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An *N*-Heterocyclic Carbene−Disilyne Complex and Its Reactivity toward $ZnCl_2$

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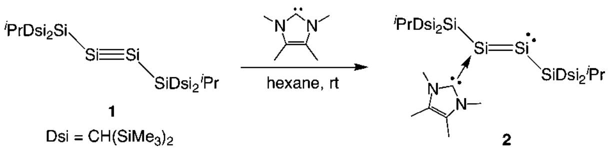
Abstract: The reaction of disilyne **1** with 1,3,4,5-tetramethylimidazol-2-ylidene (an *N*-heterocyclic carbene, NHC) produced the disilyne−NHC complex **2**, RLSi═SiR**:** (R = $Si^iPr[CH(SiMe_3)_2]_2$, L = NHC), with a *trans* geometry of the Si═Si moiety and lone-pair electrons residing on one of the double-bonded Si atoms. Upon complexation of **2** with $ZnCl_2$, the disilyne−NHC−$ZnCl_2$ complex **3** was produced, in which the Si═Si bond adopted the *cis* geometry.

The chemistry of N-heterocyclic carbenes (NHCs) has grown rapidly since the isolation of bottleable NHCs in 1991,[1] and numerous applications of NHCs have been reported.[2] In particular, NHCs are widely used as ligands for transition metal complexes because of their strong two-electron donor character.[2c,d] Recently, the strong σ-donation of NHCs has been applied to stabilize low-coordinate main group element compounds.[3] Remarkably, Robinson et al. described an isolable NHC-supported **:**Si═Si**:** compound with silicon in the formal oxidation state of zero.[4a] A silanone with a Si═O double bond[4b,c,h] and dihalosilylenes[4d−f] have also been isolated and structurally characterized using NHC ligands. Very recently, Filippou et al. reported a molybdenum silylidyne complex and its NHC adduct.[4g] However, the interaction of NHCs with heavier group 14 alkyne analogues, including disilyne with silicon−silicon triple bonds, has remained elusive and could open a new field of low-coordinate chemistry.

Very recently, the chemistry of the heavy alkyne analogues of Si, Ge, Sn, and Pb has been developed.[5] In 2004, we[6a] and Wiberg's group[6b] independently reported the synthesis of disilyne derivatives with silicon−silicon triple bonds, which were stabilized by very bulky silyl groups. Later, Tokitoh's group reported a disilyne bearing two very bulky aryl groups.[6c] The structure of disilyne **1**, RSi≡SiR (R = $Si^iPr[CH(SiMe_3)_2]_2$), shows *trans*-bending of the silicon−silicon triple bond, which results in two nondegenerate occupied π-molecular orbitals (MOs) and two unoccupied antibonding π^*-MOs.[6a] In particular, the energy of the LUMO is significantly lowered, and the one-electron reduction of **1** using ^tBuLi followed by hydrogen abstraction easily occurs to give the lithium salt of disilenide RHSi═SiRLi.[7] In this Communication, we describe the reaction of NHCs with disilyne **1** to produce an NHC−disilyne complex. Upon complexation with $ZnCl_2$, an NHC−disilyne−$ZnCl_2$ complex with unexpected *cis*-geometry of its Si═Si double bond was obtained, which we also report in this paper.

The reaction of disilyne **1** with an equivalent amount of the NHC 1,3,4,5-tetramethylimidazol-2-ylidene[8] in hexane immediately proceeded at room temperature to give a reddish-brown solution, from which the disilyne−NHC 1:1 complex **2** was isolated as air- and moisture-sensitive brown crystals in 81% yield (Scheme 1).[9] No evidence of a disilyne−NHC 1:2 complex was observed when an excess amount of NHC was used.

Scheme 1. Synthesis of the Disilyne−NHC Complex **2** from **1**



The molecular structure of **2** was determined by X-ray crystallography, and its crystal structure is shown in Figure 1.[9] The NHC coordinates to one of the Si atoms of the disilyne skeleton, and the five-membered ring of the NHC is nearly perpendicular to the Si1−Si2 bond, with the N1−C35−Si1−Si2 torsion angle being 79.00(14)°. The sum of the bond angles around the Si1 atom (359.16°) shows the planarity, and the four Si atoms are nearly coplanar, with a Si3−Si1−Si2−Si4 torsion angle of 165.12(2)°. The C35−Si1 bond length (1.9221(16) Å) is close to the Si−C(carbene) bond length of the NHC-supported L′**:**Si═Si**:**L′ compound (1.9271(15) Å)[4a] (L′ = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) and the $R_2(L)Si═O$ compound (1.930(2) Å)[4b,h] (L = 1,3,4,5-tetramethylimidazol-2-ylidene; $R_2 = CH\{[C(Me)=N(aryl)]-C(=CH_2)N(aryl)\}$, aryl = 2,6-$^iPr_2C_6H_3$). As expected, the Si1−Si2 bond length (2.1989(6) Å) is longer than the Si≡Si triple bond length of disilyne **1** (2.0622(9) Å)[6a] but close to the length of the Si═Si double bond of the solvent-separated ion pair of the disilenides, $RHSi═SiR^-\cdot Li(dme)_3^+$ (2.2034(9) Å)[7] and L′**:**Si═Si**:**L′ (2.2294(11) Å).[4a]

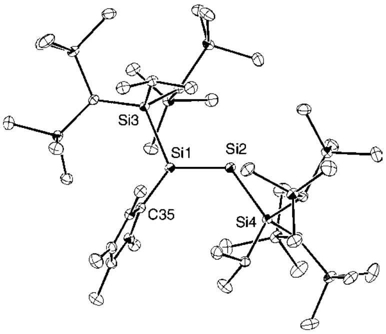


Figure 1. ORTEP drawing of **2** (30% thermal ellipsoids). Hydrogen atoms and the pentane molecule as a crystallization solvent are omitted for clarity. Selected bond lengths (Å), angles (deg), and torsion angles (deg): C35−Si1 = 1.9221(16), Si1−Si2 = 2.1989(6), Si1−Si3 = 2.4195(6), Si2−Si4 = 2.3905(6); C35−Si1−Si2 = 126.82(5), C35−Si1−Si3 = 121.39(5), Si2−Si1−Si3 = 110.95(2), Si1−Si2−Si4 = 120.35(2); Si3−Si1−Si2−Si4 = 165.12(2), C35−Si1−Si2−Si4 = 4.39(7).

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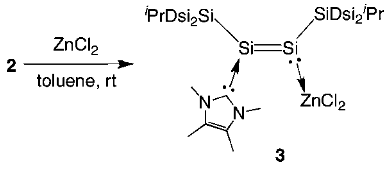
The ^{29}Si NMR spectrum of **2** (THF-d_8) shows characteristic signals of low-coordinate Si atoms at 28.7 ppm (NHC-*Si*═Si) and 276.3 ppm (NHC-Si═*Si*). However, the former is shifted upfield from that of RHSi═SiRLi, whereas the latter is shifted downfield (124.7 ppm for the H-substituted Si atom and 165.0 ppm for the Li-substituted Si atom in benzene-d_6). The high-field shift of the NHC-coordinated Si atom is similar to that of L′**:**ClSi−SiCl**:**L′ (38.4 ppm), and the signal for the low-coordinate Si2 atom is also close to that of L′**:**Si═Si**:**L′ (224.5 ppm).[4a] These spectroscopic data also indicate that the NHC−disilyne complex **2** has the structure RLSi═SiR**:**, the lone-pair electrons residing on the low-coordinate Si2 atom.[10] Theoretical calculations and chemical reactivity also support this structure.

Density functional theory calculations on the Me$_3$Si-substituted model compound **2′** were carried out to elucidate the electronic structure of the disilyne−NHC complex. Although the Si1−Si2−Si4 bond angle (102.20°) of the optimized structure of **2′** (B3LYP/6-31G(d)) is narrower than that indicated by the X-ray data (120.35(2)°), apparently because of the steric release from the bulky ^{i}PrDsi$_2$Si to the smaller Me$_3$Si groups, the other structural parameters are reproduced well (see Supporting Information). Selected MOs (B3LYP/6-31G(d)) of the model compound **2′** are depicted in the Supporting Information. The HOMO and LUMO correspond to the Si−Si π bonding and antibonding orbitals, respectively. The HOMO−1 involves an n-orbital with the lone-pair of electrons on the Si2 atom. The UV−vis spectrum of **2** shows an absorption at 409 nm (ε 10000) with a shoulder (ca. 440 nm) that can be assigned to the $\pi-\pi^*$ (HOMO to LUMO) and n$-\pi^*$ (HOMO−1 to LUMO) transitions, respectively.

The reaction of **2** with a Lewis acid was examined to see the reactivity of the lone-pair electrons on the Si2 atom. The reaction of **2** with ZnCl$_2$ in toluene afforded a pale orange solution of the disilene **3** by complexation of the lone-pair electrons on the Si2 atom with ZnCl$_2$ (Scheme 2).[9] The ^{29}Si NMR signals of the skeletal Si atoms of **3** appeared at 66.9 (NHC-*Si*═Si) and 190.8 ppm (NHCSi═*Si*ZnCl$_2$), which lie in the typical region for Si═Si double-bonded compounds.[11]

Scheme 2. Synthesis of the Disilyne−NHC−ZnCl$_2$ Complex **3** from **2**



The structure of **3** was unambiguously determined by X-ray crystallography (Figure 2).[9] Surprisingly, the two bulky ^{i}PrDsi$_2$Si− groups are arranged in the *cis*-orientation, with large bond angles for Si2−Si1−Si3 (143.83(5)°) and Si1−Si2−Si4 (135.43(5)°). Although the interatomic N1(N2)···Zn distances (3.31 and 3.35 Å) are much longer than the sum of the covalent radius of N−Zn (1.95 Å),[12] an attractive interaction between the NHC skeleton and a Zn moiety, such as an electrostatic interaction (Zn1(δ+)···N1(N2)(δ−), C36(C37)(δ+)···Cl1(Cl2)(δ−)), may induce a preference for the *cis*-form of **3**.[13] The Si1−Si2 bond length of **3** (2.2006(13) Å) is almost the same as that of **2** (2.1989(6) Å); the Si═Si double bond length is not affected by the complexation with ZnCl$_2$. The C35−Si1 bond length of **3** (1.917(3) Å) is also comparable to that of **2** (1.9221(16) Å). The Si2−Zn1 bond length (2.3954(10)) is within the reported range for Si−Zn bond lengths (2.34−2.45 Å).[14]

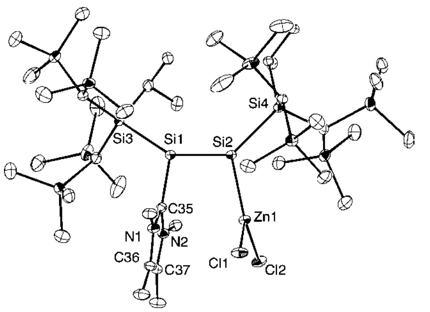


Figure 2. ORTEP drawing of **3** (30% thermal ellipsoids). Hydrogen atoms and the benzene molecule as a crystallization solvent are omitted for clarity. Selected bond lengths (Å), angles (deg), and torsion angles (deg): C35−Si1 = 1.917(3), Si1−Si2 = 2.2006(13), Si1−Si3 = 2.4511(13), Si2−Si4 = 2.3947(12), Si2−Zn1 = 2.3954(10); C35−Si1−Si2 = 98.93(10), C35−Si1−Si3 = 112.67(11), Si2−Si1−Si3 = 143.83(5), Si1−Si2−Si4 = 135.43(5), Si1−Si2−Zn1 = 102.92(4), Si4−Si2−Zn1 = 121.39(4); Si3−Si1−Si2−Si4 = 32.96(13), C35−Si1−Si2−Zn1 = 1.99(11).

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Supporting Information Available: Experimental procedure for **2** and **3**, computational results on model compounds **2′** and **3′** (*cis* and *trans*), and tables of crystallographic data, including atomic positional and thermal parameters for **2** and **3** (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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