

Synthesis, structure, and reactivity of novel iron(II) complexes with a five-membered chelate ligand $\kappa^2(\text{Si},\text{N})\text{-SiMe}_2\text{O}(2\text{-C}_5\text{H}_4\text{N})$

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Abstract

Photolysis of $\text{Cp}'(\text{CO})_2\text{FeSiMe}_2\text{O}(2\text{-C}_5\text{H}_4\text{N})$ (**1a**: $\text{Cp}' = \eta^5\text{-C}_5\text{H}_5$ (Cp), **1b**: $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$ (Cp*)) afforded $\text{Cp}'(\text{CO})\text{Fe}[\kappa^2(\text{Si},\text{N})\text{-SiMe}_2\text{O}(2\text{-C}_5\text{H}_4\text{N})]$ (**2a**: $\text{Cp}' = \text{Cp}$, **2b**: $\text{Cp}' = \text{Cp}^*$) in good yield each. These cyclic compounds also formed in moderate yields through photoreaction of $\text{Cp}'(\text{CO})_2\text{FeSiMe}_3$ with $\text{HSiMe}_2\text{O}(2\text{-C}_5\text{H}_4\text{N})$ (**3**). Single-crystal X-ray diffraction study confirmed the structure of **2b** containing a five-membered chelate ring comprised of Fe, Si, O, C, and N. Complexes **2a** and **2b** were thermally stable and did not react with slight excess of PR_3 (R = Me, Ph) in benzene-*d*₆ solution below 80 °C. Above 80 °C, **2a** reacted slowly with PR_3 to give $\text{Cp}(\text{CO})(\text{PR}_3)\text{FeSiMe}_2\text{O}(2\text{-C}_5\text{H}_4\text{N})$ (**6**: R = Me, **7**: R = Ph) accompanied by the cleavage of the Fe–N bond. These results indicate that both Fe–Si bond and Fe–N bond in **2** are notably sturdy.

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1. Introduction

Over the last few decades, the synthesis and reactivity of transition metal silyl complexes have received significant attention, since these complexes are assumed to be key intermediates in the various metal-mediated transformation reactions of organosilicon compounds [1]. Efforts in this area revealed that silyl ligands have an exceptionally strong σ -donating and *trans*-influencing ability. Taking account of these characters, silyl ligands are also expected to exhibit strong *trans*-effect. Therefore, our recent studies have focused on the utilization of silyl groups as ancillary ligands to greatly accelerate the generation of highly reactive, unsaturated metal centers. To avoid the cleavage of the metal–silicon bonds, the *Si,P* chelate-type ligands $\kappa^2(\text{Si},\text{P})\text{-R}_2\text{Si}(\text{CH}_2)_2\text{PR}_2'$ have been developed [2,3]. In complexes containing these ligands, loss of the silyl group from the metal center is effectively retarded and we were able to find some interesting reactivities of them: The silylir-

idium(I) complex $\text{Ir}[\kappa^2(\text{Si},\text{P})\text{-Me}_2\text{Si}(\text{CH}_2)_2\text{PPh}_2](\text{PMe}_3)_3$ catalyzes the isomerization of HPhMeSiSiMe_3 to $\text{HMe}_2\text{SiSiMe}_2\text{Ph}$ [3c]. The coordinatively unsaturated square-planar silylrhodium(I) complex $\text{Rh}[\kappa^2(\text{Si},\text{P})\text{-Me}_2\text{Si}(\text{CH}_2)_2\text{PPh}_2](\text{PMe}_3)_2$ can be isolated and causes dehydrogenative coupling of a monohydrosilane to give a disilane [3e]. These reactions occur under mild conditions (25–45 °C), which might be attributable to the strong σ -donating ability and *trans*-effect of silyl ligands.

On the other hand, there are only a few examples of Si- and N-coordinated bidentate ligands. It is well known that amine ligands are good σ -donors but are poor π -acceptors compared with phosphine ligands. Thus, complexation of silicon and nitrogen atoms with a metal could generate a more electron-rich metal center than that of silicon and phosphorus atoms. The complexes $\text{M}[\kappa^2(\text{Si},\text{N})\text{-SiMe}_2(8\text{-quinolyl})]_3$ (M = Rh, Ir) and $\text{Cp}_2\text{Ti}[\kappa^2(\text{Si},\text{N})\text{-SiMe}_2(2\text{-C}_5\text{H}_4\text{N})]$ were synthesized and characterized by X-ray crystal structure analysis [4,5], but little has been known about their reactivity. Harrod et al. reported that the pyridine part in $\text{Cp}_2\text{Ti}[\kappa^2(\text{Si},\text{N})\text{-SiMe}_2(2\text{-C}_5\text{H}_4\text{N})]$ was labile and was reversibly replaced by two-electron donor ligands such as PMe_3 and

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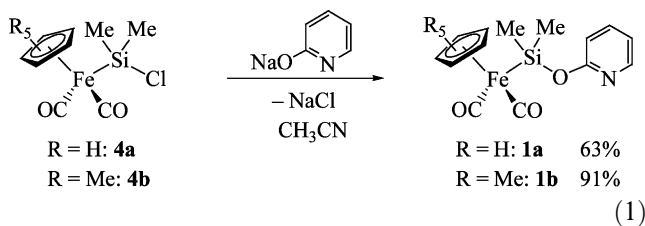
pyridine [5]. More recently, Tilley et al. successfully synthesized a complex containing an NSiN tridentate ligand, $\text{Ir}(\text{H})(\text{Cl})(\text{cyclooctene})[\kappa^3(\text{Si}, \text{N}, \text{N})\text{-SiMe}(\text{8-quinolyl})_2]$, in which the $\text{Ir}(\text{NSiN})$ fragment is chemically robust [6].

We encountered the formation of a novel iron complex $\text{Cp}^*(\text{CO})\text{Fe}[\kappa^2(\text{Si}, \text{N})\text{-SiMe}_2\text{O}(2\text{-C}_5\text{H}_4\text{N})]$ during research on the thermal- and photochemical reactions of $\text{Cp}^*(\text{CO})\text{Fe}(\text{H})\{\text{SiMe}_2\text{O}(2\text{-C}_5\text{H}_4\text{N})\}_2$ [7]. This finding prompted us to start examining the utility of the Si, N chelate ligand. This paper describes the synthesis, structure, and reactivity of iron complexes having the five-membered chelate ligand $\kappa^2(\text{Si}, \text{N})\text{-SiMe}_2\text{O}(2\text{-C}_5\text{H}_4\text{N})$.

2. Results and discussion

2.1. Synthesis of (2-pyridyloxy)silyl complexes (**1a** and **1b**)

Treatment of $\text{Cp}'(\text{CO})_2\text{FeSiMe}_2\text{Cl}$ (**4a**: $\text{Cp}' = \text{Cp}$, **4b**: $\text{Cp}' = \text{Cp}^*$) with an equimolar amount of $\text{NaO}(2\text{-C}_5\text{H}_4\text{N})$ in refluxing acetonitrile gave **1a** and **1b** in 63 and 91%, respectively (Eq. (1)). The elemental analysis and mass spectral data supported the molecular formula of each complex.



However, the tautomerism between 2-hydroxypyridine and 2-pyridone has been well known [8], so that we had to consider another possible structure for **1**, i.e. the keto-form depicted in Fig. 1.

To determine which structure **1** adopts, we carried out an X-ray crystal structure analysis of **1b**. The ORTEP drawing is shown in Fig. 2 and selected bond lengths and angles are listed in Table 1.

Complex **1b** proved to take the enol-form with an Fe-Si-O(1)-C(3)-N linkage at least in the solid state. The interatomic distance between Fe and N is 3.8266(18) Å, indicating no bonding interaction between them. The Fe-Si bond length (2.2990(6) Å) is one of the shortest

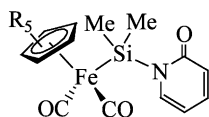


Fig. 1. Keto-forms of **1a** ($\text{R} = \text{H}$) and **1b** ($\text{R} = \text{Me}$).

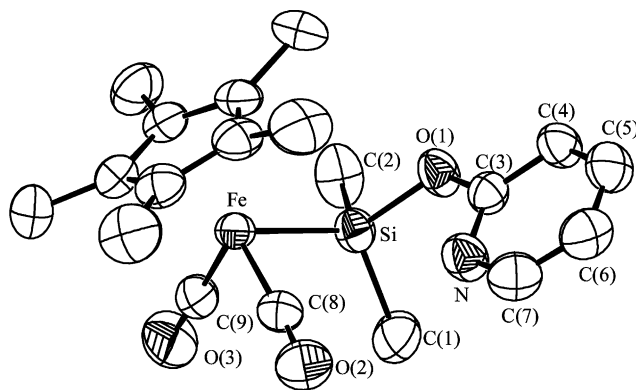


Fig. 2. ORTEP drawing of **1b** with 50% thermal ellipsoids.

Table 1

Selected bond lengths (Å) and angles (°) for complexes **1b** and **2b**

	1b	2b
<i>Bond lengths</i>		
Fe–Si	2.2990(6)	2.2640(10)
Si–C(1)	1.871(2)	1.873(4)
Si–C(2)	1.875(2)	1.874(4)
Si–O(1)	1.7070(14)	1.743(3)
O(1)–C(3)	1.347(2)	1.320(4)
N(1)–C(3)	1.315(2)	1.341(4)
C(3)–C(4)	1.385(3)	1.401(5)
C(4)–C(5)	1.372(3)	1.357(6)
C(5)–C(6)	1.368(3)	1.373(6)
C(6)–C(7)	1.360(3)	1.355(5)
C(7)–N	1.340(3)	1.359(4)
Fe–C(8)	1.743(2)	1.720(4)
Fe–C(9)	1.738(2)	^a
Fe–N	3.8266(18) ^b	1.999(3)
C(8)–O(2)	1.143(2)	1.160(4)
C(9)–O(3)	1.145(2)	^a
<i>Bond angles</i>		
Fe–Si–O(1)	117.98(6)	98.36(9)
Fe–Si–C(1)	114.75(9)	118.41(14)
Fe–Si–C(2)	112.49(8)	129.10(16)
C(1)–Si–C(2)	105.27(13)	102.7(2)
Si–O(1)–C(3)	125.34(12)	116.7(2)
O(1)–C(3)–N	117.33(16)	117.9(3)
O(1)–C(3)–C(4)	119.07(17)	120.8(4)
C(3)–C(4)–C(5)	118.11(19)	120.1(4)
C(4)–C(5)–C(6)	119.3(2)	118.7(4)
C(5)–C(6)–C(7)	118.2(2)	119.3(4)
C(6)–C(7)–N	124.2(2)	123.5(4)
C(7)–N–C(3)	116.62(18)	117.1(3)
Fe–C(8)–O(2)	174.7(2)	175.9(3)
Fe–C(9)–O(3)	178.0(2)	^a
Fe–N–C(7)		121.5(2)
Si–Fe–C(8)	87.99(7)	86.89(12)
Si–Fe–C(9)	83.51(7)	^a
Si–Fe–N		81.00(8)
C(8)–Fe–C(9)	95.10(10)	^a
C(8)–Fe–N		96.36(14)

^a C(9) of **1b** is in a carbonyl ligand, while C(9) of **2b** is in the Cp^* ligand. The data for the latter are intentionally omitted to avoid confusion.

^b This is the interatomic distance between Fe and N.

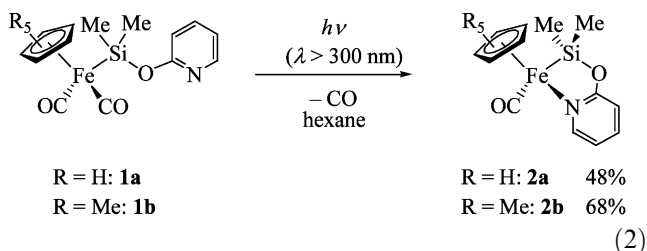
among those known for dimethylsilyliron complexes (2.30–2.46 Å) [9]. On the other hand, the Si–O bond length in **1b** (1.7070(14) Å) is longer than those in the normal alkoxy silanes (1.58–1.65 Å) [10]. These structural features are attributable to the electron-withdrawing effect of a 2-pyridyloxy group on the silicon atom. Thus, when an electron-withdrawing group is attached to silicon, the strong π -interaction between $M(d\pi)$ and $SiX(\sigma^*)$ (X = the electron-withdrawing group) arises, which makes the M–Si and Si–X bond lengths shorter and longer, respectively.

The spectroscopic features of **1** also support that **1** takes the enol-form in solution. Thus, the IR spectra of **1a** and **1b** in hexane solution as well as in the solid state exhibit no C=O stretching bands characteristic of the keto-form. In the ^{13}C -NMR spectra of **1a** and **1b**, the chemical shift of one of the pyridine ring carbon falls in the range 147–148 ppm, which is characteristic of the α -CH carbon in alkoxy pyridines (the enol-form) and are out of the range for *N*-alkylpyridones (the keto-form, 140–141 ppm) [11]. Furthermore, Cragg et al. have shown that the trimethylsilyl derivative of 2-pyridone, which is closely related to **1**, exists only in enol-form in solution [12].

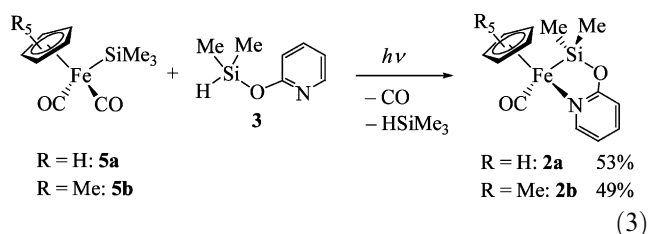
In the ^{29}Si -NMR spectra, the signals appear at 71.9 ppm (**1a**) and 72.5 ppm (**1b**), which can be assigned to the silicon atoms directly bound to iron.

2.2. Synthesis of complexes **2a** and **2b** having a $\kappa^2(\text{Si}, \text{N})$ - $\text{SiMe}_2\text{O}(2\text{-C}_5\text{H}_4\text{N})$ ligand

Photoreactions of **1a** and **1b** in C_6D_6 solution were carried out and monitored by ^1H -NMR spectroscopy. The reactions proceeded cleanly to give **2a** and **2b** with evolution of CO gas (Eq. (2)). Irradiation of **1a** and **1b** in large scale and subsequent work-up of the resulting solution afforded red crystals of **2a** and **2b** in 48 and 68% yields, respectively. These complexes are more air-sensitive than the corresponding silyl complexes **1a** and **1b**. Complexes **2** are the first example of a Group 8 metal complex having a $\kappa^2(\text{Si}, \text{N})$ -ligand.



Complexes **2** were also synthesized by irradiation of $\text{Cp}'(\text{CO})_2\text{FeSiMe}_3$ and $\text{HSiMe}_2\text{O}(2\text{-C}_5\text{H}_4\text{N})$ (**3**) in hexane in moderate yields (Eq. (3)).



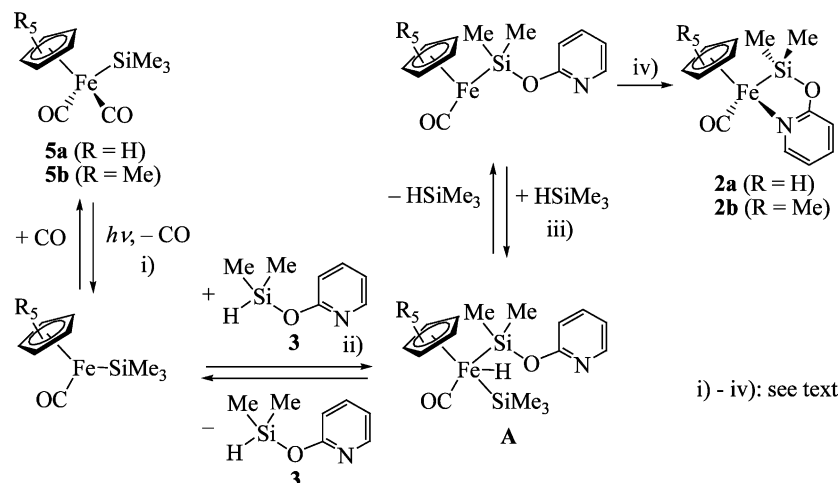
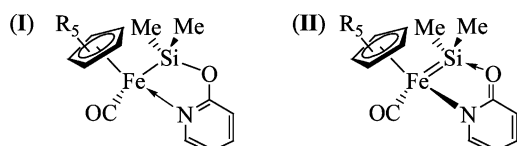
The mechanism of the exchange of silyl groups between hydrosilane and $\text{Cp}'(\text{CO})_2\text{FeSiR}_3$ has been thoroughly investigated by various groups [13]. Based on their studies, we propose the formation mechanism of **2** described in Scheme 1.

It consists of four paths; (i) photo-induced elimination of one CO ligand, (ii) H–Si oxidative addition of hydrosilane **3** to give a hydridobis(silyl)iron (IV) complex **A**, (iii) reductive elimination of trimethylsilane, and (iv) coordination of the pyridyl nitrogen to the metal center. The intermediate $\text{Cp}(\text{CO})\text{Fe}(\text{H})(\text{SiMe}_3)\{\text{SiMe}_2\text{O}(2\text{-C}_5\text{H}_4\text{N})\}$ (**A**) was not detected spectroscopically, probably due to the facile reductive elimination of either HSiMe_3 or $\text{HSiMe}_2\text{O}(2\text{-C}_5\text{H}_4\text{N})$ (**3**) [7,13].

Each IR spectrum of **2a** and **2b** shows only one intense band in the terminal CO region (**2a**: 1884 cm^{-1} , **2b**: 1886 cm^{-1} in KBr pellet), in accord with the structure having only one CO ligand. In the ^1H - and ^{13}C -NMR spectra, the two Me groups on Si are chemically equivalent in **1** but inequivalent in **2**, which is consistent with the formation of a chelate ring containing a chiral Fe atom. In the ^{29}Si -NMR spectra, the signals of **2** are substantially downfield shifted (113.5 ppm (**2a**), 114.4 ppm (**2b**)) compared with those of **1** (71.9 ppm (**1a**), 72.5 ppm (**1b**)). The ^{29}Si signals of donor-stabilized dimethylsilyleneiron complexes usually appear in the region of 92–127 ppm [14]. Thus, there seems to be a significant contribution from a donor-stabilized silylene complex form (**II**) in the bonding mode of **2** (Fig. 3).

2.3. Crystal structure of **2b**

An ORTEP drawing of **2b** is shown in Fig. 4. Selected bond lengths and angles are listed in Table 1. The molecule contains a five-membered chelate ring which consists of Fe, Si, O(1), C(3), and N. A couple of enantiomers, based on a chiral iron center, makes a racemic body in the unit cell. The Fe–Si bond length in **2b** (2.2640(10) Å) is considerably shorter than that in **1b** (2.2990(6) Å) and comparable to those in the donor-stabilized silyleneiron complexes (2.20–2.29 Å) [14]. This suggests that the Fe–Si bond of **2b** bears a significant unsaturated bond character. On the other hand, the Si–O(1) distance in **2b** (1.743(3) Å) is longer than those in **1b** (1.7070(14) Å) and the normal alkoxy silanes (1.58–1.65 Å) [10], indicating the dative bond character of Si–O(1). These structural features

Scheme 1. A plausible mechanism for formation of **2** from **5**.Fig. 3. Two important canonical forms for **2a** ($R = H$) and **2b** ($R = Me$). (I) Silyl complex form; (II) silylene complex form (dative bonds are emphasized).

further support the consideration that the bonding mode of **2b** is significantly contributed by the silylene complex form (keto-form) **II** in Fig. 3. To estimate the s -character of the silicon atom in donor-stabilized silylene ligands, the sum of three bond angles around silicon is often used [14]. Ideally, it becomes 360° for sp^2 -hybridized silicon atom and 328° for sp^3 -hybridized one. In **2b**, the sum of the three bond angles around silicon, i.e. Fe–Si–C(1), Fe–Si–C(2), and C(1)–Si–C(2), is $350.2(5)^\circ$, that is much larger than those in usual silyl complexes (e.g. **1b**, $332.5(3)^\circ$). This also indicates that the silicon atom in **2b** is significantly contributed by sp^2 -hybridization. The large contribution

of the form **II** is partly because the coordination of N to Fe makes the metal center more electron-rich, which then enhances the back-donation from Fe(d_π) to Si–O(σ^*) in comparison with **1a** and **1b**.

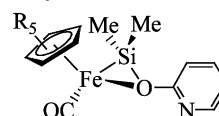
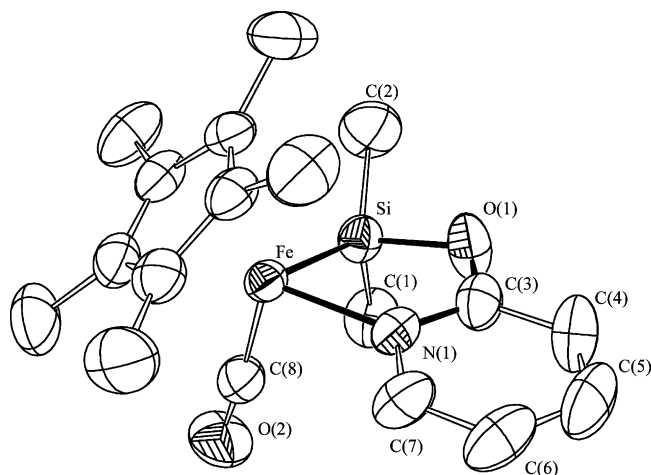
The Fe–N bond ($1.999(3) \text{ \AA}$) in **2b** is shorter than that in the pyridine iron complexes ($2.22 \text{ \AA}$ in average) [15]. Although, to our knowledge, there is no X-ray characterized amidoiron complex, the Fe–N bond length of **2b** is likely to be a mean value between dative and covalent bonds.

The distance of the C(3)–O(1) bond in the chelate ring of **2b** ($1.320(4) \text{ \AA}$) is nearly equal to that of **1b** ($1.347(2) \text{ \AA}$), and also those of 2-methoxypyridines {e.g. 2-methoxy-3,5-dinitropyridine ($1.312(5) \text{ \AA}$) [16] and Co(MeO(2- C_5H_4N)) $_2$ Cl $_2$ ($1.350(6)$ and $1.344(6) \text{ \AA}$) [17]} and to that of bridged η^2 -2-pyridonato ligands in Ru $_2(\mu\text{-O}(2\text{-}C_5H_4N))_2(\text{CO})_4(\text{HO}(2\text{-}C_5H_4N))_2$ ($1.305(3)$ and $1.301(3) \text{ \AA}$) [18]. In addition, these are distinctly longer than the C=O bond length of 2-pyridone ($1.251(1) \text{ \AA}$) [19]. Therefore, a single line is appropriate to draw the C–O bond next to the pyridine ring in **2b**.

For **2**, an isomer having an Fe–Si–O three-membered chelate ring illustrated in Fig. 5 is conceivable, but formation of such an isomer was not confirmed by NMR spectroscopy. This is attributable to the ring strain of the three-membered ring and the low affinity of oxygen toward Fe in **2**.

2.4. Reactivity of the $Fe[\kappa^2(\text{Si}, N)\text{-SiMe}_2\text{O}(2\text{-}C_5H_4N)]$ chelate in **2**

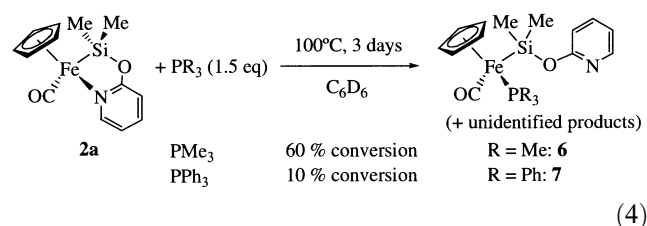
Complexes **2a** and **2b** are air-sensitive but thermally stable. The reactivity of **2a** under various reaction

Fig. 5. A possible isomer of **2** ($R = H, Me$) having an Fe–Si–O three-membered ring.Fig. 4. ORTEP drawing of **2b** with 50% thermal ellipsoids.

conditions is summarized in Table 2. Heating a benzene-*d*₆ solution of **2** in a sealed tube did not lead to decomposition even after 1 week at 90 °C.

Lability of the pyridine part in the chelate ligand [$\kappa^2(\text{Si},\text{N})\text{-SiMe}_2\text{O}(2\text{-C}_5\text{H}_4\text{N})$] of **2** was examined using tertiary phosphines as reactants. It is well known that coordination of PR_3 to an unsaturated $\text{Cp}'(\text{CO})\text{FeSiR}_3''$ species affords $\text{Cp}'(\text{CO})(\text{PR}_3)\text{FeSiR}_3''$ [20]. Therefore, if the Fe–N bond cleaves in the presence of PR_3 , coordination of PR_3 will occur. Complexes **2a** and **2b** actually did not react with PMe_3 and PPh_3 at room temperature. Heating the benzene-*d*₆ solution of **2a** in the presence of 1.5 equivalents of PMe_3 at 80 °C also did not show any change in the ¹H-NMR spectrum. However, upon heating this solution at 100 °C for 3 days, 60% of **2a** was converted to a phosphine-coordinated product **6** with formation of a small amount of unidentified products (Eq. (4)). Complex **6** was characterized by the NMR spectral data. In the ²⁹Si-NMR spectrum of the reaction mixture, a new doublet signal appeared at 79.7 ppm (²*J*_{PSi} = 44 Hz). The coupling constant is comparable to that in $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe-SiMe}_3$ (30 Hz) [21] and $\text{Cp}(\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2)\text{FeSiMe}_3$ (46 Hz) [21], which strongly supports the formation of **6**. In the ³¹P-NMR spectrum, a new signal appeared at 33.6 ppm. The chemical shift is characteristic of PMe_3 coordinated to Fe, e.g. $\text{Cp}^*(\text{CO})(\text{PMe}_3)\text{FeMe}$ (36.0 ppm) [22] and $\text{Cp}(\text{PMe}_3)_2\text{FeSiH}_3$ (32.5 ppm) [23]. The reaction of **2a** with 1.5 equivalents of PPh_3 proceeded more slowly to convert ca. 10% of **2a**, after 3 days at 100 °C, into a PPh_3 -coordinated product **7** (Eq. (4)). Further thermal reaction at higher temperatures led to decomposition of both **2a** and **7**. Complex **2b** is less reactive toward PPh_3 than **2a**. Thus, the benzene-*d*₆ solution of **2b** with five equivalents of PPh_3 did not change after 7 days at 150 °C. The lack of reactivity of **2b** may be ascribed to the steric protection by the Cp^*

ligand.



Complex **2a** is stable in the presence of MeOH below 80 °C. On the other hand, when **2a** was treated with a MeOH solution of NaOMe in the presence of PPh_3 , the reaction completed within 1 h at room temperature to give $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeH}$ (**8**) [24] and $\text{SiMe}_2(\text{OMe})_2$, quantitatively. This reaction would begin with the cleavage of the Fe–Si bond, which is caused by the nucleophilic attack of methoxide onto silicon, as illustrated in Scheme 2. Another mechanism, a reaction beginning with replacement of the pyridine part of **2a** by PPh_3 or MeOH, is strongly refuted with regard to the poor reactivity of **2a** toward MeOH in the presence of PPh_3 without NaOMe. Formation of $\text{MeOSiMe}_2\text{O}(2\text{-C}_5\text{H}_4\text{N})$ (**9**) was expected in Scheme 2 but was not confirmed spectroscopically. The compound would subsequently be converted to $\text{SiMe}_2(\text{OMe})_2$ through the nucleophilic substitution of an $\text{O}(2\text{-C}_5\text{H}_4\text{N})$ group by a MeO group of MeOH. Actually, an authentic sample of **9** was found to react with a mixture of MeOH and small amount of NaOMe rapidly (<10 min at room temperature) to give $\text{SiMe}_2(\text{OMe})_2$.

2.5. Conclusion

We successfully synthesized iron complexes **2a** and **2b** with the novel five-membered chelate ligand $\kappa^2(\text{Si},\text{N})\text{-SiMe}_2\text{O}(2\text{-C}_5\text{H}_4\text{N})$, in which coordination of the pyridine nitrogen atom is quite strong and inert to substitution (up to 80 °C). Above 80 °C, the iron–nitrogen bond in **2a** started to cleave and phosphine-substituted products **6** and **7** were formed. Cleavage of the iron–silicon bond in **2a** occurred easily by the direct nucleophilic attack of NaOMe onto the silicon, although a weaker nucleophile MeOH did not react with **2a** at room temperature. Employment of complexes containing the *Si,N*-chelate ligand to catalysis is under investigation.

3. Experimental

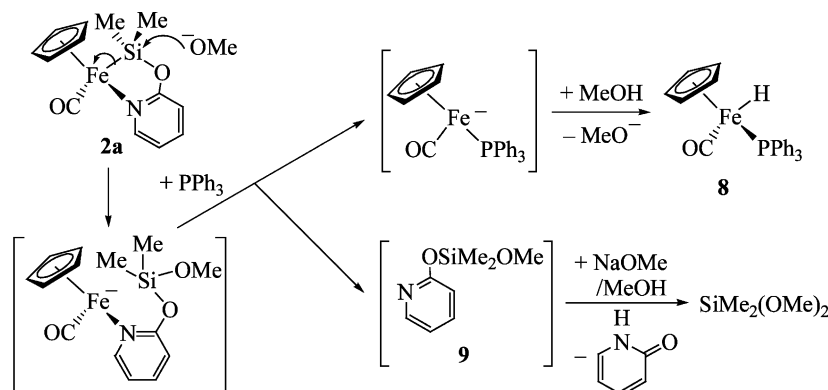
3.1. General comments

All reactions and manipulations were carried out using high-vacuum line techniques, standard Schlenk techniques, or in a glovebox under an atmosphere of N_2 .

Table 2
Reactivity of **2a** in the presence of reactants ^a

Reactant (molar ratio vs. 2a)	Temperature and time	Reactivity (conversion ratio of 2a)
None	90 °C, 7 days	Non-reactive
PMe_3 (1.5)	80 °C, 5 h	Non-reactive
	100 °C, 3 days	Reactive (60%)
PPh_3 (1.5)	80 °C, 5 h	Non-reactive
	100 °C, 7 days	Poorly reactive (13%)
MeOH (1.3)	80 °C, 5 h	Non-reactive
MeOH (1.3)+ PPh_3 (1.5)	80 °C, 5 h	Non-reactive
MeOH (9)+ PPh_3 (3)	Room temperature, 24 h	Poorly reactive (3%)
MeOH (9)+ PPh_3 (3)+NaOMe (0.7)	Room temperature, <1 h	Highly reactive (100%)

^a 0.06–0.09 mol l^{−1} benzene-*d*₆ solution, in a vacuum-sealed glass tube.



Scheme 2. A possible mechanism for the reaction of **2a** with $\text{MeOH} + \text{NaOMe} + \text{PPh}_3$.

The compounds $\text{Cp}(\text{CO})_2\text{FeSiMe}_2\text{Cl}$ (**4a**) [25], $\text{Cp}^*(\text{CO})_2\text{FeSiMe}_2\text{Cl}$ (**4b**) [26], $\text{Cp}(\text{CO})_2\text{FeSiMe}_3$ (**5a**) [20a], $\text{Cp}^*(\text{CO})_2\text{FeSiMe}_3$ (**5b**) [20b], $\text{Cp}^*(\text{CO})_2\text{FeMe}$ (**10**) [27], and $\text{MeOSiMe}_2\text{Cl}$ [28] were synthesized according to published methods. Acetonitrile (CaH_2), chlorodimethylsilane (CaH_2), Et_3N (Na), ether (Na-benzophenone-ketyl), hexane (Na-benzophenone-ketyl), MeOH ($\text{Mg}(\text{OMe})_2$), THF (Na-benzophenone-ketyl), and benzene- d_6 (K mirror) were distilled from the drying agents indicated in parentheses. Hexamethylbenzene and 2-hydroxypyridine were sublimed before use. Sodium hydride in oil was repeatedly washed with hexane, and used immediately after it was dried. PPh_3 was recrystallized from EtOH and dried under vacuum prior to use. PMe_3 was purchased from Aldrich, and used as received. ^1H -, ^{13}C -, ^{29}Si -, and ^{31}P -NMR spectra were recorded on a Bruker ARX-300 spectrometer at 300, 75.5, 59.6, and 121.5 MHz, respectively. ^1H -, ^{13}C -, and ^{29}Si -NMR spectra were referenced to SiMe_4 . ^{31}P -NMR spectra were referenced to 85% H_3PO_4 . IR spectra were run on a Horiba FT-200 or Horiba FT-730 spectrometer as either solids (KBr pellet) or neat liquid (NaCl plate). UV–vis absorption spectra were measured on a Shimadzu Multispec 1500 spectrometer. Mass spectra (EI, 70 eV) were obtained on a Shimadzu GCMS QP-5050 or a Hitachi M-2500S spectrometer. Irradiation was carried out with an Ushio UV-450 450 W medium-pressure Hg lamp placed in a water-cooled quartz jacket. Sample solutions were irradiated in Pyrex tubes.

Elemental analysis and mass spectroscopic data for isolated compounds are listed in Table 3. The ^{29}Si -, ^{31}P -NMR, IR, and UV–vis spectroscopic data of new compounds are listed in Table 4.

3.2. Synthesis of $\text{Cp}(\text{CO})_2\text{FeSiMe}_2\text{O}(2\text{-C}_5\text{H}_4\text{N})$ (**1a**)

$\text{NaO}(2\text{-C}_5\text{H}_4\text{N})$ was prepared by treatment of equimolar amounts of sodium hydride and 2-hydroxypyridine in refluxing ether, dried under vacuum, and stored under N_2 . Complex **4a** (542 mg, 2.00 mmol) was treated with the above-mentioned $\text{NaO}(2\text{-C}_5\text{H}_4\text{N})$ (255 mg, 2.18

mmol) in refluxing Et_3N (30 ml). After 2 h, it was allowed to cool to room temperature (r.t.) and the solvent was removed under reduced pressure. The residue was extracted with three 5 ml portions of hexane and the insoluble materials were filtered off with a D3 sintered glass filter and washed with additional three 5 ml portions of hexane. All solvents were removed under reduced pressure. The reddish brown residue was crystallized from hexane at -75°C to afford **1a** (415 mg, 1.26 mmol, 63%) as yellowish–brown crystals. M.p.: 37°C . ^1H -NMR (C_6D_6): δ 0.97 (s, 6H, SiMe_2), 4.15 (s, 5H, C_5H_5), 6.42 (ddd, 1H, $J = 7.1, 5.1, 0.8$ Hz, $\text{OC}_5\text{H}_4\text{N}$), 6.62 (dd, 1H, $J = 8.2, 0.8$ Hz, $\text{OC}_5\text{H}_4\text{N}$), 7.03 (ddd, 1H, $J = 8.2, 7.1, 2.1$ Hz, $\text{OC}_5\text{H}_4\text{N}$), 8.12 (dd, 1H, $J = 5.1, 2.1$ Hz, $\text{OC}_5\text{H}_4\text{N}$). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): δ 9.8 (SiMe_2), 83.7 (C_5H_5), 113.5, 116.6, 138.8, 147.5, 163.6 (pyridine ring), 215.3 (FeCO).

3.3. Synthesis of $\text{Cp}^*(\text{CO})_2\text{FeSiMe}_2\text{O}(2\text{-C}_5\text{H}_4\text{N})$ (**1b**)

Complex **1b** (725 mg, 1.82 mmol) was synthesized in 91% yield by a procedure analogous to that for **1a**, using **4b** (680 mg, 2.00 mmol) and $\text{NaO}(2\text{-C}_5\text{H}_4\text{N})$ (263 mg, 2.25 mmol). Recrystallization from hexane at -30°C gave yellow crystals of **1b**. M.p.: 69°C . ^1H -NMR (C_6D_6): δ 1.04 (s, 6H, SiMe_2), 1.51 (s, 15H, C_5Me_5), 6.43 (ddd, 1H, $J = 7.2, 5.0, 0.6$ Hz, $\text{OC}_5\text{H}_4\text{N}$), 6.63 (dd, 1H, $J = 8.2, 0.6$ Hz, $\text{OC}_5\text{H}_4\text{N}$), 7.08 (ddd, 1H, $J = 8.2, 7.2, 2.0$ Hz, $\text{OC}_5\text{H}_4\text{N}$), 8.19 (dd, 1H, $J = 5.0, 2.0$ Hz, $\text{OC}_5\text{H}_4\text{N}$). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): δ 8.7 (SiMe_2), 9.6 (C_5Me_5), 95.2 (C_5Me_5), 113.2, 116.2, 138.5, 147.8, 163.9 (pyridine ring), 217.3 (FeCO).

3.4. Synthesis of $\text{HSiMe}_2\text{O}(2\text{-C}_5\text{H}_4\text{N})$ (**3**)

A 300 ml three-necked flask equipped with a pressure-equalized dropping funnel, an ice-cooled condenser, and a magnetic stirring bar was charged with a solution of chlorodimethylsilane (5.46 g, 57.8 mmol, 1.15 equivalents) and Et_3N (5.85 g, 57.7 mmol, 1.15 equivalents) in 60 ml of THF. To it was added dropwise a solution of 2-

Table 3
Elemental analysis and mass spectroscopic data for isolated compounds

Complex	Formula	Anal. Found (Calc.)			Mass spectra (EI, 70 eV) (<i>m/z</i>)	
		C (%)	H (%)	N (%)		
Cp(CO) ₂ FeSiMe ₂ O(2-C ₅ H ₄ N) (1a)	C ₁₄ H ₁₅ FeNO ₃ Si	50.95 (51.08)	4.57 (4.59)	4.27 (4.25)	301 (M ⁺ – CO, 7) 258 (M ⁺ – 2CO – Me, 5)	273 (M ⁺ – 2CO, 31) 152 (M ⁺ – Cp(CO) ₂ Fe, 100)
Cp*(CO) ₂ FeSiMe ₂ O(2-C ₅ H ₄ N) (1b)	C ₁₉ H ₂₅ FeNO ₃ Si	57.46 (57.15)	6.19 (6.31)	3.51 (3.51)	371 (M ⁺ – CO, 5) 341 (M ⁺ – CO – 2Me, 16)	343 (M ⁺ – 2CO, 10) 152 (M ⁺ – Cp*(CO) ₂ Fe, 100)
Cp(CO)Fe[κ ² (<i>Si,N</i>)-SiMe ₂ O(2-C ₅ H ₄ N)] (2a)	C ₁₃ H ₁₅ FeNO ₂ Si	51.64 (51.84)	5.09 (5.02)	4.67 (4.65)	301 (M ⁺ , 16) 258 (M ⁺ – CO – Me, 20) 152 (M ⁺ – Cp(CO)Fe, 59)	273 (M ⁺ – CO, 100) 208 (M ⁺ – CO – Cp, 16)
Cp*(CO)Fe[κ ² (<i>Si,N</i>)-SiMe ₂ O(2-C ₅ H ₄ N)] (2b)	C ₁₈ H ₂₅ FeNO ₂ Si	57.78 (58.22)	6.77 (6.79)	3.73 (3.77)	371 (M ⁺ , 12) 341 (M ⁺ – 2 Me, 100) 152 (M ⁺ – Cp*(CO)Fe, 33)	343 (M ⁺ – CO, 35) 190 (11)
HsiMe ₂ O(2-C ₅ H ₄ N) (3)	C ₇ H ₁₁ NOSi	54.62 (54.86)	7.33 (7.23)	9.10 (9.14)	153 (M ⁺ , 40) 138 (M ⁺ – Me, 100)	152 (M ⁺ – H, 47)
MeOSiMe ₂ O(2-C ₅ H ₄ N) (9)	C ₈ H ₁₃ NO ₂ Si	52.26 (52.43)	7.18 (7.15)	7.78 (7.64)	183 (M ⁺ , 26) 152 (M ⁺ – OMe, 11)	168 (M ⁺ – Me, 100)

hydroxypyridine (4.76 g, 50.0 mmol) in 60 ml of THF over 45 min at r.t. with stirring. After further stirring for 3 h, white precipitates were filtered off and washed with three 10 ml portions of hexane. The filtrate and washings were combined and all volatiles were removed from the solution under reduced pressure (at > 20 Torr) to yield a yellow oil. Fractional distillation of the oil afforded colorless liquid of **3** (5.39 g, 35.2 mmol) in 70% yield. B.p.: 90 °C/24 Torr. ¹H-NMR (C₆D₆): δ 0.39 (d, ³J_{HH} = 2.8 Hz, 6H, SiMe₂), 5.34 (septet, ³J_{HH} = 2.8 Hz, 1H, SiH), 6.39 (ddd, 1H, *J* = 7.1, 5.3, 0.7 Hz, OC₅H₄N), 6.58 (dd, 1H, *J* = 8.3, 0.7 Hz, OC₅H₄N), 7.00 (ddd, 1H, *J* = 8.3, 7.1, 2.0 Hz, OC₅H₄N), 8.00 (dd, 1H, *J* = 5.3, 2.0 Hz, OC₅H₄N). ¹³C{¹H}-NMR (C₆D₆): δ –1.2 (SiMe₂), 112.5, 117.1, 139.1, 147.5, 163.1 (pyridine ring).

3.5. Synthesis of Cp(CO)Fe[κ²(*Si,N*)-SiMe₂O(2-C₅H₄N)] (**2a**)

3.5.1. Method A (from **1a**)

An H-shaped glass tube (6 mm i.d.) connected to a ground glass joint through a Teflon needle valve was charged with a solution of **1a** (165 mg, 0.501 mmol) in 4 ml of hexane. The solution was degassed by freeze–pump–thaw technique and the needle valve was closed. The tube was irradiated at 10 °C. The reaction mixture was degassed every 20 min of irradiation by freeze–pump–thaw technique. After irradiation for 60 min, the tube was flame-sealed on a vacuum line. The reaction mixture was warmed to 60 °C to dissolve the red precipitates and then gradually cooled down and

Table 4
²⁹Si-, ³¹P-NMR, IR, and UV–vis spectroscopic data for new compounds

Complex	δ		IR (KBr), ν _{FeC–O} (cm ^{–1})	UV–vis (hexane), λ _{max} (nm) (log ε)
	²⁹ Si-NMR (C ₆ D ₆)	³¹ P-NMR (C ₆ D ₆)		
Cp(CO) ₂ FeSiMe ₂ O(2-C ₅ H ₄ N) (1a)	71.9		1992 vs, 1938 vs	271 (3.9), 313 (3.3)
Cp*(CO) ₂ FeSiMe ₂ O(2-C ₅ H ₄ N) (1b)	72.5		1981 vs, 1923 vs	254 (3.9), 285 (3.7), 340 (3.1)
Cp(CO)Fe[κ ² (<i>Si,N</i>)-SiMe ₂ O(2-C ₅ H ₄ N)] (2a)	113.5		1884 s	246 (3.8), 323 (3.3), 405 (2.9)
Cp*(CO)Fe[κ ² (<i>Si,N</i>)-SiMe ₂ O(2-C ₅ H ₄ N)] (2b)	114.4		1886 s	255 (3.8), 339 (3.3), 427 (2.9)
HsiMe ₂ O(2-C ₅ H ₄ N) (3)	3.6		ν _{SiH} 2156 s ^c	
Cp(CO)(PMe ₃)FeSiMe ₂ O(2-C ₅ H ₄ N) (6)	79.7 ^a	33.6		
Cp(CO)(PPh ₃)FeSiMe ₂ O(2-C ₅ H ₄ N) (7)	77.2 ^b	80.6	1903 s	
MeOSiMe ₂ O(2-C ₅ H ₄ N) (9)	–1.2		ρ _{SiOMe} 1190 m ^c	

^a ²J_{PSi} = 44 Hz.

^b ²J_{PSi} = 36 Hz.

^c IR value of **3** and **9** were measured in NaCl plate.

stored at $-30\text{ }^{\circ}\text{C}$ for 2 days to afford red crystals. Its mother liquor was removed by decantation and the crystals were washed several times with hexane, and dried under vacuum to give red crystals of **2a** (72 mg, 0.24 mmol, 48%). M.p.: $128\text{ }^{\circ}\text{C}$ (dec.). $^1\text{H-NMR}$ (C_6D_6): δ 0.92, 1.05 (s, s, 3Hx2, SiMe₂), 4.09 (s, 5H, C₅H₅), 5.72 (ddd, 1H, $J = 7.4, 5.9, 1.3$ Hz, OC₅H₄N), 6.33 (dd, 1H, $J = 8.2, 1.3$ Hz, OC₅H₄N), 6.55 (ddd, 1H, $J = 8.2, 7.4, 1.7$ Hz, OC₅H₄N), 7.73 (dd, 1H, $J = 5.9, 1.7$ Hz, OC₅H₄N). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (C_6D_6): δ 8.8 (SiMe), 9.1 (SiMe), 80.4 (C₅H₅), 111.0, 114.2, 138.0, 155.7, 170.7 (pyridine ring), 223.4 (FeCO).

3.5.2. Method B (from **5a** with hydrosilane **3**)

A solution of **5a** (1.02 g, 4.09 mmol) and **3** (789 mg, 5.15 mmol) in 7 ml of hexane was irradiated in a manner similar to that of **1a** as described above, except that the solution was degassed every 1 h of irradiation, and total period of irradiation was 4 h. Crystallization from hexane at $-75\text{ }^{\circ}\text{C}$ gave deep red crystals of **2a** (655 mg, 2.17 mmol, 53%).

3.6. Synthesis of $\text{Cp}^*(\text{CO})\text{Fe}[\kappa^2(\text{Si},\text{N})\text{-SiMe}_2\text{O}(2\text{-C}_5\text{H}_4\text{N})]$ (**2b**)

3.6.1. Method A (from **1b**)

Photolysis of **1b** (202 mg, 0.507 mmol) was carried out in a manner similar to that of **1a** to yield red crystals of **2b** (128 mg, 0.345 mmol, 68%). M.p.: $112\text{ }^{\circ}\text{C}$ (dec.). $^1\text{H-NMR}$ (C_6D_6): δ 0.94, 1.04 (s, s, 3Hx2, SiMe₂), 1.54 (s, 15H, C₅Me₅), 5.88 (ddd, 1H, $J = 7.4, 5.9, 1.0$ Hz, OC₅H₄N), 6.37 (dd, 1H, $J = 8.1, 1.0$ Hz, OC₅H₄N), 6.59 (ddd, 1H, $J = 8.1, 7.4, 1.6$ Hz, OC₅H₄N), 7.77 (dd, 1H, $J = 5.9, 1.6$ Hz, OC₅H₄N). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (C_6D_6): δ 7.3 (SiMe), 9.9 (SiMe), 10.5 (C₅Me₅), 89.8 (C₅Me₅), 110.5, 114.6, 137.6, 154.5, 170.6 (pyridine ring), 224.4 (FeCO).

3.6.2. Method B (from **5b** with hydrosilane **3**)

Photolysis of **5b** (640 mg, 2.00 mmol) and **3** (388 mg, 2.53 mmol) was carried out in a manner similar to that of **5a** and **3** to give red crystals of **2b** (360 mg, 0.970 mmol, 49%).

3.6.3. Method C (from **10** with hydrosilane **3**)

Photolysis of **10** (131 mg, 0.500 mmol) and **3** (85 mg, 0.55 mmol) was carried out in a manner similar to that of **5b** and **3**. Recrystallization from hexane at $-75\text{ }^{\circ}\text{C}$ afforded red crystals of **2b** (64 mg, 0.17 mmol, 34%).

3.7. Thermal reaction of **2**

A Pyrex NMR tube (5 mm o.d.), which was connected to a ground glass joint through a Teflon needle valve, was charged with a benzene-*d*₆ solution of **2a** (6 mg, 0.02 mmol) and internal standard hexamethylbenzene (1 mg,

0.06 mmol). The solution was degassed by freeze–pump–thaw technique and the tube was flame-sealed on a vacuum line. The sample was heated and the reaction was monitored by $^1\text{H-NMR}$ spectroscopy. The reaction did not occur below $90\text{ }^{\circ}\text{C}$ for 7 days.

A vacuum-sealed NMR tube containing a benzene-*d*₆ solution of **2b** (8 mg, 0.02 mmol) and hexamethylbenzene was also prepared in a similar manner. The sample was heated and the reaction was monitored by $^1\text{H-NMR}$ spectroscopy. The reaction did not occur below $90\text{ }^{\circ}\text{C}$ for 7 days.

3.8. Reaction of **2** with PPh_3

A vacuum-sealed NMR tube containing a benzene-*d*₆ solution of **2a** (6 mg, 0.02 mmol), PPh_3 (8 mg, 0.03 mmol), and hexamethylbenzene was prepared in a manner analogous to Section 3.7. The sample was heated and the reaction was monitored by $^1\text{H-}$ and $^{31}\text{P-NMR}$ spectroscopy. The reaction did not occur below $80\text{ }^{\circ}\text{C}$. Complex **2a** was gradually converted to a single product $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeSiMe}_2\text{O}(2\text{-C}_5\text{H}_4\text{N})$ (**7**) above $100\text{ }^{\circ}\text{C}$. The reaction did not complete within 7 days at $100\text{ }^{\circ}\text{C}$. The yield of **7** was 13%, and 87% of **2a** still remained intact after 7 days at $100\text{ }^{\circ}\text{C}$. When the mixture was heated to $150\text{ }^{\circ}\text{C}$, black precipitates formed. In addition, the NMR signals broadened, although **2a** was still a major component after 2 days at $150\text{ }^{\circ}\text{C}$. Complex **7**: $^1\text{H-NMR}$: δ 0.65, 0.79 (s, s, 3Hx2, SiMe), 4.30 (s, 5H, Cp), 6.4–8.2 (m, 19H, OC₅H₄N + PPh_3).

A vacuum-sealed NMR tube containing a benzene-*d*₆ solution of **2b** (8 mg, 0.02 mmol), PPh_3 (24 mg, 0.09 mmol), and hexamethylbenzene prepared in a similar manner was also heated and the reaction was monitored by $^1\text{H-}$ and $^{31}\text{P-NMR}$ spectroscopy. The reaction did not occur below $150\text{ }^{\circ}\text{C}$ for 8 days.

3.9. Reaction of **2a** with PMe_3

A vacuum-sealed NMR tube containing a benzene-*d*₆ solution of **2a** (7 mg, 0.02 mmol), PMe_3 (2.5 mg, 0.03 mmol), and hexamethylbenzene was prepared in a manner similar to that for **2a** and PPh_3 . The sample was heated and the reaction was monitored by $^1\text{H-}$ and $^{31}\text{P-NMR}$ spectroscopy. The reaction did not occur at $80\text{ }^{\circ}\text{C}$ and was slow at $100\text{ }^{\circ}\text{C}$. After 3 days heating at $100\text{ }^{\circ}\text{C}$, 60% of **2a** was converted to $\text{Cp}(\text{CO})(\text{PMe}_3)\text{FeSiMe}_2\text{O}(2\text{-C}_5\text{H}_4\text{N})$ (**6**) with formation of a little amount of unidentified products. Complex **6**: $^1\text{H-NMR}$ (C_6D_6): δ 0.97, 0.99 (s, s, 3Hx2, SiMe), 1.03 (d, 9H, $^2J_{\text{PH}} = 9.2$ Hz, PMe_3), 4.18 (d, 5H, $^3J_{\text{PH}} = 1.4$ Hz, C₅H₅), 6.44 (ddd, 1H, $J = 7.1, 4.8, 1.1$ Hz, OC₅H₄N), 6.63 (dd, 1H, $J = 8.2, 1.1$ Hz, OC₅H₄N), 7.09 (ddd, 1H, $J = 8.2, 7.1, 2.2$ Hz, OC₅H₄N), 8.19 (dd, 1H, $J = 4.8, 2.2$ Hz, OC₅H₄N).

3.10. Reaction of **2a** with MeOH in the absence of PPh₃

A vacuum-sealed NMR tube containing a benzene-*d*₆ solution of **2a** (6 mg, 0.02 mmol), MeOH (1.0 μ l, 0.02 mmol), and hexamethylbenzene was prepared in a manner similar to that of **2a** and PPh₃. The sample was heated and the reaction was monitored by ¹H-NMR spectroscopy. The reaction proceeded slowly at 100 °C. After 8 days at 100 °C, 17% of **2a** reacted and SiMe₂(OMe)₂ was formed in 12% yield. The resultant product containing Fe was not characterized.

3.11. Reaction of **2a** with MeOH in the presence of PPh₃

A vacuum-sealed NMR tube containing a benzene-*d*₆ solution of **2a** (6 mg, 0.02 mmol), MeOH (1.0 μ l, 0.02 mmol), PPh₃ (8 mg, 0.03 mmol), and hexamethylbenzene was prepared in a manner similar to that of **2a** and PPh₃. The reaction did not occur after 5 h at 80 °C.

Another sealed tube containing a benzene-*d*₆ solution of **2a** (8 mg, 0.02 mmol), MeOH (10 μ l, 0.25 mmol, nine equivalents), PPh₃ (20 mg, 0.075 mmol), and hexamethylbenzene was prepared in the same manner. After 24 h at r.t., 3% of **2a** reacted and small amount of Cp(CO)(PPh₃)FeH (**8**) [24] and SiMe₂(OMe)₂ formed.

3.12. Reaction of **2a** with NaOMe–MeOH in the presence of PPh₃

A vacuum-sealed NMR tube containing a benzene-*d*₆ solution of **2a** (8 mg, 0.02 mmol), NaOMe (1.0 mg, 0.019 mmol, 0.7 equivalents), MeOH (10 μ l, 0.25 mmol, nine equivalents), PPh₃ (20 mg, 0.075 mmol), and hexamethylbenzene was prepared in a manner similar to that of **2a** and PPh₃. The reaction completed within 1 h at r.t. Quantitative formation of Cp(CO)(PPh₃)FeH (**8**) [24] and SiMe₂(OMe)₂ was confirmed by ¹H-NMR spectroscopy.

3.13. Synthesis of MeOSiMe₂O(2-*C*₅H₄N) (**9**)

Silane **9** was synthesized by a procedure analogous to that for **3**, using MeOSiMe₂Cl (2.93 g, 23.5 mmol), Et₃N (2.37 g, 23.5 mmol), and 2-hydroxypyridine (1.91 g, 20.0 mmol). Fractional distillation afforded a colorless liquid of **9** (2.04 g, 11.1 mmol) in 56% yield. B.p.: 115 °C/12 Torr. ¹H-NMR (C₆D₆): δ 0.44 (s, 6H, SiMe₂), 3.57 (s, 3H, OMe), 6.39 (ddd, 1H, *J* = 7.3, 5.0, 0.8 Hz, OC₅H₄N), 6.60 (dd, 1H, *J* = 8.2, 0.8 Hz, OC₅H₄N), 7.01 (ddd, 1H, *J* = 8.2, 7.3, 2.0 Hz, OC₅H₄N), 7.97 (dd, 1H, *J* = 5.0, 2.0 Hz, OC₅H₄N). ¹³C{¹H}-NMR (C₆D₆): δ -2.0 (SiMe₂), 50.8 (OMe), 112.7, 117.2, 139.1, 147.5, 162.5 (pyridine ring).

3.14. Reaction of **9** with NaOMe–MeOH

To a benzene-*d*₆ solution of **9** (5 mg, 0.03 mmol), and hexamethylbenzene was added MeOH (11 μ l, 0.27 mmol) and the reaction was monitored at r.t. by ¹H-NMR spectroscopy. After 1 h, 7% of **9** had reacted. Then, to it was added powdered NaOMe (1.0 mg, 0.019 mmol) at r.t. The reaction completed within 10 min to give SiMe₂(OMe)₂ quantitatively.

3.15. X-ray crystal structure determination of **1b** and **2b**

Single crystals of **1b** and **2b** were obtained by recrystallization of the isolated products. A suitable part of each crystal was cut out with blade and mounted on a glass capillary. The intensity data were collected on a Rigaku Raxis-Rapid Imaging Plate diffractometer with graphite monochromated Mo-K α radiation at 20(2) °C. The space group was determined based on the systematic absences. The structures were solved by

Table 5
Crystal data and structural refinement for complexes **1b** and **2b**

	1b	2b
Formula	C ₁₉ H ₂₅ FeNO ₃ Si	C ₁₈ H ₂₅ FeNO ₂ Si
Formula weight	399.34	371.33
Crystal size (mm)	0.3 $\times$ 0.3 $\times$ 0.2	0.1 $\times$ 0.1 $\times$ 0.1
Color of crystals	Yellow	Red
Temperature (°C)	20(2)	20(2)
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (#14)	<i>P</i> 2 ₁ / <i>c</i> (#14)
<i>a</i> (Å)	9.2384(3)	13.9956(5)
<i>b</i> (Å)	13.4781(4)	7.9981(3)
<i>c</i> (Å)	16.5016(5)	16.9069(7)
β (°)	97.3323(12)	95.4819(6)
<i>V</i> (Å ³)	2037.91(11)	1883.87(12)
<i>Z</i>	4	4
<i>D</i> _{calc} (g cm ⁻³)	1.302	1.309
Absorption coefficient (mm ⁻¹)	0.815	0.872
θ Range for data collection	1.96–27.48	1.46–27.48
<i>hkl</i> limits	–11, 11; –17, 17; –21, 21	–18, 18; –10, 10; –21, 21
Reflections collected	19014	15904
Independent reflections	4647 (<i>R</i> _{int} = 0.0392)	4296 (<i>R</i> _{int} = 0.0555)
Reflections with <i>I</i> > 2 σ (<i>I</i>)	4065	3024
Number of parameters	226	208
<i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0348 ^a <i>wR</i> ₂ = 0.0920 ^b	<i>R</i> ₁ = 0.0481 ^a <i>wR</i> ₂ = 0.1001 ^c
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0418 <i>wR</i> ₂ = 0.0968	<i>R</i> ₁ = 0.0811 <i>wR</i> ₂ = 0.1222
Goodness-of-fit on <i>F</i> ²	1.040	1.043
Largest difference peak and hole (e Å ⁻³)	0.238; –0.275	0.308; –0.364

$$^a R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|.$$

$$^b wR_2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}; \quad w^{-1} = \sigma^2(F_o^2) + (0.0515P)^2 + 0.5670P; \quad P = (F_o^2 + 2F_c^2)/3.$$

$$^c wR_2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}; \quad w^{-1} = \sigma^2(F_o^2) + (0.0416P)^2 + 2.1377P; \quad P = (F_o^2 + 2F_c^2)/3.$$

Patterson and Fourier transform methods, and all non-hydrogen atoms were refined by full-matrix least-squares techniques with anisotropic displacement parameters using SHELXL-97 [29]. All hydrogen atoms were placed at their geometrically calculated positions ($d_{\text{CH}} = 0.96 \text{ \AA}$ for methyl hydrogen atoms and $0.93 \text{ \AA}$ for aromatic hydrogen atoms) and refined riding on the corresponding carbon atoms with isotropic thermal parameters ($U = 1.5U(\text{C}_{\text{methyl}})$ and $1.2U(\text{C}_{\text{aromatic}})$). The final R indices against reflections with $I > 2\sigma(I)$ were $R_1 = 0.0348$ and $wR_2 = 0.0920$ for **1b**, and $R_1 = 0.0481$ and $wR_2 = 0.1001$ for **2b**. The crystal data and analytical conditions are listed in Table 5.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 193001 for compound **1b** and CCDC no. 193002 for compound **2b**. Copies of this information may be obtained upon application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1RZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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