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

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Abstract: *Reaction of carbene-stabilized disilicon (**1**) with $Fe(CO)_5$ gives the 1:1 adduct $L{:}Si{=}Si[Fe(CO)_4]{:}L$ ($L{:}=C\{N(2,6\text{-}Pr^i_2C_6H_3)CH\}_2$) (**2**) at room temperature. At raised temperature, however, **2** may react with another equivalent of $Fe(CO)_5$ to give $L{:}Si[\mu\text{-}Fe_2(CO)_6](\mu\text{-}CO)Si{:}L$ (**3**) through insertion of both CO and $Fe_2(CO)_6$ 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-disilenide 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] disilenides,[10] carbene-disilyne complex,[11] carbene-coordinated disilenyl 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 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 $[L{:}Ge\text{-}Fe(CO)_4]_2$ cluster unambiguously features both π-type (bridging) and σ-type (terminal) $Fe(CO)_4$-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 $Si_2Fe(CO)_4$ (**2**) and $Si[\mu\text{-}Fe_2(CO)_6](\mu\text{-}CO)Si$ (**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.

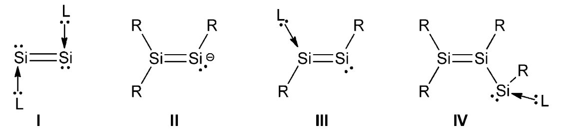

Figure 1. Silicon–silicon doubly bonded compounds containing silicon lone electron pairs. **I**: carbene-stabilized disilicon; **II**: disilenides; **III**: carbene–disilyne complex; **IV**: carbene-coordinated disilenyl silylene (L:=carbene).

Reaction of **1** with $Fe(CO)_5$ 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 $Fe(CO)_5$ 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 $Fe(CO)_5$ 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 $Fe(CO)_5$ is a prerequisite for the synthesis of **3**. Compound **3** may also be prepared (42% yield) by reaction of **1** with excess $Fe(CO)_5$ 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, $L{:}Fe(CO)_4$ ($L{:}=C\{N(2,6\text{-}Pr^i_2C_6H_3)CH\}_2$) was isolated as a byproduct.

The X-ray structure[16] of **2** reveals that the L_2Si_2 ($L{:}=C\{N(2,6\text{-}Pr^i_2C_6H_3)CH\}_2$) moiety acts as a silicon-based σ-donor to bind one $Fe(CO)_4$ unit (Figure 2). The exclusive formation of the 1:1 adduct (**2**), even with excess $Fe(CO)_5$, may be largely ascribed to the substantial steric repulsion

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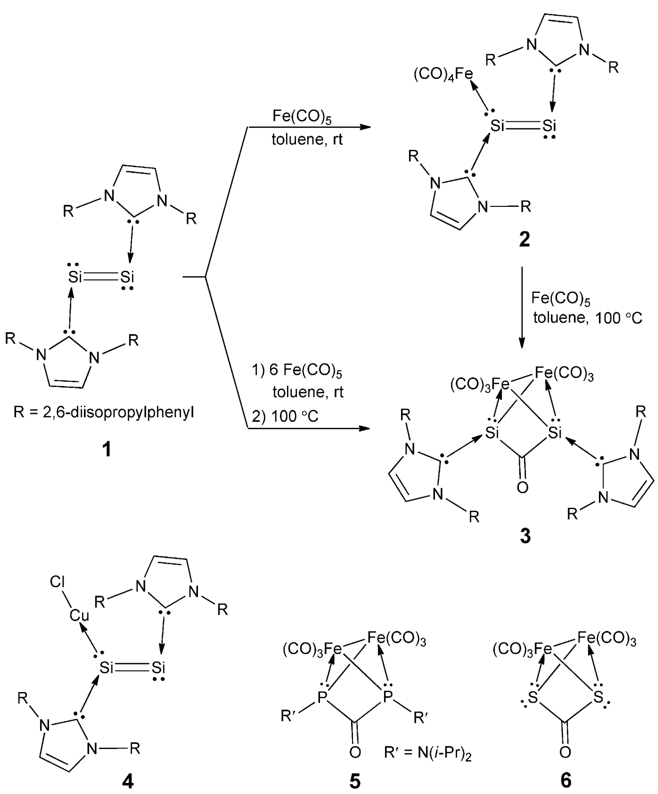

Scheme 1. Synthesis of **2** and **3**, and relevant compounds **4**, **5**, and **6**.

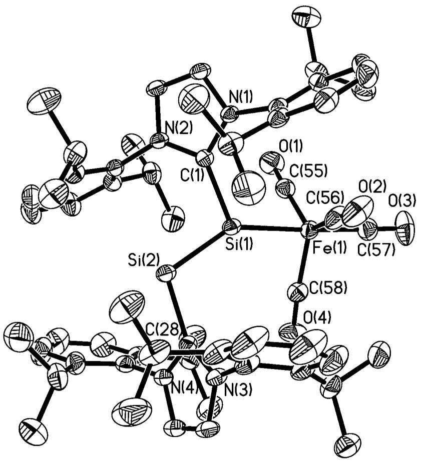

Figure 2. Molecular structure of **2**. Thermal ellipsoids represent 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Si(1)–Si(2) 2.1951(12), Si(1)–C(1) 1.942(3), Si(2)–C(28) 1.940(3), Si(1)–Fe(1) 2.3265(10), Fe(1)–C(57) 1.753(4); C(1)-Si(1)-Si(2) 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 [L′Ge[Fe(CO)$_4$]$_2$ has been isolated from the reaction of small carbene (L′ = :C{(Pr^i)NC(Me)}$_2$)-stabilized Ge$_2$ with Fe$_2$(CO)$_9$.[15] The Si–Fe bond [2.3265(10) Å] in **2**, though shorter than the computed values for **2-Me** (L: = :C[N(Me)CH]$_2$) (2.364 Å)[17] and for H$_2$Si[Fe(CO)$_4$] (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)$_4$ (NHSi = :Si[(*t*-Bu)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 ^{29}Si NMR resonance (226.7 ppm in C$_6$D$_6$), **2** gives two upfield-shifted ^{29}Si NMR resonances (201.3 and 142.5 ppm in [D$_8$]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 L:SiCl$_2$[Fe(CO)$_4$] (L: = :C{N(2,6-Pr$^i_2$C$_6$H$_3$)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** (L: = :C[N(Me)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** (L: = :C[N(Ph)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

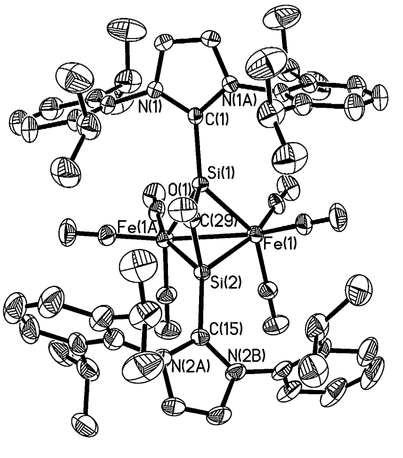

Figure 3. Molecular structure of **3**. Thermal ellipsoids represent 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Si(1)···Si(2) 2.5206(13), Si(1)-C(1) 1.933(3), Si(2)-C(15) 1.935(3), C(29)-O(1) 1.194(4), Si(1)-C(29) 1.957(3), Si(2)-C(29) 1.937(4), 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 $Fe_2(CO)_6$ units are inserted between the two L:Si ($L\!: = C\{N(2,6\text{-}Pr^i{}_2C_6H_3)CH\}_2$) 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 ^{13}C 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] ($L\!: = \,\colon C[N(Me)CH]_2$, optimized in C_2 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 $Fe_2(CO)_6$ 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-$Fe_2(CO)_6$](μ-CO)Si core in **3** is isoelectronic to the inorganic core in RP[μ-$Fe_2(CO)_6$](μ-CO)PR [R = N(Pr^i)$_2$ (**5**),[25] Scheme 1] and S[μ-$Fe_2(CO)_6$](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., $(C_5F_6)Fe_2(CO)_7$].[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 $Fe_2(CO)_6$ 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 Gaussian 94 and Gaussian 09 programs: M. J. Frisch, et al., Gaussian 94, Revision B.3; Gaussian Inc.: Pittsburgh, PA, **1995**; Gaussian 09, revision D.01; Gaussian, Inc.: Wallingford, CT, **2013**. See the Supporting Information for the full citations.

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