outer orbitals are shown. The thickness of the diagonal lines are in direct proportion with the percentage of the fragment orbitals in the [L:(Cl)Si−Si(Cl):L] orbitals.

orbital in character, respectively. It becomes immediately obvious that the (Cl)Si−Si(Cl):L fragment is a much worse σ acceptor than the [$SiCl_4$], because it has an empty high lying 31a orbital which is mainly a Si p AO. The fragment orbital analysis shows that the occupied orbitals 47a and 48a of 2-Me contain very small contributions from mixing of the two orbitals; 19a of L: and 31a of (Cl)Si−Si(Cl):L contribute 6 and 9% to the 47a, and 3 and 5% to the 48a. Likewise, it can be argued that the dominant contributions to the stabilization of complex 2-Me, which arises from the orbital interactions, do not come from closed shell donor−acceptor interactions depicted in the DCD model.

Fragment Orbital Analysis for 3-Me Built from [$C(CHNCH_3)_2$:Si=Si] and [:$C(CHNCH_3)_2$]. To analyze the factors related to the bonding situation of the Si−$C_{carbene}$ bond in 3-Me, the bonding analysis was carried out to look at the interactions between one L: and the Si=Si:L fragment, the same computation procedure as in 2-Me. The orbital interactions between the L: and the Si=Si:L fragments are displayed in Figure 4. The geometries of the two fragments are from the optimized structure of 3-Me at C_i symmetry.[1] Figure 4 gives the orbital interactions with only a symmetry contribute to the stabilizing orbital interaction term. The occupied 19a (HOMO) of the L: fragment and the virtual 24a (LUMO) of the Si=Si:L fragment are mainly the carbene lone-pair orbital and the Si p orbital in character, respectively. Like 2-Me, the Si=Si:L fragment should not be a good σ acceptor, because it has an empty high-lying 24a orbital that is mainly a Si p AO. The fragment orbital analysis shows that the occupied orbitals 32a, 37a, 39a, and 40a of 3-Me contain small contributions from mixing of the two orbitals; 19a of L: and 24a of Si=Si:L contribute 21 and 2% to the 32a, 8 and 3% to the 37a, 11 and 10% to the 39a, and 4 and 3% to the 40a. The donor−acceptor interactions are stronger in 3-Me than in the other two complexes, 1-Me and 2-Me. However, this comparison is somewhat misleading, as the orbital overlap ⟨19a|24a⟩ of 3-Me is negative, an antibonding interaction; the corresponding orbital overlap ⟨10a|9a⟩ of 1-Me is the largest (see Table 1). The contributions of the stabilizing orbital interaction arise from the sum of all orbital interactions with appropriate symmetry, and it can reasonably be argued that the dominant contributions do not come from closed shell donor−acceptor interactions depicted in the DCD model for all the three complexes, 1-Me, 2-Me, and 3-Me.

3.2. Energy Decomposition Analysis. Fragment orbital analysis shows that the donor−acceptor description is not valid for these complexes. To gain a deeper insight into the nature of the Si−$C_{carbene}$ bond, we have performed an energy decomposition analysis (EDA) of the Si−$C_{carbene}$ bond interaction energy (ΔE_{int}) which come not only from orbital interactions but also from electrostatic bonding. Table 1 shows the results of the partitioning of the interaction energies, E_{int} (Si−$C_{carbene}$), into the three terms, ΔE_{Pauli}, ΔE_{elstat}, and ΔE_{orb}. The calculated absolute values of ΔE_{elstat} and ΔE_{orb} are always higher than the bonding energy, ΔE_{int}. Only one attractive term, either ΔE_{elstat} or ΔE_{orb}, would not

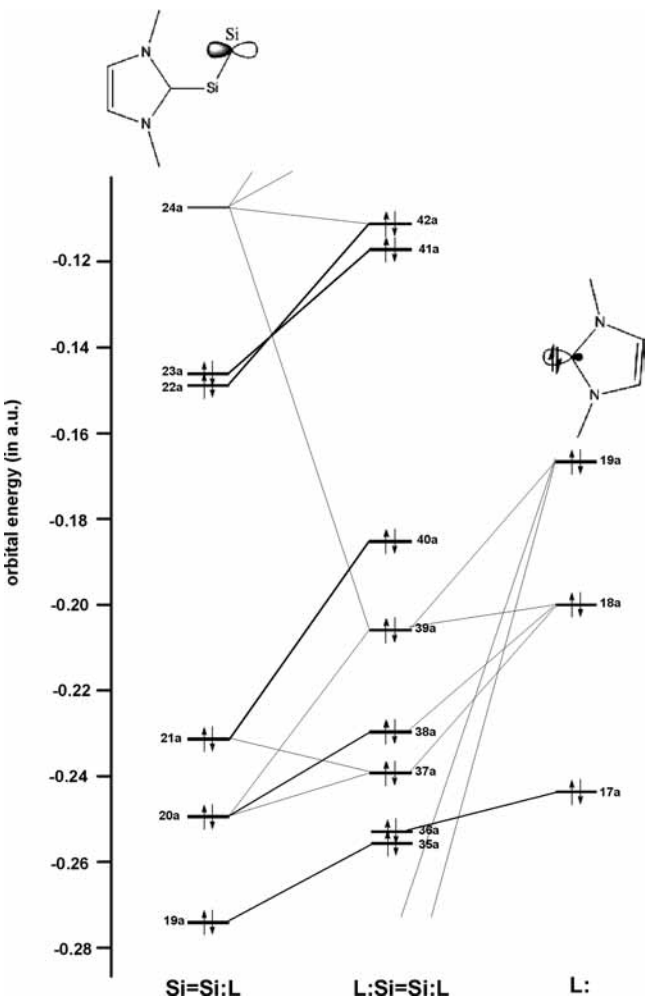

Figure 4. Orbital correlation diagram built from [Si═Si:L] and [L:]. Only some important outer orbitals are shown. The thickness of the diagonal lines are in direct proportion with the percentage of the fragment orbitals in the [L:Si═Si:L] orbitals.

TABLE 1: Energy Decomposition Analysis at BP86/TZ2P of the Si−$C_{carbene}$ Bond in the Complexes 1-Me, 2-Me, and 3-Me (All Energies in kcal/mol)

	L:SiCl4 (1-Me)	L:(Cl)Si−Si(Cl):L (2-Me)	L:Si═Si:L (3-Me)
ΔE_{int}	−68.64	−46.03	−44.77
ΔE_{Pauli}	237.19	230.21	212.50
ΔE_{elstat}[a]	−170.51 (55.8%)	−152.40 (55.2%)	−143.63 (55.8%)
ΔE_{orb}[a]	−135.32 (44.2%)	−123.84 (44.8%)	−113.64 (44.2%)
Δa (σ)	−118.39	−123.84	−113.64
Δb (σ)	−16.93		
orbital overlap	⟨10a|9a⟩ 0.390	⟨19a|31a⟩ 0.371	⟨19a|24a⟩ −0.374

[a] The value in parentheses gives the percentage contribution to the total attractive interactions ($\Delta E_{elstat} + \Delta E_{orb}$).

lead to Si−$C_{carbene}$ bonding between the fragments. A reasonable consideration of all three terms results in the conclusion that the ionic contribution, the covalent contribution, and the Pauli repulsion leads to a net bonding which is <0.3($\Delta E_{elstat} + \Delta E_{orb}$). Table 1 shows that, for all the three complexes, 1-Me, 2-Me, and 3-Me, it holds that $\Delta E_{elstat} < \Delta E_{orb}$, i.e., the electrostatic bonding given by ΔE_{elstat} is larger than the covalent bonding given by ΔE_{orb}. The EDA results suggest that the Si−$C_{carbene}$ bonding in 1-Me, 2-Me, and 3-Me have more electrostatic than covalent character. The contributions of the ΔE_{orb} term to the total attractive interactions are 44.2% for 1-Me, 44.8% for 2-Me, and 44.2% for 3-Me. The covalent bonding comes completely from the σ orbitals. It does not follow that the stabilizing orbital interactions are given by Si ← $C_{carbene}$ σ-donation and the Si → $C_{carbene}$ π-back-donation. We want to point out that the total attractive interactions in 1-Me ($\Delta E_{int} = -68.64$ kcal/mol) are much stronger than in 2-Me ($\Delta E_{int} = -46.03$ kcal/mol) and 3-Me ($\Delta E_{int} = -44.77$ kcal/mol). The stronger net attraction comes mainly from the significantly stronger electrostatic interaction in 1-Me than in 2-Me and 3-Me. This is because there are four chlorine atoms to attract electrons toward themselves in the covalent Si−C bonds of the fragment $SiCl_4$ in 1-Me, which strengthen the electrostatic interaction between the $SiCl_4$ and the nucleophilic carbene fragment in 1-Me. It can be concluded that, without the stabilizing contribution of ΔE_{elstat}, 1-Me, 2-Me, and 3-Me would not be stable complexes. Even the molecules, which are usually considered as covalently bonded, like N_2 and O_2, would not be bonded without the attraction that comes from the ΔE_{elstat} term.[11] It is worth also pointing out that the solid lines that connect the parent carbene orbitals with the MOs of 1-Me, 2-Me, and 3-Me are all downward, whereas those that connect the parent orbitals of the silicic fragments with the MOs of 1-Me, 2-Me, and 3-Me are all upward (see Figures 2−4). 1-Me, 2-Me, and 3-Me should therefore be best described as stabilized carbene complexes rather than carbene-stabilized complexes. Moreover, the orbital interactions between the silicic and carbene fragments are seem to be of the pattern of the energy raising of metal d-orbitals in a spherical ligand field in the crystal field theory, which says that the interaction between a transition metal and ligands arises from the attraction between the positively charged metal cation and negative charge on the nonbonding electrons of the ligands. It gives a coherent picture of the bonding interactions, viz., the electrostatic attraction (ΔE_{elstat}) plays an important or even dominant role for the interatomic attraction in the stable silicon complexes and it is the interplay of all the three terms ΔE_{orb}, ΔE_{Pauli}, and ΔE_{elstat} that determines the bond situations in 1-Me, 2-Me, and 3-Me.

4. Conclusions

The nature of the Si−$C_{carbene}$ bonds in the 1-Me, 2-Me, and 3-Me complexes that serve as model compounds for the recently synthesized silicon−carbene complexes is very different from the qualitatively assumed models such as the popular DCD model of Si ← $C_{carbene}$ σ-donation and the Si → $C_{carbene}$ π-back-donation. Inspection of the orbital correlation diagrams shows that the dominant contributions to the stabilization of all the three complexes, which arise from the orbital interactions, come not from donor−acceptor interactions depicted in the DCD model. The electrostatic attraction and the Pauli repulsion must be considered for a true understanding of the chemical bonding. The energy decomposition analysis indicates that for the silicon−carbene complexes, the carbenes are more electrostatically than covalently bonded to the silicon fragments. The electrostatic term ΔE_{elstat} contributes more than 50% to the attractive interactions. Thus, according to the EDA model, the binding interactions have a significant ionic component. The features of the orbital correlation diagrams indicate that the silicon−carbene complexes, L:$SiCl_4$, L:(Cl)Si−Si(Cl):L, and L:Si═Si:L, are better described as stabilized carbene complexes.

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