

Transition-Metal-Mediated Cleavage of a Si=Si Double Bond**

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Abstract: Reaction of carbene-stabilized disilicon (**1**) with $\text{Fe}(\text{CO})_5$ gives the 1:1 adduct $\text{L}:\text{Si}=\text{Si}[\text{Fe}(\text{CO})_4]:\text{L}$ ($\text{L}:=\text{C}[\text{N}(2,6\text{-Pr}_2\text{C}_6\text{H}_3)\text{CH}]_2$) (**2**) at room temperature. At raised temperature, however, **2** may react with another equivalent of $\text{Fe}(\text{CO})_5$ to give $\text{L}:\text{Si}[\mu\text{-Fe}_2(\text{CO})_6](\mu\text{-CO})\text{Si}:\text{L}$ (**3**) through insertion of both CO and $\text{Fe}_2(\text{CO})_6$ into the Si_2 core, which represents the first experimental realization of transition metal-carbonyl-mediated cleavage of a Si=Si double bond. The structures and bonding of both **2** and **3** have been investigated by spectroscopic, crystallographic, and computational methods.

The chemistry of silicon–silicon multiple bonds, inspired by the seminal synthesis of the first disilene,^[1] has been extensively developed over the past three decades.^[2] A variety of disilene-transition metal complexes have been reported, similar to alkene-transition metal complexes, wherein the disilene moiety engages the metal in a η^2 -fashion.^[2g,3] Based on the Dewar–Chatt–Duncanson model, these disilene-transition metal complexes have typically been classified as either metallacycles or π -complexes.^[2g,4] Interestingly, an η^1 -disilene zirconium complex was reported to readily isomerize to give the corresponding cyclic silyl complex through 1,2-addition of a methyl C–H bond to the Si=Si bond.^[5] Cleavage of silicon–silicon double bonds by main group (or organic) species has been well explored.^[2a,d,6] While η^2 -disilene transition metal complexes have been reported to react with main group (or organic) species to cleave silicon–silicon bonds,^[2d,3b,k] notably, the direct cleavage of a Si=Si double bond by transition metal species has not been reported.

Silylenes are the silicon analogues of carbenes.^[7] Consequently, transition metal complexes of silylenes^[3i,8] have attracted considerable attention due to their pivotal roles in catalysis.^[8a,g] In contrast to the abundance of disilenes and silylenes, there exists only a small group of organosilicon compounds (i.e., carbene-stabilized disilicon (**1**),^[9] disilene,^[10] carbene-disilyne complex,^[11] carbene-coordinated disilyl silylene^[12]) that contain two types of reactive sites: a) the Si=Si double bond; b) the silicon-based lone pair(s)

(Figure 1). As diphosphenes,^[13] these compounds may exhibit versatile coordination modes and unusual reactivity towards various transition metal species. While a carbene-disilyne complex has been reported to act as a σ -donor to coordinate ZnCl_2 ,^[11] our recent variable-temperature NMR analysis

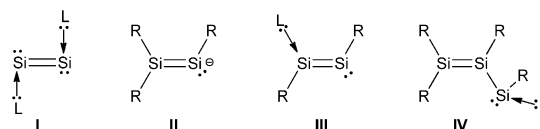


Figure 1. Silicon–silicon doubly bonded compounds containing silicon lone electron pairs. I: carbene-stabilized disilicon; II: disilenes; III: carbene-disilyne complex; IV: carbene-coordinated disilyl silylene ($\text{L}:=\text{carbene}$).

suggested the possible interconversion of σ – π coordination modes of carbene-stabilized disilicon-copper chloride complex (**4**), which, however, only exhibits the σ -bonding mode in the solid state.^[14] Interestingly, carbene-stabilized $[\text{L}:\text{Ge}-\text{Fe}(\text{CO})_4]_2$ cluster unambiguously features both π -type (bridging) and σ -type (terminal) $\text{Fe}(\text{CO})_4$ -coordination modes in the solid state.^[15] These exciting discoveries encouraged us to examine the reactivity of **1** with iron pentacarbonyl. Herein, we report the syntheses,^[16] molecular structures,^[16] and computations^[17] of carbene-stabilized $\text{Si}_2\text{Fe}(\text{CO})_4$ (**2**) and $\text{Si}[\mu\text{-Fe}_2(\text{CO})_6](\mu\text{-CO})\text{Si}$ (**3**). To the best of our knowledge, the synthesis of **3** represents the first example of transition metal-carbonyl-mediated cleavage of a Si=Si double bond.

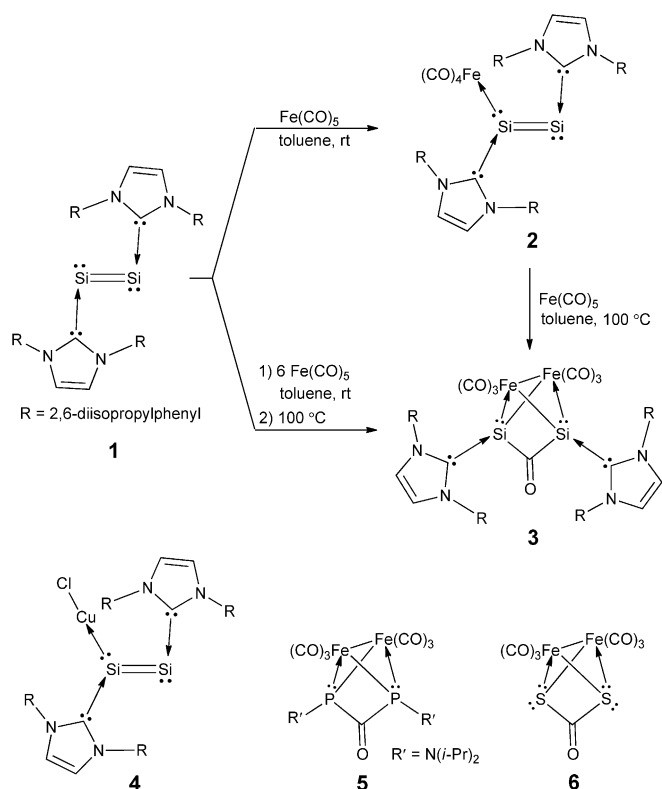
Reaction of **1** with $\text{Fe}(\text{CO})_5$ in a 1:1 ratio in toluene at room temperature gave **2** as a dark purple crystalline solid (81 % yield) (Scheme 1).^[16] Compound **3** was synthesized by reaction of **2** with one equivalent of $\text{Fe}(\text{CO})_5$ at 100 °C overnight and isolated as an orange crystalline solid in 97 % yield (Scheme 1). However, thermal reaction of **2** in the absence of $\text{Fe}(\text{CO})_5$ resulted only in the decomposition of **2** and the formation of free carbene ligand. In addition, we did not observe the reaction of **2** with CO gas. These results suggest that the addition of the second equivalent of $\text{Fe}(\text{CO})_5$ is a prerequisite for the synthesis of **3**. Compound **3** may also be prepared (42 % yield) by reaction of **1** with excess $\text{Fe}(\text{CO})_5$ in toluene at room temperature over one day and subsequent heating of the mixture in an oil bath at 100 °C over an additional 24 h (Scheme 1). In this synthetic route, $\text{L}:\text{Fe}(\text{CO})_4$ ($\text{L}:=\text{C}[\text{N}(2,6\text{-Pr}_2\text{C}_6\text{H}_3)\text{CH}]_2$) was isolated as a byproduct.

The X-ray structure^[16] of **2** reveals that the L_2Si_2 ($\text{L}:=\text{C}[\text{N}(2,6\text{-Pr}_2\text{C}_6\text{H}_3)\text{CH}]_2$) moiety acts as a silicon-based σ -donor to bind one $\text{Fe}(\text{CO})_4$ unit (Figure 2). The exclusive formation of the 1:1 adduct (**2**), even with excess $\text{Fe}(\text{CO})_5$, may be largely ascribed to the substantial steric repulsion

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Scheme 1. Synthesis of **2** and **3**, and relevant compounds **4**, **5**, and **6**.

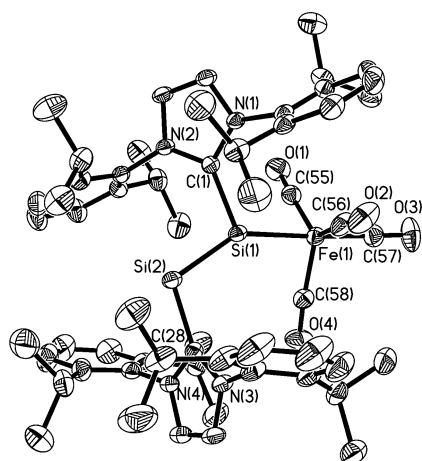


Figure 2. Molecular structure of **2**. Thermal ellipsoids represent 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Si(1)–Si(2) 2.1951(12), Si(1)–C(1) 1.942(3), Si(2)–C(28) 1.940(3), Si(1)–Fe(1) 2.3265(10), Fe(1)–C(57) 1.753(4); C(1)–Si(1)–Si(2) 101.66(9), Si(1)–Si(2)–C(28) 106.54(10), Si(2)–Si(1)–Fe(1) 144.41(5), C(1)–Si(1)–Fe(1) 113.40(9).

between the carbene ligands and Fe(CO)_4 unit. Indeed, the 1:2 adduct $[\text{L}'\text{Ge[Fe(CO)}_4\text{]}_2]$ has been isolated from the reaction of small carbene ($\text{L}' = \text{:C}(\text{Pr}^i)\text{NC}(\text{Me})_2$)-stabilized Ge_2 with $\text{Fe}_2(\text{CO})_9$.^[15] The Si–Fe bond [2.3265(10) Å] in **2**, though shorter than the computed values for **2-Me** ($\text{L}' = \text{:C}[\text{N}(\text{Me})\text{CH}]_2$) (2.364 Å)^[17] and for $\text{H}_2\text{Si[Fe(CO)}_4\text{]}$ (2.41 Å),^[18] is somewhat longer than those for silylene- Fe(CO)_4 complexes [2.196–2.294 Å].^[19] Notably, the short

Si–Fe bond (2.196 Å) in NHSi:Fe(CO)_4 ($\text{NHSi} = \text{Si}[(t\text{-Bu})\text{NCH}]_2$) may be attributed to iron-to-silicon π back-bonding.^[19a] The Si=Si bond [2.1951(12) Å] and Si–C bonds (1.941 Å, av) in **2** are similar to those for **1**^[9] [$d_{\text{Si=Si}} = 2.2294(11)$ Å; $d_{\text{Si-C}} = 1.9271(15)$ Å], **2-Me**^[17] [$d_{\text{Si=Si}} = 2.215$ Å; $d_{\text{Si-C}} = 1.954$ Å, av], and **4**^[14] [$d_{\text{Si=Si}} = 2.2061(12)$ Å; $d_{\text{Si-C}} = 1.928$ Å, av]. In contrast to **4**, which only exhibits a singlet-shifted ^{29}Si NMR resonance (226.7 ppm in C_6D_6), **2** gives two upfield-shifted ^{29}Si NMR resonances (201.3 and 142.5 ppm in $[\text{D}_8]\text{THF}$), suggesting that the asymmetrical structure of **2** exists not only in the solid state but also in solution. The lack of dynamic complexation behavior of **2** may be ascribed to the steric bulk of the Fe(CO)_4 unit. The terminal carbonyl ^{13}C NMR resonance of **2** (218.7 ppm) is close to that for **3** (221.1 ppm) and for $\text{L:SiCl}_2[\text{Fe(CO)}_4]$ ($\text{L} = \text{:C}[\text{N}(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)\text{CH}]_2$) (215.0 ppm).^[20]

DFT computations at the B3LYP/6-311 + G** level were performed on the simplified model **2-Me** (optimized in C_1 symmetry).^[17] In contrast to the Si–Cu bond in **4-Me** ($\text{L} = \text{:C}[\text{N}(\text{Me})\text{CH}]_2$) that is highly polarized (78%) towards silicon, natural bond orbital (NBO)^[21] analysis shows that the Si–Fe single bond [Wiberg bond index (WBI) = 0.69] in **2-Me** is only slightly polarized (51%) towards silicon (Figure S1c in the Supporting Information).^[17] The 1.75 WBI of the silicon–silicon bond in **2-Me** compares to that in **1-Ph** ($\text{L} = \text{:C}[\text{N}(\text{Ph})\text{CH}]_2$) (1.73 WBI)^[9] and in **4-Me** (1.63 WBI),^[14] suggesting the presence of a Si=Si double bond in **2**. Similar to **4-Me**, the Si–Si σ -bonding orbital in **2-Me** (Figure S1a)^[17] involves the overlap of the approximately sp^2 -hybridized Si(1) atomic orbital (35.9% s, 63.9% p, 0.2% d) with the Si(2) atomic orbital that bears predominantly p character (16.8% s, 82.7% p, 0.5% d). The Si–Si π -bonding orbital in **2-Me** (Figure S1b)^[17] is of nearly pure p character (98.7%).

The X-ray structure^[16] of **3** (Figure 3) indicates that one equivalent of **1** may react with two equivalents of Fe(CO)_5 at

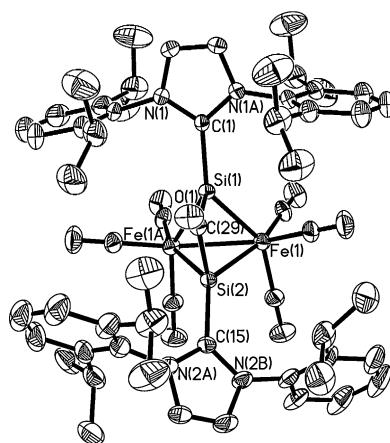


Figure 3. Molecular structure of **3**. Thermal ellipsoids represent 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Si(1)–Si(2) 2.5206(13), Si(1)–C(1) 1.933(3), Si(2)–C(15) 1.935(3), C(29)–O(1) 1.194(4), Si(1)–C(29) 1.957(3), Si(2)–C(29) 1.937(4), Si(1)–Fe(1) 2.2867(8), Si(2)–Fe(1) 2.2930(8), Fe(1)–Fe(1A) 2.6658(8); C(1)–Si(1)–Fe(1) 134.11(6), C(1)–Si(1)–C(29) 114.21(15), Si(1)–C(29)–Si(2) 80.67(14), Si(1)–Fe(1)–Si(2) 66.79(3), Si(1)–Fe(1)–Fe(1A) 54.34(2).

raised temperature through cleavage of the Si=Si double bond in **1**. Consequently, both CO and Fe₂(CO)₆ units are inserted between the two L:Si (L: = C[N(2,6-Pr₂C₆H₃)CH]₂) fragments. The reactions between CO and silicon compounds are only scarcely documented.^[22] Scheschkewitz et al. reported the direct carbonylation of cyclotrisilenes with CO.^[22a] Sekiguchi et al. achieved a disilyl ketone (**7**) through CO insertion into the strained silicon–silicon bond of silyl-substituted 1,4-disila.^[22b] Silylene–CO complexes were only observed in hydrocarbon matrices at 77 K.^[22c] While the formation of **7** has been suggested to involve a biradical intermediate, the relevant mechanism of the formation of **3** remains unclear. The Si(1)–C(29) and Si(2)–C(29) bonds [1.957(3) and 1.937(4) Å] in **3** are marginally shorter than those attached to the C=O group in **7** [1.9730(17) and 1.9807(16) Å]. Both the ¹³C NMR resonance (247.5 ppm) and IR stretching band (1628 cm^{−1}) of the bridging CO in **3** are comparable to those for **7** (260.3 ppm and 1673 cm^{−1}, respectively).^[22b] The computed IR absorption (1636 cm^{−1}) of the bridging C=O in **3-Me** model^[17] (L: = C[N(Me)CH]₂, optimized in C₂ symmetry) is also consistent with that of **3**. The non-bonded silicon–silicon distance in **3** (2.5206 Å) is obviously longer than the sum of silicon covalent radii (2.34 Å).^[23] Each silicon atom in **3** shares three valence electrons with the Fe₂(CO)₆ fragment through a Si–Fe covalent bond and a Si–Fe donor–acceptor bond. The Si–Fe bonds [2.2867(8) and 2.2930(8) Å] in **3** are not only close to the computed values for the **3-Me** model (2.319 and 2.320 Å), but also among those for silylene–Fe(CO)₄ complexes [2.196–2.294 Å].^[19] However, they are obviously shorter than the reported iron–silyl bonds (2.493 Å, av) in *cis*-[Fe(xantsil)(CO)₄].^[24] With the valence electrons contributed from the carbene ligands, the Si[μ-Fe₂(CO)₆](μ-CO)Si core in **3** is isoelectronic to the inorganic core in RP[μ-Fe₂(CO)₆](μ-CO)PR [R = N(Pr)₂ (**5**)],^[25] Scheme 1 and S[μ-Fe₂(CO)₆](μ-CO)S (**6**)^[26] (Scheme 1). The Fe–Fe bond in **3** [2.6658(8) Å] is about 0.08 Å shorter than that of **3-Me** (2.739 Å).^[17] However, the Fe–Fe bond length decreases from **3** [2.6658(8) Å] to **5** [2.603(2) Å], and then to **6** [2.488(1) Å]. Meanwhile, the IR stretching band of the bridging C=O group is blue-shifted from **3** (1628 cm^{−1}) to **5** (1720 cm^{−1}) and then to **6** (1775 cm^{−1}).

NBO analysis shows that the Si–Fe bonds in **3-Me** (one is shown as Figure S2a)^[17] are polarized (53.3% and 56.4%) towards iron. The WBIs (0.63–0.68) of the Si–Fe bonds in **3-Me** are similar to that for **2-Me** (0.69). The 0.36 WBI of the Fe–Fe bond in **3-Me** (Figure S2b)^[17] is consistent with those (0.34–0.35) of the iron–iron single bonds in the singlet binuclear iron carbonyl complexes [i.e., (C₅F₆)Fe₂(CO)₇].^[27]

Compound **3** was prepared by reaction of **1** with Fe(CO)₅ through isolable intermediate **2**. In contrast to **4**, compound **2** does not exhibit dynamic complexation behavior, which may be due to the strong steric repulsion between the carbene ligands and Fe(CO)₄ fragment. The transformation of **2** to **3** involves the insertions of both CO and Fe₂(CO)₆ into the two L:Si units, which represents the first realization of transition-metal-carbonyl-mediated cleavage of a Si=Si double bond.

Keywords: carbenes · cleavage reactions · insertion · iron · silicon

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- [16] See the Supporting Information for synthetic and crystallographic details. CCDC 1052619 (**2**) and 1052620 (**3**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.
- [17] Computations: The structures of the simplified **2-Me** and **3-Me** models were optimized at the B3LYP/6-311+G** DFT level with the Gaussian94 and Gaussian09 programs: M. J. Frisch, et al., Gaussian94, Revision B.3; Gaussian Inc.: Pittsburgh, PA, **1995**; Gaussian09, revision D.01; Gaussian, Inc.: Wallingford, CT, **2013**. See the Supporting Information for the full citations.
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