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Synthesis and characterization of a series of sila-bridged diiron complexes $(E)[(\eta^5\text{-}t\text{-BuC}_5H_3)Fe(CO)]_2(\mu\text{-CO})_2$ ($E = Me_2Si$, $Me_2SiSiMe_2$, $Me_2SiOSiMe_2$). The molecular structures of *cis*- and *trans*-$(Me_2Si)[\eta^5\text{-}t\text{-BuC}_5H_3)Fe(CO)]_2(\mu\text{-CO})_2$

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Abstract

Binuclear iron complexes $(E)[(\eta^5\text{-}t\text{-BuC}_5H_3)Fe(CO)]_2(\mu\text{-CO})_2$ [$E = Me_2Si$ (**1**), $Me_2SiOSiMe_2$(**3**)] were prepared by reaction of $Fe(CO)_5$ with the corresponding cyclopentadienyl ligands in boiling xylene. Like the analogue $(Me_2SiSiMe_2)[(\eta^5\text{-}t\text{-BuC}_5H_3)Fe(CO)]_2(\mu\text{-CO})_2$ (**2**) reported previously, they are also found to exist as a mixture of *cis* and *trans* isomers that have been separated by preparative TLC. To examine the effect of larger substituents on the formation of isomers, the analogue $(Me_2Si)[\{\eta^5\text{-}C_5H_3(t\text{-heptyl})\}Fe(CO)]_2(\mu\text{-CO})_2$ (**4**) was also synthesized by the same approach. The molecular structures of *cis*- and *trans*-$(Me_2Si)[(\eta^5\text{-}t\text{-BuC}_5H_3)Fe(CO)]_2(\mu\text{-CO})_2$ have been determined by X-ray diffraction. © 1998 Elsevier Science S.A.

Keywords: Cyclopentadienyl; Iron; Metal carbonyl; Sila-bridged; X-ray diffraction

1. Introduction

There is considerable attention being focused presently on the synthesis and study of ring-linked binuclear iron complexes [1–9]. These systems are suitable for studying interactions between two metal reaction sites, since the existence of a bridge inherently holds the two metals in close proximity. When a suitable substituent is introduced on the cyclopentadienyl ring in this species, it is conceivable that the bridging linkage will force the two substituents to adopt both *cis* and *trans* arrangements to each other. In this paper, we describe the synthesis of sila-bridged binuclear iron complexes $(E)[(\eta^5\text{-}t\text{-BuC}_5H_3)Fe(CO)]_2(\mu\text{-CO})_2$ [$E = Me_2Si$, $Me_2SiOSiMe_2$]. The objective is to explore the effect of the *tert*-butyl substituent on this type of complexes.

2. Experimental details

Schlenk and vacuum line techniques were employed for all manipulations of air- and moisture-sensitive compounds. Reaction solvents were distilled from appropriate drying agents under argon before use. Tetrahydrofuran, toluene and xylene were distilled from sodium/benzophenone ketyl and purged with an argon atmosphere before use. $t\text{-BuC}_5H_5$ [10], 6,6-dimethyl fulvene [11], and $t\text{-BuC}_5H_4Me_2SiOSiMe_2C_5H_4t\text{-Bu}$ [12] were prepared according to literature methods. Proton (^1H NMR) spectra were obtained on a Bruker AC-P200 spectrometer using $CHCl_3$ (δ: 7.24) as an internal standard. Elemental analyses were performed by a Perkin-Elmer 240 C analyzer. Infrared spectra were obtained as KBr disk and recorded on a Nicolet

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Table 1
^{1}H NMR, UV–vis and IR spectral data for all of complexes

Compound	^{1}H NMR δ, ppm CDCl$_3$	IR υ(CO), cm^{-1} (KBr disc)		λ, nm (ϵ, L mol^{-1} cm^{-1})[a] CH$_2$Cl$_2$	
1c	0.29, 0.34 (s, s, 6H, SiMe$_2$) 1.35 (s, 18H, *t*-Bu)	2032(m)	1975(s)	233(20000)	288(10000)
	4.82, 4.89, 5.38 (s, s, s, 6H, Cp)	1934(s)	1770(s)	348(8600)	
1t	0.32 (s, 6H, SiMe$_2$) 1.34 (s, 18H, *t*-Bu)	1975(s)	1934(m)	234(24000)	287(12000)
	4.84 (s, 4H, Cp) 5.38 (s, 2H, Cp)	1811(m)	1762(s)	348(11000)	
2c[b]	0.23 (s, 12H, SiMe$_2$) 1.33 (s, 18H, *t*-Bu)	1983(s)	1934(m)	233(20000)	
	4.63, 5.23 (d, s, 6H, Cp)	1795(m)	1754(s)	362(6800)	
2t[b]	0.18, 0.28 (s, s, 12H, SiMe$_2$) 1.33 (s, 18H, *t*-Bu)	1983(s)	1926(m)	233(17000)	
	4.58, 5.26 (s, s, 6H, Cp)	1770(s)		359(5500)	
3c	0.09, 0.55 (s, s, 12H, SiMe$_2$) 1.30 (s, 18H, *t*-Bu)	1983(s)	1934(m)	234(32000)	294(14000)
	3.75, 4.80, 5.08 (d, s, d, 6H, Cp)	1770(s)		352(12000)	
3t	0.31 (s, 12H, SiMe$_2$) 1.35 (s, 18H, *t*-Bu)	1992(s)	1944(m)	233(28000)	
	4.29, 4.38, 5.16 (d, s, d, 6H, Cp)	1799(m)	1756(s)	353(11000)	
4c	0.29, 0.34 (s, s, 6H, SiMe$_2$) 0.85 (t, 6H, $C(CH_3)_2(CH_2)_3\underline{CH_3}$)	1983(s)	1942(m)	233(15200)	
	1.25–1.42 (m, 24H, $\underline{C(CH_3)_2(CH_2)_3}CH_3$)	1770(s)		287(7600)	
	4.78, 4.86, 5.36 (s, s, s, 6H, Cp)			348(6600)	
4t	0.32 (s, 6H, SiMe$_2$) 0.85 (t, 6H, $C(CH_3)_2(CH_2)_3\underline{CH_3}$)	1975(s)	1934(s)	234(22000)	
	1.24–1.41 (m, 24H, $\underline{C(CH_3)_2(CH_2)_3}CH_3$)	1770(s)		288(11700)	
	4.80, 4.83, 5.35 (s, s, s, 6H, Cp)			350(9700)	

[a] Absorption in the visible region was not obtained due to much weaker intensity.
[b] Ref. [13].

5DX FT-IR spectrometer. UV–vis spectra were recorded on a Shimadzu UV-240 spectrometer.

2.1. Preparation of (Me$_2$Si)[(η^5-t-BuC$_5$H$_3$)Fe(Co)]$_2$(μ-Co)$_2$ (1)

A solution of 8.0 g (65.6 mmol) of *t*-BuC$_5$H$_5$ in 60 ml of THF, cooled to -20°C, was treated dropwise ($\sim$30 min) with 34.5 ml of 1.90 M hexane-solution of BuLi (65.6 mmol) to give a light-yellow solution, which was allowed to rise to room temperature and then stirred for an additional 4 h. The mixture was cooled again to -20°C and a solution of 4.2 g (32.8 mmol) of Me$_2$SiCl$_2$ in 20 ml of THF was added dropwise ($\sim$30 min). The reaction mixture was slowly warmed to room temperature and stirred for 2 h and was subsequently refluxed for an additional 4 h. Water (100 ml) was added to the mixture. The aqueous layer was separated and extracted twice with 60 ml of ether. The organic and ether extracts were combined and dried with sodium sulfate overnight. The solvent was removed under reduced pressure, and the residue was introduced to a silica column in the minimum of hexane. Elution with hexane developed a light yellow band which afforded 6.0 g (61%) of yellow oil. It can be used in the following reaction without further purification.

A solution of 2.50 g (8.3 mmol) of *t*-BuC$_5$H$_4$Me$_2$SiC$_5$H$_4$*t*-Bu and 4.16 g (21.2 mmol) of Fe(CO)$_5$ in 30 ml of xylene was refluxed for 12 h. The solvent was removed under vacuum to give a dark-red crude product, which was then introduced to an alumina column in the minimum amount of dichloromethane. Elution with petroleum ether–dichloromethane (3:1) gave a red band that afforded 2.00 g (46%) of violet-red crystals of **1** as a mixture of *cis* and *trans* isomers, which were later separated by preparative TLC (silica G). 1.00 g of deep-red crystals (**1**) was dissolved in a

Table 2
Crystallographic data for **1c** and **1t**

	1c	**1t**
Formula	$C_{24}H_{30}Fe_2O_4Si$	$C_{24}H_{30}Fe_2O_4Si$
Formula weight	522.28	522.28
Space group	$P2_1/c$	$P2_1/n$
Crystal system	Monoclinic	Monoclinic
Z	4	4
a (Å)	8.499(2)	7.272(2)
b (Å)	14.071(5)	17.586(4)
c (Å)	21.237(6)	19.307(6)
α (°)	90	90
β (°)	97.57(3)	97.58(2)
γ (°)	90	90
Volume (Å^3)	2517(1)	2447(1)
d_{calc} (g cm^{-1})	1.378	1.417
Crystal size (mm)	0.20 × 0.20 × 0.30	0.20 × 0.20 × 0.30
Radiation (Å^3)	MoKα(0.71073)	MoKα(0.71073)
μ (cm^{-1})	12.25	12.60
Data collection method	$\omega-2\theta$	$\omega-2\theta$
Max 2θ (°)	49.9	49.9
Total no. of observations	3515	3397
No. of unique data, $I > 3\sigma(I)$	2691	2412
Final no. of variables	281	280
Max. residual density, $e^-/$Å^3	0.25	0.32
R[a]	0.031	0.031
R_w[b]	0.042	0.040
Goodness-of-fit	1.60	1.48

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

Table 3
Selected bond lengths (Å) and angles (°) for **1c**

Bond distances			
Fe(1)–Fe(2)	2.5251(8)	Fe(1)–C(1)	1.927(4)
Fe(1)–C(2)	1.930(4)	Fe(1)–Cp(1)[a]	1.750
Fe(1)–C(3)	1.749(4)	Fe(2)–C(2)	1.915(4)
Fe(2)–C(1)	1.922(4)	Fe(2)–Cp(2)[a]	1.748
Fe(2)–C(4)	1.745(4)	C(1)–O(1)	1.178(4)
C(2)–O(2)	1.164(4)	C(3)–O(3)	1.153(4)
C(4)–O(4)	1.149(4)	Si–C(7)	1.880(4)
Si–C(18)	1.864(4)		
Bond angles			
Fe(2)–Fe(1)–C(7)	96.46(10)	Fe(1)–Fe(2)–C(18)	96.07(9)
Fe(2)–Fe(1)–C(3)	101.6(1)	Fe(1)–Fe(2)–C(4)	101.5(1)
Fe(1)–C(1)–Fe(2)	82.0(2)	Fe(1)–C(2)–Fe(2)	82.1(2)
Fe(1)–C(7)–Si	119.3(2)	Fe(2)–C(18)–Si	120.1(2)
C(7)–Si–C(18)	106.0(2)		

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

minimum volume of dichloromethane and chromatographed by preparative TLC (silica G) to develop two red bands. The first band gave 0.41 g (41%) of dark-red crystals (**1t**); the second band gave 0.52 g (52%) of purple-red crystals (**1c**). For **1t**: mp 217–9°C. Anal. Calcd for $C_{24}H_{30}Fe_2O_4Si$: C, 55.19; H, 5.79. Found: C, 55.23; H, 5.62. For **1c**: mp 193–5°C. Anal. Calcd for $C_{24}H_{30}Fe_2O_4Si$: C, 55.19; H, 5.79. Found: C, 55.26; H, 5.65.

2.2. Preparation of $(Me_2SiOSiMe_2)[(\eta^5\text{-}t\text{-}BuC_5H_3)Fe(Co)]_2(\mu\text{-}Co)_2$ (**3**)

A solution of 4.00 g (10.6 mmol) of t-$BuC_5H_4Me_2SiOSiMe_2C_5H_4$$t$-Bu and 4.16 g (21.2 mmol) of $Fe(CO)_5$ in 30 ml of xylene was refluxed for 12 h. The solvent was removed under vacuum to give a dark-red crude product, which was then introduced to an alumina column in the minimum amount of dichloromethane. Elution with petroleum ether–dichloromethane (3:1) gave a red band which afforded 2.20 g (35%) of violet-red crystals of **3**. The ^{1}H NMR spectrum of **3** indicated that it was a mixture of two isomers, which could not be separated by general chromatographic methods due to their almost equal R_f. Prolonged attempts to recrystallise **3** from diluted CH_2Cl_2-hexane solution at −20°C afforded the crystals with two different shapes. Thus, pure **3c** (red prism) and **3t** (black octahedron) were separated by the mechanical method according to their different shapes. For **3c**: mp 171–3°C. Anal. Calcd for $C_{26}H_{36}Fe_2O_5Si_2$: C, 52.36; H, 6.08. Found: C, 52.33; H, 6.14. For **3t**: mp 141–3°C. Anal. Calcd for $C_{26}H_{36}Fe_2O_5Si_2$: C, 52.36; H, 6.08. Found: C, 52.13; H, 6.43.

Table 4
Selected bond lengths (Å) and angles (°) for **1t**

Bond distances			
Fe(1)–Fe(2)	2.5249(9)	Fe(1)–C(1)	1.922(4)
Fe(1)–C(2)	1.936(4)	Fe(1)–Cp(1)[a]	1.747
Fe(1)–C(3)	1.742(5)	Fe(2)–C(2)	1.937(4)
Fe(2)–C(1)	1.947(4)	Fe(2)–Cp(2)[a]	1.745
Fe(2)–C(4)	1.754(5)	C(1)–O(1)	1.172(4)
C(2)–O(2)	1.174(4)	C(3)–O(3)	1.160(5)
C(4)–O(4)	1.147(5)	Si–C(6)	1.866(4)
Si–C(17)	1.870(4)		
Bond angles			
Fe(2)–Fe(1)–C(6)	95.8(1)	Fe(1)–Fe(2)–C(17)	96.3(1)
Fe(2)–Fe(1)–C(3)	101.1(1)	Fe(1)–Fe(2)–C(4)	102.5(1)
Fe(1)–C(1)–Fe(2)	81.5(2)	Fe(1)–C(2)–Fe(2)	81.4(2)
Fe(1)–C(6)–Si	120.4(2)	Fe(2)–C(17)–Si	119.9(2)
C(6)–Si–C(17)	105.7(2)		

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

Table 5
Atomic coordinates and thermal parameters for **1c** with estimated standard deviations in parentheses

Atom	x	y	z	B_{eq}
Fe(1)	0.42935(6)	0.54386(4)	0.27028(2)	2.88(1)
Fe(2)	0.36771(5)	0.47570(4)	0.37427(2)	2.61(1)
Si	0.1344(1)	0.67224(8)	0.32998(5)	3.71(3)
O(1)	0.6024(3)	0.6278(2)	0.3848(1)	4.87(7)
O(2)	0.2941(4)	0.3539(2)	0.2641(1)	4.74(7)
O(3)	0.7254(4)	0.4486(2)	0.2560(2)	6.27(9)
O(4)	0.6330(4)	0.3477(2)	0.4056(2)	5.88(9)
C(1)	0.5137(4)	0.5735(3)	0.3567(2)	3.39(9)
C(2)	0.3396(4)	0.4233(3)	0.2903(2)	3.08(8)
C(3)	0.6072(5)	0.4861(3)	0.2612(2)	3.89(10)
C(4)	0.5266(4)	0.3978(3)	0.3935(2)	3.70(10)
C(5)	0.4478(5)	0.6443(3)	0.1984(2)	4.4(1)
C(6)	0.3946(5)	0.6908(3)	0.2499(2)	3.79(9)
C(7)	0.2488(4)	0.6498(3)	0.2615(2)	3.37(9)
C(8)	0.2115(4)	0.5785(3)	0.2132(2)	3.59(9)
C(9)	0.3330(5)	0.5746(3)	0.1742(2)	3.87(10)
C(10)	0.3284(6)	0.5181(4)	0.1126(2)	5.6(1)
C(11)	0.2750(8)	0.5844(5)	0.0582(2)	8.9(2)
C(12)	0.489(1)	0.4817(7)	0.1042(3)	13.6(3)
C(13)	0.226(2)	0.4326(7)	0.1125(4)	21.3(5)
C(14)	0.2108(7)	0.7818(3)	0.3727(2)	6.3(1)
C(15)	--0.0780(6)	0.6762(4)	0.3013(3)	6.7(1)
C(16)	0.2918(4)	0.4714(3)	0.4652(2)	3.17(9)
C(17)	0.2825(4)	0.5651(3)	0.4424(2)	3.14(8)
C(18)	0.1756(4)	0.5687(2)	0.3845(2)	2.88(8)
C(19)	0.1167(4)	0.4734(2)	0.3738(2)	2.80(8)
C(20)	0.1867(4)	0.4130(3)	0.4227(2)	2.83(8)
C(21)	0.1428(5)	0.3105(3)	0.4346(2)	3.68(9)
C(22)	0.0404(6)	0.3115(3)	0.4880(2)	5.5(1)
C(23)	0.2907(6)	0.2510(3)	0.4570(3)	6.2(1)
C(24)	0.0503(7)	0.2681(3)	0.3752(2)	6.5(1)

2.3. Preparation of $(Me_2Si)[\{\eta^5\text{-}C_5H_3(t\text{-}heptyl)\}Fe(Co)]_2(\mu\text{-}Co)_2$ (**4**)

46.0 ml of 1.62 M hexane-solution of BuLi (74.5 mmol), cooled to −20°C, was treated dropwise (∼30 min) with a solution of 8.0 g (75 mmol) of C_8H_{10} (6,6-dimethyl fulvene) in 30 ml of THF to give a light-yellow solution, which was allowed to rise to room temperature and then stirred for an additional 1 h, subsequently refluxed for an additional 4 h. The mixture was cooled again to −20°C, and a solution of 4.8 g (37.0 mmol) of Me_2SiCl_2 in 25 ml of THF was added dropwise (~ 30 min). The reaction mixture was slowly warmed to room temperature and stirred 2 h, subsequently refluxed for an additional 2 h. Water (100 ml) was added to the mixture. The aqueous layer was separated and extracted twice with 60 ml of ether. The organic and ether extracts were combined and dried with sodium sulfate overnight. The solvent was removed under reduced pressure. The residue was distilled under vacuum (130–8°C/0.2 Torr) to yield 7.0 g (51%) of (*t*-heptyl)$C_5H_4Me_2SiC_5H_4$(*t*-heptyl) as a yellow liquid, which was used in the following reaction without further purification.

A solution of 2.00 g (5.5 mmol) of (*t*-heptyl)$C_5H_4Me_2SiC_5H_4$(*t*-heptyl) and 2.14 g (10.9 mmol) of $Fe(CO)_5$ in 35 ml of xylene was refluxed for 10 h. The solvent was removed under vacuum to give a dark-red crude product, which was then introduced to an alumina column in the minimum amount of dichloromethane. Elution with petroleum ether–dichloromethane (3:1) gave a red band that afforded 1.50 g (45%) of violet-red crystals of **4** as a mixture of *cis* and *trans* isomers that were later separated by preparative TLC (silica G). 1.20 g of deep-red crystals (**4**) was dissolved in a minimum volume of dichloromethane and chromatographed by preparative TLC (silica G) to develop two red bands. The first band gave 0.95 g (79%) of dark-red crystals (**4t**); the second band gave 0.09 g (8%) of purple-red crystals (**4c**). For **4c**: mp 142–4°C. Anal. Calcd for $C_{30}H_{42}Fe_2O_4Si$: C, 59.42; H, 6.98. Found: C, 59.37; H, 6.60. For **4t**:mp 122–3°C. Anal. Calcd for $C_{30}H_{42}Fe_2O_4Si$: C, 59.42; H, 6.98. Found: C, 59.47; H, 6.68.

All of the complexes previously unreported were characterized by IR, ^1H NMR, UV–vis and elemental analyses. The characterized data are in good agreement with their formulation. ^1H NMR, UV–vis and IR data for carbonyl stretching region of all of complexes are shown in Table 1, which includes some data of the previously reported complex **2** for comparison [13].

2.4. Crystallographic studies

A summary of the crystallographic results is presented in Table 2. Crystals of **1c** and **1t** suitable for X-ray diffraction were obtained from hexane/dichloromethane solution. All data sets were collected on a Rigaku AFC7R diffractometer with graphite monochromated Mo–Kα radiation. The structures of **1c** and **1t** were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan crystallographic solftware package of Molecular Structure. Neutral atom scattering factors were taken from the tabulation of Cromer and Waber [14]. Selected bond lengths and bond angles for **1c** and **1t** are shown in Tables 3 and 4, respectively, and atom coordinates for **1c** and **1t** are presented in Tables 5 and 6, respectively.

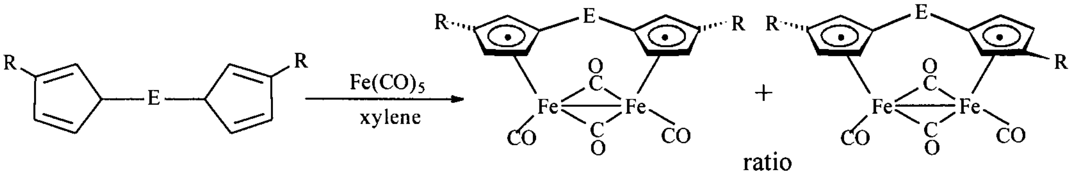
Table 6
Atomic coordinates and thermal parameters for **1t** with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	B_{eq}
Fe(1)	0.05123(7)	0.53312(3)	0.31247(3)	2.55(1)
Fe(2)	−0.01244(7)	0.47165(3)	0.19354(3)	2.60(1)
Si	−0.1189(2)	0.66392(6)	0.18533(6)	3.08(3)
O(1)	0.3596(4)	0.5361(2)	0.2302(2)	4.65(8)
O(2)	−0.2547(4)	0.4246(2)	0.2963(2)	4.76(8)
O(3)	0.2413(6)	0.4104(2)	0.3931(2)	7.3(1)
O(4)	0.1519(5)	0.3220(2)	0.2160(2)	6.2(1)
C(1)	0.2101(6)	0.5196(2)	0.2414(2)	3.07(10)
C(2)	−0.1327(5)	0.4585(2)	0.2765(2)	2.97(9)
C(3)	0.1677(6)	0.4601(3)	0.3610(2)	4.2(1)
C(4)	0.0885(6)	0.3815(3)	0.2083(2)	3.7(1)
C(5)	0.1211(5)	0.6504(2)	0.3214(2)	2.71(9)
C(6)	−0.0561(5)	0.6421(2)	0.2801(2)	2.60(9)
C(7)	−0.1741(5)	0.6065(2)	0.3247(2)	3.19(10)
C(8)	−0.0707(5)	0.5927(2)	0.3901(2)	3.19(10)
C(9)	0.1162(5)	0.6202(2)	0.3888(2)	2.60(9)
C(10)	0.2670(6)	0.6263(2)	0.4505(2)	3.26(10)
C(11)	0.2565(7)	0.7071(3)	0.4783(3)	5.5(1)
C(12)	0.4587(5)	0.6147(3)	0.4281(2)	4.4(1)
C(13)	0.2392(7)	0.5701(3)	0.5083(2)	5.1(1)
C(14)	0.0665(7)	0.7234(3)	0.1554(2)	4.9(1)
C(15)	−0.3521(6)	0.7087(3)	0.1720(3)	4.9(1)
C(16)	−0.2677(5)	0.5128(2)	0.1394(2)	2.75(9)
C(17)	−0.1270(5)	0.5701(2)	0.1395(2)	2.77(9)
C(18)	0.0153(5)	0.5379(2)	0.1038(2)	3.31(10)
C(19)	−0.0358(6)	0.4629(2)	0.0841(2)	3.5(1)
C(20)	−0.2138(5)	0.4464(2)	0.1054(2)	3.02(9)
C(21)	−0.3337(6)	0.3767(2)	0.0869(2)	3.8(1)
C(22)	−0.4664(9)	0.3961(3)	0.0236(4)	9.3(2)
C(23)	−0.2200(9)	0.3097(4)	0.0700(5)	11.8(3)
C(24)	−0.439(1)	0.3553(4)	0.1441(4)	10.9(2)

3. Results and discussion

3.1. Synthesis and characterization of complexes **1**, **3** and **4**

Synthesis of the diiron complex $(Me_2Si)[(\eta^5\text{-}C_5H_4)Fe(CO)]_2(\mu\text{-}CO)_2$ via heating a solution of $Fe(CO)_5$ and $C_5H_5Me_2SiC_5H_5$ in xylene was reported 20 years ago [1,15]. The same approach is successful for the *tert*-butyl substituted analogue $(Me_2Si)[(\eta^5\text{-}t\text{-}BuC_5H_3)Fe(CO)]_2(\mu\text{-}CO)_2$ (**1**). Thus, when the ligand *t*-$BuC_5H_4Me_2SiC_5H_4$*t*-Bu and a slight excess of $Fe(CO)_5$ was heated in boiling xylene for 12 h, a 46% yield of **1** was obtained. It should be noted that complex **1** exists as a mixture of two isomers [*cis*-**1** (**1c**), *trans*-**1**



			ratio	
R=t-Bu	E=Me_2Si	**1c**	5 / 4	**1t**
R=t-Bu	E=$Me_2SiSiMe_2$	**2c**	5 / 3.5	**2t**
R=t-Bu	E=$Me_2SiOSiMe_2$	**3c**	5 / 2	**3t**
R= t-heptyl	E=Me_2Si	**4c**	1 / 10	**4t**

Scheme 1.

(**1t**)] [1]. This is consistent with the case appearing in the previously reported complex $(Me_2SiSiMe_2)[(\eta^5\text{-}t\text{-}BuC_5H_3)Fe(CO)]_2(\mu\text{-}CO)_2$ (**2**) [13]. Pure *cis*- and *trans* isomers were separated by preparative TLC. *cis* isomer (**1c** is violet-red, prism crystals, while *trans* isomer (**1t**) is dark-red, hexagonal plate crystals. Both of them are air-stable in the solid state but air-sensitive in solution. Their IR and ^{1}H NMR spectra exhibited considerable differences. In the ^{1}H NMR spectrum of **1t**, the silicon methyl groups exhibited only a singlet (δ 0.32 ppm) attributable to the chemical equivalence of two silicon methyl groups resulting from the C_2 symmetry of **1t**. This is different from two singlets (δ 0.29, 0.34 ppm) in the ^{1}H NMR spectrum of **1c**. In addition, the bridging carbonyl groups in the IR spectrum of **1t** gave rise to two absorptions (1811, 1762 cm^{-1}), different from the one carbonyl absorption (1770 cm^{-1}) of **1c**. Both of their molecular structures were determined by single crystal X-ray diffraction.

Complex **3** was similarly prepared as a mixture of *cis* and *trans* isomers [*cis*-**3** (**3c**), *trans*-**3** (**3t**)] [2], which could not be separated by general chromatographic methods owing to their almost equal R_f values. Prolonged attempts to recrystallise **3** from diluted CH_2Cl_2-hexane solution at −20°C afforded the crystals with two different shapes. Thus, pure **3c** (red prism) and **3t** (black octahedron) were separated by the mechanical method according to their different shapes. Their IR and ^{1}H NMR spectra exhibited considerable differences. In the ^{1}H NMR spectrum of **3t**, the silicon methyl groups exhibited only a singlet (δ 0.32 ppm) attributable to an accidental degeneracy. This is different from two singlets (δ 0.09, 0.55 ppm) in the ^{1}H NMR spectrum of **3c**. In addition, the bridging carbonyl groups in the IR spectrum of **3t** gave rise to two absorptions (1799, 1756 cm^{-1}), different from the one carbonyl absorption (1770 cm^{-1}) of **3c**.

The *tert*-heptyl substituted cyclopentadienyl ligand was prepared by reaction of Me_2SiCl_2 with the corresponding cyclopentadienyl anion, formed via addition of BuLi to 6,6-dimethyl fulvene. Reaction of this ligand with $Fe(CO)_5$ in xylene solution afforded the binuclear iron complex $(Me_2Si)[\{\eta^5\text{-}C_5H_3(t\text{-heptyl})\}Fe(CO)]_2(\mu\text{-}CO)_2$ (**4**) in 45% yield. Like the analogue **1**, **4** is also a mixture of *cis*- and *trans* isomers (**4c** and **4t**). Pure **4c** and **4t** were separated by preparative TLC. **4c** is a violet-red solid, while **4t** is dark-red cube-like crystals. Unlike **1**, the IR spectra of **4c** and **4t** exhibited the same bridging carbonyl absorption at 1770 cm^{-1}, which is obviously the result when the long chain *tert*-heptyl groups reduce the difference of the molecular symmetry of the two isomers.

As seen from Scheme 1, the *cis*:*trans* ratio is increased from 5:4 for **1** to 5:2 for **3** as the bridge was lengthened. A possible factor for this is that the increase of the bridge length enlarges the dihedral angle (81.54° in **1c** and 91.95° in **2c**), thus reducing the steric interaction between two *cis tert*-butyl substituents and a bridging carbonyl group (C(13)...O(2), 3.38 Å; C(24)...O(2), 3.55 Å), which finally results in the existence of the *cis* isomer in relatively larger amount. When the *tert*-butyl substituents are replaced by *tert*-heptyl groups in the Me_2Si bridged analogues, the amount of the *trans* isomer greatly outnumbers that of the *cis* isomer (*trans*:*cis* = 10:1). It is likely that the *cis* arrangement of two very bulky substituents in shorter distance (Me_2Si) will result in severe steric repulsion so that **4** is forced to exist as the *trans* isomer in overwhelmingly larger amount. In the ^{1}H NMR spectra of the Me_2Si and $Me_2SiOSiMe_2$ bridged complexes, all of *cis* isomers exhibited two singlets for silicon methyl groups, while all of *trans* isomers displayed one singlet for silicon methyl groups. In contrast to the situation for the Me_2Si and $Me_2SiOSiMe_2$ bridged analogues, the *cis* isomer of the $Me_2SiSiMe_2$ bridged analogue **2** indicated one singlet, while its *trans* isomer showed two singlets for silicon methyl groups. The difference of

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[1] The *cis* isomer (**1c**) was designated according to the *cis* arrangement of two *tert*-butyl groups substituted at the identical position of the corresponding Cp rings, which was confirmed by single crystal X-ray diffraction. The *trans* isomer (**1t**) was similarly designated in contrast to the *cis* isomer.

[2] The *cis* isomer (**3c**) was designated by comparing its ^{1}H NMR spectrum with that of trimethyl silyl substituted analogue *cis*-$(Me_2SiOSiMe_2)[\{\eta^5\text{-}C_5H_3(SiMe_3)\}Fe(CO)]_2(\mu\text{-}CO)_2$, the molecular structure of which has been determined by X-ray diffraction. The *trans* isomer (**3t**) was designated in contrast to the *cis* isomer [16].

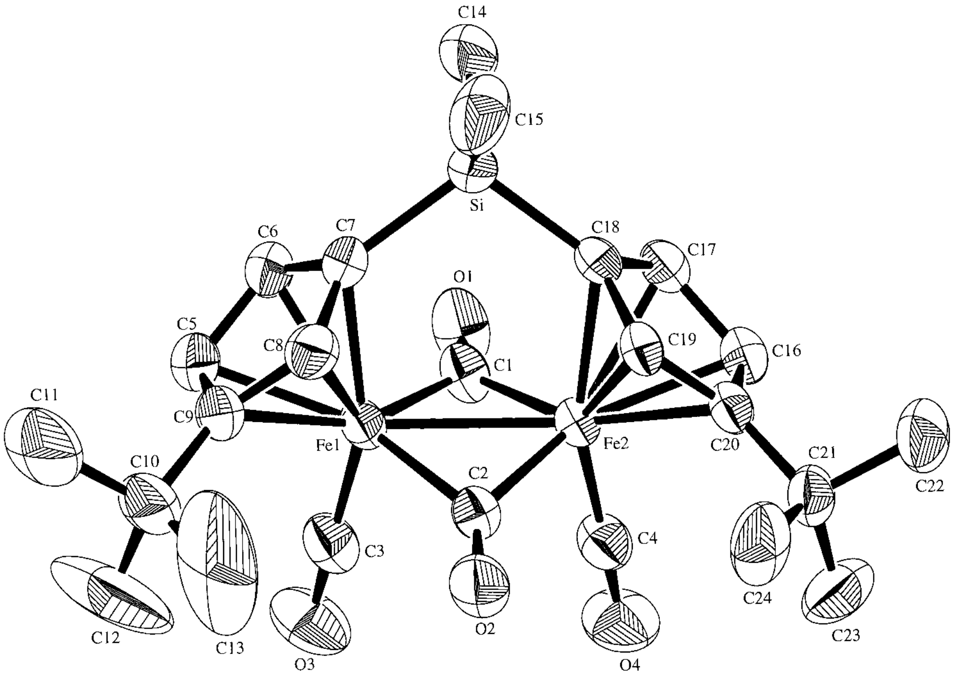

Fig. 1. Molecular structure of *cis*-$(Me_2Si)[(\eta^5\text{-}t\text{-}BuC_5H_3)Fe(CO)]_2(\mu\text{-}CO)_2$ (**1c**).

^1H NMR signals reveals that the *cis* isomer (**2c**) undergoes the same accidental degeneracy as the case appearing in **3t**. In addition, it is found that the differences of the chemical shifts between two singlets for silicon methyl groups range from 0.05 to 0.46 ppm as the silicon bridges are lengthened from Me_2Si to $Me_2SiOSiMe_2$. It appears that the extent of the equivalence of the silicon methyl groups is closely related to the bridge length.

Data in Table 1 indicate that the UV–visible spectra of all of *cis* and *trans* isomers show considerable similarity. Assignment of the near-UV absorption (at 348 nm for **1**, at mean 361 nm for **2**, at 352 nm for **3** and at mean 349 nm for **4**) to the σ_b-σ^* transition of

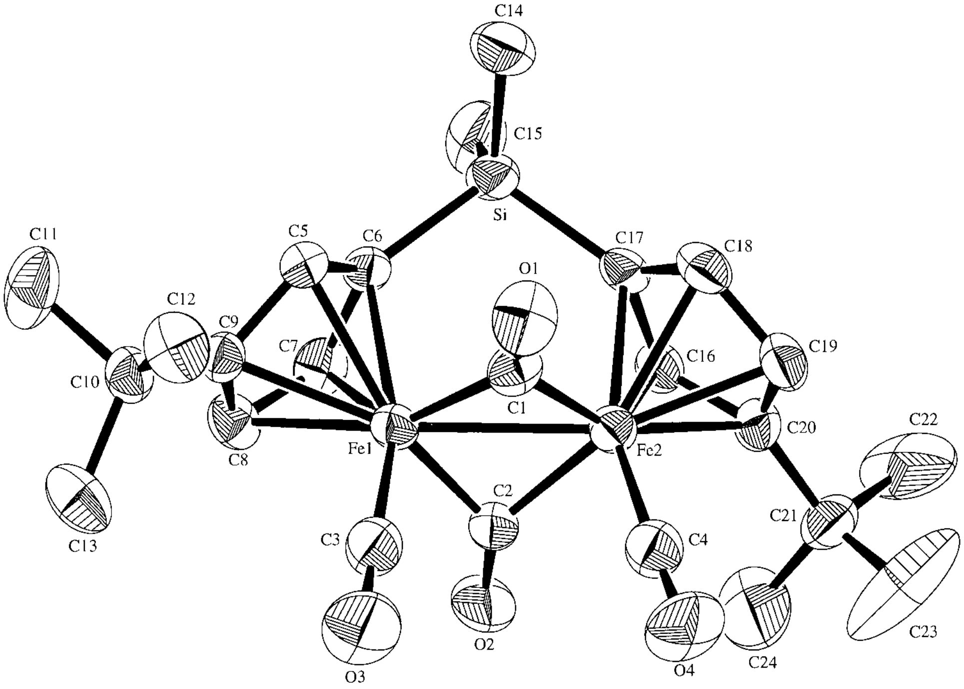

Fig. 2. Molecular structure of *trans*-$(Me_2Si)[(\eta^5\text{-}t\text{-}BuC_5H_3)Fe(CO)]_2(\mu\text{-}CO)_2$ (**1t**).

the bridged species, associated with the Fe–Fe bond, is suggested. This assignment is made on the basis of the spectra of the analogue $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ [17–19]. The electronic spectrum of complex **2** shows a red shift of nearly 10 nm compared with those of **1**, **3** and **4**. It is likely that the $\sigma_{Si-Si}-\pi$ conjugation in **2** may play an important role in this shift [20,21].

3.2. *Crystal and molecular structures of cis and trans isomers (**1c** and **1t**)*

The molecular structure of **1c** is presented in Fig. 1. The molecule of **1c** has mirror symmetry except for some twist about the Me_2Si bridge, with the two *tert*-butyl groups oriented in the same direction. The Fe–Fe distance [2.5251(8) Å] is longer than that in the parent analogue [2.512(3) Å] [1], presumably as a consequence of the bulky *tert*-butyl substitution. The dihedral angle between the cyclopentadienyl rings is 81.54°, smaller than those in many analogues: e.g., 92.8°, *cis*-$[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4]$ [22]; 97.2°, $[(\eta^5,\eta^5\text{-}C_5H_4SiMe_2C_5H_4)Fe_2(CO)_4]$ [1]; and 88.8°, $[\eta^5,\eta^5\text{-}C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4]Fe_2(CO)_4$ [23]; 109°, $[(CH_3)_2C(\eta^5\text{-}C_5H_4)_2]Fe_2(CO)_4$ [24]. The *tert*-butyl substituents should be responsible for this difference. The angle between the $Fe_2(\mu\text{-}CO)$ planes is 158°, close to that in the parent analogue (160°). The Si atom deviates from the linked cyclopentadienyl planes by 0.200 Å and 0.165 Å, respectively.

The molecular structure of **1t** is presented in Fig. 2. The molecule of **1t** has approximately C_2 symmetry in the solid, with the two *tert*-butyl groups being a *trans* arrangement. The Fe–Fe distance [2.5249(9) Å] is nearly equal to that in **1c**, but longer than that in the parent analogue [2.512(3) Å] [1], presumably as a result of the bulky *tert*-butyl substitution. The dihedral angle between the cyclopentadienyl rings is 81.82°, nearly close to the smallest value, 73.2° in $[(CH_2)_3\{\eta^5\text{-}C_5Me_4)_2\}Fe_2(CO)_4$, among the complexes of this type reported so far [25]. The Si atom deviates from the linked cyclopentadienyl planes by 0.164 Å and 0.182 Å, respectively. The remaining molecular parameters are almost equivalent to those in **1c**.

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