

257. The Crystal Structure of (1,1'-ferrocenediyl)diphenylsilane

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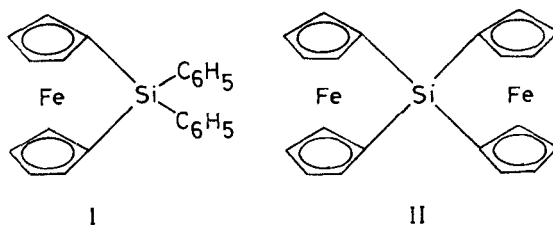
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Summary. The crystal structure of (1,1'-ferrocenediyl)diphenylsilane has been determined from analysis of photographic X-ray data. The crystal system is orthorhombic, $a = 14.18(2)$, $b = 12.54(2)$, $c = 9.28(1)$ Å, space group $Pnma$ with four formula units. The molecule has crystallographic m (C_s) symmetry with atoms Fe and Si lying in the mirror plane, which bisects the two phenyl groups. The planar cyclopentadienyl rings are bridged by a single silicon atom, and are tilted 19.2° with respect to one another. The Fe-C(Cp) distances vary from 2.01(1) to 2.11(1) Å. The bridging angle C(1)-Si-C(1') is 99.1° , while the Si-C(sp²) bond lengths range from 1.86 to 1.88 Å. The exocyclic C(1)-Si bond makes an angle of 40° with respect to the plane of the cyclopentadienyl ring.

Introduction. - The crystal structures of several bridged ferrocenes have been determined, the shortest bridges containing two atoms [1]. Recently two ferrocenophanes which contain silicon as the only bridging atom have been prepared. They are (1,1'-ferrocenediyl)diphenylsilane, (I), and bis(1,1'-ferrocenediyl)silane, (II), [2].

In compounds containing bridges of less than four carbon atoms the cyclopentadienyl (Cp) rings are tilted with respect to one another. The largest angles of tilt, 23° to 24° , have been found for bis(pentalenyl)-iron [3] and 1,1'-tetramethylethyleneferrocene [4], and more recently ferrocenophanethiazine 1,1-dioxide [5]. All have bridges of two atoms. Here we report on the crystal structure of (1,1'-ferrocenediyl)-diphenylsilane, (I).



Experimental. - The crystals of $(C_5H_4)_2FeSi(C_6H_5)_2$, compound (I), were rod-like, red and air stable. Preliminary oscillation, *Weissenberg* and precession photographs indicated an orthorhombic cell: $a = 14.18(2)$, $b = 12.54(2)$, $c = 9.28(1)$ Å, $V = 1723$ Å³, space group $Pna2_1$ or

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Pnma (the latter confirmed by structure analysis), $D_x = 1.42$, $Z = 4$, ($C_{22}H_{18}FeSi$, Mol.-Wt. = 366.3), $D_c = 1.418$, $\mu_{CuK\alpha} = 78 \text{ cm}^{-1}$. The layers hk0–hk8 and h0l–h1l were recorded by the equi-inclination *Weissenberg* method, using Ni-filtered $CuK\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) on multiple-film packs. The films were scanned by the *Science Research Council* service (Great Britain), with an *Optronics P-1000 Photoscan*. The intensities were corrected for *Lorentz*-polarization effects but not for absorption. A total of 588 unique observed reflections were obtained after inter-layer scaling and merging of equivalent reflections.

Structure Analysis and Refinement. – The position of all the non-hydrogen atoms were obtained from *Patterson* and *Fourier* syntheses. Refinement was initially by isotropic full-matrix least-squares, finally by anisotropic block-diagonal least-squares. Atomic scattering factors were taken from [6]. No attempt was made to locate the hydrogen atoms.

Refinement was terminated at $R = 6.8\%$ and $R_w = 9.0\%$ (average parameter shift ≤ 0.2 e.s.d.). The weighting scheme used in the final stages of refinement was $\sqrt{w} = F_0/24$ if $F_0 \leq 24$, otherwise $\sqrt{w} = 24/F_0$. The final positional parameters are given in Table 1. Structure factor tables and final anisotropic vibrational parameters are available from the authors.

Table 1. *Final positional parameters* $\times 10^4$ (standard deviations in parentheses)

	x/a	y/b	z/c
Fe	2550 (2)	1/4	4406 (3)
Si	4190 (3)	1/4	3301 (5)
C(1)	3439 (7)	1358 (8)	3841 (11)
C(2)	3176 (8)	1241 (8)	5333 (11)
C(3)	2232 (8)	1068 (11)	5422 (15)
C(4)	1867 (8)	1053 (11)	3983 (13)
C(5)	2594 (7)	1234 (9)	3034 (12)
C(6)	4351 (10)	1/4	1310 (16)
C(7)	4429 (8)	1539 (10)	559 (12)
C(8)	4621 (8)	1537 (10)	– 924 (12)
C(9)	4744 (12)	1/4	– 1634 (19)
C(10)	5271 (10)	1/4	4367 (16)
C(11)	5672 (8)	1545 (8)	4760 (10)
C(12)	6489 (8)	1539 (9)	5513 (12)
C(13)	6906 (13)	1/4	5893 (18)

Results and Discussion. – The final interatomic distances and angles are given in Tables 2 and 3. Deviations of various atoms from different least-squares planes in the molecule are given in Table 4. The Figure shows the atom-labelling scheme used, and illustrates some interesting intramolecular distances and angles. Crystallographic requirements impose m (C_s) symmetry for the molecule. The mirror plane, in which lie atoms Fe and Si, bisects each phenyl ring. The molecule also has pseudo C_{2v} symmetry with an approximate 2-fold axis, on which lie atoms Fe and Si, and a second approximate mirror plane containing atoms Fe, Si, C(1) and C(1'). The deviation from pure C_{2v} symmetry is indicated by the deviation of different atoms from this second 'mirror' plane (see Table 4).

Table 2. *Bond lengths* (Å) (standard deviations in parentheses)

Fe ... Si	2.636 (5)	C(1)—C(2)	1.445 (15)	C(6)—C(7)	1.397 (14)
Fe—C(1)	2.014 (11)	C(2)—C(3)	1.417 (18)	C(7)—C(8)	1.404 (16)
Fe—C(2)	2.023 (11)	C(3)—C(4)	1.440 (18)	C(8)—C(9)	1.388 (15)
Fe—C(3)	2.082 (13)	C(4)—C(5)	1.409 (16)	C(10)—C(11)	1.385 (13)
Fe—C(4)	2.114 (13)	C(5)—C(1)	1.465 (15)	C(11)—C(12)	1.397 (16)
Fe—C(5)	2.036 (11)	Si—C(1)	1.881 (11)	C(12)—C(13)	1.399 (15)
		Si—C(6)	1.862 (15)	C(1) ... C(1')	2.86
		Si—C(10)	1.881 (15)	C(2) ... C(2')	3.16
				C(3) ... C(3')	3.59
				C(4) ... C(4')	3.63
				C(5) ... C(5')	3.17

Table 3. *Bond angles* (degrees) (standard deviations in parentheses)

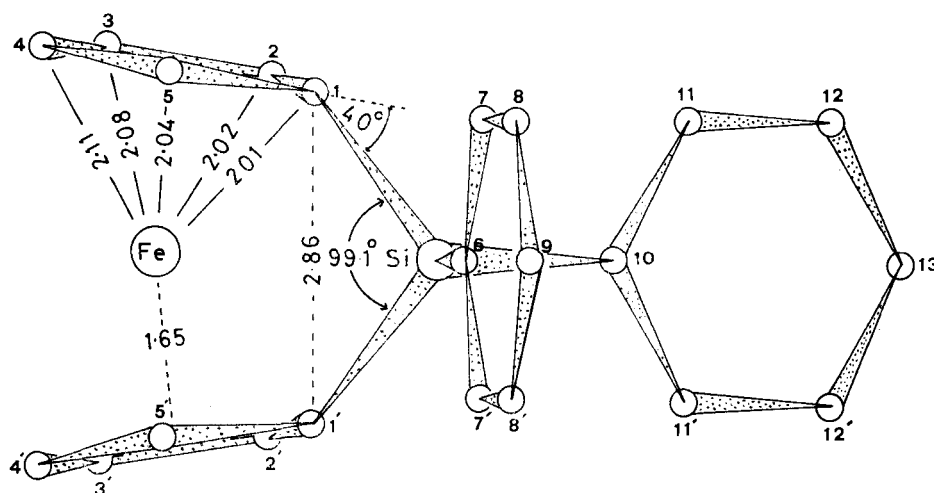
C(1)—Si—C(6)	109.9 (3)	C(3)—C(4)—C(5)	106.9 (5)
C(1)—Si—C(1')	99.1 (3)	C(4)—C(5)—C(1)	110.5 (5)
C(1)—Si—C(10)	111.3 (3)	C(7)—C(6)—C(7')	119.2 (4)
C(6)—Si—C(10)	114.4 (4)	C(6)—C(7)—C(8)	120.5 (4)
Si—C(1)—C(2)	119.5 (4)	C(7)—C(8)—C(9)	119.3 (2)
Si—C(1)—C(5)	116.7 (4)	C(8)—C(9)—C(8')	121.0 (4)
Si—C(6)—C(7)	120.4 (3)	C(11)—C(10)—C(11')	119.6 (9)
Si—C(10)—C(11)	120.2 (7)	C(10)—C(11)—C(12)	120.5 (6)
C(5)—C(1)—C(4)	104.4 (5)	C(11)—C(12)—C(13)	120.2 (7)
C(1)—C(2)—C(3)	109.7 (7)	C(12)—C(13)—C(12')	118.9 (12)
C(2)—C(3)—C(4)	108.5 (7)		

Table 4. *Various least-squares planes in the molecule*

Plane:	C(1), C(2), C(3), C(4), C(5).
Equation:	$0.157x - 0.986y - 0.057z + 1.082 = 0$
Deviations:	C(1), 0.00; C(2), 0.00; C(3), -0.01; C(4), 0.00; C(5), 0.00; Si, -1.21.
(± 0.01 Å)	
Plane:	Fe, Si, C(1), C(1').
Equation:	$-0.388x - y - 0.992z + 5.248 = 0$.
Deviations:	Fe, 0.01; Si, 0.02; C(1), -0.01; C(1'), -0.01; C(2), -1.14; C(3), -0.67; C(4), 0.77;
(± 0.01 Å)	C(5), 1.16; C(6), 1.63; C(7), 2.22; C(8), 3.38; C(9), 3.92; C(10), -1.52; C(11), -2.08; C(12), -3.20; C(13), -3.76.
Plane:	C(6), C(7), C(8), C(9), C(8'), C(7').
Equation:	$-0.979x + y - 0.206z + 6.535 = 0$.
Deviations:	C(6), -0.02; C(7), 0.01; C(8), 0.02; C(9), -0.03; C(8'), 0.02; C(7'), 0.01; Si, -0.17.
(± 0.01 Å)	
Plane:	C(10), C(11), C(12), C(13), C(12'), C(11').
Equation:	$0.503x + y - 0.864z - 0.415 = 0$.
Deviations:	C(10), 0.01; C(11), 0.01; C(12), 0.00; C(13), 0.00; C(12'), 0.00; C(11'), 0.01;
(± 0.01 Å)	Si, 0.06.

The cyclopentadienyl rings, related by the crystallographic mirror plane and hence eclipsed, are planar and inclined at an angle of 19.2° to one another. The Fe–C(Cp) distances vary from 2.01 to 2.11 Å, with an average value of 2.05 Å. The Fe–Cp(centroid) distance is 1.65 Å, while the Cp(centroid)–Fe–Cp(centroid) angle is 167.3° . The average Cp ring C–C distance is 1.43 Å, with an average ring angle of 108.0° . The inter-ring C...C' distances vary from 2.86 to 3.63 Å. This geometry is similar to that found for other bridged ferrocene compounds [3–5].

There is clearly no bonding between atoms Fe and Si as the interatomic distance (2.68 Å) is appreciably longer than the theoretical bond length calculated from metallic covalent radii (2.37 Å) [7].



Molecular structure of (1,1'-ferrocenediyl)diphenylsilane

The C(1)–Si–C(1') bridging angle is 99.1° , hence the silicon atom has a distorted tetrahedral coordination (see Table 3). The Si–C bond lengths, whose average is 1.875 Å, are normal for Si–C(sp²) bonds [8] [9]. The phenyl groups are planar (Table 4) and their bond lengths and angles normal (Tables 2 and 3). The exocyclic C(6)–Si bond makes an angle of 5° with the plane of the phenyl group, while the bond C(10)–Si makes an angle of 2° with the corresponding phenyl group.

Strain in bridged ferrocene compounds is related to (a) the angle of tilt of the Cp rings, (b) the bond-angle distortion at the bridging atoms, and (c) the deviation of the exocyclic bonds from the Cp planes. In the title compound factor (c) is dominant, as the exocyclic bond (C(1)–Si) makes an angle of 40° with the Cp plane. The largest such angle reported previously was only *ca.* 12° [4]. The relatively small ring tilt in (I) can be explained by the fact that any increase (retaining the Fe–Cp(centroid) distance of 1.65 Å, common to Cp₂Fe structures) would shorten the C(1)...C(1') distance. In unstrained compounds the normal separation of parallel aromatic rings

is 3.4 Å [10]. In bridged ferrocenes the shortest inter-ring C...C separation observed so far is 2.7 Å, [4]. In compound I it is 2.86 Å. Hence the repulsion energy between the Cp rings appears to be of more importance than the degree of strain at C(1).

For compounds (I) and (II) the ¹H-NMR. chemical shift differences between the α- and β-Cp hydrogen atoms are 0.37 and 0.15 ppm, respectively. It has been suggested [11] [12] that these chemical shift differences are roughly proportional to the ring tilt, and thus a smaller ring tilt would be predicted for (II) than for (I). However, this interpretation has been questioned [13].

In the electronic spectra of ferrocenophanes, the position and intensity of the 440 nm band are particularly sensitive to ring tilt [14]. The spectra of (I) and (II) in this region are very similar [2], so on this basis similar structural features are expected. Crystallographic studies on compound (II) and others in this series are continuing.

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