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SYNTHESIS AND CRYSTAL STRUCTURES OF TWO IRON DERIVATIVES OF PERMETHYLCYCLOPENTASILANE

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Summary

Reaction of dodecamethylcyclohexasilane with Me_3SiCl and $AlCl_3$ produces a mixture of cyclo-$Si_5Me_9SiMe_2Cl$ (Ia) and cyclo-$Si_5Me_8ClSiMe_2Cl$ (III). Treatment with $[Fe(CO)_2Cp]^-$ produced cyclo-$Si_5Me_9SiMe_2[Fe(CO)_2Cp]$ (II) and cyclo-$Si_5Me_8[Fe(CO)_2Cp]SiMe_2[Fe(CO)_2Cp]$ (IV). The structures of II and IV were determined by single crystal X-ray diffraction. Compound II crystallizes in the monoclinic space group $P2_1/c$ with a 21.531(9) Å, b 9.865(4) Å, c 13.917 Å, β 101.67(2)°, V 2895(2) Å^3 and with $Z = 4$. Compound IV crystallizes in the monoclinic space group $P2_1/c$ with a 7.923(2) Å, b 22.504(9) Å, c 19.168(7) Å, β 92.86(3)°, V 3413(2) Å^3 and with $Z = 4$. The cyclopentasilane fragment of II is in a C_s conformation, with four silicon atoms coplanar and the remaining silicon 1.02 Å out of the plane, forming a dihedral angle of 137°. In the silicon ring the average Si—Si—Si bond angle is 104(2)° and the average Si—Si bond length is 2.356(10) Å. In compound IV the second iron atom is attached at the 2 position on the cyclopentasilane ring, which is in a distorted C_s conformation with average Si—Si bond length 2.326(2) Å and average Si—Si—Si bond angle 104(2)°.

Introduction

Although the spectroscopic properties of permethylpolysilanes have been studied in some detail [1,2], relatively little structural data is yet available for these molecules. X-ray crystal structures of the monocyclic $(Me_2Si)_6$ [3] and $[Me(t\text{-}Bu)Si]_4$ [4] as well as the [3.3.1]-bicyclic polysilane Si_9Me_{16} [5] have been obtained. An electron diffraction study of the unsubstituted molecule Si_5H_{10} [6] and crystal structures for the related organosilicon compounds $(Ph_2Si)_4$ [7] and $(Ph_2Si)_5$ [8] have also been reported. The structures of these polysilanes are remarkably similar to those of the corresponding cycloalkanes.

Because $(Me_2Si)_5$ plays a key role in permethylpolysilane chemistry [1,2], its structure is particularly important. Several attempts were made to obtain dif-

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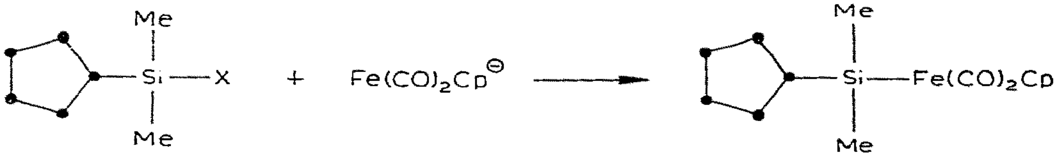
fraction patterns for this compound, all unsuccessful *. Known derivatives of $(Me_2Si)_5$ which might be suitable for X-ray crystallographic study include compounds of type I **. In such molecules, the long Si—Si bond from the silicon ring to the *exo*-silicon should ensure that the conformation of the ring will not be seriously affected by the substituent. Compound Ia was prepared according to the method of Ishikawa and Kumada [10] and then converted to its cyclopentadienyliron derivative (II) [11] in order to impart greater crystallinity to the molecule (eq. 1).



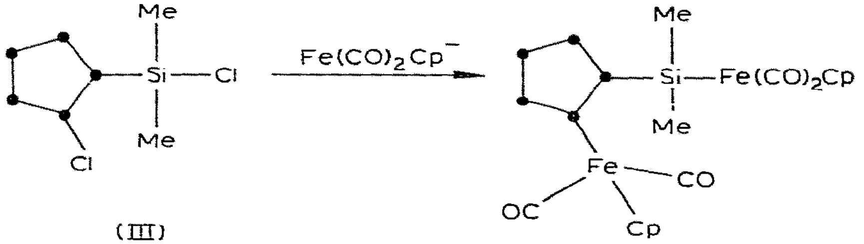
(1)

(I)

(II)

(Ia, X = Cl)

The reaction mixture containing Ia also contains a substantial amount of a dichloro isomer III. When the unpurified reaction was treated with $Fe(CO)_2Cp^-$, a compound with two iron atoms was also isolated (eq. 2). An X-ray crystal structure showed that IV has the structure shown above and must therefore arise from the dichloro isomer III.



(2)

(III)

(IV)

Experimental

All reactions were carried out under a nitrogen atmosphere at ambient temperatures. Solvents were freshly distilled just prior to use. Infrared spectra were determined on a Perkin—Elmer 457 grating infrared spectrometer. ^1H NMR spectra were run on JEOL MH-100 or Brüker 270 spectrometers in benzene-d_6. Mercury was purchased from D.F. Goldsmith and sodium from Mallinckrodt, and both were used without further purification. $[CpFe(CO)_2]_2$ was purchased from Alfa and was recrystallized from $CHCl_3$. Alumina (neutral) was purchased

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* Recently it has been found that $(Me_2Si)_5$ exists in a plastic crystalline state above —39°C [9].

** Each dot represent a silicon atom with sufficient methyl groups attached to bring the total valency of silicon to 4.

from Fisher Scientific and was oven dried at 100°C before use. $(SiMe_2)_6$ was prepared by a published procedure [11].

Synthesis of $Si_6Me_{11}Cl$ and $Si_6Me_{10}Cl_2$

A 250 ml flask, equipped with a magnetic stirring bar and nitrogen inlet, was charged with $(Me_2Si)_6$ (30 g, 86 mmol), Me_3SiCl (120 ml, 0.95 mol), and $AlCl_3$ (0.5 g, 3.7 mmol). The mixture was stirred at room temperature and monitored by VPC using a 6′ × 1/8″ column packed with 5% QF-1 on Chromosorb W. The reaction was allowed to proceed until very little $(Me_2Si)_6$ remained. Approximately 60% of the product was the monochlorinated species Ia and the rest was shown by mass spectroscopy to be the dichlorinated species III. The crude reaction mixture was subjected to a Kugelrohr distillation to separate the products from the nonvolatile residue, yielding approximately 29 g of white solid (47 mmol Ia, 30 mmol III).

Synthesis of cyclo-$Si_5Me_9SiMe_2[Fe(CO)_2Cp]$ (II) and cyclo-$Si_5Me_8[Fe(CO)_2Cp]$-$SiMe_2[Fe(CO)_2Cp]$ (IV)

The procedure of King [12] was generally followed. An amalgam was made by the slow addition of sodium (0.5 g, 17.4 mmol) to mercury (4 ml, 0.27 mol) in a 100 ml three-necked flask fitted with a stopcock at the bottom, and equipped with a mechanical stirrer and addition funnel. After the amalgam cooled, a solution of $[CpFe(CO)_2]_2$ (1 g, 2.87 mmol) was added rapidly dropwise. The reaction mixture was stirred for 1 h, and the excess amalgam was then drained through the bottom stopcock. A solution of 2 g chlorosilane (3.2 mmol I, 2.1 mmol III) in 20 ml THF was added slowly dropwise. After being stirred for 4 h, the solution turned from deep red to yellow green. An equal volume of hexane was added to precipitate any salts, and the mixture was filtered under N_2. The solvent was removed under vacuum.

The residue was dissolved in 4 ml THF, loaded on a 2 1/2′ × 3/4″ alumina column, and eluted with a mixture of 60% hexane, 40% diethyl ether. Two yellow bands were observed, and each was collected in a number of fractions. Recrystallization from hexane of fractions from the first band gave crystalline orange II (~1 g, 60%): m.p. 64.5—66.5°C; ^1H NMR (C_6D_6): δ 4.27 (5H), 0.85 (6H), 0.53 (12H), 0.43 (6H), 0.41 (6H), 0.39 (3H) ppm; IR (C_6D_6): 2950m, 2890w, 2800vw, 2005vs, 1950vs, 1915w, 1400w, 1260m, 1245m, 1015m, 687w, 646m, and 593s cm^{-1}; Anal. Found: C, 42.06; H, 7.38; Si, 33.28; $C_{24}H_{40}Fe_2O_4Si_6$ calcd.: C, 42.34; H, 7.44; Si, 33.10%; mass spectrum, parent ion peak at *m/e* 510. From the second band similar recrystallization yielded powdery yellow IV (~0.5 g, 40%): m.p. 137—141°C (with decomposition); ^1H NMR (C_6D_6): δ 4.55 (5H), 4.42 (5H), 1.06 (3H), 0.99 (3H), 0.67 (3H), 0.63 (3H), 0.57 (3H), 0.48 (12H) cm^{-1}; IR (C_6D_6): 2950m, 2890w, 2795vw, 1400w, 1260w, 1245m, 1015m, 1000m, 830s, 800s, 762s, 695s and 590s cm^{-1}; Anal. Found: C, 43.07; H, 6.25; Si, 25.28. $C_{18}H_{28}FeO_2Si_6$ calcd.: C, 42.84; H, 6.00; Si, 25.05%; mass spectrum, parent ion peak *m/e* 672.

Recrystallization for X-ray diffraction analysis

Crystallization of II was carried out by dissolving the pure compound in liquid butane at —78°C under an argon atmosphere followed by an exchange to

TABLE 1

CRYSTALLOGRAPHIC DATA FOR cyclo-$Si_5Me_9SiMe_2[Fe(CO)_2Cp]$ AND cyclo-$Si_5Me_8[Fe(CO)_2Cp]SiMe_2[Fe(CO)_2Cp]$

	cyclo-$Si_5Me_9SiMe_2$-$[Fe(CO)_2Cp]$	cyclo-Si_5Me_8-$[Fe(CO)_2Cp]SiMe_2[Fe(CO)_2Cp]$
mp (°C)	64.5—66.5	137—141 (dec.)
Crystal growing temperature (°C)	0	23
Data collection temperature (°C)	22	22
Radiation (graphite monchromator) (Å)	0.71069	0.71069
Scan speed (deg/min)	2—24	2—24
Range of 2θ (deg)	$3 < 2\theta < 50$	$3 < 2\theta < 50$
Total independent reflections	5254	4508
Independent observed reflections $[I > 26(I)]$	3296	2932
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
Equiv. positions	$\pm[x,y,z;\ -x,\ ½+y,\ ½-z]$	$\pm[x,y,z;\ ½-x,\ ½+y,\ ½-z]$
Systematic absences	$0k0$: k odd $h0l$: l odd	$0k0$: k odd $h0l$; $h+l$ odd
a (Å)	21.531(9)	7.923(2)
b (Å)	9.865(4)	22.504(9)
c (Å)	13.917(2)	19.168(7)
β (deg)	101.67(2)	92.86(3)
V (Å^3)	2895(2)	3413(2)
calcd density (g/cm^3)	1.76	1.97
R_1 (F)	4.08	3.15
R_2 (F)	4.90	3.83
Data/parameter ratio	13.5	10.4

an ice bath (at ~0°C) with the butane vapor being allowed to bleed slowly through a gas bubbler. This procedure yielded one very large crystal along with several smaller ones; a crystal suitable for X-ray diffraction was cleaved from the large one.

Crystallization of IV was carried out by sweeping argon over a saturated solution of the compound in hexane at 22°C. Many small crystals were isolated and one of these was selected for X-ray study. Crystals of both compounds were sealed in Lindemann glass capillaries under argon.

The crystallographic data are given in Table 1.

Structure solution and refinement

The crystals for each structure determination were mounted on a Syntex P$\bar{1}$ diffractometer. The crystal symmetry and lattice parameters for both structures were confirmed by axial photographs about each axis [13]. Intensity data were collected using the θ—2θ scan technique. A periodic monitoring of two standard reflections during the data collection of both data sets showed no indication of crystal decay in the X-ray beam.

The structures were solved by direct methods (MULTAN) [14]. In cyclo-$Si_5Me_9SiMe_2[Fe(CO)_2Cp]$, the first E-map located the iron and four of the silicon atoms. After three Fourier maps, the coordinates of all other nonhydrogen atoms were found. For cyclo-$Si_5Me_8[Fe(CO)_2Cp]SiMe_2[Fe(CO)_2Cp]$, the positions of all the iron and silicon atoms were found in the first E-map, while those for the carbon atoms were determined in three successive Fourier maps.

TABLE 2

ATOMIC COORDINATES AND TEMPERATURE PARAMETERS FOR cyclo-$Si_5Me_9SiMe_2[Fe(CO)_2Cp]$

A. Atomic coordinates (Å) (×10^4)

Atom	x	y	z
Fe(1)	849.0(3)	3099.7(6)	1820.2(4)
Si(1)	1308.8(5)	969.0(11)	1672.9(8)
Si(2)	2312.6(5)	691.6(10)	2729.5(7)
Si(3)	2543.1(5)	−1596.5(11)	3106.2(8)
Si(4)	3616.5(8)	−1593.9(12)	3909.7(9)
Si(5)	4060.8(6)	309.3(13)	3299.1(10)
Si(6)	3232.1(9)	1352.1(12)	2172.3(11)
C(1)	1404(2)	642(5)	380(3)
C(2)	790(2)	−459(4)	1947(4)
C(3)	2350(2)	1524(5)	3975(3)
C(4)	2033(2)	−2306(5)	3936(3)
C(5)	2442(2)	−2644(4)	1954(3)
C(6)	3680(3)	−1441(6)	5263(4)
C(7)	4026(3)	−3201(6)	3674(5)
C(8)	4721(3)	−161(7)	2687(5)
C(9)	4373(3)	1538(6)	4318(5)
C(10)	3229(3)	689(6)	910(4)
C(11)	3379(2)	3217(5)	2147(5)
C(12)	1662(2)	3958(5)	1484(5)
C(13)	1139(3)	4400(5)	815(3)
C(14)	1597(3)	4381(5)	2413(4)
C(15)	1019(3)	5107(5)	2292(5)
C(16)	748(2)	5120(5)	1322(5)
C(17)	174(2)	2421(5)	1060(4)
O(1)	−272(2)	2008(4)	558(3)
O(18)	661(2)	2463(5)	2884(3)
O(2)	534(2)	2041(4)	3592(2)

B. Anisotropic temperature parameters (×10^4) [a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	44.3(3)	51.8(4)	55.3(4)	−3.6(3)	11.6(3)	−6.9(3)
Si(1)	46.1(6)	47.3(6)	49.5(6)	−9.4(5)	12.0(5)	−6.9(5)
Si(2)	43.8(6)	43.4(6)	48.8(6)	−6.4(5)	15.5(5)	−6.4(5)
Si(3)	60.0(7)	44.3(6)	53.7(7)	−9.2(5)	20.0(5)	−0.2(5)
Si(4)	59.1(7)	57.4(8)	72.2(8)	4.0(8)	18.5(7)	7.4(8)
Si(5)	46.2(7)	71.1(2)	82.8(7)	−1.3(8)	20.0(7)	14.2(7)
Si(6)	48.4(6)	57.8(7)	83.3(9)	−4.0(5)	23.6(6)	19.2(6)
C(1)	84(3)	68(3)	58(3)	−3(3)	15(2)	−12(2)
C(2)	61(3)	62(3)	96(4)	−19(2)	15(2)	−2(3)
C(3)	76(3)	82(3)	66(3)	7(3)	8(2)	−26(3)
C(4)	85(3)	83(3)	63(3)	−20(3)	24(2)	10(3)
C(5)	103(4)	56(3)	78(3)	−14(3)	35(3)	−10(2)
C(6)	75(3)	139(5)	79(4)	−15(3)	9(3)	18(3)
C(7)	106(5)	83(4)	176(6)	25(4)	24(4)	−5(4)
C(8)	71(4)	175(6)	138(5)	31(4)	54(4)	56(5)
C(9)	86(4)	99(4)	132(5)	−27(3)	−6(4)	9(4)
C(10)	88(4)	143(5)	80(4)	9(4)	42(3)	37(4)
C(11)	62(3)	76(4)	212(7)	−14(3)	25(4)	41(4)
C(12)	51(3)	53(3)	132(5)	−6(2)	31(3)	5(3)
C(13)	88(4)	73(3)	73(3)	−13(3)	26(3)	−2(3)
C(14)	90(4)	62(3)	91(4)	−36(3)	−14(3)	10(3)
C(15)	109(4)	60(3)	103(4)	−15(3)	45(4)	−30(3)
C(16)	71(3)	63(3)	114(5)	8(3)	12(3)	11(3)
C(17)	62(3)	76(3)	75(3)	−3(3)	5(2)	0(3)
O(1)	76(2)	129(3)	114(3)	−26(2)	−21(2)	−11(3)
O(18)	54(3)	70(3)	70(3)	−8(2)	19(2)	−14(2)
O(2)	98(2)	111(3)	69(2)	−20(2)	39(2)	−4(2)

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[a] The form of this anisotropic temperature correction is $\exp[-2\pi^2(U_{11}h^2a^{\star 2} + U_{22}k^2b^{\star 2} + U_{33}l^2c^{\star 2} + 2U_{12}hka^{\star}b^{\star} + 2U_{13}hla^{\star}c^{\star} + 2U_{23})klb^{\star}c^{\star}]$.

TABLE 3

INTERATOMIC DISTANCES (Å) FOR cyclo-$Si_5Me_9SiMe_2[Fe(CO)_2Cp]$

Fe(1)—Si(1)	2.350(1)	Si(2)—C(3)	1.905(4)
Fe(1)—C(12)	2.081(4)	Si(3)—C(4)	1.882(4)
Fe(1)—C(13)	2.085(5)	Si(3)—C(5)	1.882(5)
Fe(1)—C(14)	2.082(4)	Si(4)—C(6)	1.866(5)
Fe(1)—C(15)	2.095(5)	Si(4)—C(7)	1.875(6)
Fe(1)—C(16)	2.107(5)	Si(5)—C(8)	1.859(5)
Fe(1)—C(17)	1.749(5)	Si(5)—C(9)	1.883(6)
Fe(1)—C(18)	1.729(5)	Si(6)—C(10)	1.873(5)
Si(1)—Si(2)	2.371(1)	Si(6)—C(11)	1.868(5)
Si(2)—Si(3)	2.347(2)	C(12)—C(13)	1.377(7)
Si(2)—Si(6)	2.359(2)	C(12)—C(14)	1.303(7)
Si(3)—Si(4)	2.355(2)	C(15)—C(16)	1.358(7)
Si(4)—Si(5)	2.343(2)	C(14)—C(15)	1.416(7)
Si(5)—Si(6)	2.360(2)	C(17)—O(1)	1.141(5)
Si(1)—C(1)	1.880(4)	C(18)—O(2)	1.153(5)
Si(1)—C(2)	1.884(4)		

Full matrix isotropic refinement of II resulted in $R_1(F)$ = 10.7% and $R_2(F)$ = 13.7% while an analogous refinement of IV gave $R_1(F)$ = 8.5% and $R_2(F)$ = 11.0%.

Atomic coordinates were then calculated for each hydrogen atom on the basis of an idealized C—H distance of 0.95 Å. A trigonal arrangement was

TABLE 4

SELECTED INTRAMOLECULAR ANGLES (deg) FOR cyclo-$Si_5Me_9SiMe_2[Fe(CO)_2Cp]$

X—X—C angles [a]		X—X—X angles [a]	
Si(1)—Fe(1)—C(17)	85.3(2)	Fe(1)—Si(1)—Si(2)	113.35(5)
Si(1)—Fe(1)—C(18)	85.7(1)	Si(1)—Si(2)—Si(3)	111.99(5)
Fe(1)—Si(1)—C(1)	111.5(2)	Si(1)—Si(2)—Si(6)	118.98(6)
Fe(1)—Si(1)—C(2)	111.9(2)	Si(3)—Si(2)—Si(6)	100.68(6)
Si(2)—Si(1)—C(1)	108.1(2)	Si(2)—Si(3)—Si(4)	104.35(6)
Si(2)—Si(1)—C(2)	106.9(2)	Si(3)—Si(4)—Si(5)	105.20(6)
Si(1)—Si(2)—C(3)	112.3(2)	Si(4)—Si(5)—Si(6)	106.32(6)
Si(3)—Si(2)—C(3)	104.1(2)	Si(2)—Si(6)—Si(5)	103.48(6)
Si(6)—Si(2)—C(3)	107.2(2)		
Si(2)—Si(3)—C(4)	111.8(2)	X—C—X and C—X—C angles [a]	
Si(2)—Si(3)—C(5)	110.8(2)		
Si(4)—Si(3)—C(4)	110.3(2)	Fe(1)—C(17)—O(1)	178.4(5)
Si(4)—Si(3)—C(5)	109.8(2)	Fe(1)—C(18)—O(2)	179.7(4)
Si(3)—Si(4)—C(6)	110.1(2)	C(17)—Fe(1)—C(18)	94.0(2)
Si(3)—Si(4)—C(7)	111.5(2)	C(1)—Si(1)—C(2)	104.5(2)
Si(5)—Si(4)—C(6)	110.4(2)	C(4)—Si(3)—C(5)	109.7(2)
Si(5)—Si(4)—C(7)	111.9(2)	C(6)—Si(4)—C(7)	107.7(3)
Si(4)—Si(5)—C(8)	111.9(2)	C(8)—Si(5)—C(9)	108.4(3)
Si(4)—Si(5)—C(9)	110.6(2)	C(10)—Si(6)—C(11)	107.1(3)
Si(6)—Si(5)—C(8)	110.5(2)		
Si(6)—Si(5)—C(9)	109.0(2)	C—C—C angles	
Si(2)—Si(6)—C(10)	111.6(2)		
Si(2)—Si(6)—C(11)	115.7(2)	C(13)—C(12)—C(14)	108.1(4)
Si(5)—Si(6)—C(10)	109.3(2)	C(12)—C(13)—C(16)	108.3(4)
Si(5)—Si(6)—C(11)	109.5(2)	C(12)—C(14)—C(15)	107.0(4)
		C(14)—C(15)—C(16)	108.2(5)
		C(13)—C(16)—C(15)	108.4(5)

[a] X = Fe, Si or O.

TABLE 5

DISTANCES (Å) OF ATOMS OUT OF VARIOUS MOLECULAR PLANES AND DIHEDRAL ANGLES (deg) BETWEEN VARIOUS PLANES FOR cyclo-Si$_5$Me$_9$SiMe$_2$[Fe(CO)$_2$Cp]

Plane Si(3),Si(4),Si(5),Si(6)		Plane C(12),C(13),C(14),C(15),C(16)	
Atoms	Distance	Atoms	Distance
Si(2)	−1.023	C(12)	0.003
Si(3)	0.002	C(13)	−0.005
Si(4)	−0.003	C(14)	−0.001
Si(5)	0.003	C(15)	−0.002
Si(6)	−0.002	C(16)	0.004
Plane C(6),Si(4),Si(5),C(9)		**Plane C(7),Si(4),Si(5),C(8)**	
C(6)	−0.001	C(7)	−0.004
Si(4)	0.001	Si(4)	0.006
Si(5)	−0.001	Si(5)	−0.006
C(9)	0.001	C(8)	0.004

Atoms defining plane 1	atoms defining plane 2	Dihedral angle
Si(3),Si(4),Si(5),Si(6)	C(12),C(13),C(14),C(15),C(16)	100.6
Si(3),Si(4),Si(5),Si(6)	Si(2),Si(3),Si(6)	137.0

TABLE 6

ATOMIC COORDINATES AND TEMPERATURE PARAMETERS FOR cyclo-Si$_5$Me$_8$[Fe(CO)$_2$Cp]-SiMe$_2$[Fe(CO)$_2$Cp]

A. Atomic coordinates (Å) (×10^4)

Atom	*x*	*y*	*z*
Fe(1)	3323.2(7)	2458.2(2)	835.4(3)
Fe(2)	1886.9(7)	5622.2(2)	1410.6(3)
Si(1)	2218.3(12)	3405.6(4)	1052.0(5)
Si(2)	3586.6(12)	3956.4(4)	1963.7(5)
Si(3)	2300.2(12)	4869.5(4)	2261.6(5)
Si(4)	3901.3(14)	5157.9(5)	3280.5(5)
Si(5)	4588.8(15)	4251.6(5)	3829.7(5)
Si(6)	3776.3(16)	3481.1(5)	3062.6(5)
C(1)	−70(5)	3368(2)	1289(2)
C(2)	2230(6)	3858(2)	221(2)
C(3)	5867(5)	4128(2)	1770(2)
C(4)	220(5)	4653(2)	2655(2)
C(5)	2523(6)	5617(2)	3848(2)
C(6)	5866(6)	5602(2)	3152(2)
C(7)	6927(6)	4198(2)	4055(2)
C(8)	3446(6)	4189(2)	4673(2)
C(9)	5432(7)	2881(2)	3094(2)
C(10)	1761(7)	3137(2)	3346(2)
C(11)	4944(6)	2533(2)	24(2)
C(12)	5563(5)	2881(2)	584(2)
C(13)	5884(5)	2504(2)	1153(2)
C(14)	5499(6)	1925(2)	940(3)
C(15)	4926(6)	1939(2)	247(3)
C(16)	2597(6)	5911(2)	428(2)
C(17)	2736(6)	6380(2)	889(3)
C(18)	3917(6)	6221(2)	1434(2)
C(19)	4507(5)	5655(2)	1295(2)
C(20)	3685(6)	5455(2)	677(2)
C(21)	2383(5)	2231(2)	1587(2)
O(1)	1736(5)	2063(1)	2074(2)
C(22)	1479(6)	2374(2)	321(2)
O(2)	249(5)	2317(2)	−21(2)
O(23)	176(5)	5195(2)	1104(2)
O(3)	−980(4)	4929(1)	898(2)
O(24)	701(6)	5978(2)	2020(2)
O(4)	−129(5)	6225(1)	2408(2)

TABLE 6 (continued)

B. Anisotropic temperature parameters ($\times 10^4$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	44.9(3)	35.9(3)	45.7(3)	−6.7(3)	12.1(3)	−6.0(2)
Fe(2)	45.7(3)	34.0(3)	35.4(3)	−2.6(3)	1.6(2)	5.2(2)
Si(1)	33.0(6)	38.3(6)	35.8(5)	−4.1(5)	1.6(4)	−2.0(5)
Si(2)	29.9(5)	33.7(5)	33.6(5)	−1.1(4)	2.8(4)	−0.8(4)
Si(3)	31.0(5)	32.9(5)	33.2(5)	−0.8(4)	3.2(4)	2.1(4)
Si(4)	49.6(7)	38.8(6)	36.5(6)	1.2(5)	−3.4(5)	−2.1(5)
Si(5)	56.3(7)	46.8(7)	32.8(6)	6.6(5)	−1.3(5)	1.6(5)
Si(6)	72.7(8)	37.7(6)	35.9(6)	5.2(6)	1.5(5)	2.8(5)
C(1)	37(2)	58(3)	70(3)	−3(2)	1(2)	−6(2)
C(2)	66(3)	59(3)	46(2)	2(2)	−2(2)	2(2)
C(3)	36(2)	57(3)	75(3)	−2(2)	5(2)	−12(2)
C(4)	42(2)	52(2)	57(2)	1(2)	11(2)	10(2)
C(5)	88(4)	62(3)	55(3)	22(3)	0(2)	−4(2)
C(6)	71(3)	70(3)	64(3)	−24(3)	−16(2)	6(2)
C(7)	76(3)	86(4)	65(3)	14(3)	−7(3)	4(3)
C(8)	100(4)	65(3)	44(2)	4(3)	15(2)	3(2)
C(9)	132(5)	64(3)	51(3)	39(3)	−12(3)	0(2)
C(10)	119(4)	60(3)	66(3)	−23(2)	25(3)	1(2)
C(11)	69(3)	93(4)	59(3)	2(3)	31(2)	0(3)
C(12)	48(3)	54(3)	74(3)	−11(2)	24(2)	−7(2)
C(13)	45(3)	78(3)	71(3)	−4(2)	7(2)	−3(3)
C(14)	58(3)	53(3)	114(4)	9(2)	26(3)	4(3)
C(15)	66(3)	75(4)	97(4)	−6(3)	27(3)	−43(3)
C(16)	81(4)	87(4)	41(3)	−25(3)	0(2)	23(3)
C(17)	85(4)	43(3)	80(3)	−12(2)	11(3)	18(2)
C(18)	75(3)	62(3)	51(3)	−31(3)	9(2)	−4(2)
C(19)	49(3)	71(3)	63(3)	−8(2)	13(2)	20(2)
C(20)	84(4)	61(3)	58(3)	−26(3)	38(3)	−14(2)
C(21)	59(3)	42(2)	63(3)	−1(2)	14(2)	−6(2)
O(1)	110(3)	66(2)	73(2)	−5(2)	42(2)	14(2)
C(22)	71(3)	58(3)	63(3)	−11(3)	9(3)	−19(2)
O(2)	80(3)	118(3)	93(3)	−16(2)	−27(2)	−36(2)
O(23)	53(3)	48(2)	42(2)	2(2)	−1(2)	12(2)
O(3)	63(2)	77(2)	78(2)	−22(2)	−19(2)	9(2)
O(24)	63(3)	39(2)	61(3)	0(2)	6(2)	5(2)
O(4)	95(3)	70(2)	90(3)	18(2)	30(2)	−6(2)

assumed for the cyclopentadiene hydrogens, and a regular staggered tetrahedral geometry for the methyl hydrogens. These coordinates together with an assigned isotropic temperature factor of 6.0 Å^2 were added to both least squares sets as fixed-atom contributions. After two additional cycles of isotropic refinement, convergence was obtained in each case. For II, $R_1(F)$ decreased to 9.3% and $R_2(F)$ = 11.4%, while for IV the new discrepancy indices were $R_1(F)$ = 8.6% and $R_2(F)$ = 9.3%.

Further full-matrix refinement with varying positional and anisotropic thermal parameters for all nonhydrogen atoms together with continued fixed-atom contributions for the hydrogen atoms (whose positions were recalculated every other cycle due to shifts in the carbon positions) was subsequently carried out for both structures. Convergence for II yielded $R_1(F)$ = 4.1% and $R_2(F)$ = 4.9% and for IV $R_1(F)$ = 3.2% and $R_2(F)$ = 3.8%.

Least-squares refinement was based on the minimization of $\Sigma\omega_i(|F_0| - |F_c|)^2$ with individual weights $\omega_i = 1/\sigma(F_0)^2$. Atomic scattering factors used for

TABLE 7

INTERATOMIC DISTANCES (Å) FOR cyclo-$Si_5Me_8[Fe(CO)_2Cp]SiMe_2[Fe(CO)_2Cp]$

Fe(1)—Si(1)	2.350(1)	Si(1)—C(2)	1.890(4)
Fe(2)—Si(3)	2.363(1)	Si(2)—C(3)	1.902(4)
Fe(1)—C(11)	2.073(4)	Si(3)—C(4)	1.910(4)
Fe(1)—C(12)	2.091(4)	Si(4)—C(5)	1.887(4)
Fe(1)—C(13)	2.091(4)	Si(4)—C(6)	1.876(4)
Fe(1)—C(14)	2.102(5)	Si(5)—C(7)	1.881(5)
Fe(1)—C(15)	2.096(4)	Si(5)—C(8)	1.880(4)
Fe(2)—C(16)	2.095(4)	Si(6)—C(9)	1.881(5)
Fe(2)—C(17)	2.103(4)	Si(6)—C(10)	1.878(5)
Fe(2)—C(18)	2.098(4)	C(11)—C(12)	1.398(6)
Fe(2)—C(19)	2.100(4)	C(11)—C(15)	1.403(7)
Fe(2)—C(20)	2.085(4)	C(12)—C(13)	1.395(6)
Fe(2)—C(23)	1.740(4)	C(13)—C(14)	1.394(6)
Fe(2)—C(24)	1.732(5)	C(14)—C(15)	1.384(7)
Fe(1)—C(21)	1.732(4)	C(16)—C(17)	1.377(6)
Fe(1)—C(22)	1.732(5)	C(16)—C(20)	1.408(7)
Si(1)—Si(2)	2.362(1)	C(17)—C(18)	1.413(6)
Si(2)—Si(3)	2.376(1)	C(18)—C(19)	1.389(6)
Si(2)—Si(6)	2.360(1)	C(19)—C(20)	1.396(6)
Si(3)—Si(4)	2.366(1)	C(21)—O(1)	1.151(5)
Si(4)—Si(5)	2.355(1)	C(22)—O(2)	1.154(5)
Si(5)—Si(6)	2.355(2)	C(23)—O(3)	1.147(5)
Si(1)—C(1)	1.893(4)	C(24)—O(4)	1.159(5)

all nonhydrogen atoms are from Cromer and Mann [15], while those for the hydrogen atoms are from Stewart et al. [16]. The positional and thermal parameters from the output of the final least-squares cycle are listed for II and IV in Tables 2 and 6, respectively. Interatomic distances and angles with esd's are listed in Tables 3 and 4 for II and Tables 7 and 8 for IV. A listing of the observed and calculated structure factor amplitudes is available from the authors on request.

Discussion

Cyclo-$Si_5Me_9SiMe_2[Fe(CO)_2Cp]$ (II)

In this molecule the cyclopentasilane moiety adopts a puckered C_s conformation as shown in Figs. 1 and 2. Four silicon ring atoms, Si(3), Si(4), Si(5), Si(6) are coplanar within ±0.003 Å, as seen in the appropriate least-squares plane presented in Table 5. The remaining silicon ring atom, Si(2), is displaced by 1.023 Å from this plane.

The mean value of the Si—Si—Si angles in the cyclopentasilane is 104.0°, which is close to the average values of 104.3° in Si_5H_{10} and 104.5 in $(Ph_2Si)_5$. The torsional angles Si(6), Si(2), Si(3), Si(4) and Si(5), Si(6), Si(2), Si(3) are 42.8 and 42.2° respectively, quite similar in magnitude to the torsional angles which measure the puckering in Si_5H_{10} (41.5—44.1°) and in $(Ph_2Si)_5$ (37.0 and 41.9°).

The mean Si—Si bond length in II of 2.356 Å is slightly longer than that reported for $(H_2Si)_5$ and slightly shorter than that for $(Ph_2Si)_5$ (Table 10). Si—Si bonds in the latter compound have an average length of 2.396 Å and are the longest ones yet known [8]. The increasing Si—Si bond length going from

TABLE 8

SELECTED INTRAMOLECULAR ANGLES (deg) FOR cyclo-$Si_5Me_8[Fe(CO)_2Cp]SiMe_2[Fe(CO)_2Cp]$

X—X—C angles [a]		X—X—X angles [a]	
Fe(1)—Si(1)—C(1)	111.8(1)	Fe(1)—Si(1)—Si(2)	116.46(5)
Fe(1)—Si(1)—C(2)	108.8(1)	Fe(2)—Si(3)—Si(2)	120.03(5)
Fe(2)—Si(3)—C(4)	111.3(1)	Fe(2)—Si(3)—Si(4)	115.04(5)
Si(1)—Fe(1)—C(21)	86.6(1)	Si(1)—Si(2)—Si(3)	116.43(5)
Si(1)—Fe(1)—C(22)	83.6(1)	Si(1)—Si(2)—Si(6)	115.40(5)
Si(3)—Fe(2)—C(23)	85.2(1)	Si(3)—Si(2)—Si(6)	100.75(5)
Si(3)—Fe(2)—C(24)	85.8(1)	Si(2)—Si(3)—Si(4)	102.53(5)
Si(2)—Si(1)—C(1)	104.8(1)	Si(3)—Si(4)—Si(5)	103.91(5)
Si(2)—Si(1)—C(2)	108.6(1)	Si(4)—Si(5)—Si(6)	107.46(5)
Si(1)—Si(2)—C(3)	111.5(1)	Si(2)—Si(6)—Si(5)	103.53(5)
Si(3)—Si(2)—C(3)	107.1(1)		
Si(6)—Si(2)—C(3)	104.3(1)	X—C—X and C—X—C angles [a]	
Si(2)—Si(3)—C(4)	105.3(1)		
Si(4)—Si(3)—C(4)	100.5(1)	Fe(1)—C(21)—O(1)	177.6(4)
Si(3)—Si(4)—C(5)	108.9(1)	Fe(1)—C(22)—O(2)	179.9(5)
Si(3)—Si(4)—C(6)	116.9(1)	Fe(2)—C(23)—O(3)	177.9(4)
Si(5)—Si(4)—C(5)	109.8(1)	Fe(2)—C(24)—O(4)	177.6(4)
Si(5)—Si(4)—C(6)	110.2(2)	C(21)—Fe(1)—C(22)	93.2(2)
Si(4)—Si(5)—C(7)	111.0(2)	C(23)—Fe(2)—C(24)	92.5(2)
Si(4)—Si(5)—C(8)	110.0(1)	C(1)—Si(1)—C(2)	105.7(2)
Si(6)—Si(5)—C(7)	109.0(2)	C(5)—Si(4)—C(6)	107.0(2)
Si(6)—Si(5)—C(8)	110.7(2)	C(7)—Si(5)—C(8)	108.7(2)
Si(2)—Si(6)—C(9)	111.5(2)	C(9)—Si(6)—C(10)	107.2(2)
Si(2)—Si(6)—C(10)	115.3(2)		
Si(5)—Si(6)—C(9)	109.9(2)	C—C—C angles	
Si(5)—Si(6)—C(10)	109.3(2)		
		C(12)—C(11)—C(15)	107.9(40
		C(11)—C(12)—C(13)	107.7(4)
		C(12)—C(13)—C(14)	108.1(4)
		(C13)—C(14)—C(15)	108.4(4)
		C(11)—C(15)—C(14)	107.9(4)
		C(17)—C(16)—C(20)	108.2(4)
		C(16)—C(17)—C(18)	108.1(4)
		C(17)—C(18)—C(19)	107.8(4)
		C(16)—C(20)—C(19)	107.8(4)
		C(18)—C(19)—C(20)	108.1(4)

[a] X = Fe, Si or O.

$(H_2Si)_5$ to II to $(Ph_2Si)_5$ probably results from steric repulsions of the groups attached to silicon. The average bond length in II is also intermediate between that found for $[Me(t\text{-}Bu)Si]_4$ and $(Me_2Si)_6$ (Table 10).

The electronic spectra and other properties of cyclopolysilanes have been interpreted in terms of a structure for $(Me_2Si)_5$ which is much more nearly planar than those for $(Me_2Si)_6$ or $(Me_2Si)_7$ [1]. The crystal structure data for II allow an estimate of the ring puckering in methylcyclopentasilanes. Following Bucourt [18], we will use the average of the absolute values of the torsional angles as a measure of deviation from planarity *. The degree of distortion from planarity, measured in this way, is given for several ring compounds in Ta-

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* Other methods of measuring nonplanarity, for example deviation from a mean plane, give results qualitatively similar to those in the table. For a discussion see ref. 18.

TABLE 9

DISTANCES (Å) OF ATOMS OUT OF VARIOUS MOLECULAR PLANES AND DIHEDRAL ANGLES (deg) BETWEEN VARIOUS PLANES FOR cyclo-Si_5Me_8[Fe(CO)$_2$Cp]SiMe$_2$[Fe(CO)$_2$Cp]

Plane Si(3),Si(4),Si(5),Si(6)		Plane C(6),Si(4),Si(5),C(7)	
Atoms	Distance	Atoms	Distance
Si(2)	1.055	C(6)	0.009
Si(3)	—0.051	Si(4)	—0.014
Si(4)	0.080	Si(5)	0.014
Si(5)	—0.081	C(7)	—0.009
Si(6)	0.052		
Plane Si(4),Si(5),Si(6)		**Plane C(5),Si(4),Si(5),C(8)**	
Si(2)	0.783	C(5)	—0.021
Si(3)	—0.355	Si(4)	0.033
		Si(5)	—0.033
		C(8)	0.021
Plane Si(3),Si(5),Si(6)			
Si(2)	0.999		
Si(4)	0.229		

Atoms defining plane 1	Atoms defining plane 2	Dihedral angle
Si(3),Si(4),Si(5),Si(6)	C(11),C(12),C(13),C(14),C(15)	164.8
Si(3),Si(4),Si(5),Si(6)	C(16),C(17),C(18),C(19),C(20)	158.8
Si(3),Si(4),Si(5),Si(6)	Si(2),Si(3),Si(6)	135.7
Si(3),Si(5),Si(6)	Si(2),Si(3),Si(6)	138.6

TABLE 10

AVERAGE Si—Si BOND LENGTHS AND INTRAMOLECULAR Si—Si—Si ANGLES FOR SOME SILICON COMPOUNDS [a]

	$(Si—Si)_{ave}$ (Å)	$(SiSiSi)_{ave}$ (deg)	Ref.
II [b]	2.353(2)	104.0(6)	this work
IV [b]	2.363(1)	104.0(5)	this work
$(H_2Si)_5$	2.342(3)	104.3(7)	6
$(Ph_2Si)_5$	2.396(4)	104.5(3)	8
$(Ph_2Si)_4$	2.377(1)	89.6(2)	7
$(Me_2Si)_6$	2.338(1)	111.9(4)	3
$(t\text{-}BuMeSi)_4$	2.377(1)	87.0(2)	4
Si_9Me_{16}	2.343(6)	112(4)	5
Elemental Si	2.352		17
Expected from covalent radii	2.34		

[a] Values in parentheses are average esd's. [b] Values for ring silicons only.

ble 12. The average of magnitudes of torsional angles for II, as well as for the cyclopentasilanes studied previously, is approximately 27°. This amount of ring puckering is similar to that for cyclopentane, and is about half as large as that found for $(Me_2Si)_6$, which has an average torsional angle of 53.5° (Table 12).

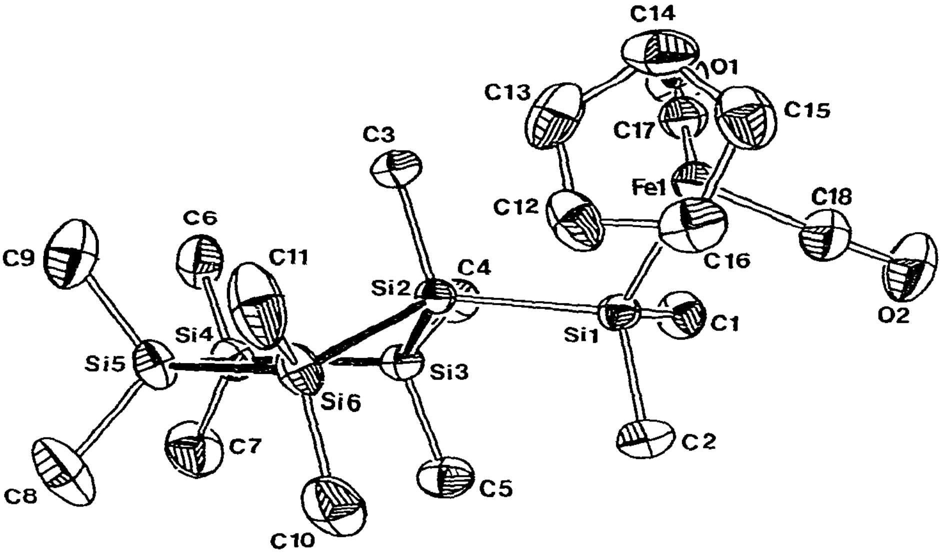

Fig. 1. ORTEP drawing of cyclo-$Si_5Me_9SiMe_2[Fe(CO)_2Cp]$ showing the conformation of the polysilane ring (darkened lines); 30% probability ellipsoids are shown.

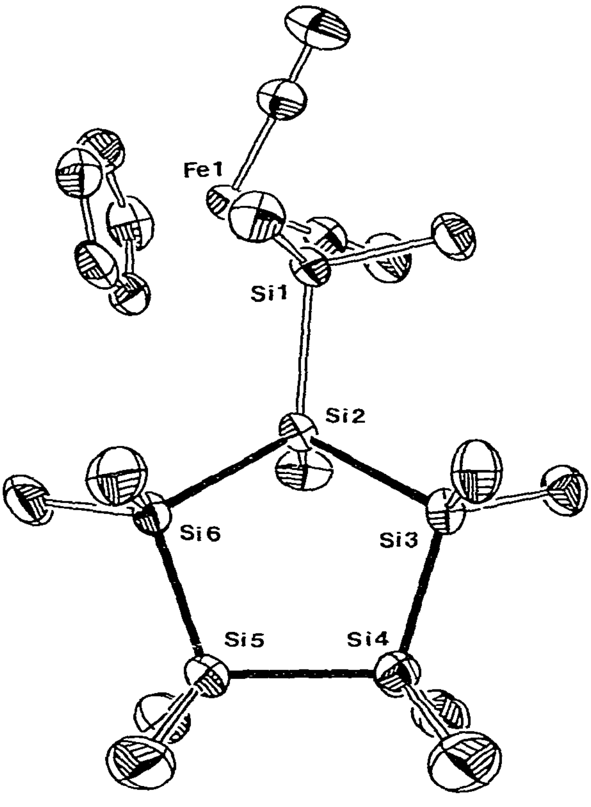

Fig. 2. ORTEP drawing of cyclo-$Si_5Me_9SiMe_2[Fe(CO)_2Cp]$ viewed perpendicular to the cyclopentasilane ring; 30% probability ellipsoids are shown.

TABLE 11

MAGNITUDES OF TORSIONAL ANGLES (deg) FOR cyclo-$Si_5Me_9SiMe_2[Fe(CO)_2Cp]$ (II) AND cyclo-$Si_5Me_8[Fe(CO)_2Cp]SiMe_2[Fe(CO)_2Cp]$ (IV)

Atoms	Torsional angle (°)	
	II	IV
Si(2)—Si(3)—Si(4)—Si(5)	27.0	34.2
Si(3)—Si(4)—Si(5)—Si(6)	0.3	8.9
Si(4)—Si(5)—Si(6)—Si(2)	26.2	20.0
Si(5)—Si(6)—Si(2)—Si(3)	42.2	40.6
Si(6)—Si(2)—Si(3)—Si(4)	42.8	46.5

Smith et al. [6] estimated the energy difference between the C_s and C_2 conformations in Si_5H_{10} to be 1.2 to 2.2 kcal/mol but were unable to assign the structure unambiguously. In $(Ph_2Si)_5$, the silicon skeleton is found to be intermediate between the C_s and C_2 conformations. The C_s conformation of II is apparently the result of a balance between steric interactions and ring strain. Table 5 shows the methyl groups on Si(4) and Si(5) to be eclipsed. Puckering of the ring leads to a staggered conformation of the methyl groups on other silicons, but results in a relatively acute Si(3)—Si(2)—Si(6) ring angle of 100.7°.

Cyclo-$Si_5Me_8[Fe(CO)_2Cp]SiMe_2[Fe(CO)_2Cp]$ (IV)

In IV, replacement of the *trans*-methyl substituent at Si(3) of the five-membered ring of II by the second $Fe(CO)_2Cp$ group results in a distorted C_s ring conformation. A comparison of the corresponding ring torsional angles for II and IV (Table 11) reveals the effect of the iron attached to the silicon ring in IV. The average torsional angle is only slightly greater in IV than in II, but the four ring silicon atoms [Si(3), Si(4), Si(5), Si(6)] are no longer coplanar in IV (see Figs. 3 and 4, and Table 9). The ring atom Si(2) is again displaced far from the mean plane defined by the other four silicon atoms in the ring. The average

TABLE 12

AVERAGE MAGNITUDES OF RING TORSIONAL ANGLES (deg) FOR SOME FIVE- AND SIX-MEMBERED CYCLIC COMPOUNDS [a]

Compound	Angle (°)	Ref.
cyclo-$Si_5Me_9SiMe_2[Fe(CO)_2Cp]$ (II)	27.7	this work
cyclo-$Si_5Me_8[Fe(CO)_2Cp]SiMe_2[Fe(CO)_2Cp]$ (IV)	30.0	this work
$(H_2Si)_5$	26.7	6
$(Ph_2Si)_5$	27.0	8
C_5H_{10}, C_s conformation	26.1	21
C_5H_{10}, C_2 conformation	27.2	21
(+)-1,2-*trans*-$C_5H_8(COOH)_2$	26.2	20
$(Me_2Si)_6$	53.5	3
C_6H_{12}	55.9	22

[a] Averages of the absolute magnitudes of the torsional angles of the form Si(1)Si(2)Si(3)Si(4) for the polysilanes and C(1)C(2)C(3)C(4) for the cycloalkanes.

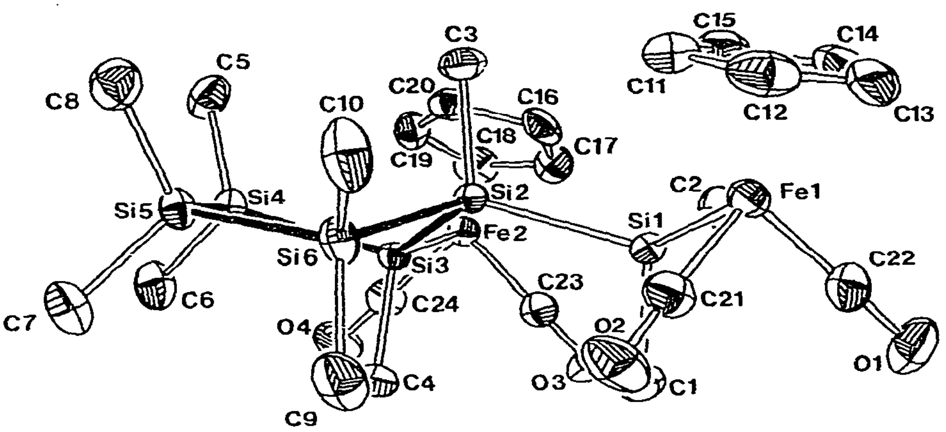

Fig. 3. ORTEP drawing of cyclo-$Si_5Me_8[Fe(CO)_2Cp]SiMe_2[Fe(CO)_2Cp]$ showing the conformation of the polysilane ring (darkened lines); 30% probability ellipsoids are shown.

Si—Si—Si angles and Si—Si bond lengths in the cyclopentasilane ring of IV are similar to those found for II. The steric effect of the bulky iron group attached to Si(3) may be reflected in the fact that the Si(3)—Si(4) and Si(3)—Si(2) bonds are slightly longer than the others in the ring (Table 9).

In both structures, the bond lengths and angles determined for the $[Fe(CO)_2Cp]$ fragments are typical. The Si—Fe bond length of 2.363 Å found in cyclo-$Si_5Me_8[Fe(CO)_2Cp]SiMe_2[Fe(CO)_2Cp]$ is the longest yet reported, but

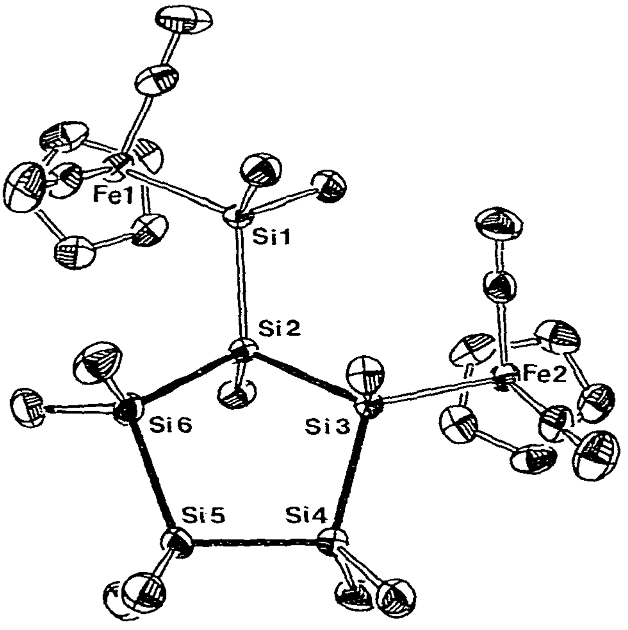

Fig. 4. ORTEP drawing of cyclo-$Si_5Me_8[Fe(CO)_2Cp]SiMe_2[Fe(CO)_2Cp]$; 30% probability ellipsoids are shown.

this may be at least partially due to the fact that the silicon is substituted with less electronegative groups than those in the other Si—Fe structures [19]. An analysis of intermolecular nonbonding distances for II and IV shows the absence of serious interactions, and therefore packing effects on geometry are presumed to be minimal.

A comparison of the structure of IV with that of (+)-1,2-*trans*-cyclopentane dicarboxylic acid [20] further demonstrates the structural similarity between cyclosilane and cycloalkane rings. Both molecules are *trans* substituted, and have maximum ring torsional angles near 40°. The smallest angles and longest bond lengths in the rings occur at the substituted atoms. The average Si—Si—Si bond angle of 103.6° for IV is very similar to the average C—C—C angle in the disubstituted organomolecule of 104.5°. Bond angles in the ring vary from 100.8° to 107.5° in IV, versus 101.8 to 107.3° for the cyclopentane derivative. The average torsional angle of 30.0° for IV is similar to the corresponding value of 26.2° in the organic species. Thus disubstitution appears to have a similar effect on the conformation of five-membered rings in both the carbon and silicon series.

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