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Article

Chemistry of the Si–Si and Fe–Fe Bonds in the Cyclic Structure $(Me_2SiSiMe_2)[\eta^5\text{-}C_5H_4Fe(CO)_2]_2$. Selective Cleavage of the Fe–Fe Bond by I_2 and Unexpected Properties of the Iodide

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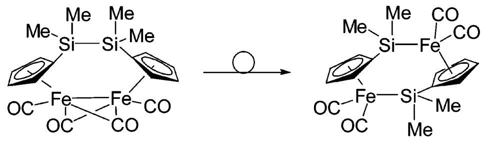
The Si–Si bond in the title cyclic structure (**1**) exhibited unexpected stability toward I_2. Thus, the reaction of **1** with 1 equiv of I_2 in chloroform resulted in selective cleavage of the Fe–Fe bond to afford diiodide $(Me_2SiSiMe_2)[\eta^5\text{-}C_5H_4Fe(CO)_2I]_2$ (**2**) with retention of the Si–Si bond. When excess (2–4 equiv) I_2 was used to react with **1** in either benzene or chloroform, iodonium-bridged diiron complex $\{(Me_2SiSiMe_2)[\eta^5\text{-}C_5H_4Fe(CO)_2]_2I^+\}(I_5^-)$ (**4**) was obtained, in which the Si–Si bond was still retained. It is noteworthy that **4** contains a counteranion I_5^- rather than the expected I_3^-, which is the first example for an iodonium-bridged diiron complex to combine a polyiodide anion larger than I_3^-. UV irradiation of **2** did not affect the stability of the silicon–silicon bond and, in the presence of PR_3, resulted in CO substitution to give $(Me_2SiSiMe_2)[\eta^5\text{-}C_5H_4Fe(CO)(PR_3)I]_2$ (**5**, R = Ph; **6**, R = OPh). The molecular structure of **2** was determined by the X-ray diffraction method. It is noteworthy that the structure of **2** does not take the expected anti conformation but adopts a gauche one. The length of the Si–Si bond of **2** [2.353(3) Å] is about the same as that of **1** [2.346(4) Å], which can be direct evidence to demonstrate that the Si–Si bond in the cyclic structure of **1** is not subject to significant ring strain. The molecular structure of **4** was also determined by the X-ray diffraction method. It is noted that the structure of **4** contains an abnormally large $Fe–I^+–Fe$ bond angle of 121.25(7)°. Of particular interest is the observation that the I_5^- anions of **4** are self-assembled into novel layered, two-dimensional networks with the $(Me_2SiSiMe_2)[\eta^5\text{-}C_5H_4Fe(CO)_2]_2I^+$ cations as the template.

Introduction

Scheme 1



1

Silicon–silicon bond-bridged dicyclopentadienyltetracarbonyldiiron complexes have received considerable attention recently due to coexistence of the silicon–silicon and iron–iron bonds in the cyclic structure which leads to the interesting thermal metathesis reaction between the two bonds (Scheme 1). This reaction was first reported by us for the title complex (**1**) in 1993.[1] Since then, much effort in this area has been devoted to explore the scope of this reaction in related systems. For example, the possibilities of the reaction in acyclic systems[2,3] and in cyclic structures similar to that of **1** but containing a Ge–Ge bond in place of the Si–Si bond[4–6] or a Ru–Ru bond in place of the Fe–Fe bond[7,8] have been examined. Mechanistic details have also been under thorough investigation, which has resulted in recognition of the intramolecular nature[9,10] and the interesting regioselective features[10] of this reaction. All the evidence obtained up to now has demonstrated that it is the

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cyclic structure that is responsible for this reaction's taking place. But the specific aspect of the cyclic structure that allows the reaction to take place is still in question.

To examine whether the silicon−silicon and iron−iron bonds in the cyclic structure have unusual properties, we have undertaken a study on the reaction of **1** with I_2. This study is so devised because both silicon−silicon and iron−iron bonds in other systems have been shown to be susceptible to cleavage by I_2. For example, the reaction of $Me_3SiSiMe_3$ with I_2 is an effective route to generate Me_3SiI.[11] On the other hand, the reaction of $[CpFe(CO)_2]_2$ with I_2 has been well established to produce the iodide $CpFe(CO)_2I$[12] and in the presence of excess I_2 in nonpolar solvent (such as benzene) to afford the iodonium-bridged diiron complex $\{[CpFe(CO)_2]_2I^+\}(I_3^-)$ containing I_3^- as the counteranion.[13] Thus, the coexistence of the silicon−silicon and iron−iron bonds in the molecule of **1** raises a question about which of the two bonds will be preferentially cleaved upon interaction with I_2. Herein, we report the results of our study, which demonstrates that only the iron−iron bond can be cleaved by I_2 whereas the silicon−silicon bond remains unchanged, showing unexpected stability of the silicon−silicon bond. The selective cleavage of the iron−iron bond provides the ring-opened product. The molecular structure of this product has been determined and compared with the structure of **1** to get information about the suspected ring strain in the cyclic structure, especially at the silicon−silicon bond. Photochemical properties of the ring-opened product have also been examined. Also reported in this paper is the isolation of the iodonium-bridged diiron complex which unexpectedly contains I_5^- as the counteranion. The molecular structure study of this product has revealed that the I_5^- anions are self-assembled into novel layered two-dimensional networks composed solely of iodine atoms.

Experimental Section

General Methods. All reactions were carried out under an argon atmosphere by using standard Schlenk techniques. ^1H NMR spectra were recorded on a Varian Unity-plus 400 or a Bruker AC-P200 spectrometer. IR spectra were recorded using a Bruker Smart 1000 instrument. Elemental analyses were performed using a Vario EL instrument. Chloroform was dried by refluxing over P_2O_5 and distilled under an inert atmosphere. Benzene was dried by refluxing with sodium in the presence of benzophenone and distilled before use. Complex **1** was synthesized as reported previously.[1] Other chemicals were purchased and used without further purification.

Synthesis of ($Me_2SiSiMe_2$)[η^5-$C_5H_4Fe(CO)_2I$]$_2$ (2). To a Schlenk flask were added 0.24 g of **1** (0.50 mmol), 0.13 g of I_2 (0.50 mmol), and 10 mL of chloroform. The mixture was stirred at room temperature overnight. The resulting solution was washed with a saturated solution of sodium sulfite and then with water and dried over anhydrous sodium sulfate. After removal of sodium sulfate by filtration, the solvent was evaporated under reduced pressure to give a solid residue, which was purified through a column (neutral Al_2O_3, chloroform) to give a brown band. Collection of this band gave 0.18 g (77% yield) of **2** as dark crystals, mp 143−145 °C. ^1H NMR: $CDCl_3$, δ 0.46 (s, 12H, SiMe), 4.90 (dd, $J = 1.5$, 1.5 Hz, 4H, Cp), 5.16 (dd, $J = 1.5$, 1.5 Hz, 4H, Cp); acetone-d_6, δ 0.52 (s, 12H, SiMe), 5.30 (dd, $J = 2.0$, 2.0 Hz, 4H, Cp), 5.38 (dd, $J = 2.0$, 2.0 Hz, 4H, Cp). ^{13}C NMR ($CDCl_3$): δ −3.75 (SiMe), 85.50, 85.68, 92.55 (Cp), 213.08 (CO). IR (KBr): ν_{CO} 2024 (s), 1983 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{20}O_4Fe_2I_2Si_2$: C, 29.94; H, 2.79; I, 35.15. Found: C, 30.44; H, 2.98; I, 35.29.

Synthesis of $\{(Me_2SiSiMe_2)[\eta^5\text{-}C_5H_4Fe(CO)_2]_2I^+\}(I_5^-)$ (4). To a Schlenk flask were added 0.12 g of **1** (0.25 mmol) and 5 mL of benzene, to which a solution of 0.13 g of I_2 (0.50 mmol) in 5 mL of benzene was added. The mixture was left at room temperature for 30 min. During this time black crystals were formed, which was collected by filtration to give 0.19 g (62%, based on **1**) of **4**, mp 93−95 °C. ^1H NMR (acetone-d_6): δ 0.65 (s, 12H, SiMe), 5.45 (dd, $J = 2.0$, 2.0 Hz, 4H, Cp), 5.86 (dd, $J = 2.0$, 2.0 Hz, 4H, Cp). IR (KBr): ν_{CO} 2011 (s), 1996 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{20}O_4Fe_2I_6Si_2$: C, 17.58; H, 1.64; I, 61.92. Found: C, 18.11; H, 1.72; I, 61.97.

When 3 or 4 equiv of I_2 was used in above reaction, quantitative yield of **4** could be obtained. Similar treatment of **1** with 2, 3, and 4 equiv of I_2 in chloroform resulted in isolation of **4** in 7%, 56%, and 83% yield, respectively.

Synthesis of ($Me_2SiSiMe_2$)[η^5-$C_5H_4Fe(CO)(PR_3)I$]$_2$ (5; R = Ph). A solution containing 0.14 g of **2** (0.20 mmol), 0.16 g of PPh_3 (0.6 mmol) and 20 mL of benzene in a Pyrex tube was irradiated using a high-pressure mercury lamp (500 W) for 3 h at room temperature. The resulting solution was transferred to another flask, where the solvent was removed under vacuum. The residue was purified through a column (neutral Al_2O_3, 1:1 petroleum ether/ether) to give 0.16 g (66% yield) of **5** as a green powder, mp 130 °C (dec). ^1H NMR ($CDCl_3$): δ 0.51, 0.52, 0.53, 0.56 (s, 3H:3H:3H:3H, SiMe), 3.50, 3.51, 3.78, 4.58, 4.61, 5.17, 5.27 (br s, 1H: 1H: 2H: 1H: 1H: 1H: 1H, Cp), 7.38, 7. 55 (m, 18H:12H, Ph). ^{13}C NMR ($CDCl_3$): δ −3.90, −3.66, −3.61 (SiMe), 78.12, 78.41, 81.18, 84.48, 84.77, 88.08, 102.12 (Cp), 128.07−136.28 (Ph), 221.38 (d, $J = 33.05$ Hz, CO). ^{31}P NMR ($CDCl_3$): δ 68.93. IR (KBr): ν_{CO} 1967 (s), 1978 (s) cm^{-1}. Anal. Calcd for $C_{52}H_{50}O_2Fe_2I_2Si_2P_2$: C, 52.46; H, 4.23. Found: C, 52.37; H, 4.36.

Synthesis of ($Me_2SiSiMe_2$)[η^5-$C_5H_4Fe(CO)(PR_3)I$]$_2$ (6; R = OPh). A solution containing 0.14 g of **2** (0.20 mmol), 0.19 g of $P(OPh)_3$ (0.6 mmol) and 20 mL of benzene in a Pyrex tube was irradiated with a high-pressure mercury lamp (500 W) for 5 h at room temperature. The solvent was removed, and the residue was purified through a short column (neutral Al_2O_3, 1:1 ether/CH_2Cl_2). The product obtained was washed with hexane to give 0.17 g (67% yield) of **6** as a yellowish powder, mp 105−107 °C. ^1H NMR ($CDCl_3$): δ 0.15, 0.20, 0.30, 0.32 (s, 3H:3H:3H:3H, SiMe), 2.53, 2.57, 4.04, 4.08, 4.32, 4.34, 4.65, 4.77 (m, 1H:1H:1H:1H:1H:1H:1H:1H, Cp), 7.21, 7.35 (m, 6H:24H, Ph). ^{13}C NMR ($CDCl_3$): δ −4.38, −4.23, −4.13 (SiMe), 75.94, 82.45, 82.89, 84.54, 86.34, 97.61 (Cp), 121.57−151.45 (Ph), 217.81 (d, $J = 47.69$ Hz, CO). ^{31}P NMR ($CDCl_3$): δ 131.30. IR (KBr): ν_{CO} 1932 (s), 1944 (s) cm^{-1}. Anal. Calcd for $C_{52}H_{50}O_8Fe_2I_2Si_2P_2$: C, 48.54; H, 3.92. Found: C, 49.11; H, 4.06.

X-ray Crystallography. Single crystals of **2** and **4** suitable for X-ray analyses were obtained from hexane and hexane/CH_2Cl_2 solution, respectively. Data collections were performed on a Brucker SMART 1000 diffractometer using a $2\theta/\omega$ scan technique with Mo Kα ($\lambda = 0.710\,73$ Å) radiation at room temperature. The structures were solved using SHELX-90 program and refined by full matrix least-squares methods on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically and

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Table 1. Crystal Data and Structure Refinement for $(Me_2SiSiMe_2)[\eta^5\text{-}C_5H_4Fe(CO)_2I]_2$ (**2**) and $\{(Me_2SiSiMe_2)[\eta^5\text{-}C_5H_4Fe(CO)_2]_2I^+\}(I_5^-)$ (**4**)

	2	**4**
formula	$C_{18}H_{20}Fe_2I_2O_4Si_2$	$C_{18}H_{20}Fe_2I_6O_4Si_2$
fw	722.02	1229.62
cryst size (mm)	0.22 × 0.20 × 0.10	0.24 × 0.20 × 0.10
cryst system	monoclinic	monoclinic
space group	$C2/c$	$P2_1$
a (Å)	11.5768(11)	8.434(4)
b (Å)	17.4149(17)	18.966(8)
c (Å)	13.6659(15)	10.336(5)
β (deg)	113.956(6)	96.686(9)
V (Å^3)	2517.8(4)	1642.1(13)
Z	4	2
ρ_{calc} (g/cm^{-3})	1.905	2.487
abs coeff (mm^{-1})	3.719	6.617
θ range (deg)	2.25−26.35	1.98−26.38
no. of reflcns collcd	5167	9591
no. of indpt reflcns	2524	5632
no. of obsd reflcns	1641	3616
goodness of fit on F^2	1.014	0.992
R1 indices [$I > 2\sigma(I)$]	0.0509	0.0504
wR2 indices (all data)	0.1355	0.1088
largest peak/hole (e Å^{-3})	0.634/−1.083	0.872/−0.810

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $(Me_2SiSiMe_2)[\eta^5\text{-}C_5H_4Fe(CO)_2I]_2$ (**2**) and $\{(Me_2SiSiMe_2)[\eta^5\text{-}C_5H_4Fe(CO)_2]_2I^+\}(I_5^-)$ (**4**)

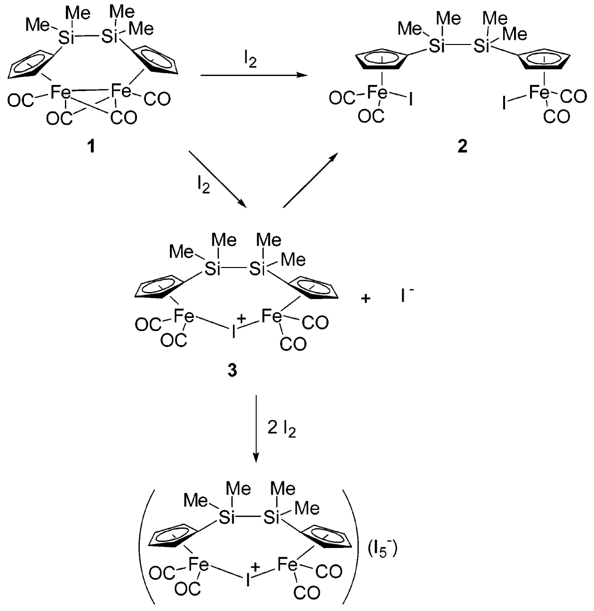
Compound **2**			
I(1)−Fe(1)	2.5969(10)	Si(1)−Si(1A)	2.353(3)
Fe(1)−C(1)	1.804(8)	Fe(1)−C(2)	1.810(10)
Si(1)−C(8)	1.857(7)	Si(1)−C(9)	1.872(8)
Si(1)−C(15)	1.883(6)	Fe(1)−C(3)	2.100(6)
Fe(1)−C(4)	2.085(6)	Fe(1)−C(5)	2.087(7)
Fe(1)−C(6)	2.103(7)	Fe(1)−C(7)	2.103(6)
C(1)−Fe(1)−I(1)	88.1(2)	C(2)−Fe(1)−I(1)	89.0(3)
C(1)−Fe(1)−C(2)	93.6(4)	C(3)−Si(1)−Si(1A)	104.52(19)
C(8)−Si(1)−Si(1)	112.2(3)	C(9)−Si(1)−Si(1)	111.1(3)
Compound **4**			
Fe(1)−I(1)	2.622(2)	Fe(2)−I(1)	2.614(2)
Si(1)−C(5)	1.888(13)	Si(2)−C(14)	1.858(13)
Si(1)−C(11)	1.828(14)	Si(1)−C(10)	1.869(15)
Si(2)−C(13)	1.866(13)	Si(2)−C(12)	1.880(13)
Fe(1)−C(1)	1.78(2)	Fe(1)−C(2)	1.799(16)
Fe(2)−C(4)	1.766(16)	Fe(2)−C(3)	1.80(2)
Si(1)−Si(2)	2.336(5)	I(2)−I(3)	3.003(2)
I(3)−I(4)	2.8596(19)	I(5)−I(6)	2.785(3)
I(4)−I(3)−I(2)	177.40(6)	Fe(1)−I(1)−Fe(2)	121.25(7)
C(1)−Fe(1)−C(2)	91.7(7)	C(1)−Fe(1)−I(1)	88.2(5)
C(2)−Fe(1)−I(1)	96.2(4)	C(4)−Fe(2)−C(3)	93.5(7)
C(4)−Fe(2)−I(1)	90.7(5)	C(3)−Fe(2)−I(1)	96.0(5)
C(5)−Si(1)−Si(2)	114.8(4)	C(14)−Si(2)−Si(1)	114.2(4)

included in the refinement processes in an isotropic manner. Crystal data and refinement details for the two structures are given in Table 1. Selected bond lengths and angles for **2** and **4** can be found in Table 2. Additional information may be found in the Supporting Information.

Results and Discussion

Iodination Reactions. The reaction of **1** with 1 equiv of I_2 in chloroform resulted in cleavage of the iron−iron bond to give diiodide $(Me_2SiSiMe_2)[\eta^5\text{-}C_5H_4Fe(CO)_2I]_2$ (**2**) as the only isolated product (Scheme 2). No product from cleavage of the silicon−silicon bond was obtained. This result is consistent with the expected property of the iron−iron bond, but the stability of the silicon−silicon bond is somewhat unexpected. A probable reason for this phenomenon may be the increased steric hindrance at the silicon−silicon bond compared to the case of $Me_3SiSiMe_3$. Electronic effects of the cyclopentadienylmetal moieties on the reactivity of the silicon−silicon bond may also exist. Similar steric and electronic effects on the reactivity of silicon−silicon bonds toward halogens have been reported in the literature.[14]

Scheme 2



1 2 3 4

When the reaction was performed in benzene in the presence of 2 equiv of I_2, iodonium-bridged diiron complex $\{(Me_2SiSiMe_2)[\eta^5\text{-}C_5H_4Fe(CO)_2]_2I^+\}(I_5^-)$ (**4**) was obtained (62% yield, based on **1**) (Scheme 2). It was found that the counteranion in this complex appeared to be I_5^-, rather than the expected I_3^- as in the case of $\{[CpFe(CO)_2]_2I^+\}(I_3^-)$.[13] The same product was obtained in quantitative yield when 3 or 4 equiv of I_2 was used. During these processes, the silicon−silicon bond still remained unchanged.

To confirm the stability of the silicon−silicon bond observed above, the reaction was monitored by the ^1H NMR spectroscopic method in chloroform-*d*. It was found that, upon being mixed with 1 equiv of I_2, **1** was quickly transformed into the iodonium-bridged intermediate $(Me_2SiSiMe_2)[\eta^5\text{-}C_5H_4Fe(CO)_2]_2I^+$ (**3**) (Scheme 1), accompanied by formation of a small amount of **2**. It was noted that the ^1H NMR spectrum of **3** exhibited a singlet for SiMe protons at 0.62 ppm and two pseudotriplets for Cp groups at 5.16 and 5.50 ppm, which was completely different in chemical shifts from those of **2** as well as of **1**. As the time prolonged, **3** was gradually transformed into **2** in about 5 min. No product from cleavage of the silicon−silicon bond was observed. When 2 equiv of I_2 was used, **3** was formed immediately but transformed into **2** slowly with a half-life time of about 40 min. This is due presumably to the formation of I_3^- which is less reactive than I^- as a nucleophile to react with **3**.[13] No cleavage of the silicon−

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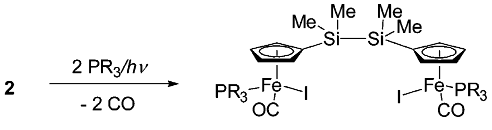
silicon bond was observed although excess I_2 was present in the reaction process. When 3 equiv of I_2 was used in the ^1H NMR experiment, **3** disappeared quickly in about 2 min. In this case, however, instead of being transformed into **2** it precipitated out through combination with I_5^- to form a large amount of crystals of **4** in the NMR tube at the end of the experiment. This formation of **4** from chloroform is unexpected and very interesting. It means that for preparation of the iodonium-bridged intermediate product it is not necessary to use a nonpolar solvent. According to this finding, larger scale preparation of **4** in chloroform was carried out. It was found that the same product **4** containing the counteranion I_5^- could be obtained in 7%, 56%, and 83% yield when 2, 3, and 4 equiv of I_2 were used, respectively.

All the results obtained above evidently demonstrate that the silicon−silicon bond is stable toward I_2. According to this stability, it looks like that there is no significant molecular strain at the silicon−silicon bond. This question will be further clarified through study of the molecular structure of **2** (see below). It is noteworthy that **4** containing the counteranion I_5^- is the first example for an iodonium-bridged diiron complex to combine with a polyiodide anion larger than I_3^-. The fact that only I_5^- but neither a smaller nor larger polyiodide anion was produced when different amounts of I_2 were used is quite interesting. The formation of the stable well-organized network of I_5^- anions (see below), especially the template effect of the $(Me_2SiSiMe_2)[\eta^5\text{-}C_5H_4Fe(CO)_2]_2I^+$ cations on the formation of the networks, should be responsible for this phenomenon.

2 and **4** were characterized by conventional elemental (C and H) analyses. For the products of **4**, iodine contents were also determined. The ^1H NMR spectrum of **2** recorded in chloroform-*d* showed, as expected, a singlet for SiMe groups and two sets of pseudotriplets for the Cp protons. The ^1H NMR spectrum of **4** in chloroform-*d* could not be obtained because it became sparingly soluble in chloroform after being precipitated from the solution. However, acetone-d_6 was found to have good solubility for **4**. The spectrum thus obtained in acetone-d_6 also showed a singlet for SiMe groups and two sets of pseudotriplets for the Cp protons. But the chemical shifts were obviously different from those of **2** recorded in chloroform-*d* as well as in acetone-d_6. The ^{13}C NMR spectrum of **2** exhibited one signal for SiMe, two signals for Cp, and one signal for CO carbon atoms at the expected chemical shifts. The ^{13}C NMR spectrum of **4** was not obtained because it was transformed gradually into **2** upon being dissolved in acetone-d_6. The IR spectra of **2** and **4** gave generally two absorption bands due to symmetrical and asymmetrical vibrations of two germinal CO groups, which is in accord with the structures.

Photochemical Reactions. The silicon−silicon bond in the cyclic structure of **1** has been known to be stable under photochemical conditions.[1] After the cyclic structure has been opened, reexamination of the stability of the silicon−silicon bond of **2** under photochemical conditions should also be of interest. It was found that upon being irradiated with a high-pressure mercury lamp the silicon−silicon bond of **2** was not affected. When the PR_3 ligand was added to the reaction system, CO substitution for the PR_3 ligand took place to give the product $(Me_2SiSiMe_2)[\eta^5\text{-}C_5H_4Fe(CO)(PR_3)I]_2$ (**5**, R = Ph; **6**, R = OPh) (Scheme 3). The formation of **5** and **6** indicates that CO loss can occur during the irradiation processes but the coordinatively unsaturated iron center thus formed is not able to cleave the silicon−silicon bond. Similar photochemical stability of silicon−silicon bonds has been observed in the system $(\eta^5\text{-} Me_3SiSiMe_2C_5H_4)Fe(CO)_2\text{-}Me$,[15,16] although silicon−silicon bonds linked to the metal atoms [e.g. $CpFe(CO)_2SiMe_2SiMe_2Fe(CO)_2Cp$[17,18]] are easily cleaved by the coordinatively unsaturated iron centers formed via CO loss under the same conditions.[19,20] It seems that the photochemical stability of silicon−silicon bonds linked indirectly to the metal atoms through Cp ligands is a common feature.

Scheme 3



5: R=Ph; **6**: R=OPh

5 and **6** were characterized by elemental analyses as well as by spectroscopic methods. ^1H NMR spectrum of **5** showed that it was a mixture of *rac* and *meso* isomers in a ratio of about 1:1. Each of the isomers should give rise to two singlets for $SiMe_2$ protons due to influence of the chiral center, and four such singlets were indeed observed for the mixture of the two isomers. The Cp groups which should exhibit four peaks for each isomer, however, gave only seven peaks for the two isomers due to accidental degeneracy. ^1H NMR spectrum of **6** showed that it was also a mixture of *rac* and *meso* isomers similar to the case of **5**. In this case, four singlets for SiMe protons and eight peaks for the Cp groups were all observed. The ^{13}C NMR spectra of **5** and **6** showed the presence of *rac* and *meso* isomers, although the numbers of the peaks were generally less than expected due to degeneracy. Only one peak could be observed for the *rac* and *meso* isomers in the ^{31}P NMR spectra of either **5** or **6** also due to degeneracy. The IR spectrum of **5** gave a narrow and strong ν_{CO} band which was split into two on the top due to the presence of the *rac* and *meso* isomers. The IR spectrum of **6** showed a situation similar to that of **5,** but the corresponding peaks appeared at higher frequencies due to lower electron-donating ability of $P(OPh)_3$ compared to that of PPh_3. Separation of the *rac* and *meso* isomers proved to be difficult due to their similarity in physical properties.

Molecular Structures. The molecular structure of **2** was determined by the X-ray diffraction method. A molecule of **2** (Figure 1) has C_2 symmetry. The conformation around the silicon−silicon bond appeared to be gauche (Figure 2) rather

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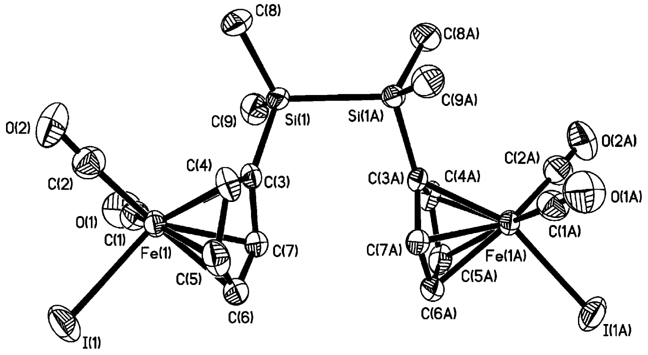

Figure 1. ORTEP plot of $(Me_2SiSiMe_2)[\eta^5\text{-}C_5H_4Fe(CO)_2I]_2$ (**2**). Thermal ellipsoids are given at the 30% probability level.

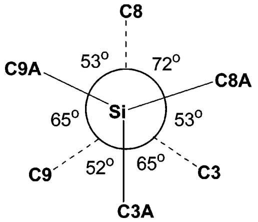

Figure 2. Newmann projection along the silicon−silicon bond axis of $(Me_2SiSiMe_2)[\eta^5\text{-}C_5H_4Fe(CO)_2I]_2$ (**2**).

than the expected anti one. The reasons for this unexpected conformation were not determined in this work. It may be stabilized either by an intermolecular interaction of crystal packing or by an intramolecularly attractive interaction between groups at two silicon atoms. The two Cp groups that are nearly parallel to each other with a dihedral angle of 10.18° may be responsible for such an attractive interaction, if it exists. The length of the Si−Si bond was determined to be 2.353(3) Å. It is interesting to compare this bond length after the cyclic structure was opened with that before opening of the cyclic structure [2.346(4) Å in **1**[1]]. In doing so, it is found that the lengths of the two Si−Si bonds are about the same within the limits of experimental errors. This is direct evidence to show that the silicon−silicon bond in the cyclic structure of **1** is not subject to significant ring strain. Although it has previously been noted that the boatlike conformation of cyclic structure of **1** may cause a certain extent of molecular strain,[1] it seems that this kind of molecular strain caused by the ring conformation is not strong enough to lead to detectable weakening of the silicon−silicon bond. This is in accord with the observed stability of the silicon−silicon bond of **1** toward I_2, taking into account the contribution of the steric and electronic effects (see above).

The molecular structure of **4** was also determined by the X-ray diffraction method. The structure of the cationic part of **4** (Figure 3) has C_1 symmetry. The lengths of the Fe−I bonds are 2.622(2) and 2.614(2) Å, which are slightly longer than the terminal Fe−I bond of **2** and the bridging Fe−I bonds [2.581(2) and 2.595(2) Å] of $\{[CpFe(CO)_2]_2I^+\}(BF_4^-)$ (**7**).[21] The length of the Si−Si bond is 2.336(5) Å, also quite close to those of **2** and **1** within the limits of experimental

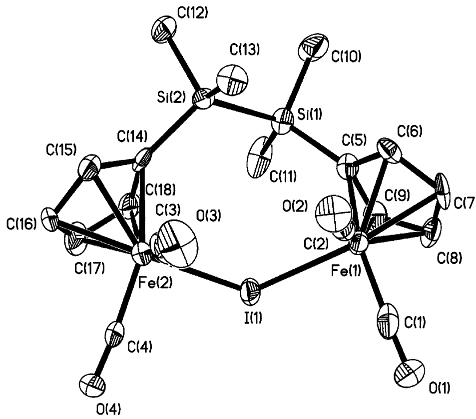

Figure 3. ORTEP plot of the cation part of $\{(Me_2SiSiMe_2)[\eta^5\text{-}C_5H_4Fe(CO)_2]_2I^+\}(I_5^-)$ (**4**). The counteranion is omitted. Thermal ellipsoids are given at the 30% probability level.

errors, indicating that there is no obvious molecular strain at the Si−Si bond in the cyclic structure of **4**. It is noteworthy that the bond angle of $Fe-I^+-Fe$ is 121.25(7)°, which is abnormally large compared to the reported angle of 110.8(1)° for the case of **7**. This difference between the two complexes indicates that the bond angle at the iodonium center is quite flexible. It has been reported[21] that the bond angle is generally sensitive to steric effects between groups attached to the iodonium center and when the attached groups are not particular bulky, this angle tends to take a value of 90° to optimize the employment of its p-orbitals. This has been observed in the case of diphenyliodonium ion (**8**), where the $C-I^+-C$ angle is 92°.[22] It is noteworthy that if solely determined according to these angles, the orbital hybridization at the iodonium center should be sp^2, sp^3, and pure p in the cases of **4**, **7**, and **8**, respectively. Thus, it will be interesting to see in the future if an even larger bond angle of 180° featuring an sp hybridization at the iodine atom could be reached in case of special steric demands.

The structure of the I_5^- anion is shown in Figure 4. As usually seen, the I_5^- anion consists of a linear I_3^- anion [I(2)−I(3)−I(4), 177.4°] and an I_2 molecule.[23] The bond lengths within the I_3^- anion [I(2)−I(3), 2.8596(19) Å, and I(3)−I(4), 3.003(2) Å] and within the I_2 molecule [I(5)−I(6), 2.785(3) Å] are also normal.

Between the I_3^- anion and the I_2 molecule, significant interaction [I(2)−I(6), 3.460 Å] and weak secondary interaction [I(3)−I(6), 4.157 Å] exist to combine the two species into a relatively discrete unit of I_5^- having approximately an L-shape [I(3)−I(2)−I(6), 79.7°].[24] It is interesting that these I_5^- units are linked together through different interactions to result in formation of a two-dimensional layered structure. The interaction scheme has been shown in Figure 4, in which each I_5^- unit is linked to the next one through significant interaction [I(2)−I(5′)/I(2‴)−I(5″), 3.578 Å] to form branched infinite chains. Cross-linking of these chains

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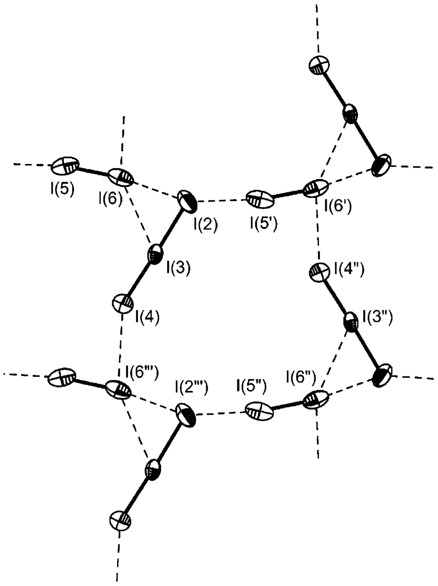

Figure 4. Structure and cross-linking scheme of the I$_5^-$ anion, showing interactions ranging up to the van der Waals distance of 4.30 Å. Thermal ellipsoids are given at the 50% probability level.

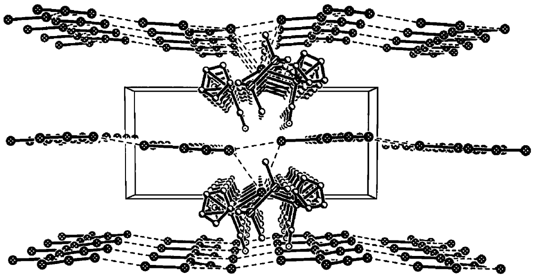

Figure 5. View of the layers of the I$_5^-$ networks along the *c*-axis, showing location of the cations between the layers in the central unit cell.

through weak secondary interactions [I(4)−I(6‴)/I(4″)−I(6′), 4.194 Å] forms the layered structure. The distance between two adjacent layers (Figure 5) is 8.434 Å. The (Me$_2$SiSiMe$_2$)-[η^5-C$_5$H$_4$Fe(CO)$_2$]$_2$I$^+$ cations are located between the layers to form a huge sandwich-like structure. The top view of the layers is illustrated in Figure 6. It shows the structure and stacking of the networks which form channels surrounded by 11 iodine atoms with a diameter of about 10 Å [I(4)−I(4″), 9.652 Å, and I(5′)−I(5″), 10.336 Å]. The cations reside in the channels. It is very impressive that the shape of the channels has a good fit with the dimensions of the cation's structure, which unambiguously demonstrates the template effects of the cations on the formation the iodine networks. Weak interactions that exist between the bridging iodonium and the network iodine atoms [I(1)−I(2), 4.210 Å, and I(1)−I(5), 4.424 Å] may contribute to the realization of the template effects. Also noticeable in Figure 4 are the bond angles [e.g.: I(3)−I(2)−I(5′), 123.8°; I(2)−I(5′)−I(6′), 169.4°; I(5′)−I(6′)−I(4″), 80.5°; I(3)−I(4)−I(6‴), 149.9°; I(4)−I(6″)−I(2″), 107.7°; I(5″)−I(2‴)−I(6‴), 153.1°] which vary considerably. This indicates that the two-dimensional networks constructed solely from iodine atoms could be rather flexible. This may provide opportunity for further tuning the network structure through modifying the cationic template.

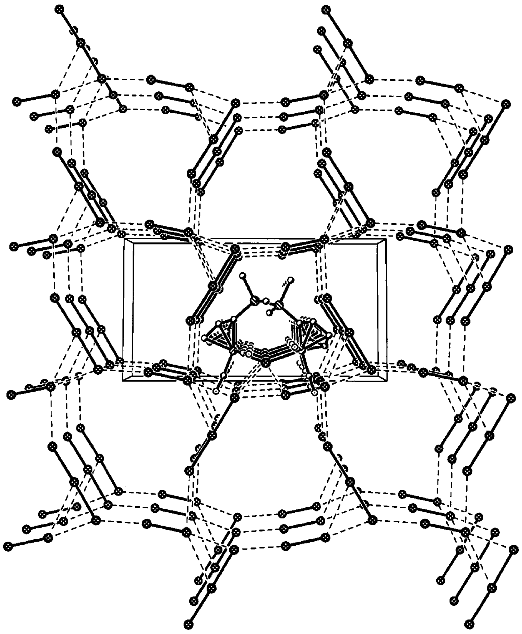

Figure 6. View of the I$_5^-$ networks along the *a*-axis, showing the channels surrounded by 11 iodine atoms. The good fit of the shape of the channels with the cation is shown in the central unit cell.

Conclusions

The silicon−silicon bond in the cyclic structure of title complex **1** has been found to be stable toward I$_2$. This has resulted in selective cleavage of the iron−iron bond by I$_2$ to give the ring-opened diiodide **2**. The molecular structure of **2** determined by the X-ray diffraction method provides direct evidence to conclude that the silicon−silicon bond in the cyclic structure of **1** is not subject to significant ring strain. This conclusion will be important for further understanding the mechanism of the thermal rearrangement reaction that occurred for the cyclic structure. Photochemical stability of the silicon−silicon bond of **2** has also been observed. It confirms that a silicon−silicon bond linked to a Cp ligand cannot be cleaved by the transition metal center even if CO loss has occurred. The study on the reaction of **1** with excess I$_2$ has also resulted in the isolation of the iodonium-bridged diiron complex **4** containing unexpectedly I$_5^-$ rather than I$_3^-$ as the counteranion. The molecular structure of **4** determined by the X-ray diffraction method shows self-assembly of the I$_5^-$ anions to form novel layered, two-dimensional networks composed solely of iodine atoms. The cationic part of the complex demonstrates obvious template effects on formation of the network structure. This template effect can well explain why the I$_5^-$ anions have always been produced when different equivalents of I$_2$ are used to react with **1**.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structural determinations of **2** and **4**. This material is available free of charge via the Internet at http://pub.acs.org.

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