

[3]Ferrocenophanes with a Tetramethyldisiloxane Bridge: Synthesis and Molecular Structure

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Summary. 6,6,8,8-Tetramethyl-7-oxa-6,8-disila[3]ferrocenophane **2** was obtained from the di(alkoxysilyl) ferrocene $(H_4C_5SiMe_2OR)_2Fe$ ($R = CH_2CH_2OCH_2CH_2OCH_2CH_2OMe$) by hydrolysis and subsequent intramolecular disiloxane formation. 2,2',3,3',4,4',5,5',6,6,8,8-Dodecamethyl-7-oxa-6,8-disila-[3]ferrocenophane **3** was formed by air oxidation of 2,2',3,3',4,4',5,5',6,6,7,7-dodecamethyl-6,7-disila[2]ferrocenophane. The crystal structures of both compounds were determined by single-crystal X-ray diffraction (**2**: $a = 8.5330(10)$, $b = 15.610(3)$, $c = 18.774(5)$ Å, $\alpha = 70.68(2)$, $\beta = 77.94(2)$, $\gamma = 75.150(10)^\circ$, $V = 2259.8(8)$ Å³, $Z = 6$, space group $P\bar{1}$, $R = 0.045$, $R_w = 0.044$; **3**: $a = 12.388(3)$, $b = 9.924(3)$, $c = 19.136(10)$ Å, $\beta = 105.11(3)^\circ$, $V = 2271.2(15)$ Å³, $Z = 4$, space group $P2_1/c$, $R = 0.076$, $R_w = 0.060$). Owing to the flexibility of the disiloxane bridge, **2** and **3** are unstrained molecules.

Keywords. Ferrocenophane; Disiloxane unit.

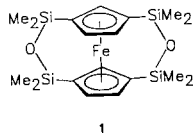
[3]Ferrocenophane mit Tetramethyldisiloxan-Brücke: Synthese und Molekülstruktur

Zusammenfassung. 6,6,8,8-Tetramethyl-7-oxa-6,8-disila[3]-ferrocenophan **2** entsteht aus dem Di(alkoxysilyl)ferrocen $(H_4C_5SiMe_2OR)_2Fe$ ($R = CH_2CH_2OCH_2CH_2OCH_2CH_2OMe$) durch Hydrolyse und anschließende intramolekulare Disiloxan-Bildung. 2,2',3,3',4,4',5,5',6,6,8,8-Dodecamethyl-7-oxa-6,8-disila[3]ferrocenophan **3** wurde durch Luftoxidation von 2,2',3,3',4,4',5,5',6,6,7,7-Dodecamethyl-6,7-disila[2]ferrocenophan erhalten. Die Kristallstrukturen beider Verbindungen wurden durch Einkristall-Röntgenstrukturanalyse bestimmt (**2**: $a = 8.5330(10)$, $b = 15.610(3)$, $c = 18.774(5)$ Å, $\alpha = 70.68(2)$, $\beta = 77.94(2)$, $\gamma = 75.150(10)^\circ$, $V = 2259.8(8)$ Å³, $Z = 6$, Raumgruppe $P\bar{1}$, $R = 0.045$, $R_w = 0.044$; **3**: $a = 12.388(3)$, $b = 9.924(3)$, $c = 19.136(10)$ Å, $\beta = 105.11(3)^\circ$, $V = 2271.2(15)$ Å³, $Z = 4$, Raumgruppe $P2_1/c$, $R = 0.076$, $R_w = 0.060$). Wegen der Flexibilität der Disiloxan-Brücke sind **2** und **3** ungespannte Moleküle.

Introduction

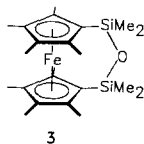
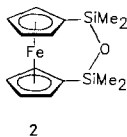
Ferrocenophanes represent a fascinating class of compounds. They have been extensively investigated over the past 35 years. The research on "all-carbon-bridged" species has culminated in the synthesis of "superferrocenophane" by Hisatome et al. [1]. Currently, heteroatom-bridged ferrocenophanes are receiving much attention due to special electronic and steric features of the bridge(s) [2]. Recently, we described the synthesis and structure of the [3] [3]ferrocenophane **1**, which is the

first example of a ferrocenophane bearing *two* disiloxane bridges; it is also the first example of a structurally characterized disiloxane-bridged ferrocenophane [3].



Compound **1** was formed from the tetra(alkoxysilyl)ferrocene $[\text{H}_3\text{C}_5(\text{SiMe}_2\text{-OR})_2]_2\text{Fe}$ ($\text{R} = \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OMe}$) [3] by hydrolysis and subsequent intramolecular disiloxane formation; diethylene glycol monomethyl ether was identified as the second reaction product.

We now wish to report the synthesis and structure of two closely related species, namely the disiloxane-bridged [3]ferrocenophanes **2** and **3**.



Results and Discussion

Compound **2** [4] is formed in analogy to **1** from the di(alkoxysilyl)ferrocene $(\text{H}_4\text{C}_5\text{SiMe}_2\text{OR})_2\text{Fe}$ ($\text{R} = \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OMe}$) upon prolonged standing in the air at room temperature; triethyleneglycol monomethyl ether is the second reaction product, as identified by $^1\text{H-NMR}$ spectroscopy.

An alternative strategy for the formation of a disiloxane-bridged species involves the insertion of oxygen into a somewhat strained disilanediyyl-bridged compound [5]. Indeed, when an acetonitrile solution of the disilanediyyl-bridged [2]ferrocenophane $(\text{Me}_4\text{C}_5\text{SiMe}_2)_2\text{Fe}$ [6] was kept in the air at room temperature for several days, crystals of the disiloxane-bridged species **3** precipitated [7].

The molecular structures of **2** and **3** (Figs. 1 and 2) were established from single-crystal X-ray diffraction data. Atomic coordinates and thermal parameters for **2** and **3** are presented in Tables 1 and 2.

For compound **2**, the asymmetric unit of the unit cell contains three crystallographically independent molecules, two of which are very similar, but not identical within the margin of error of the structure determination; the third molecule differs from the other two mainly by the significantly higher Cp-ring twist angle (7.0 *vs.* ca. 1°). **2** and **3** are virtually unstrained: for both compounds, the cyclopentadienyl rings adopt an eclipsed conformation; ring twist angles range from 1.1 to 7.0°. The cyclo-

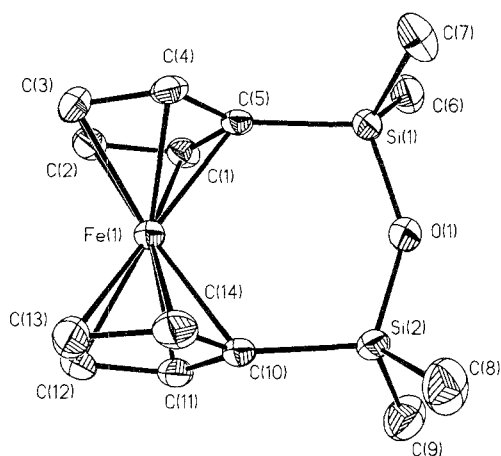


Fig. 1. Molecular structure of compound **2** (molecule 1 of three crystallographically independent molecules). Selected bond lengths (\AA) and angles ($^\circ$): C(1)–C(2) 1.422(5), C(1)–C(5) 1.444(5), C(2)–C(3) 1.419(5), C(3)–C(4) 1.422(5), C(4)–C(5) 1.429(5), C(10)–C(11) 1.442(5), C(10)–C(14) 1.434(5), C(11)–C(12) 1.422(6), C(12)–C(13) 1.412(6), C(13)–C(14) 1.437(6), Si(1)–C(5) 1.861(4), Si(1)–O(1) 1.637(3), Si(2)–C(10) 1.859(4), Si(2)–O(1) 1.630(4); O(1)–Si(1)–C(5) 110.3(2), Si(1)–O(1)–Si(2) 143.6(2), O(1)–Si(2)–C(10) 111.1(2)

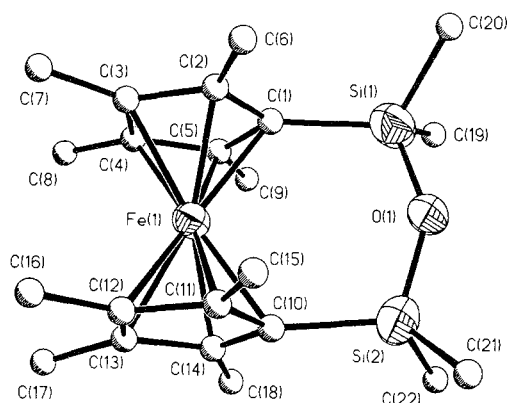


Fig. 2. Molecular structure of compound **3**. Selected bond lengths (\AA) and angles ($^\circ$) (the cyclopentadienyl units were refined as regular pentagons with C–C = 1.420 \AA): Si(1)–C(1) 1.896(14), Si(1)–O(1) 1.618(17), Si(2)–C(10) 1.886(14), Si(2)–O(1) 1.623(18); O(1)–Si(1)–C(1) 110.2(9), Si(1)–O(1)–Si(2) 139.7(9), O(1)–Si(2)–C(10) 110.4(7)

pentadienyl rings are very nearly parallel; ring tilt angles are close to zero (0.7 to 2.7°). The iron-ring centroid distance is 1.65\AA for both compounds, which is almost identical to the values observed for ferrocene and decamethyl ferrocene (1.66\AA) [8]. The Si–O–Si angles range from 139.7 to 143.6° , which is at the low end of the region typical of disiloxanes [9].

It is instructive to compare the molecular structure of the disiloxane-bridged [3]ferrocenophanes **2** and **3** with that of [3]ferrocenophane **4** and also with that of 7-oxa[3]ferrocenophane **5** (Fig. 3). Pertinent data are collected in Table 3.

It is obvious that compounds **4** and **5** are fairly strained: Their iron-ring centroid distance is 0.02\AA shorter than that found for **2** and **3**; furthermore, a considerable ring tilt is observed (7.6 and 11.9° , respectively). Additionally, the angle α (see Fig. 3), which also gives a rough measure of the molecular strain, deviates slightly more from 180° for compounds **4** and **5** than it does for **2** and **3**. The main factor for the unstrained character of **2** and **3** is the central bridge angle β , which is ca. 140° for **2** and **3**, but only 123° for **4** and a mere 114.7° for **5**. This reflects the remarkable flexibility of disiloxane units, which can easily adjust to a wide range of steric requirements [10].

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for compound **2**

	x	y	z	<i>U</i> (eq)
Fe(1)	1959(1)	7213(1)	5045(1)	21(1)
Fe(2)	1366(1)	7871(1)	1522(1)	19(1)
Fe(3)	4180(1)	7609(1)	8515(1)	20(1)
Si(1)	-1540(1)	6798(1)	4681(1)	24(1)
Si(2)	-1774(1)	8731(1)	4868(1)	26(1)
Si(3)	5061(1)	6359(1)	1872(1)	23(1)
Si(4)	4795(1)	8379(1)	1862(1)	25(1)
Si(5)	7896(1)	8251(1)	8258(1)	22(1)
Si(6)	8029(1)	6254(1)	8269(1)	23(1)
O(1)	-2210(3)	7881(2)	4676(2)	45(1)
O(2)	5407(3)	7253(2)	2045(2)	36(1)
O(3)	8561(3)	7248(2)	8088(2)	37(1)
C(1)	2040(4)	6655(2)	4192(2)	23(1)
C(2)	3515(4)	6290(3)	4524(2)	27(2)
C(3)	3105(4)	5837(2)	5309(2)	27(1)
C(4)	1376(4)	5926(2)	5459(2)	23(1)
C(5)	679(4)	6437(2)	4774(2)	20(1)
C(6)	-1848(5)	6721(3)	3755(2)	34(2)
C(7)	-2697(5)	6062(3)	5490(2)	36(2)
C(8)	-3255(5)	8959(3)	5688(2)	45(2)
C(9)	-1975(5)	9737(3)	4012(2)	44(2)
C(10)	343(4)	8428(2)	5111(2)	26(1)
C(11)	1794(4)	8618(3)	4586(2)	29(2)
C(12)	3192(5)	8214(3)	4973(3)	36(2)
C(13)	2646(5)	7775(3)	5740(3)	37(2)
C(14)	894(5)	7910(3)	5833(2)	32(2)
C(15)	1473(4)	6535(2)	2194(2)	23(1)
C(16)	88(5)	6836(2)	1799(2)	27(1)
C(17)	660(5)	7082(3)	1005(2)	30(2)
C(18)	2411(5)	6944(3)	910(2)	27(1)
C(19)	2938(4)	6599(2)	1657(2)	21(1)
C(20)	6511(5)	6131(3)	1039(2)	38(2)
C(21)	5383(5)	5367(3)	2733(2)	39(2)
C(22)	6112(5)	8954(3)	1012(2)	41(2)
C(23)	4946(5)	8672(3)	2724(2)	33(2)
C(24)	2637(4)	8745(2)	1668(2)	22(1)
C(25)	2079(4)	9103(2)	931(2)	26(1)
C(26)	339(5)	9225(3)	1036(2)	31(2)
C(27)	-215(4)	8962(3)	1829(2)	30(2)
C(28)	1181(4)	8672(2)	2220(2)	26(1)
C(29)	4539(4)	8884(2)	7841(2)	26(1)
C(30)	2894(4)	8949(2)	8203(2)	27(1)
C(31)	2912(4)	8632(3)	9005(2)	28(2)
C(32)	4595(4)	8381(2)	9129(2)	24(1)
C(33)	5617(4)	8534(2)	8409(2)	20(1)
C(34)	8714(5)	9122(3)	7418(2)	34(2)
C(35)	8652(5)	8200(3)	9130(2)	35(2)
C(36)	8808(5)	5438(3)	9145(2)	41(2)
C(37)	8968(5)	5836(3)	7431(2)	42(2)
C(38)	5772(4)	6407(2)	8396(2)	26(1)
C(39)	4689(5)	6227(3)	9104(2)	31(2)
C(40)	3044(5)	6496(3)	8952(3)	38(2)
C(41)	3042(5)	6847(3)	8154(3)	37(2)
C(42)	4711(5)	6798(3)	7803(2)	32(2)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor

Experimental Part

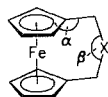
NMR: Bruker AM 300 (300.133 MHz, ^1H , ext. *TMS*). EI-MS: Varian CH5 and VG Autospec (70 eV).

2: 1.20 g (1.91 mmol) of the di(alkoxysilyl)ferrocene ($\text{H}_4\text{C}_5\text{SiMe}_2\text{OR}$)₂Fe (R = $\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{-OCH}_2\text{CH}_2\text{OMe}$) [3] are stored in the air at room temperature for several months. The oil is removed

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for compound **3**

	x	y	z	<i>U</i> (eq)
Fe(1)	2432(3)	1025(3)	2582(2)	34(1)
Si(1)	3264(7)	492(8)	1019(4)	58(4)
Si(2)	1512(7)	2671(9)	950(4)	63(4)
O(1)	2193(13)	1449(16)	696(7)	55(8)
C(1)	3410(13)	142(17)	2013(6)	36(7)
C(2)	2769	-847	2261	45(7)
C(3)	3049	-786	3029	55(8)
C(4)	3864	241	3255	40(7)
C(5)	4087	814	2628	35(7)
C(6)	1948(19)	-1826(24)	1814(12)	85(9)
C(7)	2625(22)	-1687(27)	3524(13)	135(14)
C(8)	4455(19)	552(26)	4019(11)	107(11)
C(9)	4976(22)	1841(24)	2628(13)	91(10)
C(10)	1451(11)	2411(13)	1915(6)	25(6)
C(11)	760	1427	2120	46(7)
C(12)	992	1431	2887	42(7)
C(13)	1826	2418	3156	43(7)
C(14)	2110	3024	2556	45(8)
C(15)	-108	515	1628	77(9)
C(16)	439(19)	576(25)	3347(12)	97(10)
C(17)	2247(18)	2865(24)	3969(10)	79(9)
C(18)	2845(17)	4183(22)	2640(11)	78(9)
C(19)	4479(21)	1381(28)	861(12)	121(12)
C(20)	3089(22)	-989(30)	446(13)	160(13)
C(21)	131(20)	2741(24)	296(11)	96(10)
C(22)	2205(19)	4298(25)	833(12)	97(11)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor



4 ($x = \text{CH}_2$)
5 ($x = \text{O}$)

Fig. 3. Compounds **4** and **5**. The angles α and β give an indication of the molecular strain in these compounds (α is the angle between the vector defined by the bridge atom and its Cp carbon neighbour and the plane defined by this carbon atom and its two Cp carbon neighbours; β is the central bridge angle at X)

Table 3. Compilation of parameters indicative of molecular strain for compounds **2–5**

Compound	2 ^a	3	4 ^b	5 ^b
Iron-ring centroid distance (\AA)	1.65	1.65	1.63	1.63
Cp ring tilt ($^\circ$)	0.7	0.8	2.7	11.9
Cp ring twist ($^\circ$)	7.0	1.1	1.2	1.4
$180 - \alpha$ ($^\circ$)	2.6/3.1	3.1/2.7	3.0/3.3	4.5/6.4
β ($^\circ$)	143.6	141.6	140.9	114.7

^a Three crystallographically independent molecules

^b Data taken from: Hillman M., Austin J. D. (1987) *Organometallics* **6**: 1737

from the large orange crystals by using filter paper. Yield 575 mg (95%). $^1\text{H-NMR}$ (CDCl_3): δ (ppm) = 0.27 (s, 12H, Me), 4.22 (s, 4H, CH), 4.31 (s, 4H, CH). MS: m/z (%) = 316 (100) [M^+].

3: A solution of 45 mg (0.11 mmol) of 2,2',3,3',4,4',5,5',6,6,7,7-dodecamethyl-6,7-disila[2]ferrocenophane [**6**] in 15 ml of acetonitrile is allowed to stand in the air at room temperature for several days. The

Table 4. Single-crystal X-ray diffraction study of compounds **2** and **3**: Crystal data

Compound	2	3
Empirical formula	C ₁₄ H ₂₀ FeOSi ₂	C ₂₂ H ₃₆ FeOSi ₂
Colour	orange	orange
Crystal size (mm)	0.5 × 0.7 × 0.7	0.3 × 0.3 × 0.1
Crystal system	triclinic	monoclinic
Space group	P $\bar{1}$	P2 ₁ /c
Unit cell dimensions	$a = 8.5330(10) \text{ \AA}$ $b = 15.610(3) \text{ \AA}$ $c = 18.774(5) \text{ \AA}$ $\alpha = 70.68(2)^\circ$ $\beta = 77.94(2)^\circ$ $\gamma = 75.150(10)^\circ$	$a = 12.388(3) \text{ \AA}$ $b = 9.924(3) \text{ \AA}$ $c = 19.136(10) \text{ \AA}$ $\beta = 105.11(3)^\circ$
Volume	2259.8(8) \AA^3	2271.2(15) \AA^3
Z	6	4
Formula weight	316.3	428.5
Density (calcd.)	1.395 g/cm ³	1.253 g/cm ³
Absorption coefficient (μ)	1.142 mm ⁻¹	0.774 mm ⁻¹
F(000)	996	920

Table 5. Single-crystal X-ray diffraction study of compounds **2** and **3**: Data collection

Compound	2	3
Radiation	MoK α ($\lambda = 0.71073 \text{ \AA}$)	
Temperature (K)	173	294
Monochromator	highly oriented graphite crystal	
2 θ range	3.0 to 55.0°	3.0 to 40.0°
Scan type	ω	
Scan speed	variable; 6.0 to 29.3°/min in ω	variable; 5.0 to 30.0°/min in ω
Scan range (ω)	1.40°	1.20°
Background measurement	stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time	
Standard reflexions	4 measured every 76 reflections	3 measured every 50 reflections
Index ranges	$0 \leq h \leq 11$ $-19 \leq k \leq 20$ $-23 \leq l \leq 24$	$0 \leq h \leq 11$ $0 \leq k \leq 9$ $-18 \leq l \leq 17$
Reflections collected	11127	2427
Independent reflections	10427	2137
Observed reflections (F > 5.0 σ (F))	7631	730

Table 6. Single-crystal X-ray diffraction study of compounds **2** and **3**: Structure solution and refinement

Compound	2	3
Programme package used	Siemens SHELXTL PLUS (VMS)	
Solution	direct method	
Refinement method	full-matrix least-squares	
Quantity minimized	$\sum w(F_o - F_c)^2$	
Hydrogen atoms	riding model, fixed isotropic U	
Weighting scheme	$w^{-1} = \sigma^2(F)$	
Number of parameters refined	487	104
Final <i>R</i> indices (obs. data)	<i>R</i> = 0.045 <i>R_w</i> = 0.044 <i>R_w</i> = $(\sum w(F_o - F_c)^2 / w F_o ^2)^{1/2}$	<i>R</i> = 0.076 <i>R_w</i> = 0.060
<i>R</i> indices (all data)	<i>R</i> = 0.065 <i>R_w</i> = 0.049	<i>R</i> = 0.201 <i>R_w</i> = 0.077
Goodness-of-fit	2.24	1.74
Largest and mean Δ/σ	0.003, 0.001	0.001, 0.000
Data-to-parameter ratio	15.7:1	7.0:1
Largest difference peak	0.63 e/Å ³	0.54 e/Å ³
Largest difference hole	-0.62 e/Å ³	-0.38 e/Å ³

orange crystals are isolated by filtration and dried in vacuo. Yield 20 mg (42%). ¹H-NMR (C₆D₆): δ (ppm) = 0.49 (s, 12H, SiMe₂), 1.59 (s, 12H, CMe), 1.81 (s, 12H, CMe). MS: *m/z* (%) = 428 (100) [M]⁺.

X-Ray Crystallography

The crystal structures of **2** and **3** were determined using a Syntex P2₁ four circle diffractometer. Details concerning the structure determinations are collected in Tables 4–6 [11]. Atomic scattering factors were taken from standard sources [12].

Acknowledgments

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