

# Synthesis of tetramethyldisilane-bridged bis(1-indenyl) tetracarbonyl di-iron: a novel thermal rearrangement reaction between the Si–Si and Fe–Fe bonds

Bai-Quan Wang, Shan-Sheng Xu, Xiu-Zhong Zhou \*

Department of Chemistry, Nankai University, Tianjin 300071, People's Republic of China

Received 4 December 1996; revised 3 January 1997

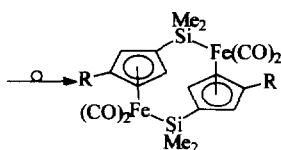
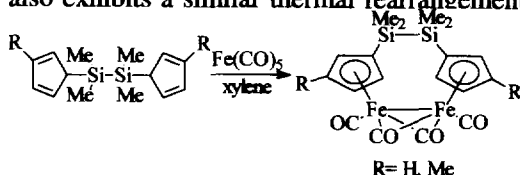
## Abstract

The title complex  $(\text{Me}_2\text{SiSiMe}_2)(\eta^5\text{-1-indenyl})\text{Fe}(\text{CO})_2(\mu\text{-CO})_2$  (**1**) was prepared by the reaction of 1,2-bis(1-indenyl)tetramethyldisilane and  $\text{Fe}(\text{CO})_5$  in refluxing heptane. Its thermal rearrangement product  $[\text{Me}_2\text{Si}(\eta^5\text{-1-indenyl})\text{Fe}(\text{CO})_2]_2$  (**2**) was also obtained from the reaction. **1** in refluxing xylene can be readily converted into **2**. The crystal structures of the *cis* isomer **1c** and the *trans* isomer **1t** were determined by X-ray diffraction. © 1997 Elsevier Science S.A.

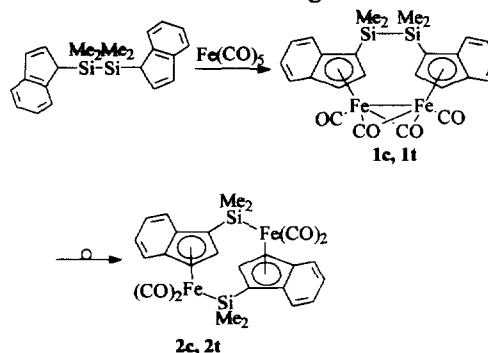
**Keywords:** Indenyl ligand; Thermal rearrangement; Crystal structure; Fe–Fe bond

## 1. Introduction

Much attention has been focused on the synthesis and reactions of a variety of metal–metal bonded transition metal complexes, especially bridged binuclear complexes, due to their structural characteristics and applications as catalysts [1–3]. For some years we have been investigating the syntheses, structures and reactions of tetramethyldisilane-bridged biscyclopentadienyl transition metal complexes [4–6]. In 1993, we reported the synthesis of  $(\text{Me}_2\text{SiSiMe}_2)[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\mu\text{-CO})_2]$  and the novel thermal rearrangement reaction between the Si–Si and Fe–Fe bonds ( $\text{R}=\text{H}$ ) [7]. Later we found that the mono-substituted cyclopentadienyl analogue also exhibits a similar thermal rearrangement [8]:



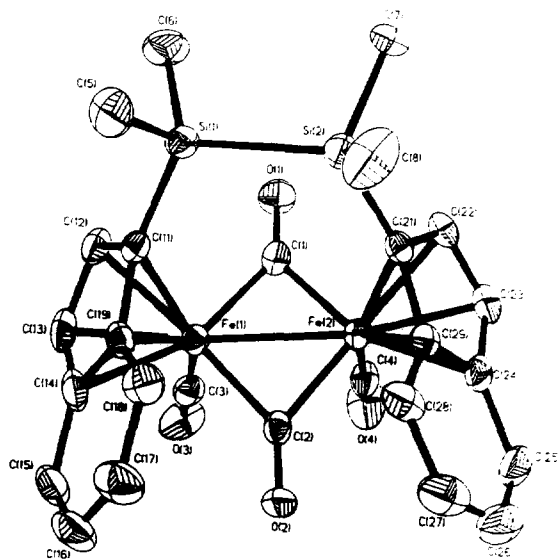
In order to further extend the area of this reaction, and owing to the similarity of indenyl and cyclopentadienyl ligands, we synthesized the tetramethyldisilane-bridged bis(1-indenyl) tetracarbonyl di-iron (**1**) and have studied the related rearrangement.



## 2. Results and discussion

In comparison with the cyclopentadienyl analogue, the tetramethyldisilane-bridged bis(1-indenyl) Fe–Fe bond complex **1** is less stable: extreme decomposition occurs in refluxing xylene. However, when heptane was used instead of xylene as the reaction medium, **1** was obtained in 12% yield, and an unexpected orange yellow product **2** was isolated in 4% yield. In order to establish the relationship between **1** and **2**, the former

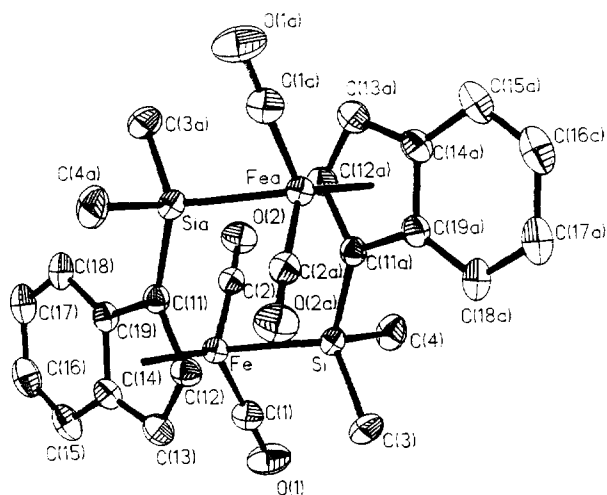
\* Corresponding author.

Fig. 1. The molecular structure of **1c**.

was refluxed in xylene for 12 h and was converted into **2** in 38% yield. Owing to the asymmetry of the indenyl ligand, both **1** and **2** can be formed as *cis* and *trans* isomers. Due to the different crystal shapes it was possible to separate a small amount of pure *cis* isomer **1c** and *trans* isomer **1t** by hand. However, only pure *trans* isomer **2t** was isolated from the rearrangement product **2** by recrystallization.

The 200 MHz  $^1\text{H}$  NMR spectrum of **1** indicates the presence of two isomers. The  $\alpha$ ,  $\beta$  protons of the five-membered rings of each isomer appear as two doublets. In the IR spectrum of **1** there are absorption peaks of bridged carbonyls at about  $1800\text{ cm}^{-1}$  and terminal carbonyls between  $1900$  and  $2000\text{ cm}^{-1}$ . After rearrangement, the absorption peaks associated with the bridged carbonyls disappeared.

The molecular structures of **1c** and **2t** were determined by X-ray diffraction (Figs. 1 and 2). The C–C bond lengths in the five-membered rings of **1c** and **2t**

Fig. 2. The molecular structure of **2t**.

are almost identical, indicating that the five-membered rings are bonded in an  $\eta^5$ -manner to the Fe atom. However, in the six-membered rings, the bond lengths of C(15)–C(16) (1.360, 1.366 Å) and C(17)–C(18) (1.363, 1.388 Å) are close to that of a double bond (1.34–1.35 Å), suggesting that the cyclic part of C(15)–C(16)–C(17)–C(18) exists as a conjugated diene system. The molecular structure of **2t** is centric symmetric. The two silicon atoms and two iron atoms are in one plane, and the two bridgehead carbon atoms of the cyclopentadienyl rings lie on different sides of the plane. These six atoms (Si, Fe, C(11), Sia, Fea and C(11a)) form a six-membered ring having a chair conformation. The structural stability of the rearrangement product is probably one of the driving forces of the thermal rearrangement reaction. Further research on the stereochemistry and mechanism of the rearrangement will be published elsewhere.

### 3. Experimental section

#### 3.1. General

All operations were carried out in an argon atmosphere. Heptane and xylene were distilled from sodium

Table 1  
Summary of crystal data and data collection and refinement for **1c** and **2t**

	<b>1c</b>	<b>2t</b>
Formula	$\text{C}_{26}\text{H}_{24}\text{Fe}_2\text{O}_4\text{Si}_2$	$\text{C}_{26}\text{H}_{24}\text{Fe}_2\text{O}_4\text{Si}_2$
$M$ ( $\text{g mol}^{-1}$ )	568.34	568.43
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/a$
$a$ (Å)	9.428(2)	9.438(3)
$b$ (Å)	9.444(2)	13.711(6)
$c$ (Å)	14.532(2)	10.225(2)
$\alpha$ (°)	90.31(1)	
$\beta$ (°)	94.28(1)	109.42(2)
$\gamma$ (°)	107.63(1)	
$V$ (Å <sup>3</sup> )	1229.1(7)	1248(1)
$Z$	2	2
$D_c$ ( $\text{g cm}^{-3}$ )	1.536	1.512
$F(000)$	584	584
Temperature (K)	299(±1)	299(±1)
$\mu$ (Mo $K\alpha$ ) ( $\text{mm}^{-1}$ )	1.309	1.286
Scan type	$\omega/2\theta$	$\omega/2\theta$
$\theta$ range (°)	0–23	2.0–25.0
Reflections collected	3577	2314
Independent reflections	3253	2036
Observed reflections [ $I \geq 3\sigma(I)$ ]	2746	1629
Number of refined parameters	307	154
Goodness of fit	2.57	1.49
$R_{\text{int}}$	0.023	0.014
Final $R$ and $R_w$	0.039 and 0.040	0.041 and 0.050
Maximum $\Delta/\sigma$	0.06	0.01
Max. residual peak ( $\text{e} \text{ \AA}^{-3}$ )	0.33	0.58

diphenylketyl under argon before use. IR spectra were recorded on a Nicolet 5DX FT-IR spectrophotometer, while  $^1\text{H}$  NMR spectra on a Jeol FX-90Q or Bruker AC-P200 instrument. 1,2-Bis(1-indenyl)tetramethyldisilane was prepared by the literature method [9].

### 3.2. Preparations of 1 and 2

1,2-Bis(1-indenyl)tetramethyldisilane (3 g, 8.66 mmol) and  $\text{Fe}(\text{CO})_5$  (3 ml, 22.22 mmol) were heated in heptane (50 ml) under reflux for 5 days. After removal of excess  $\text{Fe}(\text{CO})_5$  and solvent under vacuum, the residue was extracted with dichloromethane and filtered through a silica column ( $3 \times 35 \text{ cm}^2$ ). The first yellow band was eluted with dichloromethane/petroleum ether (1:5) and, on evaporation, yielded yellow crystals of **2** (0.185 g, 3.76%) as a mixture of *cis* and *trans* isomers. Recrystallization from

Table 2  
Atomic coordinates and thermal parameters of **1c**

Atom	x	y	z	$B_{\text{eq}}$ ( $\text{\AA}^2$ )
Fe(1)	0.37367(5)	0.37656(6)	0.31931(4)	2.407(9)
Fe(2)	0.09747(5)	0.27688(6)	0.35125(4)	2.285(9)
Si(1)	0.3071(1)	0.7228(1)	0.23897(8)	2.88(2)
Si(2)	0.0489(1)	0.6170(1)	0.24293(9)	3.15(2)
O(1)	0.2798(4)	0.5175(4)	0.4713(2)	4.77(8)
O(2)	0.1971(3)	0.1082(3)	0.2163(2)	3.75(6)
O(3)	0.4922(4)	0.1911(4)	0.4426(3)	5.44(8)
O(4)	0.1551(5)	0.0824(5)	0.4937(3)	6.08(9)
C(1)	0.2618(4)	0.4307(5)	0.4107(3)	3.10(8)
C(2)	0.2146(4)	0.2054(4)	0.2694(3)	2.69(7)
C(3)	0.4412(5)	0.2621(5)	0.3949(3)	3.30(8)
C(4)	0.1275(5)	0.1548(5)	0.4361(3)	3.48(8)
C(5)	0.3468(7)	0.8251(6)	0.1285(4)	5.2(1)
C(6)	0.3760(6)	0.8579(6)	0.3395(5)	5.3(1)
C(7)	-0.0112(6)	0.7350(6)	0.3275(6)	6.0(1)
C(8)	-0.0478(7)	0.6220(7)	0.1259(5)	6.8(1)
C(11)	0.4142(4)	0.5854(4)	0.2472(3)	2.91(7)
C(12)	0.5309(5)	0.5893(5)	0.3168(3)	3.56(9)
C(13)	0.5960(4)	0.4767(5)	0.2967(4)	4.0(1)
C(14)	0.5270(4)	0.4050(5)	0.2112(3)	3.62(8)
C(15)	0.5484(5)	0.2879(6)	0.1576(4)	4.9(1)
C(16)	0.4630(7)	0.2453(6)	0.0767(4)	5.5(1)
C(17)	0.3548(7)	0.3134(6)	0.0451(4)	5.3(1)
C(18)	0.3283(6)	0.4246(5)	0.0944(3)	3.97(9)
C(19)	0.4155(4)	0.4724(4)	0.1805(3)	3.02(8)
C(21)	-0.0169(4)	0.4214(4)	0.2841(3)	2.56(7)
C(22)	-0.0601(4)	0.3891(5)	0.3759(3)	3.02(7)
C(23)	-0.1231(5)	0.2363(5)	0.3845(3)	3.56(8)
C(24)	-0.1320(4)	0.1673(4)	0.2948(3)	3.14(8)
C(25)	-0.1938(5)	0.0171(6)	0.2635(5)	5.0(1)
C(26)	-0.1921(6)	0.0139(6)	0.1727(5)	6.0(1)
C(27)	-0.1279(6)	0.0978(7)	0.1108(4)	5.8(1)
C(28)	-0.0636(5)	0.2445(6)	0.1386(3)	4.18(9)
C(29)	-0.0670(4)	0.2816(4)	0.2333(3)	2.78(7)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as:  $B_{\text{eq}} = (4/3) \cdot [a^2 \beta(1,1) + b^2 \beta(2,2) + c^2 \beta(3,3) + ab(\cos \Gamma) \cdot \beta(1,2) + ac(\cos \beta) \cdot \beta(1,3) + bc(\cos \alpha) \cdot \beta(2,3)]$ .

Table 3  
Atomic coordinates and thermal parameters for **2t**

Atom	x	y	z	$B_{\text{eq}}$ ( $\text{\AA}^2$ )
Fe	0.43767(8)	0.45124(5)	0.77930(8)	2.76(1)
Si	0.6683(2)	0.5131(1)	0.9103(2)	2.93(3)
O(1)	0.5871(5)	0.4179(4)	0.5779(4)	6.0(1)
C(1)	0.5241(6)	0.4339(4)	0.6552(6)	3.8(1)
O(2)	0.3402(5)	0.6492(3)	0.7017(4)	4.8(1)
C(2)	0.3813(5)	0.5712(4)	0.7339(5)	3.1(1)
C(3)	0.8141(6)	0.4116(5)	0.9662(7)	4.5(2)
C(4)	0.7444(6)	0.6079(5)	0.8156(7)	4.6(1)
C(11)	0.3405(5)	0.4184(4)	0.9329(5)	2.9(1)
C(12)	0.4594(6)	0.3516(4)	0.9397(6)	3.2(1)
C(13)	0.4288(6)	0.3022(4)	0.8113(6)	3.6(1)
C(14)	0.2799(6)	0.3312(4)	0.7234(6)	3.6(1)
C(15)	0.1915(7)	0.3017(5)	0.5854(7)	4.6(2)
C(16)	0.0508(7)	0.3407(5)	0.5312(7)	5.2(2)
C(17)	-0.0064(7)	0.4109(5)	0.6041(7)	4.7(2)
C(18)	0.0786(6)	0.4431(5)	0.7355(6)	3.9(1)
C(19)	0.2260(6)	0.4016(4)	0.7985(6)	3.1(1)

dichloromethane/petroleum ether afforded pure *trans* isomer **2t**. The second red band was eluted with dichloromethane/petroleum ether (1:1) and gave 0.581 g (11.81%) of dark brown crystals of **1** as a mixture of *cis* and *trans* isomers. A small number of crystals of the pure *cis* isomer **1c** and *trans* isomer **1t** were separated by hand.

**1.** Anal. Found: C, 54.87; H, 4.21.  $\text{C}_{26}\text{H}_{24}\text{Fe}_2\text{O}_4\text{Si}_2$   
Calc.: C, 54.95; H, 4.26%. IR (KBr): [ $\nu_{\text{CO}}/\text{cm}^{-1}$ ] 1991.4 vs, 1942.2s, 1810.9s, 1769.9 vs.  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ): **1c**,  $\delta_{\text{H}}$  7.41–7.24 (m, 6H), 7.05 (d, 2H), 6.05 (d, 2.76 Hz, 2H), 5.22 (d, 2.76 Hz, 2H), 0.45 ppm (s, 12H); **1t**,  $\delta_{\text{H}}$  7.41–7.24 (m, 6H), 7.06 (d, 2H), 6.03 (d, 2.55 Hz, 2H), 5.18 (d, 2.55 Hz, 2H), 0.54 (s, 6H), 0.27 ppm (s, 6H).

**2.** Anal. Found: C, 54.69; H, 4.22.  $\text{C}_{26}\text{H}_{24}\text{Fe}_2\text{O}_4\text{Si}_2$   
Calc.: C, 54.95; H, 4.26%. IR (KBr): [ $\nu_{\text{CO}}/\text{cm}^{-1}$ ] 1983.2 vs, 1934.0 vs.  $^1\text{H}$  NMR (90 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  7.90–7.48 (m, 4H), 7.48–7.00 (m, 4H), 5.60–5.20 (broad s), 5.20–5.00 (broad s) (total 4H, 3:1), 1.01 (s), 0.56 (d), 0.32 ppm (s) (total 12H, 1:1:1). **2t**,  $\delta_{\text{H}}$  (200 MHz,  $\text{CDCl}_3$ ) 7.85–7.45 (m, 4H), 7.45–7.00 (m, 4H), 5.58–5.18 (broad s, 4H), 1.01 (s, 6H), 0.32 ppm (s, 6H).

### 3.3. Rearrangement

0.26 g of **1** was heated in refluxing xylene (20 ml) for 12 h. The dark red solution turned orange yellow and was accompanied by decomposition. After removal of solvent, the residue was extracted with  $\text{CH}_2\text{Cl}_2$ , filtered through a silica column and eluted with  $\text{CH}_2\text{Cl}_2$ /petroleum ether. The yellow band and red band afforded 75 mg of **2** and 70 mg of **1** respectively. The rearrangement yield is 37.84% based on reacted **1**.

Table 4  
Selected bond distances (Å) and bond angles (°) of **1c**

Fe(1)–Fe(2)	2.5657(5)	Si(1)–Si(2)	2.340(2)	C(14)–C(15)	1.421(6)
Fe(1)–C(11)	2.182(3)	C(11)–C(12)	1.429(4)	C(15)–C(16)	1.360(6)
Fe(1)–C(12)	2.107(3)	C(11)–C(19)	1.441(4)	C(16)–C(17)	1.412(6)
Fe(1)–C(13)	2.074(3)	C(12)–C(13)	1.419(5)	C(17)–C(18)	1.363(6)
Fe(1)–C(14)	2.176(3)	C(13)–C(14)	1.424(6)	C(18)–C(19)	1.435(4)
Fe(1)–C(19)	2.228(3)	C(14)–C(19)	1.430(5)	C(24)–C(25)	1.418(5)
Fe(2)–C(21)	2.174(3)	C(21)–C(22)	1.432(4)	C(25)–C(26)	1.351(7)
Fe(2)–C(22)	2.119(3)	C(21)–C(29)	1.439(4)	C(26)–C(27)	1.413(7)
Fe(2)–C(23)	2.091(3)	C(22)–C(23)	1.394(4)	C(27)–C(28)	1.378(6)
Fe(2)–C(24)	2.189(3)	C(23)–C(24)	1.439(5)	C(28)–C(29)	1.423(4)
Fe(2)–C(29)	2.234(2)	C(24)–C(29)	1.425(5)	Si(1)–C(11)	1.869(3)
Si(2)–C(21)	1.879(3)	Fe(1)–PL(1)	1.7739(5)	Fe(2)–PL(2)	1.7859(5)
Fe(1)–CEN(1)	1.779	Fe(2)–CEN(2)	1.790		
C(1)–Fe(1)–C(2)	96.0(1)	C(1)–Fe(2)–C(2)	96.0(1)	PL(1)–PL(2)	107.85(16)
Fe(1)–C(1)–Fe(2)	84.0(1)	Fe(1)–C(2)–Fe(2)	83.2(2)		
Si(1)–Si(2)–C(21)	116.42(8)	Si(2)–Si(1)–C(11)	114.12(8)		

PL = the plane of the five-membered ring, CEN = the center of the five-membered ring.

Table 5  
Selected bond distances (Å) and bond angles (°) of **2t**

Fe–Si	2.305(1)	Si–C(11)	1.884(5)	C(14)–C(15)	1.439(7)
Fe–C(11)	2.114(4)	C(11)–C(12)	1.432(6)	C(15)–C(16)	1.366(7)
Fe–C(12)	2.092(4)	C(12)–C(13)	1.419(7)	C(16)–C(17)	1.430(8)
Fe–C(13)	2.075(5)	C(13)–C(14)	1.449(7)	C(17)–C(18)	1.388(8)
Fe–C(14)	2.164(5)	C(14)–C(19)	1.428(6)	C(18)–C(19)	1.442(7)
Fe–C(19)	2.181(4)	C(11)–C(19)	1.456(6)	Fe–PL	1.7368(8)
Fe–CEN	1.740				
Fe–Si–C(11a)	112.2(1)	Si–Fe–C(11)	102.0(1)	Fe–C(11)–Si	132.7(2)

### 3.4. Crystallography

Crystals suitable for X-ray diffraction were obtained from dichloromethane/petroleum ether. All data were collected on the Enraf–Nonius CAD4 diffractometer with Mo K $\alpha$ : ( $\lambda = 0.71073$  Å) radiation. Empirical absorption correction was applied. The structures were solved by direct methods using the SDP-PLUS program on a PDP 11/44 computer. The full-matrix least-squares method was employed for refinement. Crystal data and some details of data collection and refinement are given in Table 1. Atomic coordinates and thermal parameters are collected in Tables 2 and 3. Selected bond lengths and bond angles are listed in Tables 4 and 5.

### Acknowledgements

We greatly appreciate financial support from the National Natural Science Foundation of China and State

Key Laboratory of Elemento–Organic Chemistry of Nankai University.

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