

# Photochemical transformation of a cyclic polysilane to a cyclic carbosilane via $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_2\text{-}$ , $\text{FpCH}_2\text{-}$ , substitution

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## Abstract

The complex  $\text{FpCH}_2\text{-c-Si}_5\text{Me}_9$  (**1**),  $\text{Fp} = (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ , was synthesized by the salt-elimination reaction between  $[\text{Fp}]^-\text{Na}^+$  and  $\text{ClCH}_2\text{-c-Si}_5\text{Me}_9$ . The complex is stable indefinitely at RT, but highly reactive toward UV irradiation to yield the rearranged product  $\text{FpSi}(\text{SiMe}_3)(\text{c-SiMe}_2\text{CH}_2(\text{SiMe}_2)_3)$  (**2**) in which the initial *exo*-cyclic methylene group has been incorporated into a 5-membered ring and an initial ring  $\text{Me}_2\text{Si}$  group becomes an *exo*-cyclic  $\text{Me}_3\text{Si}$  group. The structure of **2** was confirmed by single-crystal X-ray diffraction.

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**Keywords:** Cyclic-pentasilane; Photochemistry; Cyclic-carbotetrasilane; (Cyclopentadienyl)dicarbonyliron

## 1. Introduction

The ability of the transition metal substituents  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ ,  $\text{Fp}$ , or  $\text{FpCH}_2\text{-}$ , to produce significant and often unique photochemical transformations of polysilanes is now well-established [1]. This activity stems from the facile formation of 16-electron transients at the metal center, via carbonyl loss, that can lead to the formation of either silylene or silene transients via  $\alpha$ - or  $\beta$ -elimination processes, Scheme 1A and B, respectively. The silylene intermediates have been isolated and characterized [2,3], whereas the silene species in this system have only been observed spectroscopically by low temperature matrix isolation [4]; however, many transition metal silene complexes are reported [5]. Subsequent to their formation the silylene intermediates can either result in silylene elimination [2,3], or, via a series of 1,3 alkyl, aryl or silyl migrations in the silylsilylene metal complexes, result in isomerization reactions, Scheme 2,  $\text{R} = \text{Ph}$  pathways A/B, or silyl groups, pathway B [6].

The silene intermediates exhibit two distinct forms of chemistry, A and B below.

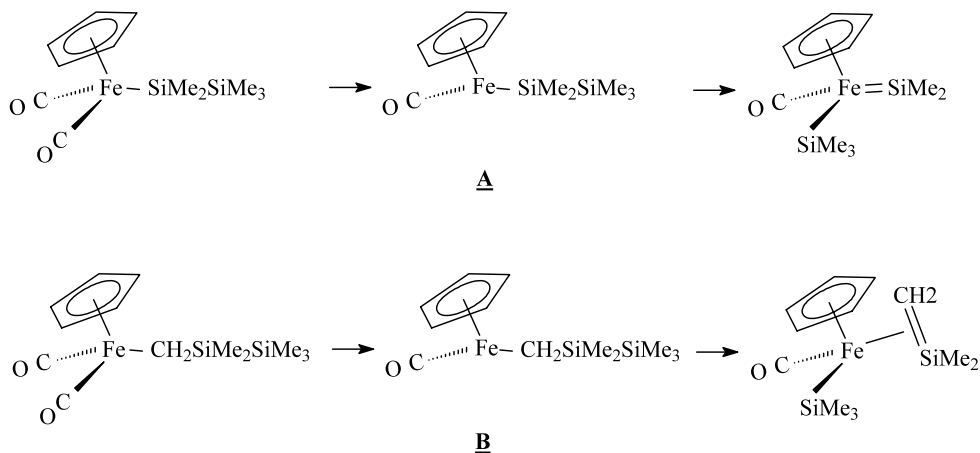
(A) In the case of monometal complexes a recoordination reaction occurs, a migration reaction induced by the return of the previously expelled CO group, in which a rearrangement has occurred to form a direct Fe–Si bond at the expense of the previous Fe–C bond, Scheme 3 [2a,7].

(B) An alternative chemistry is observed when the polysilane chains are attached to two metal centers,  $\text{FpCH}_2(\text{SiMe}_2)_n\text{CH}_2\text{Fp}$ ,  $n = 2, 3$ . In this case the coordinated silenes eliminate to stereospecifically form cyclic carbosilanes, 1,3-disilacyclobutanes and 1,2,4-trisilacyclopentanes respectively, Scheme 4 [8].

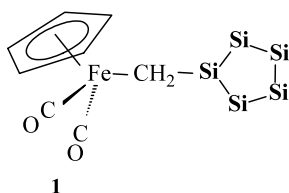
In separate chemistry we reported that when the  $\text{Fp}$  substituent is attached directly to a cyclohexasilane a photochemical rearrangement resulting in a ring contraction reaction *without* silylene elimination is observed, Scheme 5A [6a], where the bold Si represents the ring  $\text{Me}_2\text{Si}$ ,  $\text{MeSi}$  or  $\text{Si}$  groups as appropriate. This contrasts the photochemistry of the parent cyclohexasilane where ring contraction and  $\text{SiMe}_2$  elimination has been reported, Scheme 5B [9].

We now report the synthesis, elemental and spectral characterization, and photochemical treatment of an  $\text{FpCH}_2\text{-}$ substituted cyclosilane, (cyclopentadienyl)(dicarbonyliron)methyl-nonamethylcyclopentasilane,  $\text{FpCH}_2\text{-c-Si}_5\text{Me}_9$ , **1**.

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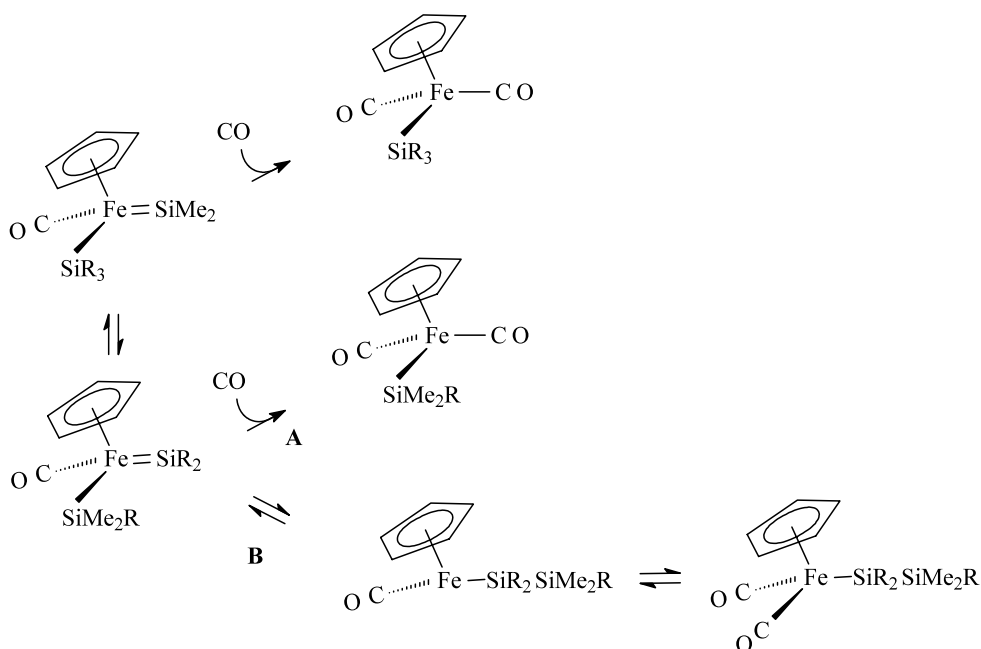


Scheme 1.



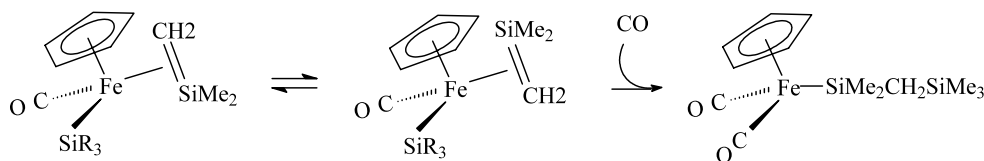
## 2. Results and discussion

The starting complex **1** was readily prepared by standard salt-elimination reaction outlined in Eq. (1).



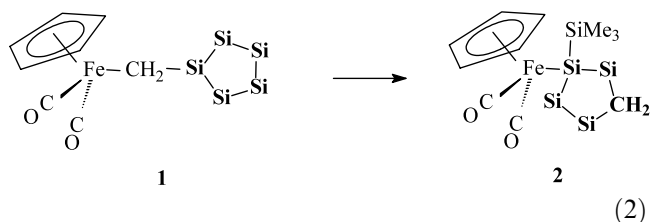
Scheme 2.

All spectroscopic and analytical details for **1** are in accord with the structure. The  $^{29}\text{Si}$ -NMR data containing resonances at  $-42.3$ ,  $-41.1$  and  $-26.2$  ppm may be analysed as belonging to the three Si atoms with respect to their location relative to the Fe atom. Thus, compared to the parent decamethylcyclopentasilane ( $\delta = -42.2$  ppm) [10]; the atom closest to Fe (Fe-CH<sub>2</sub>-Si) ( $\delta = -26.2$  ppm) has a  $\Delta\delta = 15.9$  ppm, the second furthest Si atom Fe-CH<sub>2</sub>-Si-Si is almost unchanged ( $\Delta\delta = 1.0$  ppm) and the furthest Si atom, Fe-CH<sub>2</sub>-Si-Si-Si has a small positive shift, ( $\Delta\delta = -0.2$  ppm). This progressive diminution of the effect of the metal is in keeping with all previously observed  $^{29}\text{Si}$ -NMR data for metal polysilane systems. The high field  $^{13}\text{C}$  resonance of the methylene group at  $-28.3$  ppm is also characteristic of Fe-CH<sub>2</sub> resonances.



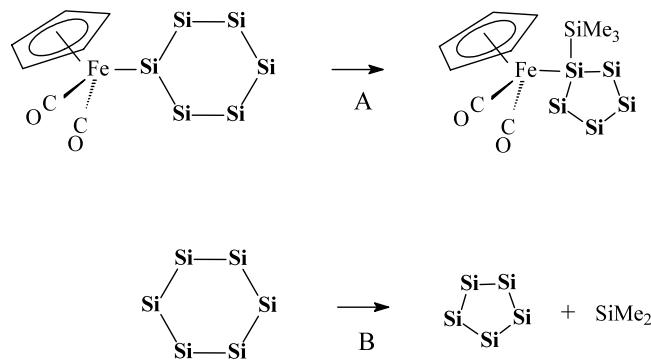
Scheme 3.

Complex **1** is relatively stable and may be stored under  $N_2$  or Ar for months in the refrigerator. However, as with other Fp-substituted polysilanes, it is extremely sensitive to ultraviolet irradiation. Thus, after 1 h of irradiation in a pyrex NMR tube it is quantitatively transformed to a single new complex **2** in high recovered yield without the appearance of any intermediate complexes. The NMR spectrum of **2** contains 5  $^{29}\text{Si}$  resonances at  $-79.0$ ,  $-33.0$ ,  $-10.4$ ,  $-5.70$  and  $2.73$  ppm, i.e. all silicon atoms are unique. The resonance at  $-79.0$  is typical of a tris-silylsubstituted silicon atom,  $\text{Si}_3\text{Si}$ , and the  $\text{Fe}-\text{CH}_2-$  methylene unit has been removed and on the basis of these data we propose that the observed chemistry is that outlined in Eq. (2).



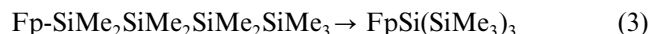
This proposal was proven correct by an X-ray diffraction analysis of a suitable crystal of **2**. The structure is presented in Fig. 1, with atomic coordinates in Table 1, and selected bond lengths and angles presented in Table 3, respectively. The data recorded in Table 3 do not exhibit any surprises in terms of the structure. All Si–Si and Si–C bond lengths and all angles are in accord with literature values and the conformation of the 5-membered ring is of the envelope type similar to those reported by Hojo et al. [11].

The mechanism for this transformation may be understood in terms of an initial  $\beta$ -elimination rearrangement followed by a sequence of  $\alpha$ -eliminations that provide a series of iron–silylene transients. These latter species undergo both 1,3-silyl (A) and alkyl (B) migra-



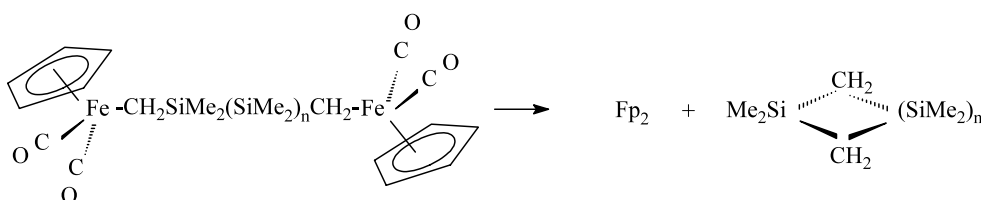
Scheme 5.

tions that eventually lead to the observed and isolated product. The reaction sequence, outlined in Scheme 6, is in accord with previous individual processes we have reported [1]. However, the reaction involving the combination of  $\beta$ - and  $\alpha$ -eliminations, and the 1,3 alkyl (silyl) shifts presents a dramatic overall chemical transformation of **1**–**2**. As is usual with related isomerization reactions, e.g. that illustrated in Eq. (3), no intermediates were observed during the NMR monitoring process. Such spectra contained only resonances associated with complexes **1** and **2**.



### 3. Experimental

All manipulations were performed under  $N_2$  or Ar atmospheres. All solvents were oxygen free and were dried by conventional methods. Starting silicon materials were purchased from Gelest, organics from Aldrich



Scheme 4.

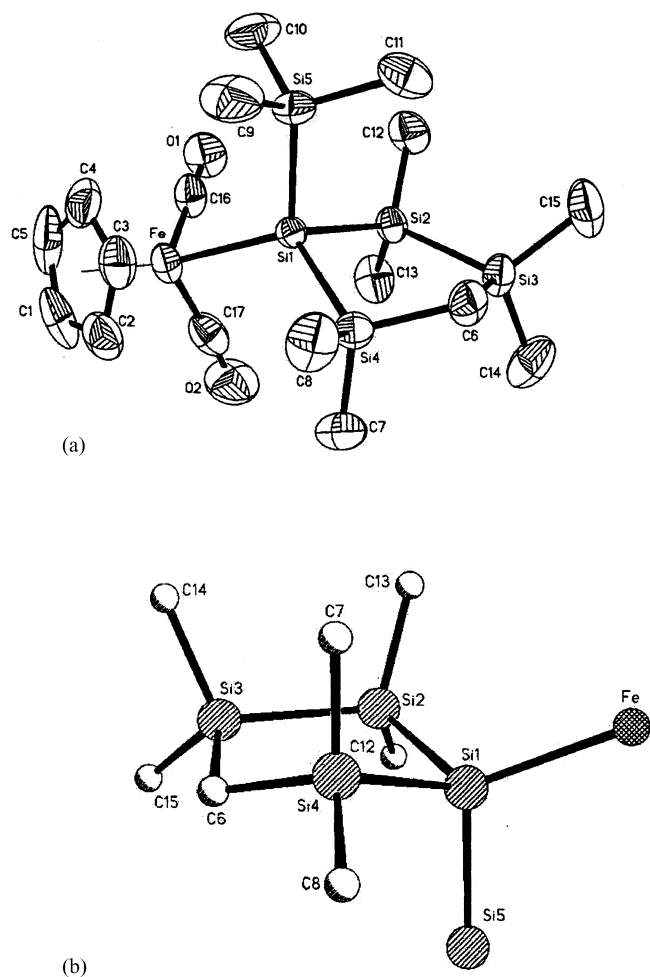


Fig. 1. (a) Molecular structure of **2**. (b) Envelope character of the 5-membered ring.

and elemental analyses were performed by Galbraith Laboratories.

### 3.1. Synthesis of $FpCH_2SiMe(SiMe_2)_4$ (**1**)

To a 20 ml THF solution of  $[(\eta^5-C_5H_5)Fe(CO)_2]^-Na^+$  prepared from 2.0 g (5.6 mmol) of  $Fp_2$  was added 3.25 g (10 mmol) of  $ClCH_2SiMe(SiMe_2)_4$  [7]. The solution was stirred for 30 min and the solvent was removed under vacuum. Extraction with hexane was followed by purification on a  $2.5 \times 10$  cm silica gel column and the orange–yellow band was eluted with hexane to yield **1** as an orange oil in 64% recovered yield. Anal. Calc. (Found), C, 43.75 (43.99); H 7.34(7.39); NMR ( $C_6D_6$ , ppm):  $^{29}Si$ ,  $-42.3$   $-41.1$ ,  $-26.2$ ;  $^{13}C$ ,  $-28.3$  ( $CH_2$ ),  $-5.94$ ,  $-5.76$  (bd),  $-5.05$ ,  $-3.17$  ( $SiMe_2$ ),  $85.5$  ( $C_5H_5$ ),  $217.9$  ( $CO$ );  $^1H$ ,  $0.10$  ( $CH_2$ ),  $0.27$  (6H,  $SiMe_2$ ),  $0.28$  (6H,  $SiMe_2$ ),  $0.32$  (12H,  $SiMe_2$ ),  $0.37$  (3H,  $SiMe$ ),  $4.17$  ( $C_5H_5$ ). IR (hexane,  $cm^{-1}$ ) 2010, 1959.

Table 1  
Crystal data and structure refinement for  $C_{17}H_{34}FeO_2Si_5$

Identification code	a: tk1
Empirical formula	$C_{17}H_{34}FeO_2Si_5$
Formula weight	466.74
Temperature (K)	296(2)
Wavelength ( $\text{\AA}$ )	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
$a$ ( $\text{\AA}$ )	13.776(4)
$b$ ( $\text{\AA}$ )	13.043(3)
$c$ ( $\text{\AA}$ )	14.219(3)
$\alpha$ ( $^\circ$ )	90
$\beta$ ( $^\circ$ )	91.13(2)
$\gamma$ ( $^\circ$ )	90
$V$ ( $\text{\AA}^3$ )	2554.4(11)
$Z$	4
$D_{\text{calc}}$ ( $\text{Mg m}^{-3}$ )	1.214
Absorption coefficient ( $\text{mm}^{-1}$ )	0.833
$F(000)$	992
Crystal size (mm)	$0.50 \times 0.40 \times 0.20$
Theta range for data collection ( $^\circ$ )	2.04–22.55
Index ranges	$0 \leq h \leq 14$ , $-3 \leq k \leq 14$ , $-15 \leq l \leq 15$
Reflections collected/unique	4601/3353 [ $R_{\text{int}} = 0.0265$ ]
Completeness to $2\theta = 22.55$	94.8%
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	3353/0/226
Goodness-of-fit on $F^2$	0.922
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0388$ , $wR_2 = 0.0990$
$R$ indices (all data)	$R_1 = 0.0626$ , $wR_2 = 0.1287$
Largest difference peak and hole ( $e \text{\AA}^{-3}$ )	0.542 and $-0.245$

### 3.2. Photolysis of $FpCH_2SiMe(SiMe_2)_4$ (**1**)

A sample of **1** (133 mg, 0.029 mmol) was dissolved in 1.5 ml of  $C_6D_6$ , placed in a pyrex nmr tube, degassed by freeze–thaw methodology, and the tube was then sealed. The sample was irradiated by a 450 watt Hanovia medium-pressure lamp at a distance of 10 cm. The progress of the reaction was monitored by  $^{29}Si$ -NMR spectroscopy. After 50 min the starting material had completely disappeared and new resonances had appeared. The solvent was removed under vacuum and the solid residue was recrystallized from a hexane/methylene chloride mixture to yield **2** as a red crystalline material in 70% yield, m.p.  $160$   $^\circ C$  (dec.). Anal. Calc. (Found): C, 43.75 (43.34), H 7.34 (7.32); NMR:  $^{29}Si$ ,  $-79.0$ ,  $-33.0$ ,  $-10.4$ ,  $-5.70$ ,  $2.73$ ;  $^{13}C$ ,  $-5.79$  ( $CH_2$ ),  $-1.26$ ,  $-0.27$ ,  $-0.11$ ,  $3.41$ ,  $4.20$  (bd),  $7.38$ ,  $82.8$ ,  $216.1$ ;  $^1H$ ,  $0.55$  ( $q$ ,  $J = 13.5$  Hz),  $0.24$  (3H),  $0.29$  (3H),  $0.31$  (9H),  $0.35$  (3H),  $0.41$  (3H),  $0.42$  (3H),  $0.43$  (3H); IR (hexane,  $cm^{-1}$ ), 1998, 1950.

#### 3.2.1. X-ray analysis of **2**: data collection

An orange fragment of approximate dimensions  $0.50 \times 0.40 \times 0.20$  mm was mounted in a random

Table 2

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{C}_{17}\text{H}_{34}\text{FeO}_2\text{Si}_5$ 

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Fe	5154(1)	437(1)	7338(1)	56(1)
Si(1)	4738(1)	2202(1)	7268(1)	39(1)
Si(2)	5960(1)	3396(1)	6885(1)	47(1)
Si(3)	5531(1)	4776(1)	7864(1)	61(1)
Si(4)	4325(1)	2955(1)	8712(1)	51(1)
Si(5)	3456(1)	2540(1)	6185(1)	57(1)
O(1)	6038(3)	839(3)	5544(3)	85(1)
O(2)	6854(3)	889(4)	8493(4)	110(2)
C(1)	4938(5)	−996(4)	7968(6)	102(2)
C(2)	4377(4)	−247(4)	8422(4)	78(2)
C(3)	3722(4)	162(4)	7756(4)	75(2)
C(4)	3881(5)	−318(5)	6888(5)	90(2)
C(5)	4626(6)	−1035(5)	7031(6)	115(3)
C(6)	4408(4)	4373(4)	8507(4)	66(1)
C(7)	5220(5)	2592(5)	9659(4)	86(2)
C(8)	3086(4)	2619(5)	9156(4)	88(2)
C(9)	2260(4)	2010(6)	6538(5)	98(2)
C(10)	3740(5)	2031(5)	4993(4)	92(2)
C(11)	3251(4)	3958(5)	6049(4)	84(2)
C(12)	6002(4)	3757(4)	5605(4)	75(2)
C(13)	7234(3)	2970(4)	7189(5)	84(2)
C(14)	6539(5)	5039(5)	8740(5)	101(2)
C(15)	5289(5)	5996(4)	7202(5)	102(2)
C(16)	5694(4)	677(3)	6251(4)	63(1)
C(17)	6179(4)	741(4)	8014(4)	74(2)

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

orientation at the tip of glass fiber for X-ray examination and data collection. All data were collected at 296 K on a Siemens R3m/v single-crystal diffractometer with graphite-monochromated Mo- $K_{\alpha}$  radiation;  $\lambda(\text{Mo}-K_{\alpha}) = 0.71073$ . Unit cell parameters and standard deviations were obtained by least-squares fit of 25 randomly selected reflections in the  $2\theta$  range of 15–30°. They indicated monoclinic symmetry which was confirmed by oscillation photographs around each crystallographic axis. Intensity data were collected in the  $\omega$ -scan mode with a scan range of 1.5° in  $\omega$  and a variable speed of 3–20° min<sup>−1</sup>. Background counts were taken with stationary crystal and total background time to scan time ratio of 0.5. Three standard reflections were monitored every 100 reflections and showed an intensity decay of less than 3% which was considered acceptable. The collection was conducted over slightly more than one quadrant of reciprocal space, in the range  $0 \leq h \leq 14$ ,  $-3 \leq k \leq 14$ ,  $-15 \leq l \leq 15$  for a total of 4802 reflections which after merging equivalents produced a set of 4610 unique reflections with an reliability parameter  $R_{\text{int}} = 2.12\%$ . The data were corrected for Lorentz and polarization effects and a semi-empirical absorption correction was also applied.

Table 3

Selected bond lengths ( $\text{\AA}$ ) and angles ( $^{\circ}$ ) for  $\text{C}_{17}\text{H}_{34}\text{FeO}_2\text{Si}_5$  (2)

Fe–C(17)	1.737(7)
Fe–C(16)	1.756(5)
Fe–C(1)	2.096(5)
Fe–C(5)	2.096(6)
Fe–C(4)	2.100(6)
Fe–C(3)	2.102(5)
Fe–C(2)	2.093(5)
Fe–Si(1)	2.3743(14)
Si(1)–Si(4)	2.3569(17)
Si(1)–Si(5)	2.3613(17)
Si(1)–Si(2)	2.3658(16)
Si(2)–C(13)	1.883(5)
Si(2)–C(12)	1.882(5)
Si(2)–Si(3)	2.3577(18)
Si(3)–C(6)	1.888(5)
Si(4)–C(6)	1.877(5)
O(1)–C(16)	1.139(6)
O(2)–C(17)	1.159(7)
Si(4)–Si(1)–Si(5)	107.47(6)
Si(4)–Si(1)–Si(2)	96.37(6)
Si(5)–Si(1)–Si(2)	104.69(6)
Si(4)–Si(1)–Fe	115.44(6)
Si(5)–Si(1)–Fe	112.70(6)
Si(2)–Si(1)–Fe	118.40(6)
C(6)–Si(3)–Si(2)	106.91(15)
C(6)–Si(4)–Si(1)	104.99(15)
Si(4)–C(6)–Si(3)	113.8(2)
O(1)–C(16)–Fe	179.5(5)
O(2)–C(17)–Fe	175.9(5)

Symmetry transformations used to generate equivalent atoms.

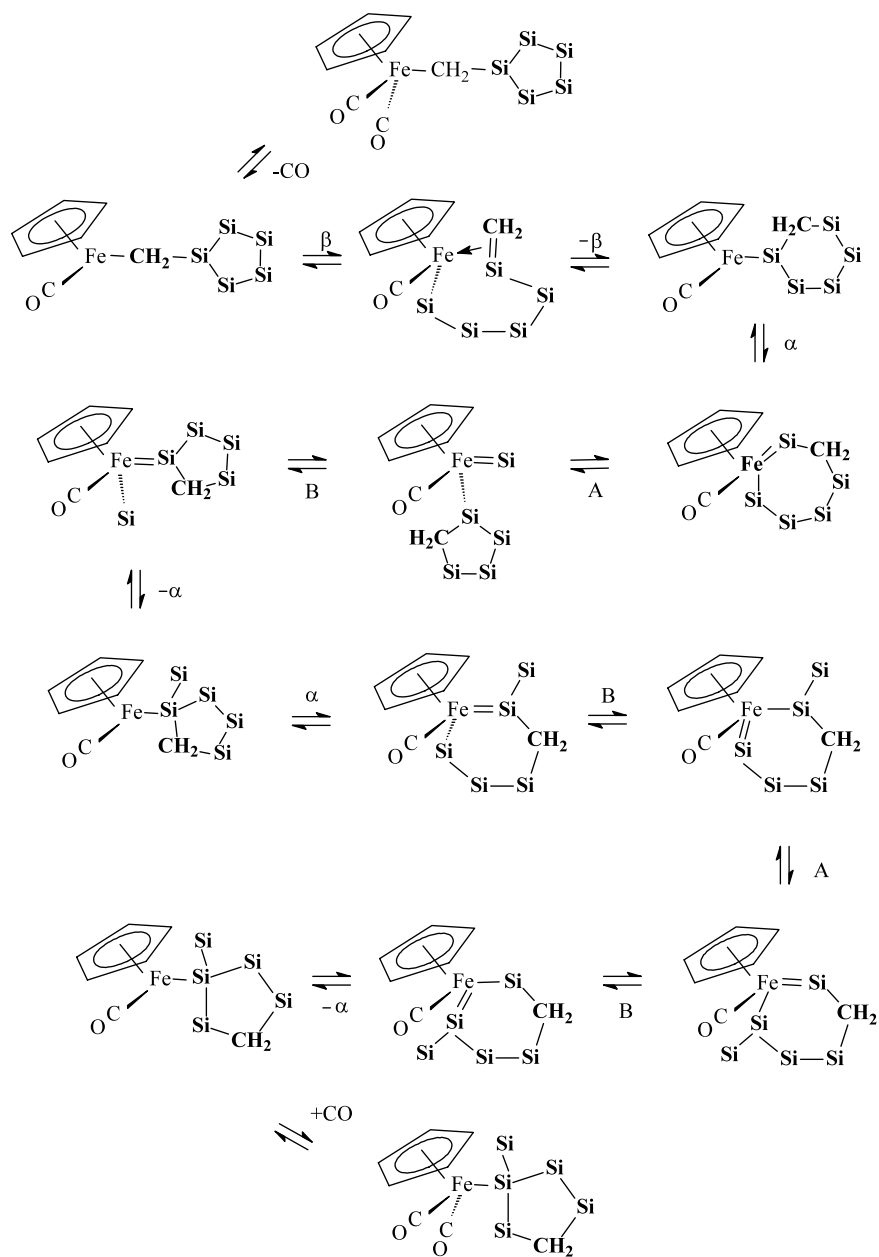
### 3.2.2. Structure refinement

Analysis of the data set based on cell parameters, systematically absent reflections and counting statistics lead to selection of space group  $P2_1/n$  (No. 14).

The structure was solved by direct methods and refined by full-matrix least-squares, based on  $F^2$ , in a PC using the SHELEX-97 public domain software package by George Sheldrick (1997). All non-hydrogen atoms were placed at calculated positions with C–H bond distances of 0.96 Å and average isotropic thermal parameters of 0.08. For the last cycle of refinement of 227 parameters and 3460 reflections, the maximum and minimum residual electron densities were 0.81 and  $-0.37$  electrons per Å<sup>3</sup> and the final  $R$ -values, as defined in SHELEX-97, were  $R = 0.0626$  and  $R_w = 0.1287$  for all data. The structure is presented in Fig. 1, with atomic coordinates in Table 2, and selected bond length and angles presented in Table 3.

### Acknowledgements

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Scheme 6.

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