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# Thermal rearrangement reaction of disilyl-bridged bis(tetramethyl cyclopentadienyl) tetracarbonyl diiron The molecular structures of $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5Me_4)Fe(CO)]_2(\mu\text{-}CO)_2$ and $[(Me_2Si)(\eta^5\text{-}C_5Me_4)Fe(CO)_2]_2$

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**Abstract**

Binuclear iron complex $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5Me_4)Fe(CO)]_2(\mu\text{-}CO)_2$ (**2**) have been prepared in good yield by thermal treatment of $Me_4HC_5(Me_2SiSiMe_2)C_5HMe_4$ with $Fe(CO)_5$. Its thermal rearrangement reaction exhibits greater difficulty in comparison with the parent complex $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5H_4)Fe(CO)]_2(\mu\text{-}CO)_2$ (**1**). Even when the reaction time was prolonged to 24 h, the rearrangement product $[(Me_2Si)(\eta^5\text{-}C_5Me_4)Fe(CO)_2]_2$ (**3**) was isolated in 3% yield. The molecular structures of **2** and **3** have been determined by X-ray diffraction. Crystals of **2** are orthorohomic, space group $P2_12_12_1$, with $a = 11.015(5)$ Å, $b = 11.020(4)$ Å, $c = 11.173(4)$ Å, $V = 1355(2)$ Å$^3$, $Z = 2$, $D_x = 1.423$ g cm$^{-3}$, $R$ ($R_w$) = 0.056 (0.064). Crystals of **3** are triclinic, space group P-1, with $a = 8.297(1)$ Å, $b = 9.988(2)$ Å, $c = 10.290(2)$ Å, $\alpha = 60.70(1)°$, $\beta = 63.79(2)°$, $\gamma = 77.41(2)°$, $V = 667.1(2)$ Å$^3$, $Z = 1$, $D_x = 1.46$ g cm$^{-3}$, $R$ ($R_w$) = 0.044 (0.031).


*Keywords:* Iron; Tetramethyl; Thermal rearrangement reaction; Metal carbonyl; Bridged complexes

## 1. Introduction

Considerable attention is currently focused on the synthesis and study of bridged binuclear iron complexes in which the two cyclopentadienyl ligands are linked by a bridge and the $Fe_2(CO)_4$ moiety is constrained to a cis configuration [1–6]. Recently our introduction of tetramethyl disilanylene as a linking group into this system led to the discovery of a novel rearrangement reaction between Si–Si and Fe–Fe bonds in $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5H_4)Fe(CO)]_2(\mu\text{-}CO)_2$ (**1**) [7]. In order to examine the effect of ring-substituents on the rearrangement reaction, we expanded this system to tetramethyl-substituted cyclopentadienyl analogue $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5Me_4)Fe(CO)]_2(\mu\text{-}CO)_2$ (**2**). We report here full details on the synthesis of **2** and its thermal rearrangement reaction.

## 2. Experimental details

Schlenk and vacuum line technique were employed for all manipulations of air- and moisture-sensitive compounds. Reaction solvents were distilled from appropriate drying agents under argon before use. Tetrahydrofuran and xylene were distilled from sodium/benzophenone ketyl and purged with argon atmosphere prior to use. $C_5Me_4H_2$ [8,9], $ClMe_2SiSiMe_2Cl$ [10] were prepared according to literature methods. Proton ($^1$H NMR) spectra were obtained on a Bruker AC-P200 spectrometer using $CHCl_3$ ($\delta$: 7.24 ppm) as an internal standard. Elemental analyzes were performed by Perkin–Elmer 240C analyzer. Infrared spectra were obtained as KBr disk and recorded on a Nicolet 5DX FT-IR spectrometer.

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### 2.1. Preparation of $HMe_4C_5Me_2SiSiMe_2C_5Me_4H$

A solution of 10.0 g (82 mmol) of $C_5Me_4H_2$ in 180 ml of THF, cooled to −20°C, was treated dropwise (~ 15 min) with 43 ml of 1.96 M hexane-solution of BuLi (84.3 mmol) to give a light-yellow solution, which was allowed to raise to room temperature and then stirred for an additional 5 h, The mixture was cooled again to −20°C and a solution of 7.6 g (40.6 mmol) of $ClMe_2SiSiMe_2Cl$ in 60 ml of THF was added dropwise (~ 1.5 h). The reaction mixture was slowly warmed to room temperature and stirred 3 h, subsequently refluxed for an additional 5 h. One hundred ml of water was added to the mixture. The aqueous layer was separated from the oil layer and extracted twice with 60 ml of ether. The oil and ether extracts were combined and dried with sodium carbonate overnight. The solvent was removed under reduced pressure to give yellow oil. Then acetone was added to the oil, subsequently cooled to −20°C. The resulting white crystals were collected by filtration and finally washed with acetone and heptane. A total of 2.5 g of white crystals was obtained in 17% yield. It was identified to be $HMe_4C_5Me_2SiSiMe_2C_5Me_4H$. Anal. Calcd for $C_{22}H_{38}Si_2$: C, 73.66; H, 10.68. Found: C, 72.98; H, 10.52. $^1H$ NMR ($CDCl_3$) $\delta$: 0.04 (s, 12H, $SiMe_2$), 1.80 (s, 12H, Cp–Me), 1.88 (s, 12H, Cp–Me), 2.73 (s, 2H, Cp–H).

Table 1
Summary of X-ray diffraction data

| | 2 | 3 |
|---|---|---|
| Formula | $C_{26}H_{36}Fe_2O_4Si_2$ | $C_{26}H_{36}Fe_2O_4Si_2$ |
| Formula weight | 580.43 | 580.43 |
| Space group | $P2_12_12_1$ | P-1 |
| Crystal system | orthorhombic | triclinic |
| $Z$ | 2 | 1 |
| $a$ (Å) | 11.015(5) | 8.297(1) |
| $b$ (Å) | 11.020(4) | 9.988(2) |
| $c$ (Å) | 11.173(4) | 10.290(2) |
| $\alpha$ (°) | 90 | 60.70(1) |
| $\beta$ (°) | 90 | 63.79(2) |
| $\gamma$ (°) | 90 | 77.41(2) |
| Volume (Å$^3$) | 1355(2) | 667.1(2) |
| $d_{calc}$ (g cm$^{-1}$) | 1.423 | 1.46 |
| Crystal size (mm) | 0.20×0.20×0.30 | 0.20×0.20×0.25 |
| Radiation (Å$^3$) | MoK $\alpha$ (0.71073) | MoK $\alpha$ (0.71073) |
| $\mu$ (cm$^{-1}$) | 11.855 | 12.04 |
| Data collection method | $\omega-2\theta$ | $\omega-2\theta$ |
| Max $2\theta$ (°) | 50.0 | 50.0 |
| Total number of observations | 1159 | 2480 |
| Number of unique data, $I>3\sigma(I)$ | 810 | 2162 |
| Final number of variables | 172 | 154 |
| $R^a$ | 0.056 | 0.044 |
| $R_w^b$ | 0.064 | 0.031 |
| Goodness-of-fit | 1.85 | 5.19 |

[a] $\Sigma\|\|F_o\|-\|F_c\|\|/\Sigma|F_o|$.
[b] $[\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$.

Table 2
Selected bond lengths (Å) and angles (°) for **2**

| | | | |
|---|---|---|---|
| *Bond distances* | | | |
| Fe(1)–Fe(1a) | 2.553(2) | Si–C(21) | 1.68(3) |
| Si–Sia | 2.153(7) | Si–C(22) | 1.88(4) |
| Fe(1)–C(1) | 1.934(8) | Si–C(21a) | 1.64(2) |
| Fe(1)–C(1a) | 1.903(8) | Si–C(22a) | 1.79(4) |
| Fe(1)–C(2) | 1.737(8) | C(1)–O(1) | 1.18(2) |
| Fe(1)–Cp(1) | 1.738[a] | C(2)–O(2) | 1.16(2) |
| *Bond angles* | | | |
| Fe(1)–C(11)–Si | 133.8(5) | Fe(1)–C(1)–Fe(1a) | 83.4(3) |
| C(11)–Si–Sia | 117.5(3) | C(21)–Si–C(22) | 100(2) |
| Fe(1a)–Fe(1)–C(11) | 108.6(2) | C(21a)–Si–C(22a) | 96(1) |

[a] The distance from the centroid of Cp ring to the linked Fe atom. C(21) and C(21a) represent two directions of this atom in the crystals, each having the occupancy of 0.5.

### 2.2. Preparation of $(Me_2SiSiMe_2)[(\eta^5-C_5Me_4)Fe(CO)]_2(\mu-CO)_2$ (2)

A solution of 2.87 g (8.0 mmol) of $HMe_4C_5Me_2SiSiMe_2C_5Me_4H$ and 3.15 g (16.1 mmol) of $Fe(CO)_5$ in 40 ml of xylene was refluxed for 5 h. The solvent was removed under vacuum giving dark brown crude product. The solids were dissolved in chloroform and then filtered to remove insoluble substance. Removal of the solvent afforded to dark-red solids and finally washed with acetone. A total of 3.0 g of black crystals was obtained in 64.7% yield for **2**: Mp > 400°C. Anal. Calcd for $C_{26}H_{36}Fe_2O_4Si_2$: C, 53.80; H, 6.25. Found: C, 53.66; H, 6.12. $^1H$ NMR ($CDCl_3$) $\delta$: 0.20 (s, 12H, $SiMe_2$), 1.88 (s, 12H, Cp–Me), 1.96 (s, 12H, Cp–Me). IR ($\nu_{CO}$, cm$^{-1}$): 1975, 1926, 1893, 1754, 1721.

### 2.3. Thermal rearrangement reaction of 2

Complex **2** (0.50 g) in 15 ml of xylene was refluxed for 24 h. The solvent was removed under vacuum. The residue was dissolved in chloroform and then filtered to remove insoluble substance. The solvent was slowly evaporated to afford 15 mg (3%) of yellow crystals of **3**: Mp 278°C (dec.). Anal. Calcd for $C_{26}H_{36}Fe_2O_4Si_2$: C, 53.80; H, 6.25. Found: C, 54.20; H, 6.33. $^1H$ NMR ($CDCl_3$) $\delta$: 0.51 (s, 12H, $SiMe_2$), 1.95 (s, 12H, Cp–Me), 1.99 (s, 12H, Cp–Me). IR ($\nu_{CO}$, cm$^{-1}$): 1975, 1934.

### 2.4. Crystallographic studies

A summary of the crystallographic results is presented in Table 1. Crystals of **2** and **3** suitable for X-ray diffraction were obtained from acetone/chloroform and chloroform solution, respectively. All data sets were

Table 3
Selected bond lengths (Å) and angles (°) for **3**

| | | | |
|---|---|---|---|
| *Bond distances* | | | |
| Fe(1)–Si(1) | 2.3307(3) | Fe(1)–Cp(1) | 1.728(1)[a] |
| Fe(1)–C(1) | 1.743(2) | C(1)–O(1) | 1.157(2) |
| Fe(1)–C(2) | 1.732(1) | C(2)–O(2) | 1.156(2) |
| *Bond angles* | | | |
| Si(1)–Fe(1)–C(1) | 88.76(3) | Fe(1)–Si(1)–C(11a) | 117.80(2) |
| Si(1)–Fe(1)–C(2) | 83.40(4) | C(20)–Si(1)–C(21) | 102.73(5) |
| C(1)–Fe(1)–C(2) | 92.56(5) | | |

[a]The distance from the centroid of Cp ring to the linked Fe atom.

collected on Enraf–Nonius CAD-4 diffractometers with graphite monochromated MoK $\alpha$ radiation. The corrections for empirical absorption was applied to intensity data. The structure was solved by a direct phase determination method and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were not included in the refinement and calculations of structure factors. Neutral atom scattering factors were taken from the tabulation of Cromer and Waber [11]. All calculations were performed on a PDP 11/14 computer using the SDP-PLUS program system. Selected bond distances and angles for **2** and **3** are given in Tables 2 and 3, respectively.

## 3. Results and discussion

### *3.1. Synthesis of complex 2 and its thermal rearrangement reaction.*

We recently reported that the diiron complex $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5H_4)Fe(CO)]_2(\mu\text{-}CO)_2$ (**1**) was synthesized by heating a solution of $Fe(CO)_5$ and $C_5H_5Me_2SiSiMe_2C_5H_5$ in xylene [7]. The same approach is successful for $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5Me_4)Fe(CO)]_2(\mu\text{-}CO)_2$ (**2**). Thus, when the ligand $HMe_4C_5Me_2Si\,SiMe_2C_5Me_4H$ and $Fe(CO)_5$ was heated at reflux in xylene for 5 h **2** was obtained in 65% yield, but no rearrangement product **3** was isolated. This is different from the case of the parent complex **1** that its rearrangement product was simultaneously obtained. In addition, it should be noted that the reaction to form **2** proceeds more readily than that to form **1**, which is attributed to the electron-donating effect of ring-methyls which enhanced the coordinative activity of the cyclopentadienyl rings. The stronger coordinative ability of this type of cyclopentadienyl ring is also reflected in shorter distance (1.738 Å) from the centroid of Cp ring to the linked Fe atom, cf. 1.756 Å, in the parent analogue **1**. To examine whether complex **2** can undergo the same rearrangement reaction as **1**, a xylene solution of isolated pure **2** was refluxed for 24 h. It was found that most of **2** decomposed, and **3** was isolated

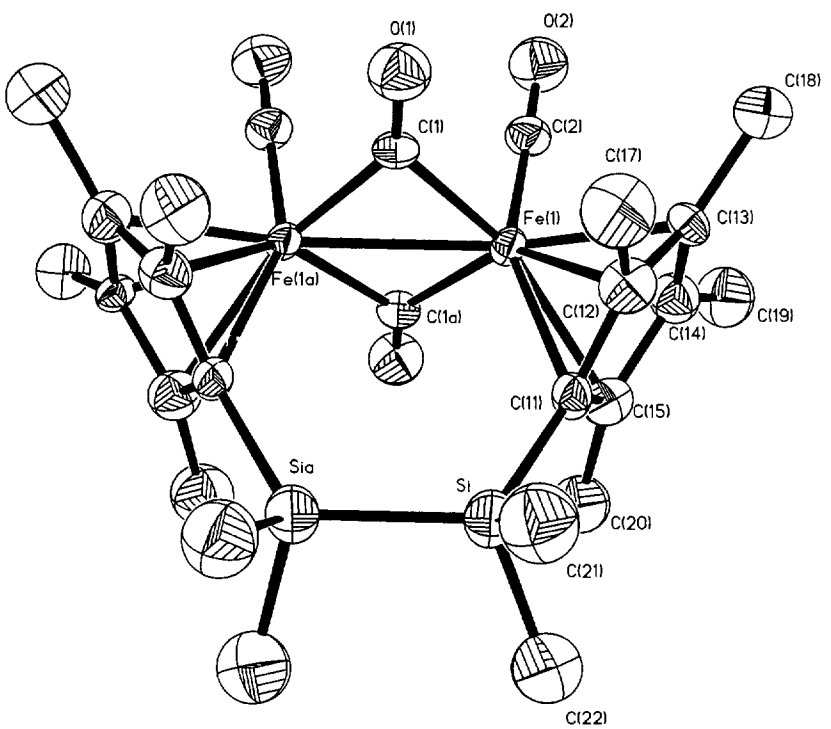
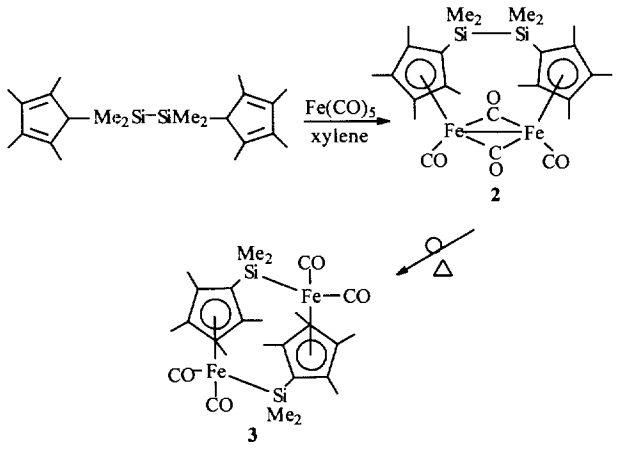



Fig. 1. Molecular structure of $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5Me_4)Fe(CO)]_2(\mu\text{-}CO)_2$ (**2**). Hydrogen atoms are omitted for clarity. C(21) and C(22) atoms represent a direction with the occupancy of 0.5.




Scheme 1.

only in rather low yield (3%) (Scheme 1). This indicates that the thermal rearrangement reaction of 2 is rather difficult. Therefore, it is possible that the steric effect of the substituted methyls retarded occurrence of this reaction.

Complex **2** is air-stable black crystals, with the melting point of over 400°C, while complex **3** is air-stable yellow crystals. They are readily soluble in xylene or $CHCl_3$, but insoluble in acetone or alkane solvents. Their $^1H$ NMR spectra are rather simple, with two singlets for the $\alpha$ and $\beta$ methyls of the cyclopentadienyl rings and one singlet for silicon methyls. IR Spectrum of **2** reveals the presence of terminal and bridging carbonyl groups, while **3** only exhibits the terminal carbonyl absorptions. This is consistent with the molecular structures of **2** and **3** determined by X-ray diffraction.

### *3.2. Crystal and molecular structures of complexes 2 and 3*

The molecular structure of **2** is presented in Fig. 1. The molecule of **2** consists of two $[(\eta^5\text{-}C_5Me_4)Fe(CO)_2]$ moieties linked by one $Me_2SiSiMe_2$ bridge and one Fe–Fe bond. **2** has $C_2$ symmetry, and the six-membered ring Fe(1)–C(11)–Si–Sia–C(11a)–Fe(1a) constituting the molecular framework adopts a hexagonal conformation (the sum of its internal angles is 719.8°, indicating the six atoms are completely planar). This is different from the parent analogue which takes a twist boat conformation [7]. The Fe–Fe bond distance [2.553(2) Å] is slightly longer than that [2.526(2) Å] in **1**, while the Si–Si bond length [2.153(7) Å] is much shorter than in **1** [2.346(4) Å]. This may be attributed to the steric effect of the crowded methyl groups. The larger steric repulsion results in a slight stretch of Fe–Fe bond and a larger compression of Si–Si bond, to reduce unfavourable non-bonded interaction. The Cp ring planes in **2** are inclined to one another at a shallower angle than is usually the case in related analogues {dihedral angle are 109.5° for **2**; cf. 85.3° in **1**; 97.2° in $(Me_2Si)[(\eta^5\text{-}C_5H_4)Fe(CO)]_2(\mu\text{-}CO)_2$ [1a]; 92.8° in cis-$[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)_2$ [12] and 88.8° in $[\eta^5,\eta^5\text{-}C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4]Fe(CO)_4$ [13]}. The Si atom deviates from the linked cyclopentadienyl plane by 0.2318 Å, and the four methyl carbon atoms deviate from the Cp ring plane by 0.0779–0.1632 Å, indicating a larger non-bonding repulsion in the two Cp rings.

The molecular structure of **3** is presented in Fig. 2. The molecule of **3** consists of two $[(Me_2Si)(\eta^5\text{-}C_5Me_4)Fe(CO)_2]$ moieties linked by two Fe–Si bonds.

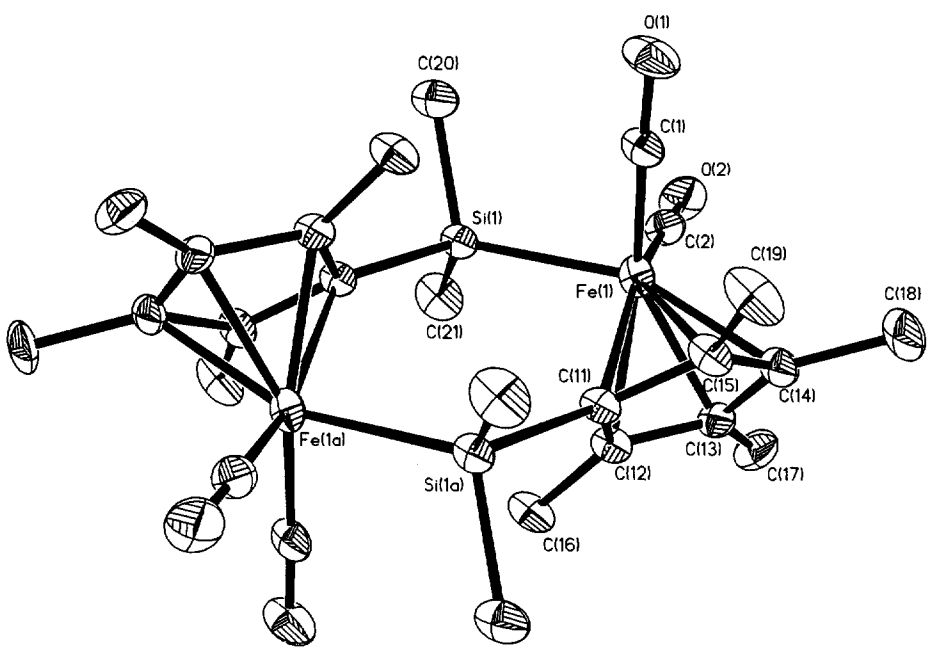



Fig. 2. Molecular structure of $[(Me_2Si)(\eta^5\text{-}C_5Me_4)Fe(CO)_2]_2$ (**3**). Hydrogen atoms are omitted for clarity.

Like many analogues [7,14–16], **3** has Ci symmetry, and the six-membered ring Fe(1)–C(11)–Si(1a)–Fe(1a)–C(11a)–Si(1) constituting the molecular framework prefers to adopt a stable chair conformation. The Fe–Si bond distance [2.3307(3) Å] is slightly longer than that [2.315(2) Å] in the parent analogue, attributable to the steric repulsion of methyl groups, and slightly shorter than those in acyclic molecules of the same type [17]. The Si atom deviates from the linked cyclopentadienyl plane by 0.4288 Å, the largest of the deviating values in many analogues, therefore reducing unfavourable non-bonded interactions and simultaneously maintaining a stable chair conformation.

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