

Communications

Intramolecular Si–Si Bond Activation by the Iron Carbonyl Unit in
an (η^4 -Silole)tricarbonyliron Complex

Zhensheng Zhang, Jianli Gu, Chengxun Zhang, and Huailin Sun*

Department of Chemistry and the State Key Laboratory of Elemento-Organic Chemistry, Nankai
University, Tianjin 300071, People's Republic of China

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Summary: Intramolecular activation of the Si–Si bond linked to an η^4 -silole ligand by a metal center was observed when 1,1-bis(trimethylsilyl)tetraphenylsilole was heated with $\text{Fe}(\text{CO})_5$ in refluxing *p*-xylene, to produce η^4 -(1-trimethylsilyl-1-methyltetraphenylsilole) $\text{Fe}(\text{CO})_3$ as the final product.

Si–Si bonds are very thermally stable, sometimes even comparable to a C–C bond, but can easily be activated by transition metals.^{1,2} This property has most frequently been observed in intramolecular processes, which has led to many

intriguing reactions in recent years.^{3–9} To date, many studies of such reactions have focused on systems containing Si–Si bonds directly linked to transition metals, initially observed independently by Pannell's and Ogino's groups in 1986.^{4,5} Also studied have been systems in which the Si–Si bonds are linked indirectly to a metal atom through an η^1 -methylene ligand, a

* To whom correspondence should be addressed. E-mail: sunhl@nankai.edu.cn.

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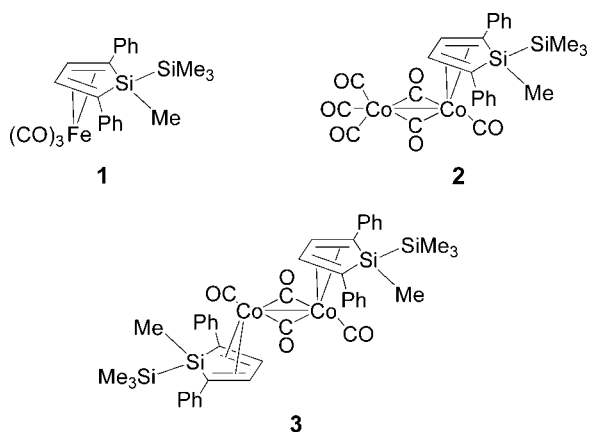
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Chart 1

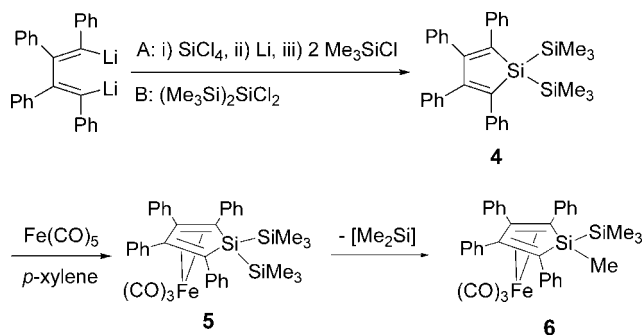


reaction first reported by Pannell and co-workers in 1974.⁶ Sakurai and co-workers in 1979 reported that the Si–Si bonds in η^4 -1,2-disilacyclohexadiene complexes could also be activated.⁷ However, study of the η^4 systems to date has been restricted to this single example. In 1993, we reported that the Si–Si bond in Si–Si-bridged bis(cyclopentadienyl)diiron complexes could be activated.^{8,9} During the mechanistic study of this reaction, it was recognized that oxidative addition to a coordinatively unsaturated iron atom was responsible for the easy activation of the Si–Si bond in this and in the systems noted above.^{8c} Thus, it is very likely that such oxidative addition might constitute a general mode of Si–Si bond activation in iron complexes.

Silacyclopentadienes (or siloles) are known η^4 ligands in transition-metal complexes, which have been studied extensively over the past few years.¹⁰ Complexes containing Si–Si bonds linked to silole ligands, e.g., **1–3** (Chart 1), were reported by Corriu and co-workers,¹¹ but for none of them was Si–Si bond cleavage by a metal species reported. On the basis of our knowledge of the Si–Si bond reactivity, we thought that this may be due to the fact that the approach of the Si–Si bond by the metal species was hindered in such compounds,¹² since the metal always was coordinated to the silole ligand from the side away from the Si–Si bond. However, if two silyl substituents were attached to the silicon atom of the silole ring, interaction of one of these Si–Si bonds with the metal species would be able to occur on coordination of the metal from either sides of the silole ring. We report here that this idea has merit and has led to the first observation of such Si–Si bond activation in an η^4 -silole complex.

Synthesis of the silole compound **4** was accomplished by starting from 1,4-dilithiotetraphenylbuta-1,3-diene, either by the three-step literature procedures (Scheme 1; path A)¹³ or by simple treatment with 2,2-dichlorohexamethyltrisilane (B).^{14a} Reaction of **4** with pentacarbonyliron was performed in refluxing *p*-xylene. The product isolated, however, was not the expected

Scheme 1. Synthesis of the Complex



complex **5** but the new complex **6**, in which one of the Si–Si bonds has been lost.^{14b}

The ¹H NMR spectrum showed the presence of two types of SiMe groups in a 1:3 ratio, in accord with the structure of **6**. The IR spectrum exhibited strong absorption of the carbonyl ligands. The molecular structure of **6**, determined by X-ray crystal diffraction (Figure 1), clearly demonstrated the presence of the methyl group at the endo position.¹⁵ The silole ligand coordinates to the iron atom in an η^4 fashion. The silicon atom of the silole ring is bent up from the plane of the diene unit with a dihedral angle of 34.5°, as has usually been observed in such complexes (within the range of 8.9–44.5°).¹⁰

The observed result showed that the endo Si–Si bond has been activated and that the trimethylsilyl group on the silole ligand has been replaced by a methyl group. It is noteworthy that the reaction occurred only at the endo Si–Si bond but not at the exo Si–Si bond. This indicates that the Si–Si bond activation has taken place intramolecularly after the iron carbonyl group coordinated to the silole ligand, as indicated in Scheme 1.

By analogy to the reaction of η^4 -1,2-disilacyclohexadiene systems,⁷ the mechanism of the present transformation can be rationalized as shown in Scheme 2. First, the η^4 – η^2 slippage of the silole

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(14) (a) Synthesis of **4** by method B: to a suspension of 1,4-dilithiotetraphenylbuta-1,3-diene in 100 mL of diethyl ether at –78 °C, obtained from 5.50 g (31 mmol) of diphenylacetylene and 0.216 g (31 mmol) of lithium according to the literature procedure,¹³ was added 3.80 g (15.5 mmol) of 2,2-dichlorohexamethyltrisilane. A 100 mL portion of THF was added, and the resulting mixture was heated to reflux for 2 h. It was cooled to room temperature and hydrolyzed with water. The organic layer was separated, washed with water, and dried over anhydrous sodium sulfate. Removal of the solvent, followed by separation through a column (silica, petroleum ether), gave 864 mg of **4** (5.7% yield) contaminated by a byproduct characterized as 1,4-bis(trimethylsilyl)tetraphenylbutadiene. The origin of the byproduct has not yet been determined. Pure **4** was obtained by fractional crystallization of the product in pentane at –20 °C. (b) Synthesis of **6**: 200 mg (0.38 mmol) of **4** and 1 mL (ca. 7 mmol) of Fe(CO)₅ were added to a flask containing 20 mL of *p*-xylene. The mixture was heated to reflux with stirring. The reaction required 100 h, as determined by ¹H NMR monitoring of its progress by periodically withdrawing samples from the reaction flask. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure (unreacted Fe(CO)₅ should be collected in a liquid nitrogen trap!) to give a solid residue. Separation of this product mixture by column chromatography (Al₂O₃, 4/1 petroleum ether/dichloromethane) gave 60 mg (25% yield) of red crystals of **6**, mp 190–192 °C. Anal. Calcd for C₃₅H₃₂O₃FeSi₂: C, 68.62; H, 5.26. Found: C, 68.76; H, 5.34. ¹H NMR (CDCl₃): δ 0.36 (s, 9H, SiMe₃), 0.92 (s, 3H, Me), 6.77–7.24 (m, 20H, Ph). ¹³C NMR (CDCl₃): δ –1.2 (Me), 0.5 (SiMe₃), 63.6 (diene), 111.0 (diene), 125.5 (Ph), 127.5 (Ph), 1127.6 (Ph), 127.9 (Ph), 130.5 (Ph), 133.0 (Ph), 134.7 (Ph), 140.2 (Ph), 211.4 (CO). ²⁹Si NMR (CDCl₃): δ –20.1 (SiMe), 18.4 (SiMe₃). IR (KBr): ν_{CO} 2033 (s), 1968 (s), 1933 (s) cm^{–1}. IR (CS₂): ν_{CO} 2035 (s), 1973 (vs) cm^{–1}.

(15) Crystallographic data for **6**: Mo K α (λ = 0.710 73 Å) radiation, monoclinic, space group *P2*₁/*n*, *a* = 8.965(3) Å, *b* = 19.433(5) Å, *c* = 18.239(4) Å, α = 90°, β = 95.184(6)°, γ = 90°, *Z* = 4, full-matrix least squares on *F*², GOF 0.974, R1 = 0.0669/wR2 = 0.1217 for 5571 reflections (*I* > 2 σ (*I*)), R1 = 0.1700/wR2 = 0.1658 for all data.

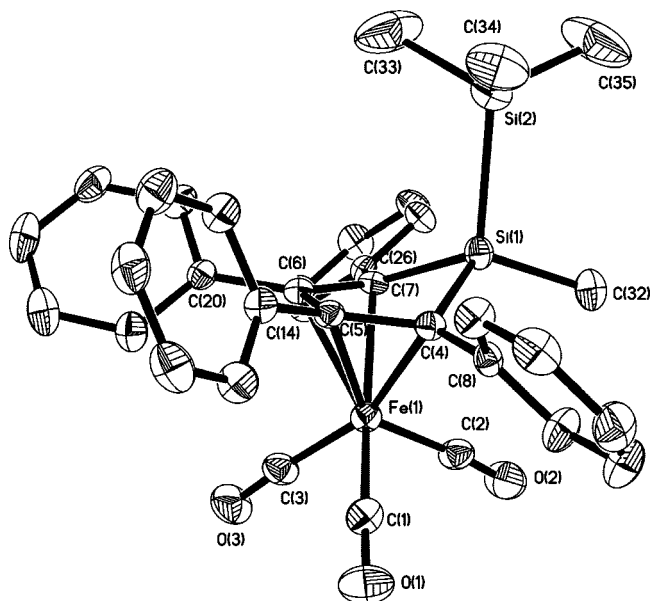
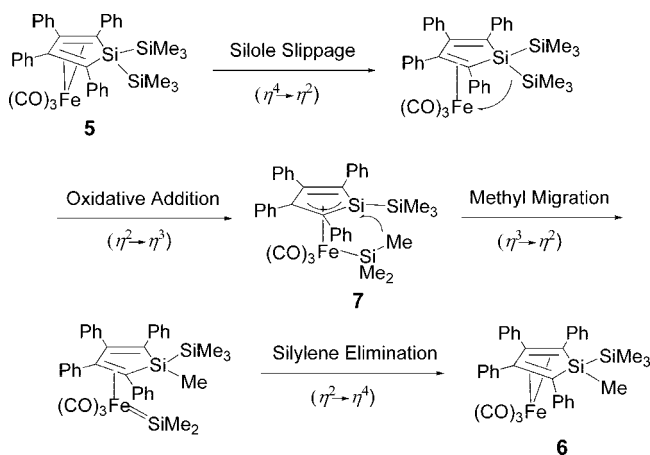


Figure 1. Molecular structure of **6** with thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): Si(1)–Si(2) = 2.385(2), Si(1)–C(32) = 1.870(6), Si(1)–C(4) = 1.860(5), Si(1)–C(7) = 1.873(6), C(4)–C(5) = 1.427(7), C(5)–C(6) = 1.447(7), C(6)–C(7) = 1.431(7), Fe(1)–C(1) = 1.772(7), Fe(1)–C(2) = 1.790(7), Fe(1)–C(3) = 1.795(7), Fe(1)–C(4) = 2.128(5), Fe(1)–C(5) = 2.060(5), Fe(1)–C(6) = 2.085(5), Fe(1)–C(7) = 2.189(5); C(1)–Fe(1)–C(2) = 96.4(3), C(1)–Fe(1)–C(3) = 88.8(3), C(2)–Fe(1)–C(3) = 95.5(3), C(4)–Si(1)–C(7) = 85.4(2), C(32)–Si(1)–Si(2) = 107.7(2).

Scheme 2. Proposed Mechanism



ligand creates a vacant coordination site at the iron atom. Oxidative addition of the Si–Si bond then takes place, giving

the η^3 -silapropenyl complex **7** as the key intermediate. Migration of the methyl group between two silicon centers of **7** produces the dimethylsilylene complex, which would easily lose the silylene, accompanied by recombination of the C–C double bond of the silole ligand.

The formation of an η^3 -silapropenyl intermediate is the critical step for Si–Si bond activation. Although η^1 -silylene, η^2 -silene, and η^4 -silatrimethylenemethane intermediates have been well documented, the formation of an η^3 -silapropenyl intermediate via Si–Si bond activation has not been easy to verify.^{16,17} Even though such intermediates have been suggested in reactions of η^4 -1,2-disilacyclohexadiene and other systems,^{7,18} the isolation of stable η^3 -silapropenyl complexes had not been successful until 2003, when Sakaba and co-workers isolated the first stable complex of this type,¹⁹ which ultimately provided a solid foundation for both the previous and present explanation of the Si–Si bond activation reactions.

The migration of the methyl group between two silicon atoms is another important process. Similar reactions recently have been of interest.²⁰ Previous attention has mainly been concentrated on alkyl or aryl migration in silyl(silylene) complexes. The only example of a silyl(η^3 -silapropenyl) complex was mentioned by Sakurai et al. in the η^4 -1,2-disilacyclohexadiene systems, which involved only the migration of the ring skeleton group and resulted in ring contraction. In the present case, the migration of a substituent on the tertiary silyl group might provide an opportunity for more convenient study of such processes.

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Supporting Information Available: CIF file giving X-ray diffraction data for **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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