

Synthesis, Characterization and Structure of an Iron-silyl Complex Containing Bis(silyl) Ligand Based on *O*-Heterocyclic Aromatics

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Abstract

The bis-(silyl)ligand based on *O*-heterocyclic aromatic backbone DBFsilH₂ (**1**) were prepared by dilithiation of the 4,5-positions of dibenzofuran using *n*-BuLi in presence of tetramethyl ethylenediamine (TMEDA) followed by addition of chlorodimethylsilane. UV irradiation of Cp*Fe(CO)₂Me and **1** in pentane produced Cp*Fe(DBFsilH)(CO)₂ (**2**). X-ray diffraction analysis ensured the structure of complex **2** along with the rigid nature of the dibenzofuran core.

Keywords: organosilicon, heterocyclic, ²⁹Si NMR, X-ray

1. Introduction

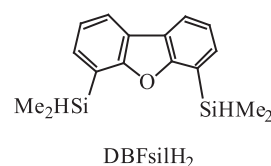
Silyl complexes with transition metals have been found important applications as catalysts in various transformations of organosilicon compounds [1], among which polymerization of hydrosilanes [2] and introduction of silicon moieties to organic compounds such as disilylations and hydrosilylation of alkenes and alkynes are most important [3]. In spite of the steady development of the chemistry of transition metal silyl complexes, there are still lots of subjects to be examined in this area. These include the mechanism of the interaction between transition metals and silicon atoms. Exceptionally strong σ -donor character and high trans influence of the silyl groups [4] introduce a marked effect on the properties of the metal complex after complexation with a silyl silicon atom with a transition metal. Steric and electronic properties of the silyl compounds will also have dramatic influence on the reactivity.

These interactions could be investigated by studying the structures, electronic properties, and reactivity of transition metal complexes having new types of silyl ligand. Therefore, synthesis of various transition metal silyl complexes and investigation of the nature of the interactions are important.

Transition metal silyl complexes can be synthesized by a number of synthetic methods. Graham et al. [5] worked with 1, 2-bis(dimethylsilyl)ethane, Sonogashira et al. [6] used 1,1'-bis(dimethylsilyl)ferrocene, and Fink et al. [7] used *O*-bis(dimethylsilyl)benzene to isolate Bis(silyl) chelate complexes by direct reactions of bis(hydrosilyl) hydrocarbons with Fe(CO)₅, Os₃(CO)₁₂, and Ru₃(CO)₁₂ where the silyl groups were constrained to *cis*-position.

Among other synthetic approaches oxidative addition of hydrosilanes to transition metal complexes [8,9] and salt elimination reactions between anionic metal complexes and halosilanes [5,10] can be mentioned. Tobita et al. has reported synthesis of an iron complex with xantsilH₂ [12] and via ultraviolet irradiation ($\lambda > 300$ nm) in Si, Si fashion [4]. Synthesis of an iron complex with a newly synthesized DBFsilH₂ ligand via oxidative addition will be discussed here.

The organosilicon compound DBFsilH₂, which has been reported earlier has been designed to achieve characteristics provided by the rigid dibenzofuran unit in the backbone (Figure 1) and to study the interaction of metal complexes with this ligand [11].



[(dibenzofuran-4,5-diyl)bis(dimethylsilyl)]

Figure 1: Bis(silyl) ligands based on rigid *O*-heterocyclic aromatics

In this paper, synthesis and characterization of an iron complex with an organosilicon ligand based on *O*-heterocyclic aromatics via oxidative addition will be reported. This compound has been fully characterized by IR, NMR, EA and X-ray crystal structure analysis.

2. Experimental

2.1 Materials and Methods

All manipulations were performed under an inert atmosphere of argon or nitrogen. Hexane and toluene were distilled from sodium benzophenone ketyl, and pentane was distilled from CaH₂ immediately before use.

C_6D_6 and $C_6D_5CD_3$ were dried over activated 4A molecular sieves or over potassium mirror and transferred into an NMR tube under vacuum for sealed tube reactions. $Cp^*Fe(CO)_2Me$ were prepared according to literature methods. $SiMe_2HCl$ and TMEDA were distilled according to standard methods. NMR measurements were performed on a Bruker ARX-300 spectrometer. IR spectra were recorded on a Horiba-730 spectrophotometer. Mass spectra were recorded on a Hitachi M-2500S spectrometer operating in the electron impact (EI) mode.

2.2 Preparation and Formulation

2.2.1 Preparation of [(dibenzofuran-4, 5- diyl)bis(dimethylsilyl)] DBFsilH₂(1) [11]

n-BuLi (142 mL of 1.49 M solution in hexane, 214 mmol) was added to a solution of dibenzofuran (15 g, 89 mmol) and TMEDA (26.9 mL, 178 mmol) in Et_2O (390 mL) and hexane (300 mL) for a period of 1 h. The color of the solution changed from yellowish brown to dark green. The mixture was then heated to 40 °C for 3 h, allowed to cool to room temperature, and then was cooled to 0 °C. $HSiMe_2Cl$ (20.3 g, 214 mmol) diluted with hexane (200 mL) was added for a period of 90 min at 0 °C. After that the reaction mixture was warm to room temperature, washed with distilled water, and dried with magnesium sulfate. The solvent was removed by a rotary evaporator and the viscous pale-yellow residue was dissolved in a minimal amount of hexane and chromatographed using silica gel with hexane as an eluent. Pale yellow liquid was obtained after removal of solvent. Yield 9.00 g (31.7 mmol, 36%). Found: C 67.98, H 7.23. Calc. for $C_{16}H_{20}OSi_2$: C, 67.55; H, 7.09. IR (hexane): 3060- 2848 (ν_{CH}), 2129 (ν_{SiH}), 1176, 1048, 910, 894, 879, 871, 856, 840, 764 (ν_{SiC}) cm^{-1} . 1H NMR (300 MHz, $CDCl_3$): δ 7.96, 7.56 (dd, $^3J = 7.2$ Hz, $^4J = 0.8$ Hz, 4 H, DBF-H), 7.31 (t, $^3J = 7.3$ Hz, 2 H, DBF-H), 4.67 (septet, $^3J = 3.7$ Hz, 2 H, SiH), 0.51 (d, $^3J = 3.7$ Hz, 12 H, $SiMe_2$). ^{13}C { 1H } NMR (75.5 MHz, $CDCl_3$): δ -3.5 ($SiMe_2$), 120.2, 122.4, 122.9, 123.2, 127.8, 128.1, 128.4, 133.5 (Ar-C). ^{29}Si { 1H } NMR (59.6 MHz, C_6D_6): δ -18.84. MS (EI) m/z : M^+ 284, 269 (M^+-CH_3), 225 (M^+-SiMe_2H), 211 (M^+-SiMe_3), 181 ($M^+-SiMe_2H-SiMeH$), 166 ($M^+-2SiMe_2H$).

2.2.2 Synthesis of $Cp^*Fe(DBFsilH)(CO)_2$ (2)

A solution of $Cp^*Fe(CO)_2Me$ (0.50 g, 1.9 mmol) and DBFsilH₂ (1.0 g, 3.5 mmol) in pentane (200 mL) was irradiated under nitrogen with a 450 W medium-pressure Hg lamp through a Pyrex glass at 8°C for 30 min. After removal of volatiles, the pale yellow residue was subjected to a silica gel flash column and eluted with hexane and hexane/ether (20:1). The yellow band was collected and the solvent was removed in vacuo. Recrystallization with toluene/hexane (1:3) gave a pale-yellow crystal of **2**. Yield: 0.32 g (0.60 mmol, 33%).

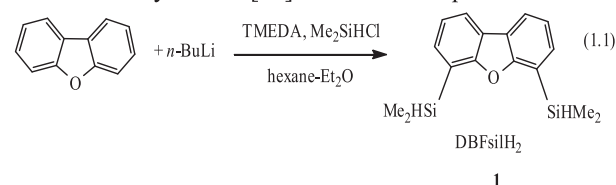
Found: C, 63.53; H, 6.51. Calc. for $C_{28}H_{34}O_3FeSi_2$: C, 63.38; H, 6.46. IR (KBr): 1967 (s, ν_{CO}), 1911 (s, ν_{CO}) cm^{-1} . 1H NMR (300 MHz, C_6D_6): δ 7.98 (dd, $J = 7.2, 1.2$ Hz, 1 H, ArH), 7.78 (dd, $J = 7.2, 1.3$ Hz, 1 H, ArH), 7.72 (dd, $J = 1.2, 7.5$ Hz, 1 H, ArH), 7.28 (t, $J = 7.4, 1$ H, ArH), 7.19 (t, $J = 7.4$ Hz, 1 H, ArH), 5.07 (m, $J = 3.75$ Hz, 1 H, SiH), 1.37 (s, 15 H, C_5Me_5), 1.13 (s, 6 H, $SiMe_2$), 0.53 (d, $J = 3.75$ Hz, 6 H, $SiMe_2$). ^{29}Si { 1H } NMR (59.6 MHz, C_6D_6): δ 35.9, -19.5. EI-Mass (70 eV): m/z M^+ 530, 515 (M^+-CH_3), 502 (M^+-CO), 474 (M^+-2CO), 459 ($M^+-2CO, -CH_3$).

2.2.3 X-ray Crystal Structure Analysis of $Cp^*Fe(DBFsilH)(CO)_2$ (2)

A single crystal of **2** for X-ray crystal structure analysis was obtained by the recrystallization from toluene/hexane (1:3). Intensity data for analysis were taken at 123.0 °C on a RAXIS-RAPID Imaging Plate diffractometer with graphite-monochromated $MoK\alpha$ radiation to a maximum 2θ value of 55.0°. A total of 44 images, corresponding to 220° oscillation angles, were collected with two different goniometer settings. Exposure time was 0.70 minutes per degree. Readout was performed in the 0.100 mm pixel mode. The structure was solved by heavy atom Patterson methods and expanded using Fourier transform techniques. All non hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Data reduction and refinement were performed using SHELX-97 software packages. Crystal data and selected bond lengths and bond angles are listed in Tables 1, 2

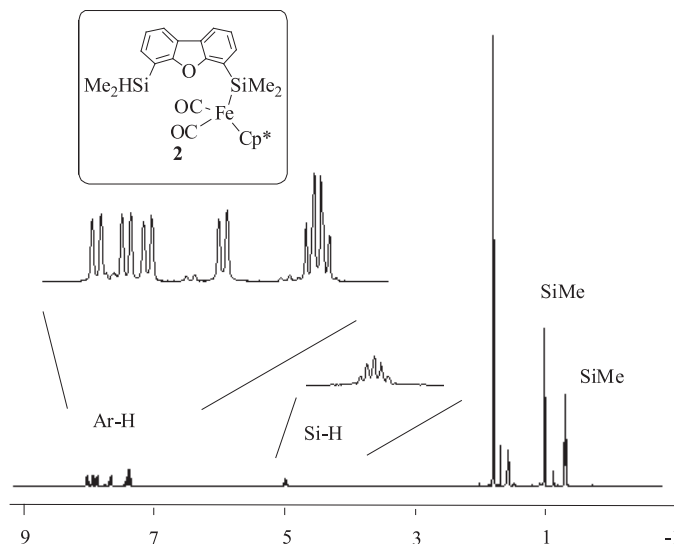
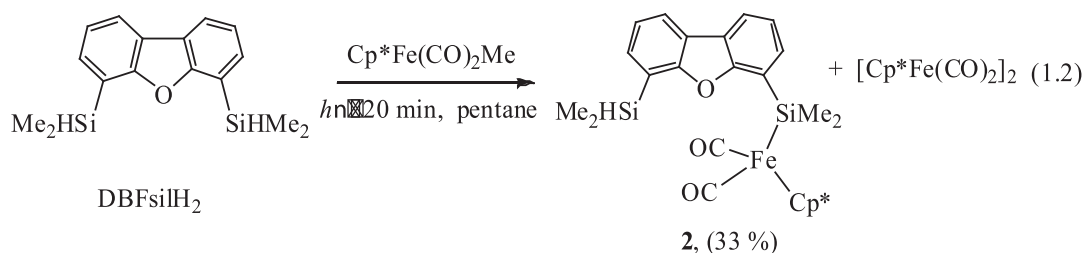
3. Results and discussion

The silyl ligand DBFsilH₂(1) was prepared by dilithiation of the corresponding *O*-heterocyclic aromatic compound dibenzofuran using *n*-BuLi in the presence of TMEDA followed by the reaction with chlorodimethyl silane [11] as shown in eqn 1.1.



1H NMR Spectrum of **1** shows signal of $SiMe_2$ protons at δ 0.36 ppm as a doublet coupled with the septet signal of SiH at δ 4.79 ($^3J_{HH} = 3.75$ Hz). The ^{29}Si { 1H } NMR. Spectrum contains a resonance at δ -18.4, the chemical shift characteristic of monohydrosilanes [standard value δ (^{29}Si) = -20.3 to -40.1] [12-15].

Twenty minutes of ultraviolet irradiation ($\lambda > 300$ nm) of a pentane solution of DBFsilH₂ (**1**) and $Cp^*Fe(CO)_2Me$ in equimolar ratio gave compound $\{Cp^*Fe(CO)_2\}(DBFsilH)$ (**2**) along with $[Cp^*Fe(CO)_2]_2$ (eq. 1.2). Compound **2** has been isolated as pale

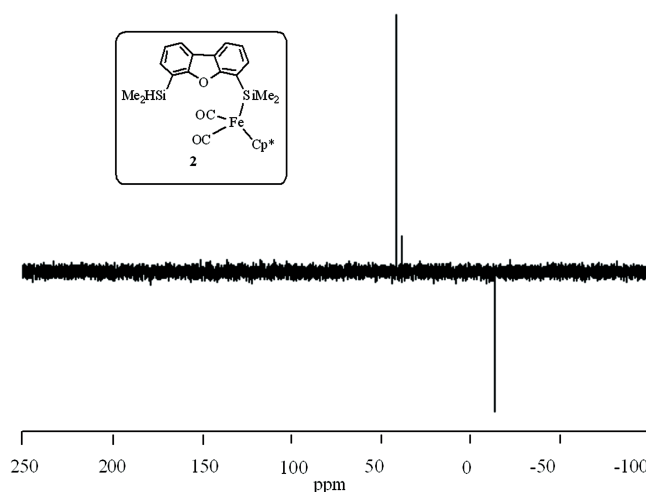
Figure 2: ¹H NMR (300 MHz, toluene-*d*₈) spectrum of (**2**)

yellow powder after repeated column chromatography using hexane-Et₂O (20: 1) as eluent. Slow evaporation of the eluent afforded pale yellow crystals of **2**. The compound was characterized by ¹H and ²⁹Si NMR, IR, elemental analysis, and X-ray crystallography.

¹H NMR spectrum (Figure 2) of compound **2** shows a singlet at 1.13 ppm for SiMe₂ region where the silyl group is bonded to the iron and a doublet for the SiMe₂ at 0.53 ppm with no direct bonding to a metal atom. The pentamethylcyclopentadienyl signal appears as a singlet at 1.37 ppm. The Si-H signal appears as a multiplet at 5.07 ppm. The ²⁹Si NMR spectrum (Figure 3) shows two

signals at 35.9 and -19.5 ppm, clearly indicating the different environments of two silyl groups. The lowfield-shifted one may correspond to the silyl group coordinated to the metal center. The IR spectrum (Figure 4) shows the CO stretching bands at 1911 and 1967 cm⁻¹.

The crystal structure of **2** is shown in Figure 5. The unit cell contains four independent molecules. The metal center attains the three-legged piano-stool geometry with two carbonyl, one silyl, and Cp* ligands. The Fe1-Si1 distance is 2.3293(15) Å that unequivocally indicates silyl characteristics. The Fe Si distances in case of usual silyl complexes are in the range of 2.22-2.41 Å.

Figure 3: ²⁹Si NMR (59.6 MHz, toluene-*d*₈) spectrum of Cp*Fe(DBFsi1H)(CO)₂ (**2**)

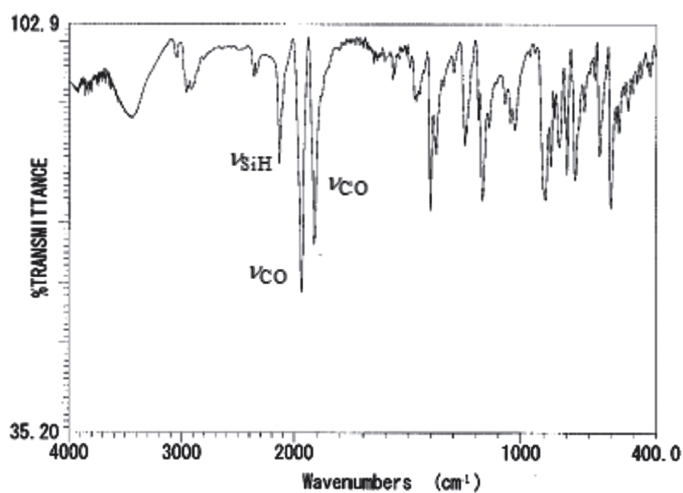
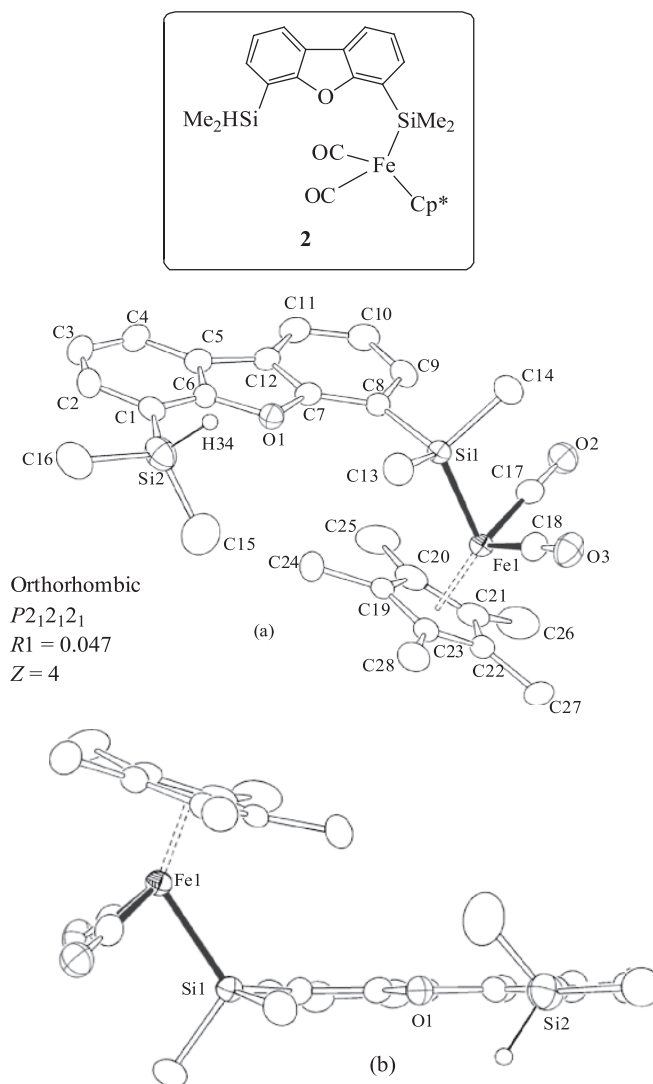
Figure 4: IR Spectrum of $\text{Cp}^*\text{Fe}(\text{DBFsiH})(\text{CO})_2$ (**2**)Figure 5: ORTEP view of $\text{Cp}^*\text{Fe}(\text{DBFsiH})(\text{CO})_2$ (**2**) with 50% thermal ellipsoids (H atoms are omitted) (a) a front view, (b) a view from the DBFsiH plane

Table 1. Crystal data and structure refinement for Cp*Fe(DBFsilH)(CO)₂

Empirical formula	C ₂₈ H ₃₄ FeO ₃ Si ₂
Formula weight	530.58
Temperature	150(2) K
Wavelength	0.71069 Å
Crystal system	orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
Unit cell dimensions	<i>a</i> = 12.8499(7) Å $\alpha = 90^\circ$ <i>b</i> = 13.0416(7) Å $\beta = 90^\circ$ <i>c</i> = 16.1539(9) Å $\gamma = 90^\circ$
Volume	2707.1(3) Å ³
<i>Z</i>	4
Density (calculated)	1.302 Mg/m ³
Absorption coefficient	0.672 mm ⁻¹
<i>F</i> (000)	1120
Crystal size	0.70 x 0.50 x 0.50 mm ³
Theta range for data collection	2.01 to 27.48°
Index ranges	0 ≤ <i>h</i> ≤ 16, 0 ≤ <i>k</i> ≤ 16, 0 ≤ <i>l</i> ≤ 20
Reflections collected	3468
Independent reflections	3468 [<i>R</i> (int) = 0.0000]
Reflections with <i>I</i> > 2σ(<i>I</i>)	3105
Completeness to θ = 27.48°	99.9 %
Max. and min. transmission	0.7298 and 0.6504
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	3468 / 0 / 320
Goodness-of-fit on <i>F</i> ²	1.244
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0470, <i>wR</i> ₂ = 0.1175
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0623, <i>wR</i> ₂ = 0.1424
Absolute structure parameter	0.46(4)
Largest diff. peak and hole	1.009 and -0.724 e Å ⁻³
$R_1 = \sum F_o - F_c / \sum F_o $ $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{0.5}$ $\text{calc } w = 1 / [\sigma^2(F_o^2) + (0.0464 P)^2 + 4.2785 P]$ where $P = (F_o^2 + 2F_c^2) / 3$.	

The distance between Fe1 and Si2 was found to be 7.457 Å which explains the non-chelating tendency of the DBFsil ligand. This large separation is due to the large distance between two silicon atoms 6.003 Å fixed by the

rigid dibenzofuran backbone. Due to the planar nature as shown in fig 5(b), the distance between the C8 and C1 is quite large 4.845 Å. The bond distance and bond angles of **2** are given in Table 2 and 3.

Table 2. Bond lengths [Å] for (2)

Fe(1)-C(18)	1.732(6)	O(1)-C(6)	1.392(6)	C(10)-C(11)	1.390(9)
Fe(1)-C(20)	2.102(5)	O(2)-C(17)	1.160(7)	C(11)-C(12)	1.371(8)
Fe(1)-C(21)	2.104(5)	O(3)-C(18)	1.169(7)	C(19)-C(20)	1.404(8)
Fe(1)-C(19)	2.114(6)	C(1)-C(6)	1.394(7)	C(19)-C(23)	1.434(9)
Fe(1)-C(23)	2.124(6)	C(1)-C(2)	1.416(7)	C(19)-C(24)	1.509(8)
Fe(1)-C(22)	2.135(5)	C(2)-C(3)	1.389(8)	C(20)-C(21)	1.438(8)
Fe(1)-Si(1)	2.3293(15)	C(3)-C(4)	1.372(9)	C(20)-C(25)	1.505(8)
Si(1)-C(14)	1.889(6)	C(4)-C(5)	1.390(8)	C(21)-C(22)	1.410(7)
Si(1)-C(1)	1.899(5)	C(5)-C(6)	1.391(7)	C(21)-C(26)	1.499(8)
Si(1)-C(13)	1.900(6)	C(5)-C(12)	1.458(8)	C(22)-C(23)	1.422(8)
Si(2)-C(15)	1.838(9)	C(7)-C(8)	1.386(8)	C(22)-C(27)	1.512(7)
Si(2)-C(16)	1.865(7)	C(7)-C(12)	1.407(7)	C(23)-C(28)	1.503(8)
Si(2)-C(8)	1.870(6)	C(8)-C(9)	1.415(8)		
O(1)-C(7)	1.387(6)	C(9)-C(10)	1.388(10)		

Table 3. Bond angles [°] for (2)

C(18)-Fe(1)-C(17)	96.9(3)	C(1)-Si(1)-Fe(1)	112.09(17)	C(20)-C(19)-C(23)	108.1(5)
C(18)-Fe(1)-C(20)	95.8(3)	C(13)-Si(1)-Fe(1)	113.0(2)	C(20)-C(19)-C(24)	125.7(6)
C(17)-Fe(1)-C(20)	122.0(2)	C(15)-Si(2)-C(16)	112.1(4)	C(23)-C(19)-C(24)	126.0(6)
C(18)-Fe(1)-C(21)	95.2(3)	C(15)-Si(2)-C(8)	110.8(3)	C(20)-C(19)-Fe(1)	70.1(3)
C(17)-Fe(1)-C(21)	159.5(3)	C(16)-Si(2)-C(8)	108.7(3)	C(23)-C(19)-Fe(1)	70.6(3)
C(20)-Fe(1)-C(21)	40.0(2)	C(7)-O(1)-C(6)	105.9(4)	C(24)-C(19)-Fe(1)	128.4(4)
C(18)-Fe(1)-C(19)	128.4(3)	C(6)-C(1)-C(2)	112.9(5)	C(19)-C(20)-C(21)	108.2(5)
C(17)-Fe(1)-C(19)	93.4(2)	C(6)-C(1)-Si(1)	128.6(4)	C(19)-C(20)-C(25)	126.4(5)
C(20)-Fe(1)-C(19)	38.9(2)	C(2)-C(1)-Si(1)	118.4(4)	C(21)-C(20)-C(25)	125.3(5)
C(21)-Fe(1)-C(19)	66.2(2)	C(3)-C(2)-C(1)	123.3(5)	C(19)-C(20)-Fe(1)	71.0(3)
C(18)-Fe(1)-C(23)	160.1(3)	C(4)-C(3)-C(2)	121.2(5)	C(21)-C(20)-Fe(1)	70.1(3)
C(17)-Fe(1)-C(23)	99.5(3)	C(3)-C(4)-C(5)	117.9(5)	C(25)-C(20)-Fe(1)	126.6(4)
C(20)-Fe(1)-C(23)	65.9(2)	C(4)-C(5)-C(6)	119.9(5)	C(22)-C(21)-C(20)	107.5(5)
C(21)-Fe(1)-C(23)	65.9(2)	C(4)-C(5)-C(12)	133.9(5)	C(22)-C(21)-C(26)	126.7(5)
C(19)-Fe(1)-C(23)	39.6(2)	C(6)-C(5)-C(12)	106.2(5)	C(20)-C(21)-C(26)	125.5(5)
C(18)-Fe(1)-C(22)	127.7(2)	C(5)-C(6)-O(1)	111.3(4)	C(22)-C(21)-Fe(1)	71.7(3)
C(17)-Fe(1)-C(22)	134.9(2)	C(5)-C(6)-C(1)	124.7(5)	C(20)-C(21)-Fe(1)	69.9(3)
C(20)-Fe(1)-C(22)	65.7(2)	O(1)-C(6)-C(1)	123.9(4)	C(26)-C(21)-Fe(1)	128.2(4)
C(21)-Fe(1)-C(22)	38.9(2)	C(8)-C(7)-O(1)	123.7(5)	C(21)-C(22)-C(23)	108.6(5)
C(19)-Fe(1)-C(22)	65.6(2)	C(8)-C(7)-C(12)	125.0(5)	C(21)-C(22)-C(27)	126.2(5)
C(23)-Fe(1)-C(22)	39.0(2)	O(1)-C(7)-C(12)	111.3(4)	C(23)-C(22)-C(27)	124.6(5)
C(18)-Fe(1)-Si(1)	81.9(2)	C(7)-C(8)-C(9)	112.8(5)	C(21)-C(22)-Fe(1)	69.4(3)
C(17)-Fe(1)-Si(1)	86.15(19)	C(7)-C(8)-Si(2)	125.3(4)	C(23)-C(22)-Fe(1)	70.1(3)
C(20)-Fe(1)-Si(1)	151.72(16)	C(9)-C(8)-Si(2)	121.8(5)	C(27)-C(22)-Fe(1)	133.2(4)
C(21)-Fe(1)-Si(1)	111.90(16)	C(10)-C(9)-C(8)	123.7(6)	C(22)-C(23)-C(19)	107.4(5)
C(19)-Fe(1)-Si(1)	149.32(18)	C(9)-C(10)-C(11)	120.5(6)	C(22)-C(23)-C(28)	124.6(6)
C(23)-Fe(1)-Si(1)	110.24(18)	C(12)-C(11)-C(10)	118.3(6)	C(19)-C(23)-C(28)	127.6(6)
C(22)-Fe(1)-Si(1)	93.35(13)	C(11)-C(12)-C(7)	119.6(5)	C(22)-C(23)-Fe(1)	70.9(3)
C(14)-Si(1)-C(1)	109.8(3)	C(11)-C(12)-C(5)	135.1(5)	C(19)-C(23)-Fe(1)	69.8(3)
C(14)-Si(1)-C(13)	104.0(3)	C(7)-C(12)-C(5)	105.3(5)	C(28)-C(23)-Fe(1)	129.7(4)
C(1)-Si(1)-C(13)	103.4(3)	O(2)-C(17)-Fe(1)	177.1(6)		
C(14)-Si(1)-Fe(1)	113.8(2)	O(3)-C(18)-Fe(1)	177.3(6)		

5. Conclusion

In this paper, synthesis and characterization of an iron complex with the bis(silyl) ligand based on *O*-heterocyclic aromatic backbone has been discussed. Due to the presence of $\text{Si}^{\text{d}+}-\text{H}^{\text{d}-}$ group, the organosilyl compound was found to be a suitable ligand precursor because of the nucleophilic nature of silicon. The new compound has been fully characterized by spectroscopic methods and X-ray analysis. The reactivity of this iron-silyl compound are now under active investigation.

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References

1. N. Auner and J. Weis (eds.), *Organosilicon Chemistry*, VCH, Weinheim, 1994.
2. Vancea, L. and Graham, W. A. G. 1974, *Inorg. Chem.*, 13, 511.
3. Fink, W., *Helv. Chem. Acta*, 1976, 59, 606.
4. Minglana, J. J. G; Okazaki, M; Hasegawa, K; Luh, L. S; Yamahira, N; Komuro, T; Ogino, H and Tobita, H., *Organometallics*. 2007, 26, 5859.
5. M. A. Brook, *Silicon in Organic, Organometallic, and Polymer Chemistry*, John Wiley and Sons, New York, p. 145, 2000.
6. (a) R. West, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F. G. A. Stone, E. W. Abel, Eds. Pergamon, Oxford, Vol.2, Chap. 4, p 365 1982. (b) P. Kochs, *Silicon in Polymer Synthesis*, H. R. Kricheldorf, Ed., Springer, Berlin, Chap. 4, p. 223, 1996.
7. (a) Speier, J. L; Webster, J. A; Barnes, G. H., *J. Am. Chem. Soc.* 1957, 79, 974. (b) C. Eaborn, R. W. Bott, *Organometallic Compounds of the Group IV Elements*, A. G. Macdiarmid, Ed., Marcel Dekker, New York Vol. 1, p. 105 1968. (c) Lukevics, E; Belyakova, Z. V; Pomerantseva, M. G and Voronkov, M. G. *Organomet. Chem. Rev.*, 1977, 5, 1.
8. S. Kotani, T. Tanizawa, K. Shiina and K. Sonogashira, *Chem. Lett.*, 1990, 1889.
9. K. Hasegawa, Undergraduate thesis, Tohoku University, 1997.
10. H. Tobita, K. Hasegawa, J.J. G. Minglana, L. S. Luh, M. Okazaki and H. Ogino, *Organometallics*, 1999, 18, 2058.

11. Begum, R., SUST Journal of Science and Technology, 2012, 16(2), 41.
12. Kolosky, T. H; Pestana, D. S; Carrol, P. J and Berry, D. H., Organometallics, 1994, 13, 489.
13. Berry, D. H; Chey, J. C; Zipin, H. S and Carroll, P. J. J. Am. Chem. Soc., 1990, 112, 452.
14. Berry, D. H; Chey, J. C; Zipin, H. S and Carroll, P. Polyhedron, 1991, J., 10, 1189.
15. Krentz, R and Pomeroy, R. K., Inorg. Chem. 1985, 24, 2976.