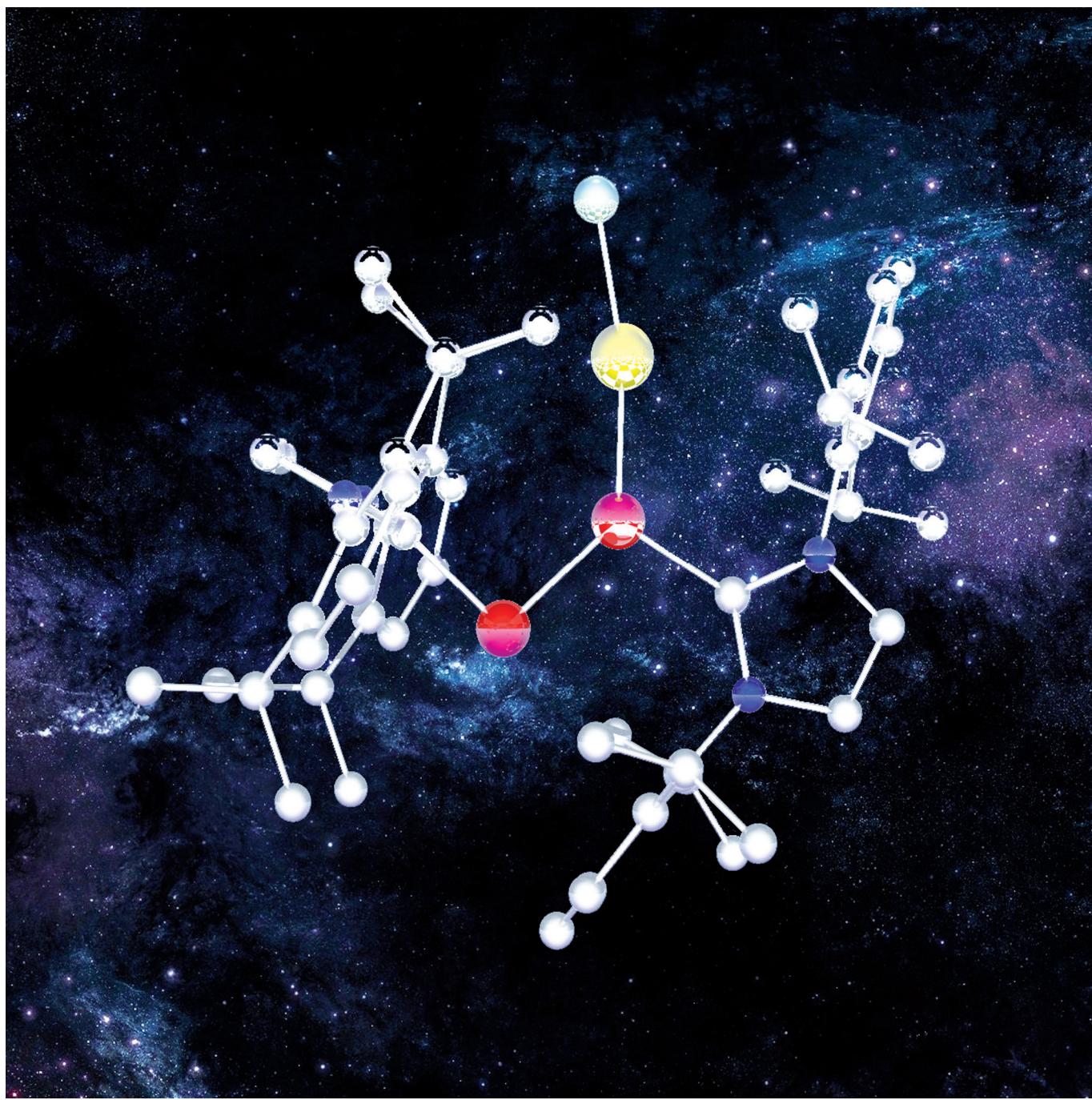


■ Computational Chemistry

Dynamic Complexation of Copper(I) Chloride by Carbene-Stabilized Disilicon

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Abstract: Reaction of N-heterocyclic-carbene (NHC)-stabilized disilicon (**1**) with CuCl gave a carbene-stabilized disilicon–copper(I) chloride complex (**2**). The nature of the structure and bonding in **2** has been investigated by crystallographic, spectroscopic, and computational methods. The dynamic complexation behavior of **2** was experimentally explored by variable-temperature NMR analysis.

The twenty-three year span between the seminal synthetic reports of the first disilene^[1] and the first disilyne,^[2] arguably, suggests both a measure of frustration and fascination associated with the chemistry of low-oxidation-state organosilicon compounds. These unsaturated molecules are intriguing not only because of the distinctive nature of the bonding but also due to the new reactivity of the disilicon cores.^[3] In addition, the silylenes (i.e., siliconocenes^[4] and diamidosilylenes^[5]) have developed into potent tools in areas, such as small-molecule activation, organic synthesis, catalysis, and transition-metal coordination chemistry.^[6]

In contrast to the large number of disilenes (Si=Si double bonds) and silylenes (electron-pair donors), only a small group of organosilicon compounds possess both silicon–silicon double bonds and silicon-based electron pair donor capabilities: disilenides (**I**),^[7] carbene–disilyne complex (**II**),^[8] carbene-coordinated disilyl silylene (**III**),^[9] and carbene-stabilized disilicon (**IV**; Figure 1; L:=carbene).^[10]

Because anionic derivatives of disilenes, disilenides (**I**)^[11] have proven to be unique organosilicon reagents.^[7] Notably, ion-separated disilenide also may be obtained by solvent coordination.^[12] Considering the π -donating capability of the Si=Si double bond, coupled with the σ -donor character of the electron lone pair(s) of silicon(s), compounds **I**–**IV** may exhibit versatile coordination modes toward various metal salts.

The only known **IV**-type example, **1**, was synthesized by potassium graphite reduction of L:SiCl₄ [L:=C{N(2,6-iPr₂C₆H₃)CH₂}].^[10] Carbene-stabilized disilicon has shown unusual reactivity toward BH₃, forming a “push-pull” stabilized parent silylene (H₂Si:).^[13] Inspired by the utilization of N-heterocyclic carbene (NHC)-copper(I) complexes in catalysis and in C–H bond activation,^[14] we investigated the behavior of **1** as a coor-

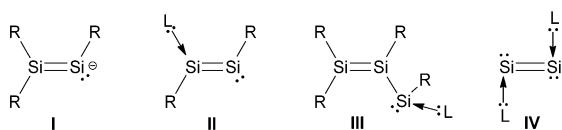


Figure 1. Donor compounds containing Si=Si double bonds.

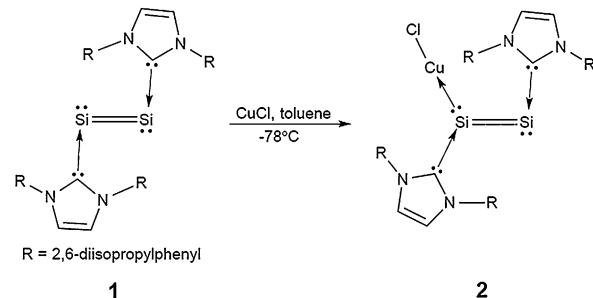
[a] Dr. M. Chen, Dr. Y. Wang, Dr. Y. Xie, Dr. P. Wei, R. J. Gilliard, Jr., N. A. Schwartz, Prof. Dr. H. F. Schaefer, III, Prof. Dr. P. v. R. Schleyer, Prof. Dr. G. H. Robinson

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dinating ligand with copper(I) chloride and now report the synthesis,^[15] structure,^[15] and related computations^[16] of carbene-stabilized disilicon–copper chloride complex (**2**).

Dark purple red crystals of **2** were isolated (51% yield) from reaction of **1** with CuCl in toluene at –78 °C (Scheme 1). Due



Scheme 1. Synthesis of carbene-stabilized disilicon:Cu^ICl complex (**2**).

to its high water sensitivity, **2** was decomposed by trace amounts of moisture to form L:CuCl [L:=C{N(2,6-iPr₂C₆H₃)CH₂}]₂ as the major by-product. However, compound **2** is thermally stable and persists in boiling C₆D₆. The stoichiometric ratio of the reactants affects the yield of **2**. Although **2** is a 1:1 adduct (L:Si=Si:L/CuCl), a better yield of **2** was achieved by combining **1** with CuCl in a 1:2 molar ratio. The possible 1:2 adduct was not formed, evidently due to the steric congestion of the two bulky carbene ligands. The copper chloride binding only shifted the ²⁹Si NMR resonance downfield marginally, from δ =224.5 ppm for **1** to 226.7 ppm for **2**, indicating a certain amount of electron donation from the Si₂ core to the copper center in **2**.

X-ray structural analysis of **2** (Figure 2) showed that CuCl is bound to only one of the two silicon atoms in the solid state^[15] (akin to the coordination of [Fe(CO)₄] to a carbene-heavier vinylidene adduct).^[17] The Si–Cu bond length [2.2081(9) Å] in **2** compares well with the Si_{sp2}–Cu distances (2.2412(8) and 2.2458(8) Å) in a lithium bis(disilyl)cuprate,^[18] but is less than the 2.43 Å sum of the silicon and copper covalent radii.^[19] The bent Si–Cu–Cl angle (167.35(5)° in **2**) contrasts with the perfectly linear fragment in [CuCl{μ-κ¹Si: κ^3 N-Si(3,5-Me₂pz)₃Mo(CO)₃}][–].^[20] Coordination of CuCl to the L:Si=Si:L fragment in **1** affects the structure and bonding of the resulting complex, **2**. Although both the imidazole rings of the two NHC ligands are perpendicular to the Si₂ core in **1**,^[10] only one imidazole ring has this arrangement in **2**. The other imidazole ring in **2** (adjacent to the Si(1) atom) is almost coplanar with the Si₂ core (the N(2)–C(1)–Si(1)–Si(2) torsion angle is –0.72°), which favors the delocalization of the p π -electrons of the Si₂ core to the empty p orbital of the carbene carbon [i.e., C(1)]. Indeed, in **2** the Si(1)–C(1) bond (1.917(3) Å) is slightly shorter than the Si(2)–C(28) bond (1.939(3) Å) in **2** and that (1.9271(15) Å) in **1**. The Si=Si double bond (2.2061(12) Å) in **2** is only slightly shorter than that (2.2294(11) Å) in **1**. Moreover, in **2** the three-coordinate Si(1) atom adopts a trigonal-planar geometry, whereas the two-coordinate Si(2) atom, as those in **1** containing lone pairs of electrons, has a bent geometry.^[10]

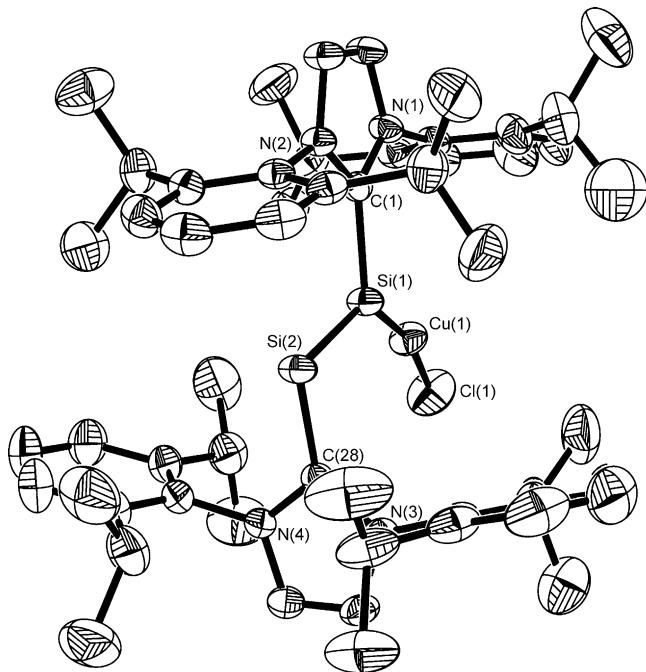


Figure 2. Molecular structure of **2**. Thermal ellipsoids represent 30% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] are as follows: Si(1)–Si(2) 2.2061(12), Si(1)–Cu(1) 2.2081(9), Si(1)–C(1) 1.917(3), Si(2)–C(28) 1.939(3), Cu(1)–Cl(1) 2.1452(11); Si(1)–Cu(1)–Cl(1) 167.35(5), C(1)–Si(1)–Si(2) 106.53(9), C(1)–Si(1)–Cu(1) 119.83(9), Si(2)–Si(1)–Cu(1) 132.41(5), C(28)–Si(2)–Si(1) 95.60(9).

DFT computations at the B3LYP/6-311 + G** level were performed on the simplified models, **2-H** ($L := :C[N(H)CH_2]$) and **2-Me** ($L := :C[N(Me)CH_2]$).^[16] The computed structural parameters of **2-Me** ($d_{\text{Si-Si}} 2.247$, $d_{\text{Si-Cu}} 2.248$, $d_{\text{Si-C}} 1.922$ Å; Cu-Si-Si bond angle 130.5°) are similar to the experimental data for **2** ($d_{\text{Si-Si}} 2.2061(12)$, $d_{\text{Si-Cu}} 2.2081(9)$, $d_{\text{Si-C}} 1.917(3)$ Å; Cu-Si-Si bond angle 132.41(5)°). However, the conformation of model **2-H** exhibited obvious differences compared with **2**.^[16] For example, **2** has C_1 symmetry, whereas **2-H** resides in C_s symmetry. Notably, the Si-Cu-Cl bond angle in **2-H** (146.8°) is considerably less than that observed for **2** (167.4°) or computed for **2-Me** (176.0°). The intramolecular N–H···Cl hydrogen bond may be a contributing factor (N–H···Cl bond lengths: Cl···H 2.51 Å, N–H···Cl 3.49 Å; N···Cl bond angle 159°).^[21]

The localized molecular orbitals (LMOs) of **2-Me** (optimized in C_1 symmetry) are shown in Figure 3. According to natural-bond-orbital (NBO)^[22] analysis, the Si–Si σ -bonding orbital is formed by an overlap of the approximately sp^2 -hybridized Si(1) atomic orbital (37.7% s, 62.0% p, 0.3% d) with the predominantly p character Si(2) atomic orbital (17.4% s, 82.1% p, 0.5% d), whereas the Si–Si π orbital has essentially pure p character (99.7%). Both the Si–Si σ and π bonds are somewhat polarized (about 55%) toward the Si(1) atom. The 1.63 Wiberg bond index (WBI) of the central silicon–silicon bond in **2-Me**, which is only slightly less than the 1.73 WBI of the **1-Ph** model,^[10] supports the Si=Si double bond character. In contrast, the Si–Cu bond is polarized more highly (78%) towards silicon. The copper hybridization (NBO) is 82.3% s, 14.5% p, and 3.2% d in

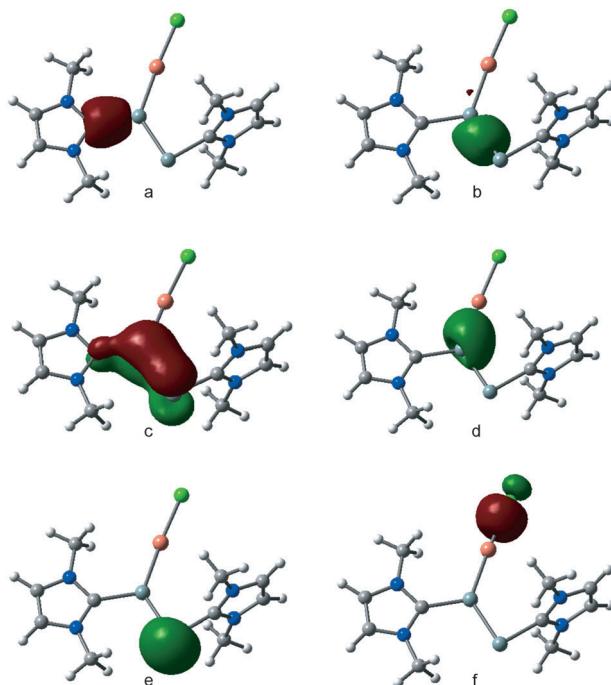


Figure 3. Localized molecular orbitals (LMOs) of model **2-Me**. a) Si–C σ -bonding orbital; b) Si–Si σ -bonding orbital; c) Si–Si π -bonding orbital; d) Si–Cu σ -bonding orbital; e) lone-pair orbital of Si; f) Cu–Cl σ -bonding orbital.

2-Me; the 0.66 WBI of its Si–Cu bond is consistent with single-bond character.

DFT computations of the simplified **2-Me** model also suggested that the carbene-stabilized disilicon–copper chloride complex may exist as either of two isomeric forms (Figure 4).^[16] Notably, the π complex **2'-Me** (a minimum with C_2 symmetry) is only 0.2 kcal mol⁻¹ higher in energy than the σ -complex minimum, **2-Me**. The side-on coordination of the $L:\text{Si}=\text{Si}:L$ ($L := :C[N(Me)CH_2]$) fragment to CuCl in **2'-Me** only results in a slight elongation of the silicon–silicon distance (to 2.295 Å from 2.2294(11) Å in **1**).^[10] Indeed, the 2.295 Å silicon–silicon bond length in **2'-Me** is similar to those reported for disilene–transition-metal π complexes.^[23] Interestingly, **2** only gave a singlet ²⁹Si NMR resonance. This, coupled with the fact that two carbene ligands are chemically equivalent in both ¹H and ¹³C NMR spectra of **2**, suggests that in solution, **2** may exist in the C_2 symmetric π -complex isomer form or rapidly equilibrate at room temperature, very likely via a π -complex intermediate (Figure 5). Indeed, σ – π rearrangements of organotransition

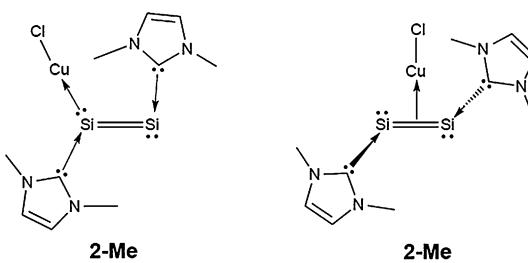


Figure 4. Isomers of the carbene-stabilized disilicon:CuCl complex.

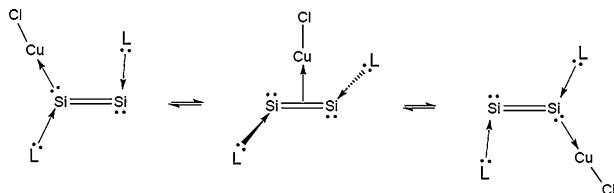


Figure 5. The proposed σ - π interconversion of **2** in solution [$L := :C\{N(2,6-iPr_2C_6H_3)CH_2\}_2$].

metal compounds are of great importance in catalytic processes.^[24]

Such dynamic complexation behavior of **2** in solution was further supported by variable-temperature (VT) ^1H NMR experiments (Figures S1–S5 in the Supporting Information).^[15] The sharp singlet resonance of the imidazole protons of **2** at 25°C broadens and then splits into two separate peaks when cooled to -66°C . These VT spectral changes are reversible. These experimental observations may be ascribed either to the slowing of the carbene–ligand rotation around the $C_{\text{NHc}}\text{—Si}$ axis in the symmetric π complex form of **2** or that the exchange shown in Figure 5 is frozen at low temperature.

Our investigation of the role of the carbene–silicon complex (**1**) as a ligand coordinating to copper chloride showed that **1** may function as a σ donor to form the asymmetric isomer of **2** in the solid state, which in solution, however, either exists as a symmetric π -complex isomer or equilibrates rapidly at room temperature, highly likely via a π -complex intermediate.

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