Cleavage of the Fe—Fe Bond of (Me$_2$SiSiMe$_2$)[η^5-C$_5$H$_4$Fe(CO)$_2$]$_2$ with Na/Hg and Molecular Structure of the Ring-Opened Complex†

SUN, Huai-Lin*(孙怀林)   ZHANG, Zhen-Sheng(张振生)   ZHOU, Xiu-Zhong*(周秀中)
*Department of Chemistry, Nankai University, Tianjin 300071, China*

The reaction of the title cyclic complex (**1**) with sodium amalgam in THF resulted in the expected cleavage of the Fe—Fe bond to afford bis-sodium salt (Me$_2$SiSiMe$_2$)[η^5-C$_5$H$_4$Fe (CO)$_2$Na]$_2$ (**4**). The latter was not isolated and was used directly to react with MeI, PhCH$_2$Cl, CH$_3$C(O)Cl, PhC(O)Cl, Cy$_3$SnCl (Cy = cyclohexyl) or Ph$_3$SnCl to afford corresponding ring-opened derivatives (Me$_2$SiSiMe$_2$)[η^5-C$_5$H$_4$Fe (CO)$_2$R]$_2$ [**5**, R = Me; **6**, R = PhCH$_2$; **7**, R = CH$_3$C(O); **8**, R = PhC (O); **9**, R = Cy$_3$Sn or **10**, R = Ph$_3$Sn]. The crystal and molecular structures of **10** were determined by X-ray diffraction analysis. The molecule took the desired *anti* conformation around the Si—Si bond. The length of the Si—Si bond is 0.2343(3) nm, which is essentially identical to that in the cyclic structure of **1** [0.2346(4) nm]. This result unambiguously demonstrates that the Si—Si bond in the cyclic structure of **1** is not subject to obvious ring strain.

Keywords   silicon, iron, sodium amalgam, X-ray diffraction

Introduction

Considerable attention has recently been paid toward the novel thermal rearrangement reaction of (Me$_2$SiSiMe$_2$) [η^5-C$_5$H$_4$Fe(CO)$_2$]$_2$ (**1**), which proceeds through metathesis of the Si—Si and Fe—Fe bonds to give -[Me$_2$Si-η^5-C$_5$H$_4$Fe(CO)$_2$SiMe$_2$-η^5-C$_5$H$_4$Fe(CO)$_2$]- (**2**) containing two Si—Fe bonds (Scheme 1). Since this reaction was first reported in 1993,[1] many efforts in this area have been devoted to explore the scopes of this reaction in related systems. For example, possibilities of the reaction in similar cyclic structures to that of **1** but containing a Ge—Ge bond[2-4] in place of the Si—Si bond or a Ru—Ru bond[5,6] in place of the Fe—Fe bond have been investigated. Mechanistic details of this reaction have also been under intensive study, which has resulted in recognition of the intramolecular nature and the interesting regioselective character.[7,8] All results obtained up to now demonstrate that it is the cyclic structure that is responsible for the reaction to take place. But what kind of property of the cyclic structure is the critical factor that leads to the taking place of the reaction is still a question.

Scheme 1

1   2
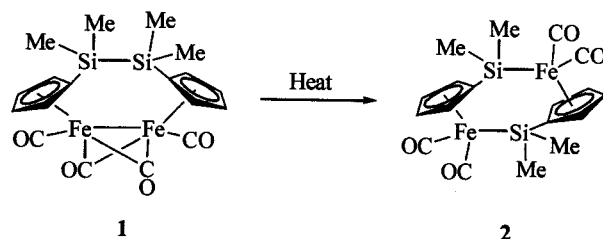
To examine if cyclic structure has any unusual properties, we have recently studied the reaction of **1** with I$_2$, which unexpectedly revealed the selective cleavage of the Fe—Fe bond with retention of the Si—Si bond to lead to the ring-opened complex (Me$_2$SiSiMe$_2$)[η^5-C$_5$H$_4$Fe-(CO)$_2$I]$_2$ (**3**).[9] It was interesting to note that **3** could be a wonderful acyclic model complex suitable for comparison with the cyclic structure of **1**. This comparison may hopefully provide the desired information about if there is significant ring strain at the Si—Si bond in the cyclic structure. However, the molecular structure of **3** determined by X-ray diffraction analysis showed an unusual gauche conformation rather than the *anti* one around the Si—Si bond. Thus, structural data of acyclic model complexes with the normal *anti* conformation are still desired. Herein, we report an alternative ring-opening method involving reductive cleavage of the Fe—Fe bond with sodium amalgam (Na/ Hg), which afforded the ring-opened bis-sodium salt (Me$_2$SiSiMe$_2$)[η^5-C$_5$H$_4$Fe(CO)$_2$Na]$_2$ (**4**) as well as a series of its derivatives (Me$_2$SiSiMe$_2$)[η^5-C$_5$H$_4$Fe(CO)$_2$R]$_2$ (**5**, R = Me; **6**, R = PhCH$_2$; **7**, R = CH$_3$C(O); **8**, R = PhC(O); **9**, R = Cy$_3$Sn or **10**, R = Ph$_3$Sn). A standard *anti* conformation was revealed by study on the molecular structure of **10**.

Experimental

All reactions were carried out under an argon atmo-

sphere by using standard Schlenk techniques. ^{1}H NMR spectra were recorded on a JEOL FX90Q or JNH-60SI spectrometer. IR spectra were recorded on a Nicolet 5DX FT-IR instrument and elemental analyses were performed using a Vario EL instrument. THF and hexane were dried by refluxing with sodium in the presence of benzophenone and distilled just before use. Complex 1 was synthesized using the reported method.[1] Other chemicals were purchased and used without further purification.

Preparation of 4

To 1% Na/Hg (30 g) in a 100-mL Schlenk flask was added 1 (0.468 g, 1.0 mmol) in THF (40 mL) while stirring magnetically. The reaction was lasted for 30 min after the addition was completed to give an orange THF solution containing a large amount of orange suspension. This solution, along with the suspension of 4, was used directly in the next reaction.

Preparation of 5—10

A typical experimental procedure is described for the synthesis of 5. The solution layer obtained above was transferred to another flask using a syringe, to which CH₃I (0.45 g, 3.0 mmol) was added with magnetically stirring at room temperature. The resulting solution, which became green, was stirred for another 30 min to complete the reaction. After removal of the solvent under reduced pressure, the residue was dissolved in a small amount of benzene and purified through a short column (neutral Al₂O₃, *n*-hexane). Collection of the yellow band gave 5 as yellow crystals. In similar manners, 6—10 were obtained as yellow crystals when PhCH₂Cl, CH₃C(O)Cl, PhC(O)Cl, Cy₃SnCl or Ph₃SnCl were used in place of CH₃I.

5   Yield 70%, m.p. 49—51 ℃; ^{1}H NMR (CDCl₃) δ: 0.31 (s, 12H, SiMe), 0.31 (s, 6H, FeMe), 4.68 (brs, 4H, Cp), 4.86 (brs, 4H, Cp); IR (KBr) ν_{co}: 1996, 1956 cm⁻¹. Anal. calcd for C₂₀H₂₆O₄Si₂Fe₂: C 48.21, H 5.26; found C 48.22, H 5.40.

6   Yield 71%, m.p. 90—92 ℃; ^{1}H NMR (CDCl₃) δ: 0.30 (s, 12H, SiMe), 2.69 (s, 4H, FeCH₂), 4.59 (brs, 4H, Cp), 4.68 (brs, 4H, Cp), 7.16—7.33 (m, 10H, Ph); IR (KBr) ν_{co}: 1995, 1931 cm⁻¹. Anal. calcd for C₃₂H₃₄O₄Si₂Fe₂: C 59.09, H 5.27; found C 59.26, H 5.27.

7   Yield 22%, m.p. 68—70 ℃; ^{1}H NMR (CDCl₃) δ: 0.31 (s, 12H, SiMe), 2.59 (s, 6H, CCH₃), 4.76 (brs, 4H, Cp), 5.03 (brs, 4H, Cp); IR (KBr) ν_{co}: 2016, 1959, 1647 cm⁻¹. Anal. calcd for C₂₂H₂₆O₆Si₂Fe₂: C 47.67, H, 4.73; found C 47.78, H 4.96.

8   Yield 44%, m.p. 130—132 ℃; ^{1}H NMR (CDCl₃) δ: 0.34 (s, 12H, SiMe), 4.83 (brs, 4H, Cp), 5.01 (brs, 4H, Cp), 7.40—7.46 (m, 10H, Ph); IR (KBr) ν_{co}: 2016, 1955, 1610 cm⁻¹. Anal. calcd for C₃₂H₃₀O₆Si₂Fe₂: C 56.65, H 4.46; found C 57.14, H

4.54.

9   Yield 79%, m.p. 193—195 ℃; ^{1}H NMR (CDCl₃) δ: 0.41 (s, 12H, SiMe), 1.20—1.95 (m, 66H, Cy), 4.52 (brs, 4H, Cp), 4.89 (brs, 4H, Cp); IR (KBr) ν_{co}: 2026, 1975 cm⁻¹. Anal. calcd for C₅₄H₈₆O₄Si₂Fe₂Sn₂: C 53.85, H 7.20; found C 53.87, H 7.47.

10   Yield 61%, m.p. 203—205 ℃; ^{1}H NMR (CDCl₃) δ: 0.37 (s, 12H, SiMe), 4.65 (brs, 8H, Cp), 7.27—7.60 (m, 30H, Ph); IR (KBr) ν_{co}: 1983, 1926 cm⁻¹. Anal. calcd for C₅₄H₅₆O₄Si₂Fe₂Sn₂: C 55.53, H 4.32; found C 55.54, H 4.91.

X-Ray crystallography

Crystals of 10 suitable for X-ray diffraction analysis were obtained from a mixed solvent of hexane and benzene. Data collection was performed on an ENRAF-NONIUS CAD-4 diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.071037 nm) using the ω-2θ scan technique at room temperature. The structure was solved by direct phase determination method. Hydrogen atoms were not found. All non-hydrogen atoms were refined by full-matrix least-squares methods with anisotropic thermal parameters. All calculations were performed on a PDP 11/4 computer using the SDP-PLUS program system. A summary of the crystallographic data is shown in Table 1. Selected bond lengths and angles are shown in Table 2.

Table 1   Crystallographic data for (Me₂SiSiMe₂)[η⁵-C₅H₄Fe(CO)₂SnPh₃]₂ (**10**)

Formula	C₅₄H₅₀Fe₂O₄Si₂Sn₂
Molecular weight	1168.24
Crystal size (mm)	0.3 × 0.2 × 0.3
Crystal system	Triclinic
Space group	*P*-1
a (nm)	0.7984(1)
b (nm)	0.9403(1)
c (nm)	1.7845(3)
α (°)	87.05(2)
β (°)	87.18(2)
γ (°)	72.15(2)
V (nm³)	1.2727
D_c (mg/mm³)	1.524
Z	1
Scan range, θ (°)	2 to 23
μ (cm⁻¹)	16.21
F(000)	586
Independent reflections	3674
Observed reflections	2830 [*I* ⩾ 3σ(*I*)]
R	0.044
wR	0.053

Table 2   Selected bond lengths (nm) and angles (°) for $(Me_2SiSiMe_2)[\eta^5-C_5H_4Fe(CO)_2SnPh_3]_2$ (**10**)

Si(1)—Si(1)	2.343(3)
Si(1)—C(21)	1.862(6)
Si(1)—C(31)	1.890(7)
Si(1)—C(32)	1.895(7)
Sn(1)—Fe(1)	0.25441(9)
Sn(1)—C(41)	0.2155(7)
Sn(1)—C(51)	0.2151(7)
Sn(1)—C(61)	0.2146(7)
Fe(1)—C(11)	0.1734(8)
Fe(1)—C(12)	0.1741(8)
Fe(1)—C(21)	0.2125(5)
Fe(1)—C(22)	0.2108(6)
Fe(1)—C(23)	0.2107(7)
Fe(1)—C(24)	0.2105(6)
Fe(1)—C(25)	0.2127(6)
Si(1)-Si(1)-C(21)	105.4(3)
Si(1)-Si(1)-C(31)	111.4(3)
Si(1)-Si(1)-C(32)	109.7(2)
Sn(1)-Fe(1)-C(11)	89.0(2)
Sn(1)-Fe(1)-C(12)	86.0(2)
C(11)-Fe(1)-C(12)	92.4(3)
Fe(1)-Sn(1)-C(41)	110.4(2)
Fe(1)-Sn(1)-C(51)	111.4(2)
Fe(1)-Sn(1)-C(61)	117.3(2)

groups. Other signals that arose from the alkyl, acyl and stannyl moieties were also observed at the expected chemical shifts. IR spectra of these products generally gave two absorption bands corresponding to the symmetrical and asymmetrical stretching vibration modes of two geminal carbonyl groups. Additional absorption bands were observed in the carbonyl absorption region for **7** and **8** due to the presence of the acyl groups. All of these results are in accord with the molecular structures of **5**—**10**.

Scheme 2

5: R = Me   X = I
6: R = PhCH$_2$ X = Cl
7: R = CH$_3$C(O)   X = Cl
8: R = PhC(O)   X = Cl
9: R = Cy$_3$Sn   X = Cl
10: R = Ph$_3$Sn   X = Cl
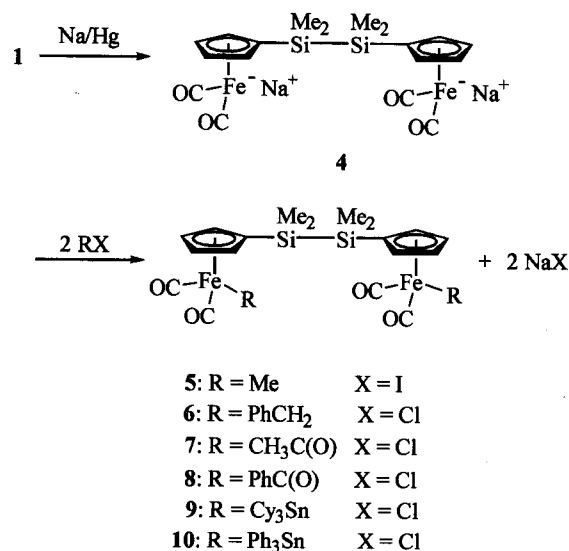
Results and discussion

Synthesis of complexes

Na/Hg has been well known to be a mild reducing agent[10] and hopefully to be able to cleave the Fe—Fe bonds with retention of the Si—Si bond of **1**. Thus, the reaction of **1** with Na/Hg was carried out in THF and found to lead to cleavage of the Fe—Fe bond to produce bis-sodium salt **4** as expected (Scheme 2). This reaction proceeded smoothly at room temperature and finished in about 30 min as indicated by disappearance of the dark-red color of **1**. At the end of the reaction, the solution became orange with a large amount of orange suspension present due to that **4** was only slightly soluble in THF. Compound **4** thus formed was not isolated and was used directly to react with a series of alkylating, acylating and stannylating agents to produce the expected ring-opened derivatives **5**—**10** (Scheme 2).

Compounds **5**—**10** were all yellow crystalline solids. They were stable enough to be handled in the air at room temperatuere during the separation and purification processes. But long-term standing in the air, especially in solutions, could cause obvious decomposition. They were characterized by elemental analyses. ^{1}H NMR spectra of them generally gave an up-field singlet due to the Si—Me protons and two sets of multiplets corresponding to the Cp

Molecular structure

The molecular structure of **10** was determined by the X-ray diffraction method. The molecule (Fig. 1) had C_i symmetry, in which two triphenylstannyl groups were linked to the iron atoms after the Fe—Fe bond was cleaved, while the Si—Si bond was still retained. Unlike the structure of **3** reported previously,[9] the molecule of **10** took the desired *anti* conformation around the Si—Si bond. The length of the Si—Si bond in this ring-opened structure was determined to be 0.2343(3) nm, which is essentially identical to that in the cyclic structure of **1** [0.2346(4) nm][1] within the limits of experimental errors. This result demonstrates that either forming or breaking of the cyclic structure does not affect the length of the Si—Si bond. Therefore, the Si—Si bond in the cyclic structure of **1** must not be subject to obvious ring strain. We have previously reported that the boat-like conformation of the six-membered cylcic structure of **1**, which consists of two silicon, two iron and two bridge-head carbon atoms, might cause certain extent of molecualr strain,[1] because groups at two silicon atoms were in eclipsed arrangement. According to the present result, it is likely that this kind of molecular strain is not so serious as to lengthen the Si—Si bond. It is also of interest here to compare the Si—Si bond length of **10** with that of **3** [0.2353(3) nm],[9] which exhibits a tendency of slightly lengthening the Si—Si bond in the
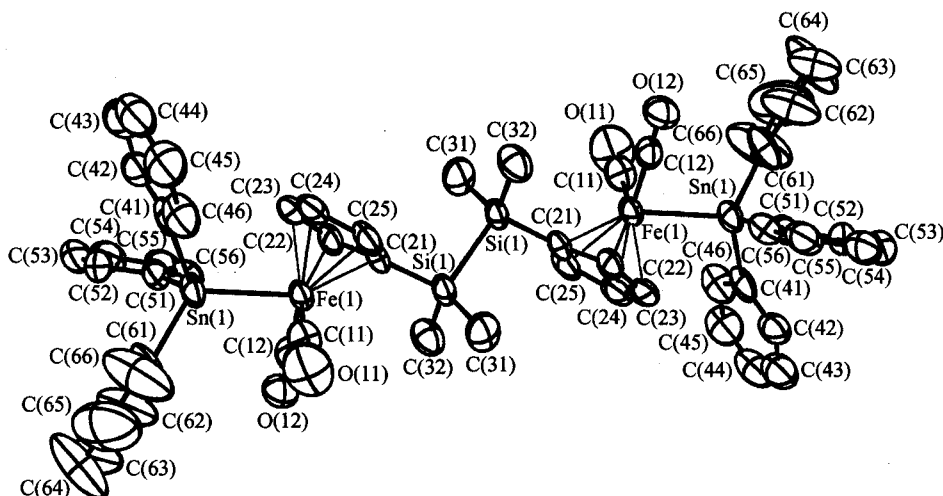
Fig. 1 Molecular structure of **10**.

case of **3**. This could be caused by the gauche conforma-
tion of **3**, which may result in weak repulsively sterric ef-
fects between the groups at two silicon atoms. Therefore,
the unusual gauche conformation should not be due to in-
tramolecular attractive effects but alternatively it most
probably was stabilized by intermolecular interactions of
crystal packing.[9] The length of the Fe—Sn bond of **10** was
determined to be 0.25441(9) nm, which is nearly the
same as that of $CpFe(CO)_2SnPh_3$ (0.2540 nm).[11] Other
bond lengths and angles are normal for this complex as
shown in Table 2.

Conclusion

The reaction of **1** with Na/Hg was found to be an ef-
fective route to cleave the Fe—Fe bond and afford the ex-
pected ring-opened products. Various alkyl, acyl and
stannyl iron derivatives could be synthesized using this
method. Molecular structure of the bis-triphenylstannyl
derivative determined by the X-ray diffraction method
demonstrated the desired *anti* conformation around the
Si—Si bond. The length of its Si—Si bond was found to
be identical to that of **1**, unambiguously demonstrating
that the cyclic structure of **1** is not subject to obvious ring
strain. This can be an evidence for ruling out the possible
mechanism involving thermally induced cleavage of the

Si—Si bond as the initial step for the novel rearrangement
from **1** to **2**.

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