

Hydrosilylation of Carbonyl Compounds with Hydrosilyliron Complexes
Catalyzed by Cationic Silyleneiron Complexes[†]Takako Muraoka,[†] Yuusaku Shimizu,[†] Hideki Kobayashi,[‡] Keiji Ueno,^{*,†} and
Hiroschi Ogino[§][†]Department of Chemistry and Chemical Biology, Graduate School of Engineering, Gunma University,
1-5-1 Tenjin-cho, Kiryu 376-8515, Japan, [‡]Department of Chemistry, Graduate School of Science,
Tohoku University, Aoba-ku, Sendai 980-8578, Japan, and [§]The Open University of Japan,
Wakaba 2-11, Mihama-ku, Chiba 261-8586, Japan

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A hydride abstraction from the hydrosilyliron complexes Cp(OC)₂FeSiR₂H (Cp = η⁵-C₅H₅, R = *p*-tolyl (**1a**), Me (**1b**)) in CD₃CN afforded cationic silyleneiron complexes [Cp(OC)₂Fe=SiR₂(NCCD₃)]⁺[B(Ar^f)₄]⁻ (Ar^f = 3,5-bis(trifluoromethyl)phenyl, R = *p*-tolyl (**2a**), Me (**2b**)). The cationic silylene complexes **2** catalyzed hydrosilylation of aldehydes and ketones with **1** to give the corresponding alkoxy-silyliron complexes **3–5** in moderate to high yield.

Introduction

Transition metal silylene complexes¹ have attracted much attention because they have been proposed as an intermediate in dehydrogenative condensation of organosilicon compounds,² redistribution of substituents on organosilicon compounds,³ and conversion of organosilylmetal complexes to monosilyl derivatives.⁴ Silylene complexes have also been suggested as an intermediate or transition state in catalytic hydrosilylation.⁵ However, there are only a few reports on the application of well-defined silylene complexes

as a catalyst for hydrosilylation.⁶ Tilley et al. reported recently that cationic silylene-ruthenium and -iridium complexes show catalytic activity for hydrosilylation of alkenes and carbonyl compounds with monosubstituted silanes RSiH₃.⁶

We previously reported the synthesis of cationic base-stabilized silyleneiron complexes [Cp(OC)₂Fe=Si(*p*-tolyl)₂(HMPA)]⁺ and [Cp(OC)₂Fe=SiMe{(2-CH₂NMe₂)C₆H₄}]⁺ (Cp = η⁵-C₅H₅, HMPA = P(O)(NMe₂)₃) by a hydride abstraction from hydrosilyliron complexes Cp(OC)₂FeSiH(*p*-tolyl)₂ (**1a**) and [Cp(OC)₂FeSiHMe{(2-CH₂NMe₂)C₆H₄}], respectively.⁷ The silylene complex coordinated by CD₃CN [Cp(OC)₂Fe=Si(*p*-tolyl)₂(CD₃CN)]⁺[B(Ar^f)₄]⁻ (**2a**, Ar^f = 3,5-bis(trifluoromethyl)phenyl) was also obtained by a hydride abstraction from **1a** with 1 equiv of Ph₃CB(Ar^f)₄ in CD₃CN. During the course of the study on the reactivity of these silyleneiron complexes, we found that **1a** was converted to alkoxy-silyliron complexes by treatment with ketones in the presence of a catalytic amount of **2a**.

Hydrosilylation catalyzed by transition metal complexes is one of the most powerful tools for synthesis of organosilicon compounds and silicon polymers and has been applied for various combinations of hydrosilanes and unsaturated organic substrates containing C=C, C≡C, C≡N, and C=O bonds.⁸ However, there are almost no examples of catalytic

[†]Part of the Dietmar Seyferth Festschrift. This paper is dedicated to Professor Dietmar Seyferth for his dedicated service to Organometallics and to the field of organometallic chemistry.

*To whom correspondence should be addressed. Tel & Fax: +81-277-30-1260. E-mail: ueno@chem-bio.gunma-u.ac.jp.

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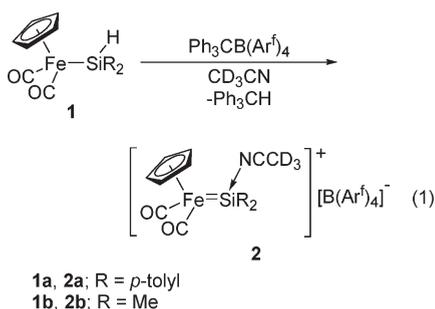
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and stoichiometric hydrosilylation directed to the functionalization of hydrosilyl fragments in transition metal silyl complexes.⁹

In this paper, we report the details of the hydrosilylation of aldehydes and ketones with hydrosilyliron complexes **1** catalyzed by cationic silyleneiron complexes **2**.

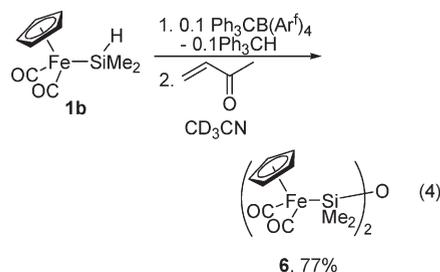
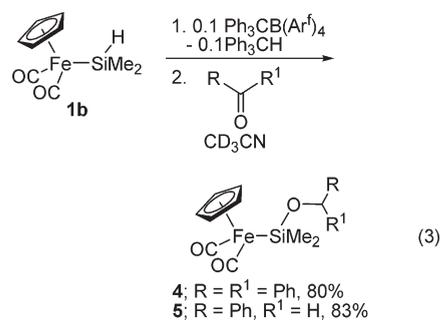
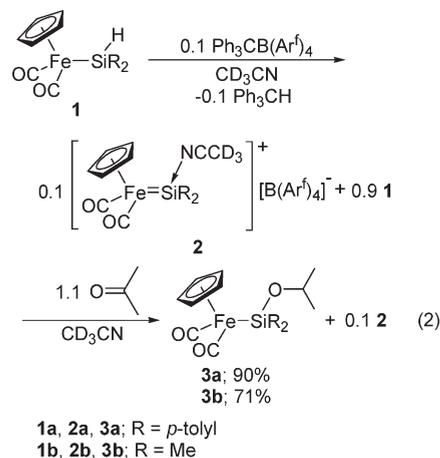
Results and Discussion

Dimethylsilyleneiron complex $[\text{Cp}(\text{OC})_2\text{Fe}=\text{SiMe}_2(\text{NCCD}_3)]^-[\text{B}(\text{Ar}^f)_4]^+$ (**2b**) was obtained almost quantitatively by the reaction of $\text{Cp}(\text{OC})_2\text{FeSiMe}_2\text{H}$ (**1b**) and 1 equiv of $\text{Ph}_3\text{CB}(\text{Ar}^f)_4$ in CD_3CN , in a similar manner to the synthesis of **2a** (eq 1). The ²⁹Si NMR spectrum of **2a** or **2b** afforded a signal assignable to the silylene fragment at 77.1 or 93.7 ppm, respectively. These are in the range of the reported resonances for the base-stabilized aryl- and alkyl-substituted silyleneiron complexes (74–160 ppm).^{7,10}



Catalytic hydrosilylation of acetone with **1a** was achieved by the following two steps: (i) addition of 0.1 equiv of $\text{Ph}_3\text{CB}(\text{Ar}^f)_4$ to 1 equiv of **1a** in CD_3CN to afford a CD_3CN solution containing 0.9 equiv of **1a**, 0.1 equiv of **2a**, and 0.1 equiv of Ph_3CH , and (ii) addition of 1.1 equiv of acetone to the reaction mixture (eq 2). The NMR spectrum of the resultant mixture revealed that it comprised $\text{Cp}(\text{OC})_2\text{FeSi}(\text{p-tolyl})_2(\text{OCHMe}_2)$ (**3a**) in 90% NMR yield and 0.1 equiv of **2a**. No reactions took place between **1a** and acetone in the absence of **2a** and between $\text{Ph}_3\text{CB}(\text{Ar}^f)_4$ and acetone in CD_3CN . Complex **2b** was also relevant to the hydrosilylation of acetone with hydrosilyliron complex **1b** to afford $\text{Cp}(\text{OC})_2\text{FeSiMe}_2(\text{OCHMe}_2)$ (**3b**) in 71% yield (eq 2). Benzophenone and benzaldehyde were hydrosilylated by **1b** in the presence of 0.1 equiv of **2b** to provide $\text{Cp}(\text{OC})_2\text{FeSiMe}_2(\text{OCHPh}_2)$ (**4**) and $\text{Cp}(\text{OC})_2\text{FeSiMe}_2(\text{OCH}_2\text{Ph})$ (**5**) in 80% and 83% NMR yields, respectively (eq 3). In contrast, the reaction of **1b** with methyl vinyl ketone under similar reaction conditions afforded not the expected alkoxy-silyliron complex but $\text{O}(\text{SiMe}_2)_2$ -bridged dimetallic complex $[\text{Cp}(\text{OC})_2\text{FeSiMe}_2]_2\text{O}$ (**6**)

in 77% yield with a concomitant formation of unidentified organic compounds (eq 4).

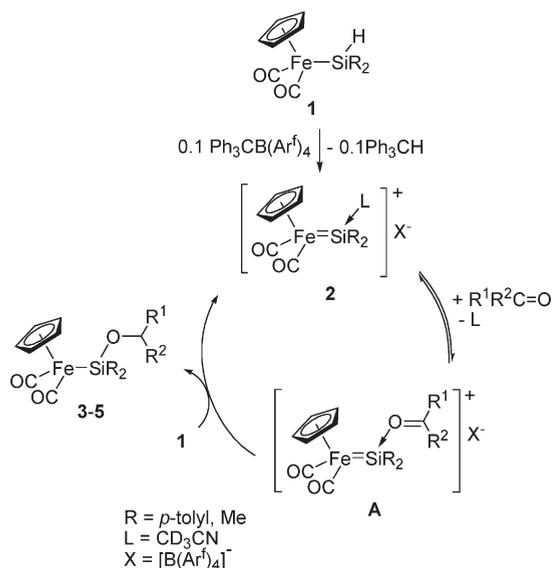


The catalytic hydrosilylation should proceed via activation of the C=O bond as a crucial process. It is well known that the silylene fragment in transition metal silylene complexes is electron deficient due to the low orbital overlapping between the empty p orbital on Si and the filled d_z orbital on the metal.^{1a} Actually, silylene complexes **2** are stabilized by the coordination of a Lewis base CD_3CN on the silylene fragment. Ketones and aldehydes could also coordinate to the electron-deficient Si to give the corresponding silylene complexes $[\text{Cp}(\text{OC})_2\text{Fe}=\text{SiR}_2(\text{O}=\text{CR}^1\text{R}^2)]^+$ (**A**), which consequently activates the carbonyl compounds. A similar activation process via coordination of carbonyl compounds to a cationic silyl fragment (silylium ion) was previously proposed as a key step in the $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed hydrosilylation.¹¹ The silylene complexes **A** were not observed by NMR; however, formation of such complexes is strongly supported by the fact that addition of 1 equiv of PPh_3 to a mixture of silylene

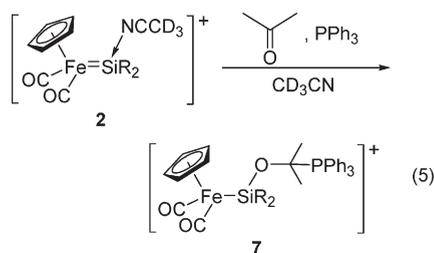
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Scheme 1. Plausible Reaction Mechanism for the Silyleneiron Complex-Catalyzed Hydrosilylation of Carbonyl Compounds


complexes **2** and acetone immediately afforded PPh₃-incorporated complexes [Cp(OC)₂FeSiR₂{OC(PPh₃)Me₂}]⁺ (R = *p*-tolyl (**7a**), Me (**7b**)) in high yield (eq 5). In the ¹³C{¹H} NMR spectrum of **7a** or **7b**, a doublet signal assignable to the PPh₃-introduced carbon was observed at 82.9 (¹J_{PC} = 64.8 Hz) or 82.1 (¹J_{PC} = 66.2 Hz) ppm, respectively. These chemical shifts and coupling constants are comparable to those observed for [RCH(OSiMe₃)PPh₃]⁺ (R = H, Et, Ph, and 4-MeC₆H₄, 58–74 ppm, ¹J_{PC} = 62–70 Hz).¹² The ²⁹Si{¹H} NMR spectrum of **7a** or **7b** also showed a doublet signal at 61.1 (³J_{PSi} = 10.8) or 76.5 (³J_{PSi} = 7.3) ppm, respectively.

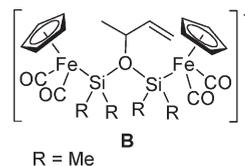


2a, 7a; R = *p*-tolyl
2b, 7b; R = Me

The formation of complex **7** shows the strong electrophilic character of the carbonyl carbon atom in **A**. The electrophilicity of the carbonyl carbon is very important to drive the catalytic cycle since no reaction occurred in the hydrosilylation for ethyl and methyl acetate with **1b** in the presence of **2b**. Thus, it is certain that complex **A** abstracts a hydride from **1** to give the corresponding alkoxy-silyliron complexes and cationic silylene complexes **2**.

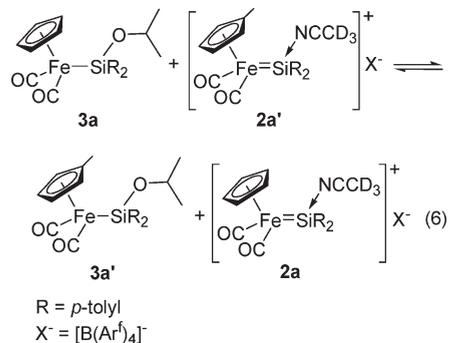
On the basis of these results, a plausible reaction mechanism for the silyleneiron complex-catalyzed hydrosilylation of carbonyl compounds is shown in Scheme 1. In the first step, CD₃CN-coordinated silyleneiron complex **2** was formed by hydride abstraction from hydrosilyliron complex **1** with Ph₃CB(Ar^f)₄. A displacement of CD₃CN with ketone or aldehyde in complex **2** resulted in the formation of intermediate **A**. A hydride

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Chart 1


abstraction from **1** by complex **A** affords hydrosilylation products **3–5** and regenerates silyleneiron complex **2**.

Complex **6**, obtained by the reaction with methyl vinyl ketone (eq 4), would be provided via the following catalytic mechanism: (i) formation of cationic disilyloxoniumdiiron complex [Cp(OC)₂FeSiMe₂]₂{μ-OCH(CH₃)CH=CH₂}⁺ (Chart 1, **B**) from silyleneiron complex **2b** and transiently produced alkoxy-silyliron complex Cp(OC)₂FeSiMe₂(OCH(CH₃)CH=CH₂), (ii) immediate decomposition of **B** to complex **6** and allylic cation (CH₂=CHCH₂CH₃⁺), and (iii) hydride abstraction by the allylic cation from complex **1b** to regenerate silyleneiron complex **2b**.¹³ The allylic cation would be converted to butene; however, it and related species were not detected in ¹H NMR or mass spectra. The formation of a cationic disilyloxoniumdiiron intermediate such as **B** is further indicated by the fact that the alkoxy group transfer reaction takes place from the alkoxy-silyliron complex to the cationic silyleneiron complex, i.e., addition of **3a** to [(η⁵-MeC₅H₄)Fe(CO)₂Si(*p*-tolyl)₂(NCCD₃)]⁺[B(Ar^f)₄]⁻ (**2a'**) in CD₃CN instantaneously gave a mixture of four silylene/silyliron complexes: **3a**, **2a'**, **2a**, and (η⁵-MeC₅H₄)Fe(CO)₂Si(*p*-tolyl)₂(OCHMe₂) (**3a'**) (eq 6).¹⁴


Experimental Section

General Procedures. All manipulations were performed using either standard Schlenk tube techniques under nitrogen, vacuum line techniques, or a drybox under nitrogen. Cp(OC)₂FeSiR₂H (R = *p*-tolyl (**1a**),¹⁵ Me (**1b**)¹⁶), Cp(OC)₂FeSiMe₂Cl,¹⁶ and Ph₃CB(Ar^f)₄ (Ar^f = 3,5-bis(trifluoromethyl)phenyl)¹⁷ were prepared according to the published procedures. Acetone was dried over Drierite followed by distillation under a nitrogen atmosphere before use. Benzaldehyde, ethyl acetate, and methyl acetate were

(13) Related hydride abstraction was reported from hydrosilane by carbocation: Kira, M.; Hino, T.; Sakurai, H. *Chem. Lett.* **1992**, 555.

(14) A similar thioalkoxy exchange reaction was reported between the thioalkoxy-silyliron complex and a cationic silyleneiron complex via the cationic disilylthiooxonium complex: Grumbine, S. K.; Tilley, T. D. *J. Am. Chem. Soc.* **1994**, *116*, 6951.

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dried over calcium hydride followed by distillation under a nitrogen atmosphere before use. Methyl vinyl ketone was dried over calcium chloride followed by distillation under a nitrogen atmosphere before use. Benzophenone was recrystallized from dry hexane before use. Toluene, Et₂O, and THF were dried by refluxing over sodium benzophenone ketyl followed by distillation under a nitrogen atmosphere before use. CH₃CN and CD₃CN were dried over calcium hydride followed by distillation under a nitrogen atmosphere before use. C₆D₆ was dried over potassium mirror followed by distillation in vacuo before use.

NMR spectra were recorded on a JEOL JNM-AL300 or a JEOL JNM-AL500 Fourier transform spectrometer at room temperature. IR spectra were recorded on a JASCO FT/IR-600 Plus spectrometer at room temperature. Elemental analyses were performed by the Center for Material Research by Instrumental Analysis, Gunma University.

General Procedure for Catalytic Hydrosilylation of Carbonyl Compounds with Hydrosilyliron Complex 1. A CD₃CN solution of Ph₃CB(Ar^f)₄ (4 mg, 4 × 10⁻⁶ mol) was added to a CD₃CN solution (total 0.5 mL) of Cp(OC)₂FeSiHMe₂ (**1b**) (9 mg, 4 × 10⁻⁵ mol) in a NMR sample tube with a Teflon vacuum valve. To this mixture was added acetone (5 μL, 7 × 10⁻³ mol), and the resultant mixture was kept for 0.5 h. Cp(OC)₂FeSiMe₂(OCHMe₂) (**3b**) was obtained in 71% yield with a trace amount of **2b** determined by ¹H NMR spectrum. Characterization of **3–6** was achieved by isolation of the silyliron complexes from the reaction mixture or comparing these spectroscopic data with those of the authentic samples prepared by the reaction of Cp(OC)₂FeSiMe₂Cl¹⁶ with the corresponding metal alkoxide.

Preparation of Cp(OC)₂FeSiR₂(OCHR')₂ (R = *p*-tolyl, R' = Me (3a**), R = Me, R' = Ph (**4**)).** To a solution of Cp(OC)₂FeSi(*p*-tolyl)₂H (**1a**) (155 mg, 4.00 × 10⁻⁴ mol) in CH₃CN (4 mL) in a 50 mL round-bottomed flask was added a CH₃CN solution (5 mL) of Ph₃CB(Ar^f)₄ (44 mg, 4.0 × 10⁻⁵ mol) with vigorous stirring. To the resultant mixture was added acetone (60.0 μL, 8.17 × 10⁻⁴ mol), and the mixture was stirred for several hours at 25 °C. After removal of volatiles from the reaction mixture in vacuo, the residue was purified by column chromatography (silica gel, eluent; toluene:hexane, 1:3), and the yellow band (R_f = 0.32) was collected. Volatiles were removed from the yellow solution to afford Cp(OC)₂FeSi(*p*-tolyl)₂(OCHMe₂) (**3a**) (69%, 109 mg, 2.44 × 10⁻⁴ mol) as yellow solids. ¹H NMR (300 MHz, CD₃CN): δ/ppm 7.51 (d, ³J_{HH} = 7.6 Hz, 4H, C₆H₄), 7.20 (d, ³J_{HH} = 7.6 Hz, 4H, C₆H₄), 4.68 (s, 5H, Cp), 3.97 (sept, ³J_{HH} = 6.0 Hz, 1H, OCH), 2.34 (s, 6H, C₆H₄CH₃), 1.04 (d, ³J_{HH} = 6.0 Hz, 6H, CMe₂). ¹³C{¹H} NMR (75.5 MHz, C₆D₆): δ/ppm 215.9 (CO), 140.5 (C₆H₄), 138.4 (C₆H₄), 134.8 (C₆H₄), 128.7 (C₆H₄), 84.5 (Cp), 65.3 (OCH), 25.7 (CMe₂), 21.4 (C₆H₄CH₃). ²⁹Si{¹H} NMR (59.6 MHz, CD₃CN): δ/ppm 51.6. IR (KBr): ν_{CO} 1990 (vs), 1925 (vs) cm⁻¹. Anal. Calcd for C₂₄H₂₆FeO₃Si: C, 64.58; H, 5.87. Found: C, 64.51; H, 5.75. In a similar manner, Cp(OC)₂FeSiMe₂(OCHPh₂) (**4**) was prepared using **1b** (187 mg, 7.92 × 10⁻⁴ mol), Ph₃CB(Ar^f)₄ (86 mg, 7.8 × 10⁻⁵ mol), benzophenone (166 mg, 9.11 × 10⁻⁴ mol), and CH₃CN (14 mL); yield 24% (73 mg, 1.7 × 10⁻⁴ mol), yellow crystals. ¹H NMR (300 MHz, CD₃CN): δ/ppm 7.44 (d, ³J_{HH} = 7.4 Hz, 4H, *o*-Ph), 7.29 (dd, ³J_{HH} = 7.4 and 7.4 Hz, 4H, *m*-Ph), 7.20 (t, ³J_{HH} = 7.4 Hz, 2H, *p*-Ph), 5.88 (s, 1H, OCH), 4.72 (s, 5H, Cp), 0.43 (s, 6H, SiMe₂). ¹³C{¹H} NMR (125.7 MHz, C₆D₆): δ/ppm 215.8 (CO), 146.0 (*ipso*-Ph), 128.5 (*m*-Ph), 127.2 (*p*-Ph), 126.7 (*o*-Ph), 83.7 (Cp), 77.3 (OCH), 8.7 (SiMe₂). ²⁹Si{¹H} NMR (99.3 MHz, C₆D₆): δ/ppm 69.6. IR (KBr) ν_{CO} 1983 (vs), 1925 (vs); ν_{SiO} 1061 (m) cm⁻¹. Anal. Calcd for C₂₂H₂₂FeO₃Si: C, 63.16; H, 5.30. Found: C, 63.18; H, 5.34.

Preparation of Cp(OC)₂FeSiMe₂(OCHRR') (R = R' = Me (3b**), R = H, R' = Ph (**5**)).** To a solution of sodium isopropoxide (2.3 × 10⁻³ mol) in 2-propanol (30 mL) in a 100 mL round-bottomed flask was added a Et₂O solution of Cp(OC)₂FeSiMe₂Cl¹⁶ (610 mg, 2.25 × 10⁻³ mol) with vigorous stirring. The resultant mixture was stirred for 3 h at 25 °C. After removal of volatiles from the reaction mixture in vacuo, the residue was extracted with hexane (30 mL). The extract was

filtrated through a glass filter. The filtrate was concentrated in vacuo, and the residue was purified by bulb-to-bulb distillation (120 °C/0.7 mmHg) to give Cp(OC)₂FeSiMe₂(OCHMe₂) (**3b**) (40%, 263 mg, 8.94 × 10⁻⁴ mol) as an orange liquid. ¹H NMR (300 MHz, CD₃CN): δ/ppm 4.84 (s, 5H, Cp), 4.07 (sept, ³J_{HH} = 6.2 Hz, 1H, OCH), 1.11 (d, ³J_{HH} = 6.2 Hz, 6H, CMe₂), 0.48 (s, 6H, SiMe₂). ¹³C{¹H} NMR (125.7 MHz, C₆D₆): δ/ppm 215.9 (CO), 83.6 (Cp), 65.3 (OCH), 26.0 (CMe₂), 9.0 (SiMe₂). ²⁹Si{¹H} NMR (99.3 MHz, C₆D₆): δ/ppm 63.3. IR (KBr): ν_{CO} 1993 (vs), 1935 (vs); ν_{SiO} 1017 (m) cm⁻¹. Anal. Calcd for C₁₂H₁₈FeO₃Si: C, 48.99; H, 6.17. Found: C, 49.47; H, 6.40. As a similar manner, Cp(OC)₂FeSiMe₂(OCH₂Ph) (**5**) was prepared using Cp(OC)₂FeSiMe₂Cl¹⁶ (500 mg, 1.85 × 10⁻³ mol), sodium benzyloxide (1.8 × 10⁻³ mol), and THF (10 mL); yield 19% (120 mg, 3.51 × 10⁻⁴ mol), 150 °C/0.7 mmHg, an orange liquid. ¹H NMR (300 MHz, CD₃CN): δ/ppm 7.20 (m, 5H, Ph), 4.85 (s, 5H, Cp), 4.71 (s, 2H, OCH₂), 0.53 (s, 6H, SiMe₂). ¹³C{¹H} NMR (125.7 MHz, C₆D₆): δ/ppm 215.7 (CO), 142.1 (*ipso*-Ph), 128.5 (*m*-Ph), 127.1 (*p*-Ph), 126.6 (*o*-Ph), 83.6 (Cp), 65.1 (OCH₂), 8.3 (SiMe₂). ²⁹Si{¹H} NMR (99.3 MHz, C₆D₆): δ/ppm 69.2. IR (KBr): ν_{CO} 1991 (vs), 1932 (vs); ν_{SiO} 1065 (m) cm⁻¹. Anal. Calcd for C₁₆H₁₈FeO₃Si: C, 56.15; H, 5.30. Found: C, 56.60; H, 5.38.

Preparation of [Cp(OC)₂FeSiMe₂]₂O (6**).** To a solution of **1b** (184 mg, 7.79 × 10⁻⁴ mol) in CH₃CN (5 mL) in a 50 mL round-bottomed flask was added a CH₃CN solution (10 mL) of Ph₃CB(Ar^f)₄ (82 mg, 7.4 × 10⁻⁵ mol) with vigorous stirring. To the resultant mixture was added a CH₃CN solution (5 mL) of benzaldehyde (100 μL, 9.8 × 10⁻⁴ mol), and then the solution was stirred for 2 h at 25 °C. After removal of volatiles from the reaction mixture in vacuo, the residue was extracted with hexane (2 mL × 5). The extract containing Cp(OC)₂FeSiMe₂(OCH₂Ph) (**5**) as a main product was hydrolyzed to afford [Cp(OC)₂FeSiMe₂]₂O (**6**) (21%, 40 mg, 8.2 × 10⁻⁵ mol) as yellow crystals. ¹H NMR (300 MHz, CD₃CN): δ/ppm 4.82 (s, 10H, Cp), 0.52 (s, 12H, SiMe₂). ¹³C{¹H} NMR (125.7 MHz, C₆D₆): δ/ppm 216.0 (CO), 83.6 (Cp), 11.3 (SiMe₂). ²⁹Si{¹H} NMR (99.3 MHz, C₆D₆): δ/ppm 54.7. IR (KBr): ν_{CO} 1985 (vs), 1917 (vs); ν_{SiO} 1045 (m) cm⁻¹. Anal. Calcd for C₁₈H₂₂Fe₂O₅Si₂: C, 44.46; H, 4.56. Found: C, 44.70; H, 4.61.

Observation of [Cp(OC)₂FeSiR₂(OC(PPh₃)Me₂)]⁺ (R = *p*-tolyl (7a**), R = Me (**7b**)).** To a CD₃CN solution of [Cp(OC)₂FeSi(*p*-tolyl)₂(NCCD₃)] [B(Ar^f)₄] (**2a**) (25 mg, 2.0 × 10⁻⁵ mol) was added a CD₃CN solution (total 0.5 mL) of 1 equiv of acetone and PPh₃ in a NMR sample tube with a Teflon vacuum valve. The formation of **7a** was identified by NMR. ¹H NMR (300 MHz, CD₃CN): δ/ppm 7.78–7.14 (m, 15H, PPh₃), 7.32–7.14 (m, 4H, C₆H₄Me), 4.50 (s, 5H, Cp), 2.33 (s, 6H, C₆H₄Me), 1.67 (d, ³J_{PH} = 17.4 Hz, 6H, CMe₂). ¹³C{¹H} NMR (75.5 MHz, CD₃CN): δ/ppm 216.8 (CO), 140.2, 139.9 (*p*-, *ipso*-C₆H₄Me), 136.2 (*p*-PPh₃), 136.1, 135.3 (*o*-, *m*-C₆H₄Me), 131.1 (d, ³J_{PC} = 11.8 Hz, *m*-PPh₃), 129.4 (d, ²J_{PC} = 12.2 Hz, *o*-PPh₃), 118.1 (d, ¹J_{PC} = 78.0 Hz, *ipso*-PPh₃), 86.6 (Cp), 82.9 (d, ¹J_{PC} = 64.8 Hz, OC(PPh₃)Me₂), 28.4 (d, ²J_{PC} = 6.6 Hz, OC(PPh₃)Me₂), 21.4 (C₆H₄Me). ³¹P{¹H} NMR (121 MHz, CD₃CN): δ/ppm 34.1. ²⁹Si{¹H} NMR (59.6 MHz, CD₃CN): δ/ppm 61.1 (d, ³J_{PSi} = 10.8 Hz). In a similar manner, **7b** was identified by NMR. ¹H NMR (300 MHz, CD₃CN): δ/ppm 8.0–7.0 (m, 15H, PPh₃), 4.65 (s, 5H, Cp), 1.79 (d, ³J_{PH} = 17.1 Hz, 6H, CMe₂), 0.59 (s, 6H, SiMe₂). ¹³C{¹H} NMR (125.7 MHz, CD₃CN): δ/ppm 216.1 (CO), 136–115 (PPh₃), 85.1 (Cp), 82.1 (d, ¹J_{PC} = 66.2 Hz, OC(PPh₃)Me₂), 28.6 (d, ²J_{PC} = 6.2 Hz, OC(PPh₃)Me₂), 12.3 (SiMe₂). ³¹P{¹H} NMR (202.5 MHz, CD₃CN): δ/ppm 30.0. ²⁹Si{¹H} NMR (99.3 MHz, CD₃CN): δ/ppm 76.5 (d, ³J_{PSi} = 7.3 Hz).

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