The Structure of the Carbene Stabilized Si$_2$H$_2$ May Be Equally Well Described with Coordinate Bonds as with Classical Double Bonds

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ⓢ Supporting Information

ABSTRACT: The cyclic alkyl(amino) carbene stabilized Si$_2$H$_2$ has been isolated in the molecular form of composition (Me-cAAC:)$_2$Si$_2$H$_2$ (**1**) and (Cy-cAAC:)$_2$Si$_2$H$_2$ (**2**) at room temperature. Compounds **1** and **2** were synthesized from the reduction of HSiCl$_3$ using 3 equiv of KC$_8$ in the presence of 1 equiv of Me-cAAC: and Cy-cAAC:, respectively. These are the first molecular examples of Si$_2$H$_2$ characterized by single crystal X-ray structural analysis. Moreover, electrospray ionization mass spectrometry and ^{1}H as well as ^{29}Si NMR data are reported. Furthermore, the structure of compound **1** has been investigated by theoretical methods. The theoretical analysis of **1** explains equally well its structure with coordinate bonds as with classical double bonds of a 2,3-disila-1,3-butadiene.

The search for stable molecules with triple bonds between the heavier group 14 atoms Si to Pb that are homologues of acetylene is a fascinating chapter of inorganic chemistry.[1] Substituted R−E≡E−R compounds with bulky R groups have been isolated and structurally characterized by Power et al. (E = Ge to Pb),[2] Sekiguchi et al.,[3a] and Wiberg et al.[3c] (E = Si). The parent E$_2$H$_2$ systems could only be prepared in low-temperature inert matrices.[4] They have been identified by comparing the experimental vibrational spectra and isotope effects with quantum chemical calculations. The experimental findings were in agreement with earlier theoretical predictions, which suggested that the geometries of E$_2$H$_2$ isomers (for E = Si to Pb) are very different from the linear structure of acetylene.[5] Chart 1 exhibits the theoretically predicted equilibrium geometries of the Si$_2$H$_2$. It was shown that the unusual
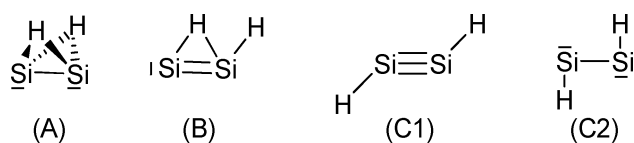
structures can be explained with the electronic state of the interacting EH fragments.[6] The carbyne CH binds through the excited $^4\Sigma^-$ state, while the heavier EH species bind through the $^2\Pi$ ground state.
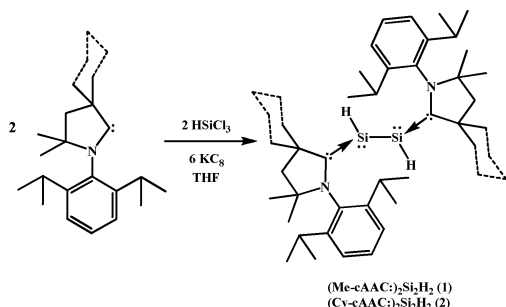
Moreover silicon hydrides are considered as existing species in the interstellar space.[7] The ultimate goal of synthetic efforts is the isolation of the silicon analogue of acetylene H−Si≡Si−H under ambient conditions, which could be achieved with the help of donor ligands (L) that stabilize highly reactive species. Numerous small molecules that are unstable as free species have been isolated in recent years substituted by ligands such as phosphanes and carbenes.[8−16] Especially N-heterocyclic carbenes (NHCs) and cAACs played an important role in the isolation of reactive silicon species.[15−17] Of particular interest for the present work are the compounds (Si$_2$Cl$_2$)-(NHC^{Dip})$_2$ and (Si$_2$Cl$_2$)(cAAC)$_2$ which were reported by Robinson et al.[8] and Roesky et al.[15] respectively. These compounds may be considered as chlorine derivatives of the sought-after disilaacetylene adducts. In addition, silicon hydride chemistry has always been an interesting topic of research and synthetic chemists have made attempts to design several silicon(II) hydrides, analogues to substituted unsaturated hydrocarbons.[18] There are few references about molecules containing silicon monohydrides,[19] but they are not representatives of Si$_2$H$_2$. Therefore, the synthesis of molecular Si$_2$H$_2$ with silicon monohydride as a building block was a challenge for synthetic chemists for several decades. Herein, we report the synthesis of *trans*-bent forms of Si$_2$H$_2$ in the compounds (Me-cAAC:)$_2$Si$_2$H$_2$ (**1**) and (Cy-cAAC:)$_2$Si$_2$H$_2$ (**2**) at ambient temperature and the complete characterization of the species in the solid state and in solution. We also provide a quantum chemical analysis of the bonding situation.

Compounds **1** and **2** were synthesized by reduction of HSiCl$_3$ with KC$_8$ in a 1:3 molar ratio in the presence of 1 equiv of Me-cAAC: and Cy-cAAC: respectively (Scheme 1; for details see Supporting Information (SI)). The reactions were conducted at −78 °C in THF and subsequently warmed to room temperature within 30 min and stirred for another 2 h to give the dark red colored solutions of **1** and **2**. They were also characterized by electrospray ionization mass spectrometry featuring the molecular ion (**1**, at *m/z* (100%) 635.5, [M + Li]$^+$; **2**, at *m/z* (100%) 733.5, [M + Na + 2H$^+$ + 2e$^-$]$^+$) (see

Chart 1. Theoretically Predicted Four Different Isomeric Forms of Si$_2$H$_2$, Dibridged (A), Monobridged (B), *trans*-Bent Species (C1 and C2)^a

^{a}Structure **C2** is a transition state, but it may become an energy minimum through stabilization by donor ligands.

Scheme 1. Syntheses of Compound 1 and 2

(Me-cAAC:)$_2$Si$_2$H$_2$ (1)
(Cy-cAAC:)$_2$Si$_2$H$_2$ (2)

SI). The experimental infrared (IR) spectra show absorption bands at 2115 and 2072 cm^{-1} respectively for **1** and **2**, which correspond to the Si−H stretching motion.[18] The ^{29}Si NMR spectra in C$_6$D$_6$ of **1** and **2** exhibit resonances at −45.50 and −41.43 ppm, respectively. The ^{13}C NMR spectra revealed resonances at 211.84 and 210.48 ppm for the carbene carbon atoms of **1** and **2**, respectively. The ^{1}H NMR spectra of **1** and **2** show slightly broadened singlets of the Si−H protons at 3.59 and 3.62 ppm, respectively. The proton coupled ^{29}Si NMR spectra exhibit J(Si,H) couplings of 163 Hz for **1** and 164 Hz for **2**. Although the magnitude of the J(Si,H) coupling constant is not a reliable measure of the Si−H bond strength or of the stability of the Si−H bond path,[20] the values for **1** and **2** are much larger than those for Si−H agostic interactions in transition metal complexes (−109 to +16 Hz).[21] Compounds **1** and **2** are stable in an inert atmosphere for more than three months in both the solid state and in solution.

We discuss the structural details of the single crystal X-ray structure of **1**, which crystallizes in the triclinic $P\bar{1}$ space group. In the asymmetric unit only half of the molecule of **1** is present with the inversion center (*i*) at the midpoint of the Si−Si bond. The X-ray single crystal structure of **1** exhibits a *trans*-bent form of Si$_2$H$_2$ where the two Me-cAAC: carbene ligands are coordinated in an antiperiplanar arrangement to the silicon atoms (Figure 1). The two planes H1Si1Si1AH1A and C1Si1Si1AC1A are twisted but not orthogonal to each other.
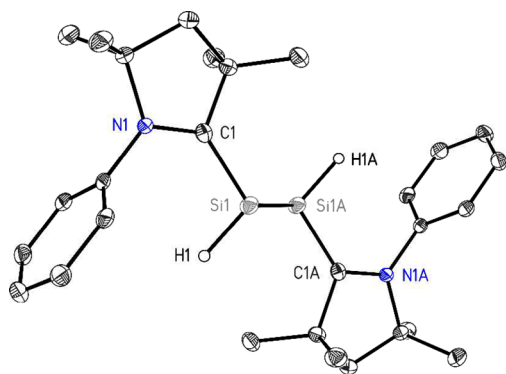
Figure 1. Crystal structure of compound **1**. Selected experimental [calculated values at M06-2X/def2-TZVPP] bond lengths (Å) and angles (deg), C-bound H atoms and isopropyl groups are omitted for clarity: Si1−Si1A, 2.3336(13) [2.339]; Si1−H1 1.437(18) [1.492]; Si1−C1, 1.8173(18) [1.822]; C1−N1, 1.362(2) [1.347]; C1−Si1−Si1A, 111.81(6) [110.4]; C1−Si1−H1, 105.6(7) [104.8]; Si1A−Si1−H1, 110.0(7) [108.5]; N1−C1−Si1, 126.47(12) [126.1]; C2−C1−Si1, 125.10(12) [108.1]; C1−Si1−Si1A−C1A, 180.0 [179.9]; H1−Si1−Si1A−H1A, 180.0 [179.9].

Thus, each Si atom in **1** is trigonally pyramidal coordinated by one hydrogen (H1 or H1A), one silicon (Si1 or Si1A), and one carbene carbon atom (C1 or C1A) (Figure 1). The sum of the three bond angles at Si1 is 327.46°, deviating considerably from a planar coordination. It is interesting to note that the Si−C bond length in **1** (1.817 Å) is very similar to the value in (Si$_2$Cl$_2$)(cAAC)$_2$ (1.823 Å/1.826 Å) but much shorter than the distance in (NHC)SiCl$_2$ (1.99 Å).[16] On the other hand the dihedral angle for the trans arrangement of H−Si−Si−H in **1** (180°) is quite different from the data for the skewed Cl−Si−Si−Cl fragment in (Si$_2$Cl$_2$)(cAAC)$_2$ (43.3°).[15]

We carried out quantum chemical calculations in order to analyze the bonding situation in the compounds (for details see SI). Figure 1 gives the calculated bond lengths and angles for **1** at the M06-2X/def2-TZVPP level of theory. They are in excellent agreement with the experimental data, except for the Si−H bond where the theoretical distance (1.492 Å) is longer than the experimental value of 1.437(18) Å. But it is well-known that X−H bonds are shortened because of asphericity effects.[22] The bond dissociation energy (BDE) for the reaction **1** → Si$_2$H$_2$(**A**) + 2 Me-cAAC: at M06-2X/def2-TZVPP amounts to D_e = 99.5 kcal/mol. Single-point energy calculations with the local coupled-cluster method at LCCSD-(T)/cc-pVTZ using the M06-2X/def2-TZVPP optimized geometry gives nearly the same value of 99.9 kcal/mol. The average BDE of the Si−C bonds of **1** is about 50 kcal/mol. This value is similar to the calculated BDE for the coordinate bond in NHC→SiCl$_2$ (42.5 kcal/mol)[17a] but much smaller than the bond dissociation energy of the H$_2$C=SiH$_2$ double bond (119 kcal/mol).[23]

Natural bond orbital (NBO) calculations suggest that the Si$_2$ fragment in **1** carries a positive partial charge of +0.62e. The Wiberg bond order for the Si−Si bond is P = 0.95. The Si−C bond has the value P= 1.26, which suggests some double bond character. Figure 2 shows the natural bond orbitals of **1** which are relevant for this study. There are four NBOs at silicon: one Si−H orbital, one Si−Si orbital, and one σ and one π orbital for the Si−C bond. Note that the Si−C σ orbital is polarized toward carbon but the π orbital is polarized toward the less electronegative silicon atom (Figure 2).

Do the σ and π orbitals of the Si−C bonds in **1** indicate a genuine electron-sharing double bond between fragments in the triplet state, or do they come from simultaneous σ donation and π back-donation? The question can be addressed with EDA (Energy Decomposition Analysis) calculations of **1** where the interacting fragments Si$_2$H$_2$ and two Me-cAAC: with the frozen geometries of the molecule are deployed in two different electronic states. The singlet states of the fragments are used to calculate the coordinate bonds. For the electron-sharing double bonds we used the quintet state of Si$_2$H$_2$ and the triplet state for the Me-cAAC: ligands. Those fragments which account for the smallest energy change by the formation of the bond are taken as an indicator for the type of interactions. It has been shown in several EDA studies that the calculated values of the orbital interactions ΔE_{orb} are a useful guide to distinguish between coordinate bonds and electron-sharing bonds.[24]

Table 1 shows the numerical results of the EDA calculations of **1** using different electronic states of the fragments. The intrinsic interaction energy ΔE_{int} for coordinate bonding (−193.0 kcal/mol) is clearly smaller than that for the electron-sharing bond (−323.5 kcal/mol). This is reasonable, because coordinate bonds A→B are always weaker than electron-sharing bonds A−B between the same atoms. Table
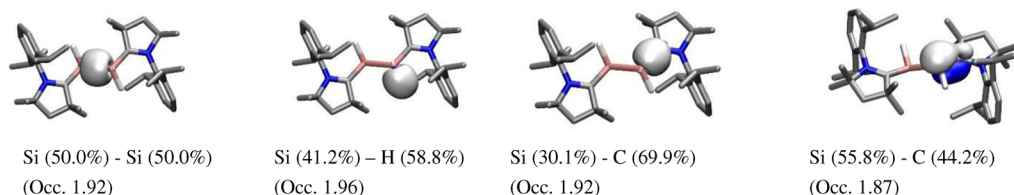
Si (50.0%) - Si (50.0%)   Si (41.2%) – H (58.8%)   Si (30.1%) - C (69.9%)   Si (55.8%) - C (44.2%)
(Occ. 1.92)   (Occ. 1.96)   (Occ. 1.92)   (Occ. 1.87)

Figure 2. Natural orbitals of the Si−Si, Si−H, and Si−C bonds of **1**.

Table 1. EDA Results of the $(Me\text{-}cAAC:)_2Si_2H_2$ at BP86-D3(BJ)/TZ2P+//M06-2X/def2-TZVPP Using Singlet or Quintet/Triplet Fragments of Si_2H_2 and $(Me\text{-}cAAC:)_2$ as Interacting Species (Energy Values Are Given in kcal mol^{-1})

	Singlet $Si_2H_2(a_g^2b_u^2a_g^2b_u^2a_g^2a_u^0b_g^0)$; Singlet $(cAAC)_2$	Quintet Si_2H_2 $(a_g^2b_u^2a_g^2b_u^1a_g^1a_u^1b_g^1)$; Triplet $(cAAC)_2$
ΔE_{int}	−193.0	−323.5
ΔE_{Pauli}	665.2	436.0
$\Delta E_{disp}{}^a$	−33.4 (3.9%)	−33.4 (4.4%)
$\Delta E_{elstat}{}^a$	−423.9 (49.4%)	−328.6 (43.3%)
$\Delta E_{orb}{}^a$	−401.0 (46.7%)	−397.5 (52.3%)

^{a}The values in parentheses give the percentage contribution to the total attractive interactions $\Delta E_{elstat} + \Delta E_{orb} + \Delta E_{disp}$.

1 shows that the weaker coordinate bonds in **1** come from the stronger Pauli repulsion ΔE_{Pauli} that is partly compensated by the stronger electrostatic attraction compared with the electron-sharing interactions. The most important result concerns the values for ΔE_{orb}. Table 1 shows that the orbital term of **1** for the coordinate bonds ($\Delta E_{orb} = -401.0$ kcal/mol) is nearly as strong as that for electron-sharing bonds ($\Delta E_{orb} = -397.5$ kcal/mol). The conclusion is that compound **1** is equally well described in terms of coordinate bonds (Me-cAAC)→(Si_2H_2)←(Me-cAAC) as with classical double bonds (Me-cAAC)═Si(H)−Si(H)═(Me-cAAC). The molecule may therefore be regarded as not only ligand stabilized disilaacetylene but also as a derivative of 2,3-disila-1,3-butadiene (Figure 3). It will be interesting to see which bonding model explains
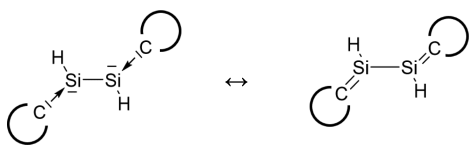
Figure 3. Two sketches of the bonding situation in **1** which according to the EDA results have nearly equal weight.

better the reactivity of the molecule. We were not able to prepare the corresponding $(Si_2H_2)(NHC)_2$ using NHC and $HSiCl_3$ directly as a precursor, unlike the preparation of the (Si_2Cl_2) species where both molecules are available.

In summary we have successfully characterized the molecule Si_2H_2 (**1** and **2**), which was stabilized by two cAAC: molecules at room temperature. The compounds (**1** and **2**) were synthesized from reduction of $HSiCl_3$ with KC_8 in the presence of cAAC:. This molecular form of Si_2H_2 is stable at room temperature under an inert atmosphere for more than three months. In addition, **1** and **2** are the first structurally characterized silicon monohydride compounds containing the *trans*-bent form of the Si_2H_2 motif. The molecular structure of the compound was confirmed by X-ray single crystal diffraction and ESI-mass spectrometry. Both compounds are further

characterized by NMR spectroscopy. The analysis of the electronic structure of **1** with modern quantum chemical methods gives detailed information in the bonding situation. From the theoretical analysis this molecule can be equally described as molecular Si_2H_2 or 2,3-disila-1-3-butadiene. The bond dissociation energy of the Si_2H_2 moiety agrees much better with the assignment of coordinate bonds.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b07361.

> Experimental and theoretical details and characterization data of compounds **1** and **2** (PDF)
> Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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