Angewandte
International Edition Chemie

Silacarbon Complexes

International Edition: DOI: 10.1002/anie.201502450
German Edition: DOI: 10.1002/ange.201502450

Stabilization of Heterodiatomic SiC Through Ligand Donation: Theoretical Investigation of $SiC(L)_2$ ($L = NHC^{Me}$, $CAAC^{Me}$, PMe_3)**

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Abstract: *Quantum chemical calculations have been carried out at the BP86/TZ2P+ level for the compounds $SiC(L)_2$ with $L = NHC^{Me}$, $CAAC^{Me}$, PMe_3 (NHC = N-heterocyclic carbene, CAAC = cyclic (alkyl)aminocarbene). The optimized geometries exhibit a trans arrangement of the ligands L at SiC with a planar coordination when $L = NHC^{Me}$ and PMe_3, while a twisted conformation is calculated when $L = CAAC^{Me}$. The bending angle L-Si-C is significantly more acute than the angle L-C-Si. Both angles become wider with the trend $PMe_3 < NHC^{Me} < CAAC^{Me}$. The latter trend is also found for the bond dissociation energies of the reaction $SiC(L)_2 \rightarrow SiC + 2\,L$, which have absolute values between $D_e = 98$–$163\ \mathrm{kcal\,mol^{-1}}$. Calculations suggest that the compounds $SiC(L)_2$ have a very large first and second proton affinity, which takes place at the central carbon and silicon atoms, respectively. Energy decomposition analyses indicate that the best description of the bonding situation in $SiC(L)_2$ features a cumulenic carbon–carbon bond and a dative carbon–silicon bond $L{=}C{=}Si\leftarrow L$ at the center.*

The chemistry of low-valent main-group elements experienced significant progress in recent years by employing σ-donor ligands (L) such as phosphines (PR_3), N-heterocyclic carbenes (NHC), and cyclic (alkyl)aminocarbenes (CAAC) as stabilizing agents.[1] The variety of ligands available nowadays and their tunable chemical features, such as σ-donor and π-acceptor character and singlet–triplet gap, have proven to be tremendously useful to achieve synthetic accomplishments. Experimental work on isolated molecules includes numerous examples where monoatomic and homodiatomic species are stabilized in complexes $L\rightarrow E_n\leftarrow L$ ($n = 1, 2$), where E_n is C_1,[2] Si_1,[3] Ge_1,[4] B_2,[5] C_2,[6] Si_2,[7] Ge_2,[8] Sn_2,[9] P_2,[10] and As_2.[11] A recent theoretical study of triphenylphosphinazine, which was originally sketched with the formula $Ph_3P{=}N{-}N{=}PPh_3$,[12] showed that it is better described as a complex $Ph_3P\rightarrow N_2\leftarrow PPh_3$ where the N_2 fragment is in the highly excited $^1\Gamma_g$ state.[13] There is only one example where a heterodiatomic molecule, namely PN, has been stabilized in the complex $NHC^{Dipp}\rightarrow PN\leftarrow CAAC^{Dipp}$ (Dipp = 2,6-diisopropylphenyl).[14] Many studies featured joint theoretical and experimental efforts, and the synthesis of some compounds was facilitated by preceding quantum chemical calculations. Examples are the carbodicarbenes $C(NHC)_2$,[2,15] the silylones SiL_2[3,16] and germylones GeL_2,[4,16b,c] and the first molecule with a boron–boron triple bond $B_2(NHC)_2$.[5,17]

Herein, we report quantum chemical calculations[18] of the heterodiatomic species SiC being stabilized by ligands $SiC(L)_2$ with $L = NHC^{Me}$, $CAAC^{Me}$, PMe_3, where Me denotes methyl substituents at the nitrogen atom(s). The homodiatomic disilicon has been isolated in the pioneering work of Robinson, who reported the synthesis of $Si_2(NHC^R)_2$ in 2008, where R denotes a bulky group.[7a] The related complex $Si_2(CAAC^R)_2$ was recently prepared.[7b] Both disilicon complexes $L\rightarrow Si_2\leftarrow L$ possess a geometry with an antiperiplanar arrangement of the carbene ligands with acute Si-Si-C angles of 93.4° ($L = NHC^R$) and between 101.2–105.1° ($L = CAAC^R$).[7] The structure and bonding situation in the disilicon complexes $Si_2(L)_2$ ($L = NHC^{Me}$, $CAAC^{Me}$) have been rationalized in terms of donor–acceptor interactions between Si_2 in the excited $^1\Delta_g$ states and the donor ligands L.[19] Calculations predicted that the dicarbon complex $C_2(NHC^{Me})_2$ has a nearly linear structure with C-C-C(NHC^{Me}) angles of 172.4°, which suggests a cumulenic bonding situation.[20] The phosphine-stabilized complex $C_2(PMe_3)_2$ was predicted to possess more acute bond angles C-C-PMe_3 of 116.2°. Experimental efforts to synthesize $C_2(NHC^R)_2$ failed,[21] but the related complex $C_2(CAAC^R)_2$ has recently been isolated by two groups.[6] The latter compound has also a nearly linear arrangement of the ligands at the central C_2 moiety where the C-C-C($CAAC^R$) bond angles were reported with 177.7° and 178.9°. A detailed bonding analysis of $C_2(NHC^{Me})_2$ and $C_2(CAAC^{Me})_2$ suggested that the compounds are well represented in terms of donor–acceptor interactions $L\rightarrow C_2\leftarrow L$ where C_2 is in the excited $^1\Delta_g$ state.[21] This explains the deviation from a perfectly linear geometry, which is expected from a genuine cumulene.

We report the theoretically predicted equilibrium structure of the compounds $SiC(L)_2$ with $L = NHC^{Me}$, $CAAC^{Me}$, PMe_3. The bare SiC molecule has only been observed in the gas phase, where it was spectroscopically identified for the first time in 1988.[22] Experimental and theoretical studies show that SiC has a $X^3\Pi$ electronic ground state.[22–24] High-level ab initio calculations suggest that the two lowest-lying electronic states are $A^3\Sigma^-$ ($T_e = 11.1\ \mathrm{kcal\,mol^{-1}}$) and $a^1\Sigma^+$ ($T_e = 14.2\ \mathrm{kcal\,mol^{-1}}$).[24] We also calculated the proton affinities of the molecules $SiC(L)_2$, which are important for experimental attempts to synthesize the molecules from

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[**] This work was financially supported by the Deutsche Forschungsgemeinschaft. D.M.A. acknowledges a postdoctoral fellowship from the DAAD (Deutscher Akademischer Austauschdienst).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201502450.

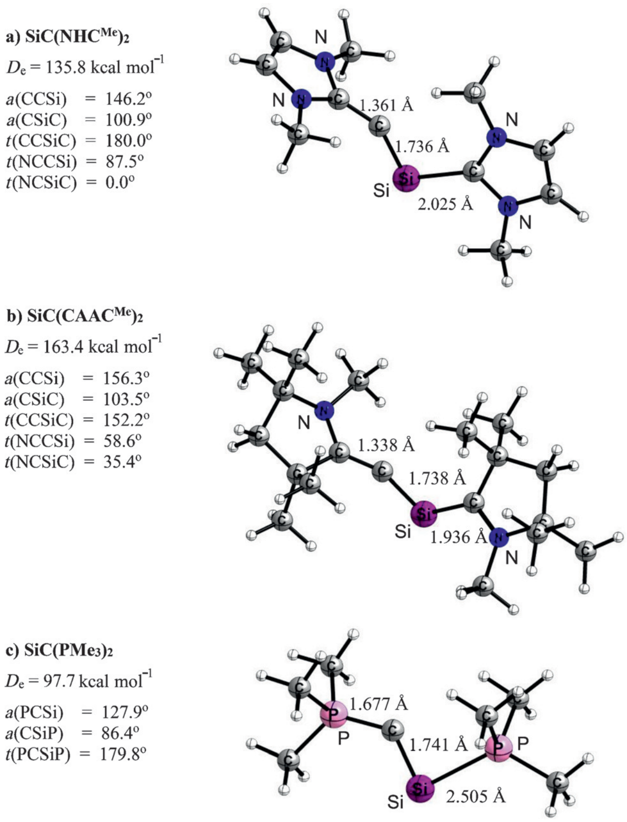

Figure 1. Optimized geometries (BP86/def2-TZVPP) and dissociation energies at (BP86/TZ2P+//BP86/def2-TZVPP) of $SiC(NHC^{Me})_2$, $SiC(CAAC^{Me})_2$, and $SiC(PMe_3)_2$.

protonated precursors. We further present a thorough bonding analysis of the electronic structure of the molecules. The results may serve as a guideline for experimental studies.

Figure 1 shows the optimized geometries of the three species $SiC(L)_2$. The calculated Si–C distances in the compounds are only slightly longer than in free $X^3\Pi$ SiC (1.730 Å). In all three molecules, the Si-bonded ligand has a very acute angle C-Si-L of between 86.4° ($L=PMe_3$) and 103.5° ($L=CAAC^{Me}$). In contrast, the C-bonded ligand exhibits a significantly larger angle Si-C-L between 127.9° ($L=PMe_3$) and 156.3° ($L=CAAC^{Me}$). The L–Si distances in $SiC(L)_2$ are clearly longer than in the disilicon complexes $Si_2(L)_2$ (Supporting Information, Table S2). The L–C bond lengths in $SiC(L)_2$ have similar values as in $C_2(L)_2$ for $L=NHC^{Me}$ and $CAAC^{Me}$ but they are clearly shorter in the former molecule when $L=PMe_3$. The calculated values for the Si–L bonds in $Si_2(L)_2$ at the same level of theory (BP86/def2-TZVPP) are 1.931 Å ($L=NHC^{Me}$), 1.880 Å ($L=CAAC^{Me}$), and 2.310 Å ($L=PMe_3$). The theoretical values for the C–L bond distances in $C_2(L)_2$ are 1.348 Å ($L=NHC^{Me}$), 1.339 Å ($L=CAAC^{Me}$) and 1.753 Å ($L=PMe_3$).

It is interesting that the plane of the NHC ligand which is bonded to the carbon end in $SiC(NHC^{Me})_2$ is nearly perpendicular to the C-C-Si plane ($t(NCCSi)=87.5°$) while the Si bonded NHC^{Me} ligand is in the C-Si-C plane ($t(NCSiC)=0.0°$). This suggests a very different orbital interaction of the two NHC^{Me} ligands with respect to the SiC moiety. The Both $CAAC^{Me}$ ligands in $SiC(CAAC^{Me})_2$ are twisted with regard to the C-C-Si and C-Si-C plane. The torsion angles are $t(NCCSi)=58.6°$ for the C-bonded ligand and $t(NCSiC)=35.4°$ for the Si-bonded ligand. Note that the torsion angle $t(CCSiC)=152.2°$ significantly deviates from the planar value of 180° which is found in $C(NHC^{Me})_2$. The twisting could come from the stronger steric interactions in the more crowded $SiC(CAAC^{Me})_2$ molecule. Figure 1 gives also the bond dissociation energies (BDEs) for the two bonds between SiC and L which exhibit the order $CAAC^{Me}$ ($D_e=163.4$ kcal mol⁻¹) > NHC^{Me} ($D_e=135.8$ kcal mol⁻¹) > PMe_3 ($D_e=97.7$ kcal mol⁻¹). The same order was found in previous theoretical studies of $Si_2(L)_2$ and $C_2(L)_2$.[19,20]

It has been reported that the dicarbon systems $C_2(NHC^R)_2$ and $C_2(CAAC^R)_2$ possess a very high basicity and that the molecules readily uptake one and two protons.[21] This is likely the reason why experimental attempts to isolate $C_2(NHC^R)_2$ via deprotonation of $[C_2H_2(NHC^R)_2]^{2+}$ have not been successful while the less basic homologue $C_2(CAAC^R)_2$ could be obtained from its protonated precursor.[6] Calculations predict that the first and second proton affinities (PAs) of $C_2(CAAC^{Me})_2$ (first PA = 285 kcal mol⁻¹; second PA = 269 kcal mol⁻¹) are clearly lower than for $C_2(NHC^{Me})_2$ (first PA = 313 kcal mol⁻¹; second PA = 290 kcal mol⁻¹).[21] We calculated the first and second PAs of $SiC(L)_2$. Table 1 shows the numerical results. The optimized geometries of the cations $[SiCH(L)_2]^+$ and the dications $[SiCH_2(L)_2]^{2+}$ are shown in Supporting Information, Figure S10. The calculations suggest that the first protonation occurs at the carbon atom of the CSi moiety while the second proton binds to Si. Comparative calculations showed that the protonation at nitrogen is energetically less favourable. The calculated first PA of $SiC(NHC^{Me})_2$ (292.6 kcal mol⁻¹) is clearly smaller than the first PA of $C_2(NHC^{Me})_2$ while the first PA of $SiC(CAAC^{Me})_2$ (283.2 kcal mol⁻¹) is slightly less than the first PA of $C_2(CAAC^{Me})_2$. The calculated data suggest that neutral $SiC(CAAC^{Me})_2$ and perhaps even $SiC(NHC^{Me})_2$ might be isolated through deprotonation of suitable precursor molecules.

Table 1: Calculated first and second proton affinities PA at BP86/def2-TZVPP.[a]

	PA1 (C)	PA1 (Si)	PA2
$SiC(NHC^{Me})_2$	292.6	268.5	169.4
$SiC(CAAC^{Me})_2$	283.2	267.0	169.0
$SiC(PMe_3)_2$	283.5	255.2	154.8

[a] Energy values are given in kcal mol⁻¹.

We analyzed the electronic structure of $SiC(L)_2$ to shed light on the bonding situation in the compounds. We first inspected the highest-lying occupied molecular orbitals (HOMOs) and the lowest-lying unoccupied orbital (LUMO) of the molecules. Figure 2 shows that the HOMO, HOMO−1, and HOMO−2 of $SiC(L)_2$ have very similar shapes, which suggests that the nature of the bonding between SiC and the ligands NHC^{Me}, $CAAC^{Me}$, and PMe_3 is very similar to each other. The HOMO−1 is clearly a Si–C π-bonding MO that extends very little to the ligands. The

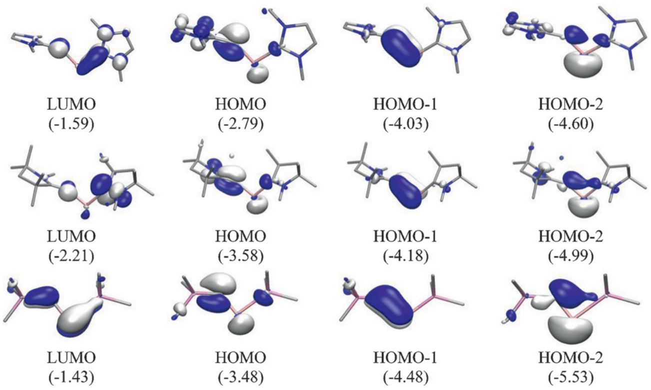

Figure 2. Plot of the LUMO and the three highest-lying occupied MOs of (top row) $SiC(NHC^{Me})_2$, (middle row) $SiC(CAAC^{Me})_2$, and (bottom row) $SiC(PMe_3)_2$. Orbital eigenvalues are given in eV.

HOMO−2 is essentially a silicon lone-pair MO where the inside lobe has some overlap with the next neighbor atoms. The HOMO has its largest extension at the carbon atom of the SiC moiety with some bonding overlap towards the ligand and a small lone-pair type appendix at Si. It has σ symmetry when the L-C-Si-L plane is taken as reference plane.

Table 2 shows some relevant atomic partial charges from NBO calculations and Wiberg bond order for bare SiC and the complexes $SiC(L)_2$. The positive charge at Si changes only slightly in the complexes but the carbon atom of the SiC acceptor fragment in $SiC(L)_2$ possesses a clearly higher negative charge than in SiC, particularly in the phosphine complex. The bond orders P(C–L) suggest a significant double-bond character, which increases for the ligands L in the order $PMe_3 < NHC^{Me} < CAAC^{Me}$. The latter trend may come from increasing π-back-donation L←CSi-L, which agrees with the partial charges q(C). The bond orders for the Si−L bonds suggest that they are single bonds with little π-bonding. The bond order for the C−Si bond becomes smaller in the complexes where it exhibits a rather uniform value between 1.54–1.57, which suggests that the net charge transfer which comes from σ donation and π back-donation is roughly the same.

Table 2: Calculated NBO partial charges q and Wiberg bond orders P at BP86/def2-TZVPP.

	q(C)	q(Si)	P(C–Si)	P(C–L)	P(Si–L)
CSi($c^1\Delta$)	−0.53	+0.53	1.86		
$[(NHC)_2SiC]$	−0.94	+0.48	1.56	1.56	0.71
$[(CAAC)_2SiC]$	−0.71	+0.58	1.54	1.75	0.92
$[(PMe_3)_2SiC]$	−1.56	+0.49	1.57	1.33	0.57

A more detailed insight into the bonding interactions between SiC and the ligands L is given by EDA (energy decomposition analysis)[25] calculations in conjunction with the NOCV (natural orbitals for chemical vacancy)[26] method. Details about the method and recent examples have been reported.[13,27] A crucial factor for the EDA-NOCV results is the choice of the interacting fragments. Figure 3 shows the MO diagram for the $X^3\Pi$ ground state and the $a^1\Sigma^+$ and $c^1\Delta$ state of SiC which are the lowest-lying singlet state that are suitable for charge donation from the ligands L→SiC←L.[28] The $a^1\Sigma^+$ state has vacant 3σ and $1\pi_g$ orbitals for admitting charge while the lowest lying acceptor orbitals in the $c^1\Delta$ state are $1\pi_u$ and $1\pi_g$. The latter state appears best for acute bonding angles which require vacant π orbitals at SiC for donor–acceptor interactions while the $a^1\Sigma^+$ state seems more appropriate when one electron pair is donated in a σ orbital and one in a π orbital.

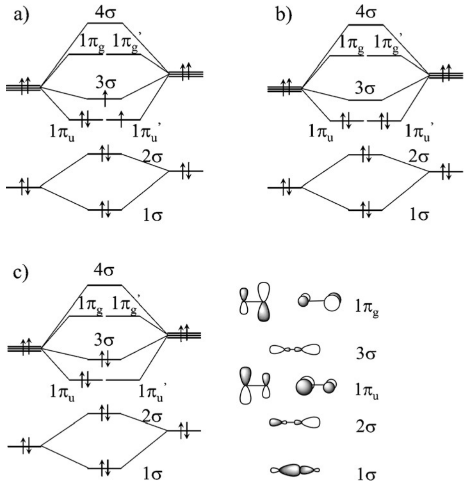

Figure 3. MO diagram of SiC in the a) $X^3\Pi$ ground state; b) $a^1\Sigma^+$ excited state; c) $c^1\Delta$ excited state. The size of the lobes qualitatively indicates the relative weight of the C and Si AO contributions.

We carried out EDA-NOCV calculations for the donor–acceptor interactions in $SiC(L)_2$ between the ligands L and SiC in two electronic states $a^1\Sigma^+$ and $c^1\Delta$. The numerical results are shown in Table 3. Inspection of the energy terms suggests that the $a^1\Sigma^+$ state of SiC is the appropriate reference state for the donor–acceptor interactions L→SiC←L for L = NHC^{Me} and $CAAC^{Me}$, while the $c^1\Delta$ state is more suitable for L = PMe_3. This becomes obvious from the absolute value of the ΔE_{orb} term which is a measure for the change in the electronic structure of the molecules upon bond formation.[15b] The smaller ΔE_{orb} values for $SiC(NHC^{Me})_2$ ($-572.7\,kcal\,mol^{-1}$) and $SiC(CAAC^{Me})_2$ ($-621.8\,kcal\,mol^{-1}$) appear with the $a^1\Sigma^+$ state of SiC while a smaller ΔE_{orb} value for $SiC(PMe_3)_2$ ($-408.7\,kcal\,mol^{-1}$) is found when the $c^1\Delta$ state is used. Irrespective of the electronic reference state of the SiC fragment, the intrinsic interaction energies ΔE_{int} between the frozen fragments exhibit the stability order $PMe_3 < NHC^{Me} < CAAC^{Me}$, which has the same trend as the bond dissociation energies D_e.

The breakdown of the ΔE_{orb} term into the most important pairwise interactions (Table 3) shows that the contribution of the L←SiC→L π-back-donation is rather small. This appears to be in conflict with the significant double bond character that is suggested by the bond orders P(L–C) in Table 2. Inspection of the four most important pairwise contributions to ΔE_{orb} shows that the EDA-NOCV results actually agree with the bond orders and that they provide a very detailed insight into the orbital interactions. Figure 4 displays the

Table 3: EDA-NOCV results of the donor–acceptor interaction of $[(L)_2SiC]$ (L = NHC^{Me}, $cAAC^{Me}$, PMe_3) at the BP86/TZ2P+ level of theory.[a]

	$c^1\Delta$			$a^1\Sigma^+$		
	NHC^{Me}	$cAAC^{Me}$	PMe_3	NHC^{Me}	$cAAC^{Me}$	PMe_3
ΔE_{int}	−182.0	−220.1	−140.4	−168.8	−207.2	−127.9
ΔE_{Pauli}	990.6	1187.9	565.1	787.6	831.8	613.2
ΔE_{elstat}[b]	−460.4 (39.3 %)	−538.9 (38.3 %)	−296.7 (42.1 %)	−383.7 (40.1 %)	−417.2 (40.2 %)	−301.7 (40.7 %)
ΔE_{orb}[b]	−712.2 (60.7 %)	−869.1 (61.7 %)	−408.7 (57.9 %)	−572.7 (59.9 %)	−621.8 (59.8 %)	−439.4 (59.3 %)
ΔE_1 $L\rightarrow SiC\leftarrow L$ (+,−) σ donation[c]	−541.6 (76.0 %)	−648.7 (74.6 %)	−297.1 (72.7 %)	−350.7 (61.2 %)	−354.7 (57.0 %)	−302.4 (68.8 %)
ΔE_2 $L\rightarrow SiC\leftarrow L$ (+,+) σ donation[c]	−72.5 (10.2 %)	−103.3 (11.9 %)	−47.4 (11.6 %)	−144.9 (25.3 %)	−165.8 (26.7 %)	−87.9 (20.0 %)
ΔE_3 $L\leftarrow SiC\rightarrow L$ $\pi_\perp$ back-donation[c]	−52.3 (7.3 %)	−54.0 (6.2 %)	−30.2 (7.4 %)	−20.0 (3.5 %)	−39.1 (6.3 %)	−21.3 (4.8 %)
ΔE_4 $L\leftarrow SiC\rightarrow L$ $\pi_\parallel$ back-donation[c]	−19.3 (2.7 %)	−28.8 (3.3 %)	−20.3 (5.0 %)	−22.2 (3.9 %)	−25.0 (4.0 %)	−9.5 (2.2 %)
ΔE_{rest}	−26.5 (3.7 %)	−34.3 (3.9 %)	−13.7 (3.3 %)	−34.9 (6.1 %)	−37.2 (6.0 %)	−18.3 (4.2 %)
$\Delta E_{prep\ CSi}$	38.8	38.6	38.4	25.6	25.7	25.9
$\Delta E_{prep\ L}$	7.4	18.1	4.3	7.4	18.1	4.3
$\Delta E_{prep\ total}$	46.2	56.7	42.7	33.0	43.8	30.2
$-D_e$	−135.8	−163.4	−97.7	−135.8	−163.4	−97.7

[a] Fragments are $(L)_2$ and SiC in the electronic states $c^1\Delta$ and $a^1\Sigma^+$. Energy values are given in kcal mol^{-1}. [b] The values in parentheses give the percentage contribution to the total attractive interactions $\Delta E_{elstat}+\Delta E_{orb}$. [c] The values in parentheses give the percentage contribution to the total orbital interactions ΔE_{orb}.

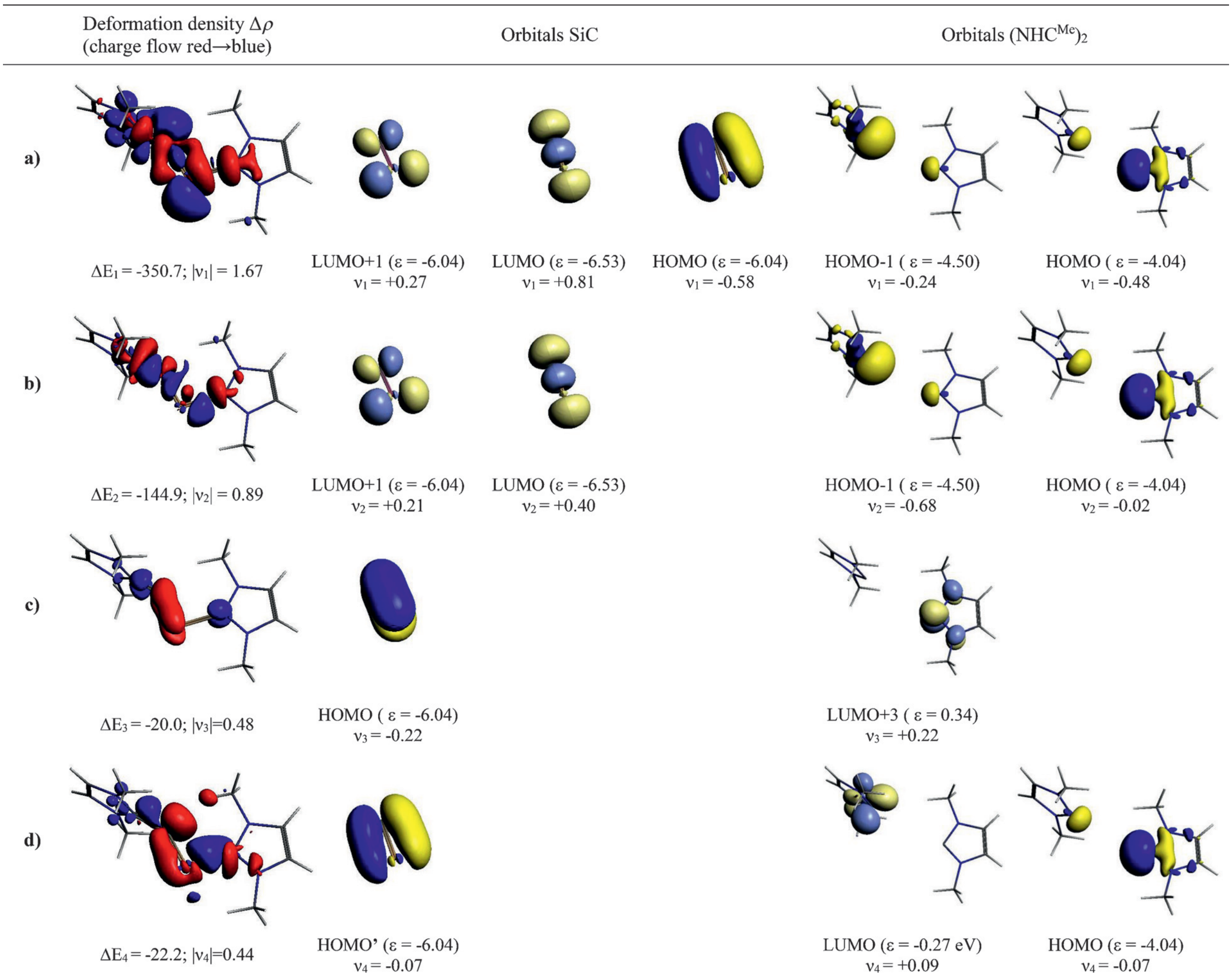

Figure 4. Plot of deformation densities Δρ of the pairwise orbital interactions in $CSi(NHC^{Me})_2$ between CSi in its $a^1\Sigma^+$ state and $(NHC^{Me})_2$ together with the associated interaction energies ΔE (in kcal mol^{-1}) and charge eigenvalues ν (in e). The charge flow is red→blue. Shape of the most important occupied and vacant orbitals and their energy eigenvalues ε (in eV) of the fragments. The charge eigenvalues ν give the amount of donated (negative numbers) and accepted electronic charge (positive numbers).

shape of the deformation densities $\Delta\rho_1-\Delta\rho_4$, which give the charge flow and the most important fragment orbitals which are involved in the pairwise donor–acceptor bonding for the complex $SiC(NHC^{Me})_2$. The results for the other systems

Table 4: EDA-NOCV results of the NHC^{Me}–Si and NHC^{Me}–C bonds of $SiC(NHC)_2$ at the BP86/TZ2P+ level of theory.[a]

	NHC^{Me} + $CSi(NHC^{Me})$		NHC^{Me} + $SiC(NHC^{Me})$	
	singlet	triplet	singlet	triplet
ΔE_{int}	−105.7	−196.6	−23.4	−175.7
ΔE_{Pauli}	930.7	333.5	227.0	168.0
ΔE_{elstat}[b]	−375.8 (36.4%)	−202.5 (38.2%)	−136.7 (55.6%)	−124.5 (36.2%)
ΔE_{orb}[b]	−655.7 (63.6%)	−327.6 (61.8%)	−109.2 (44.4%)	−219.3 (63.8%)
ΔE_{σ} σ-donation[c]	−579.3 (88.3%)	−133.0 (40.6%)	−84.7 (77.6%)	−171.9 (78.4%)
ΔE_{π} π-back-donation[c]	−54.4 (8.3%)	−157.7 (48.1%)	−5.5 (5.0%)	−31.0 (14.1%)
ΔE_{rest}	−22.0 (3.4%)	−36.9 (11.3%)	−19.0 (17.3%)	−16.4 (7.5%)

[a] Energy values are given in kcal mol^{-1}. [b] The values in parentheses give the percentage contribution to the total attractive interactions $\Delta E_{elstat}+\Delta E_{orb}$. [c] The values in parentheses give the percentage contribution to the total orbital interactions ΔE_{orb}.

$SiC(CAAC^{Me})_2$ and $SiC(PMe_3)_2$ are very similar (these are shown in the Supporting Information).

Figure 4a shows that the largest orbital interaction ΔE_1 (L→SiC←L (+,−) σ donation in Table 3) actually comes from a polarization of the in-plane orbitals of the SiC fragment, which involves an intrafragment charge transfer from the HOMO ($\nu_1 = -0.58$ e) to the LUMO ($\nu_1 = +0.81$ e). The donation that comes from the ligands comprises the out-of-phase (+,−) combination of the σ lone-pair orbitals of the NHC^{Me} ligands, which is the HOMO ($\nu_1 = -0.48$ e), and the weaker in-phase (+,+) donation, which comes from the HOMO−1 ($\nu_1 = -0.24$ e). Besides the LUMO of SiC there is also the antibonding orbital LUMO+1, which has π symmetry with respect to the free ligand, that serves as the acceptor orbital ($\nu_1 = +0.27$ e). Note that the symmetry assignments σ and π in Table 3 have been made with respect to the L-Si-C-L plane. The charge flow which is displayed by the associated deformation density $\Delta\rho_1$ (red→blue) shows that there is a strong donation from the NHC^{Me} ligand that is bonded to Si (right hand side) and a weaker donation NHC^{Me}→C (left hand side) that is coupled to a charge reorganization mainly in the SiC moiety. The shape of $\Delta\rho_1$ shows well the formation of σ-type electronic charge at the carbon and silicon atoms of SiC.

The remaining three pairs of orbital interactions can straightforwardly be explained in an analogous way. Figure 4b shows that the next strongest orbital interaction ΔE_2 (L→SiC←L (+,+) σ donation in Table 3) comes mainly from the donation of the HOMO−1 of $(NHC^{Me})_2$ ($\nu_1 = -0.68$ e) and the charge intake of the LUMO ($\nu_1 = +0.40$ e) and LUMO+1 ($\nu_1 = +0.21$ e) of SiC. The much weaker orbital interactions ΔE_3 (L←SiC→L $\pi_\perp$ back-donation) and ΔE_4 (L←SiC→L $\pi_\parallel$ back-donation) come from the donation of the degenerate π HOMO of SiC into vacant orbital of $(NHC^{Me})_2$. The two ligands are in a twisted conformation and therefore the acceptor orbitals of the NHC^{Me} moiety, which is not in the chosen plane, is a mixture of several MOs the coefficients of which are smaller than the threshold that we have chosen for the display (0.05 e).

Is it reasonable and appropriate to present the compounds $SiC(L)_2$ with donor–acceptor bonds L←SiC→L?[29] We carried out separate EDA-NOCV of $SiC(NHC^{Me})_2$ where we separately analyzed the NHC^{Me}–$SiC(NHC^{Me})$ bond and the NHC^{Me}–$CSi(NHC^{Me})$ bond. The calculations were carried out with fragments in a singlet state, which are suitable for dative bonds, and with triplet fragments, which are appropriate for electron-sharing double bonds. The results are given in Table 4. It becomes obvious that the NHC^{Me}–$SiC(NHC^{Me})$ bond is better described through interactions between closed-shell fragments (dative bonds) while the NHC^{Me}–$CSi(NHC^{Me})$ bond is better represented by electron-sharing interactions. This comes from the relative strengths of the orbital interactions ΔE_{orb} between the singlet and triplet fragments. Thus, the EDA-NOCV calculations suggest that the bonding situation in $SiC(NHC^{Me})_2$ should be represented as NHC^{Me}→SiC=NHC^{Me}. Calculations for $SiC(CAAC^{Me})_2$ failed owing to convergence problems, but since the singlet–triplet gap of CAAC is smaller than for NHC[30] it is likely that the same bonding description is appropriate for this molecule. Calculations for $SiC(PMe_3)_2$ showed a similar situation as in $SiC(NHC^{Me})_2$, that is, the triplet fragments give smaller orbital interactions than the singlet fragments when the Me_3P–$CSi(PMe_3)$ bond is analyzed while the opposite order for triplet and singlet fragments is found for the Me_3P–$SiC(PMe_3)$ bond (Supporting Information, Table S6). Thus, the best description for the bonding situation of the molecules $SiC(L_2)$ is L→SiC=L.

The EDA-NOCV results in Table 4 suggest that the NHC^{Me}→$SiC(NHC^{Me})$ donor–acceptor bond is not very strong. The interaction energy ΔE_{int} is only −23.4 kcal mol^{-1}, while the (NHC^{Me})SiC=NHC^{Me} electron-sharing bond is much stronger. This explains the results that we obtained when we optimized the geometries of the species $SiC(L)_2$ with more bulkier substituents L = NHC^{Dipp}, $CAAC^{Dipp}$, and PPh_3. The equilibrium structures of the compounds $SiC(NHC^{Dipp})_2$ and $SiC(CAAC^{Dipp})_2$ have very similar bond lengths and slightly wider angles L-Si-C and Si-C-L than in $SiC(NHC^{Me})_2$ and $SiC(CAAC^{Me})_2$ and the ligands of the latter species are more twisted with respect to the central CCSiC moiety, which may be attributed to steric repulsion. Part of the differences may also come from the fact that, because of the computational costs, we used a smaller basis set for the larger compounds. The calculated geometries of $SiC(NHC^{Dipp})_2$ and $SiC(CAAC^{Dipp})_2$ are shown in the Supporting Information, Figure S11. In contrast, the geometry optimization of $SiC(PPh_3)_2$ gave a cleavage of the Ph_3P→$SiC(PPh_3)$ donor–acceptor bond. The calculation gave free PPh_3 and $SiC(PPh_3)$ as final result of the geometry optimization. We will explore this finding in more detail in a future study.

Keywords: bonding analysis · density functional calculations · donor–acceptor interactions · silacarbon complex

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 12319–12324
Angew. Chem. **2015**, *127*, 12494–12500

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Received: March 16, 2015
Revised: June 4, 2015
Published online: July 17, 2015