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Photoreactions of silyliron(II) complexes $Cp^{\star}Fe(CO)_2SiMe_3$ ($Cp^{\star} = \eta^5$-C_5H_5, η^5-C_5Me_5) in the presence of trihydrosilanes *

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Abstract

The photochemistry of silyliron(II) complexes $Cp^{\star}Fe(CO)_2SiMe_3$ ($Cp^{\star} = \eta^5$-C_5H_5, η^5-C_5Me_5) in the presence of trihydrosilanes is described. Three types of products were observed, depending on the bulkiness of the Cp* ligands and the substituents on the trihydrosilanes: (η^5-C_5H_5)$Fe(CO)_2SiMe_3$ reacts with tert-alkylsilanes $RSiH_3$ ($R = {}^tBu$, $C(Me_2)_2H$) upon irradiation to give silylene-bridged diiron complexes (η^5-C_5H_5)$_2Fe_2(CO)_3(\mu$-SiHR) in good yields. In contrast, (η^5-C_5Me_5)$Fe(CO)_2SiMe_3$ reacts with the tert-alkylsilanes photochemically to give silyl monoiron complexes (η^5-C_5Me_5)$Fe(CO)_2SiH_2R$ exclusively. Using *p*-$TolSiH_3$ instead of tert-alkylsilane, the main photolysis product was the hydridobis(silyl)iron complex $Cp^{\star}Fe(CO)SiMe_3(H)SiH_2$-*p*-Tol. The X-ray crystal structure analysis of (η^5-C_5H_5)$_2Fe_2(CO)_3(\mu$-SiH^tBu) revealed that this complex adopts a geometry in which the two Cp rings and a Si–H bond are located on the same side with respect to the $SiFe_2C$ four-membered ring. ^{29}Si NMR spectra of the silylene-bridged diiron complexes showed signals at remarkably low field (δ 235.5–289.1 ppm). A mechanism for the formation of these silylene-bridged diiron complexes is proposed.

Introduction

The oxidative addition of Si–H bonds to low-valent metal centers is one of the most important reactions in the formation of transition-metal-to-silicon bonds. Various silyl(transition metal) complexes [1] and more recently several complexes with a M ··· H ··· Si two-electron three-center bond [2] have been synthesized by reactions of monohydrosilanes with transition-metal complexes. Silanes with more than one hydride are supposed to be useful as precursors for bridging ligands, but relatively little attention has been focused on this subject. Several oxidative

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addition reactions of dihydro- [3], trihydro- [4,5], and perhydrosilanes [6] have been reported so far to give dinuclear complexes or clusters with bridging silicon ligands.

It has been found recently that the irradiation of certain silyl(carbonyl)metal complexes, $(OC)_4CoSiMe_3$ [7], $CpFe(CO)_2SiMe_3$ ($Cp = \eta^5\text{-}C_5H_5$) [8], and $Cp'Fe(CO)_2SiMe_3$ ($Cp' = \eta^5\text{-}C_5Me_5$) [9], in the presence of monohydrosilane gives rise to silyl exchange reactions. Wrighton *et al.* demonstrated through extensive mechanistic studies that this reaction proceeded via a mechanism involving dissociative loss of CO followed by oxidative addition and reductive elimination of hydrosilane. We attempted to apply this reaction to the synthesis of polynuclear complexes by using trihydrosilanes. This paper concerns the photoreaction of $Cp^{\star}Fe(CO)_2SiMe_3$ ($Cp^{\star}$ = substituted or non-substituted cyclopentadienyl) in the presence of trihydrosilanes, the structures and properties of the products, and the reaction mechanism. Our preliminary results have already been outlined [10], and this paper presents the full details.

Experimental

General details

Standard Schlenk techniques were employed in handling organosilyl and organoiron compounds, and all manipulations were performed under a nitrogen or argon atmosphere. Reagent-grade hexane, pentane, benzene, diethylether, dibutylether, and tetrahydrofuran (THF) were distilled under a nitrogen atmosphere from sodium-benzophenone ketyl immediately before use. Chloroform-*d*, dichloromethane-d_2, and benzene-d_6 were dried over molecular sieves 4 Å. $CpFe(CO)_2SiMe_3$ (**1**) [11], $Cp'Fe(CO)_2SiMe_3$ (**2**) [12], $^tBuSiCl_3$ [13], $p\text{-}TolSiH_3$ (p-Tol = p-tolyl) [14], and $^tBuSiH_2Cl$ [15] were prepared according to published procedures. Other chemicals were purchased from Wako Pure Chemical Industries, Ltd. and used without further purification.

Photolysis was performed with an Ushio UM-452 450 W medium pressure Hg lamp placed in a water-cooled, quartz jacket. Sample solutions were irradiated in Pyrex tubes unless otherwise noted.

^1H NMR spectra were recorded on Jeol FX-90Q, Varian EM-390, or Varian XL-200 NMR spectrometers. ^{13}C NMR spectra were recorded on Jeol FX-90Q or Varian XL-200, and ^{29}Si NMR spectra on Jeol FX-90Q or Bruker AC-300 spectrometers. IR spectra were obtained on a Jasco IR-810 spectrophotometer. Mass spectra were taken on a Hitachi M-52 or Jeol JMS-HX110 mass spectrometer, and high-resolution mass spectra on a Jeol JMS-HX110 mass spectrometer.

Elemental analyses and IR data are listed in Table 1 and NMR data in Table 2.

Preparation of tert-butylsilane

A 500 ml three-necked flask equipped with a reflux condenser, topped by a dry-ice trap, a 100 ml pressure-equalizing dropping funnel, and a magnetic stirring bar, were charged with dibutyl ether (200 ml), and $LiAlH_4$ powder (11.5 g, 0.30 mol) was carefully added. The dry-ice trap was then connected over a silicone oil-filled bubbler to a trap filled with a Pd–C dispersion in methanol for the purpose of destroying pyrophoric silanes which might be generated during the following reaction.

Table 1

Yields and analytical and IR data

Compound	Yield (%)	Analyses, found (calc.) (%)		IR (cm^{-1})^{a}		
		C	H	ν(SiH)	ν(CO$_t$)	ν(CO$_b$)
^{t}BuSiH$_3$	73			2150	–	–
TxSiH$_3$	54	61.72(61.98)	13.63(13.87)	2150	–	–
Cp$_2$Fe$_2$(CO)$_3$SiH^{t}Bu (**3a**)	69^{b}	49.62(49.55)	5.01(4.89)	2074	1950 1922	1720
Cp$_2$Fe$_2$(CO)$_3$SiHTx (**3b**)	65^{b}	51.77(51.84)	5.63(5.50)	2074	1948 1926	1724
Cp'Fe(CO)$_2$SiH$_2$^{t}Bu (**4a**)	81 54^{b}, 58^{b}	57.10(57.48)	7.47(7.83)	2033	1974 1915	–
Cp'Fe(CO)$_2$SiH$_2$Tx (**4b**)	50^{b}	362.1360(362.1364)^{c}		2050	1978 1923	–
Cp'Fe(CO)$_2$SiH$_2$-*p*-Tol (**4c**)	7^{b}	58.51(61.96)	6.46(6.57)	2054	1979 1927	–
CpFe(CO)SiMe$_3$(H)SiH$_2$-*p*-Tol (**5**)^{d}	52^{b}			2087	1940	–
Cp'Fe(CO)SiMe$_3$(H)SiH$_2$-*p*-Tol (**6**)^{e}	39^{b}			2085	1919	–
Cp'Fe(CO)(SiH$_2$-*p*-Tol)$_2$H (**7**)^{f}	7^{b}			2090	1920	–
CpFe(CO)$_2$SiH$_2$^{t}Bu (**9a**)	83 4^{b}	49.74(50.01)	6.10(6.10)	2060	1996 1940	–
CpFe(CO)$_2$SiH$_2$Tx (**9b**)	5^{b}	292.0581(292.0582)^{c}		2070	1998 1944	–

[a] KBr pellet (for crystals) or neat (for an oil); CO$_t$, terminal carbonyl; CO$_b$, bridging carbonyl. [b] Yield by photochemical method. [c] Exact mass. [d] ν(FeH) 1998 cm^{-1}. [e] ν(FeH) 2052 cm^{-1}. [f] ν(FeH) 2050 cm^{-1}.

Table 2. ^1H, ^{13}C and ^{29}Si NMR data.

Compound	^1H NMR δ (ppm)	^{13}C NMR δ (ppm)	^{29}Si NMR δ (ppm)
$^tBuSiH_3$	In $CDCl_3$ 1.05 (s, 9H, ^{t}Bu) 3.46 (s, 3H, Si–H)	In $CDCl_3$ 15.0 ($\mathit{C}Me_3$) 28.5 ($C\mathit{Me}_3$)	In C_6D_6 −39.7
$TxSiH_3$	In $CDCl_3$ 0.91 (d, $J = 6.6$ Hz, 6H, $CMe_2C\mathit{Me}_2H$) 1.00 (s, 6H, $C\mathit{Me}_2CMe_2H$) 1.54 (sep, $J = 6.6$ Hz, 1H, $CMe_2CMe_2\mathit{H}$) 3.42 (s, 3H, Si–H)	In C_6D_6 19.1 ($CMe_2C\mathit{Me}_2H$) 23.1 ($\mathit{C}Me_2CMe_2H$) 24.4 ($C\mathit{Me}_2CMe_2H$) 37.1 ($CMe_2\mathit{C}Me_2H$)	In C_6D_6 −46.6
$Cp_2Fe_2(CO)_3SiH^tBu$ (**3a**)	In CS_2 1.32 (s, 9H, ^{t}Bu) 4.50 (s, 10H, Cp) 7.23 (s, 1H, Si–H)	In CD_2Cl_2 30.0 ($C\mathit{Me}_3$) 31.5 ($\mathit{C}Me_3$) 84.5 (Cp) 213.4 (CO_{term}) 277.6 (CO_{brid})	In CD_2Cl_2 254.4
$Cp_2Fe_2(CO)_3SiHTx$ (**3b**)	In CS_2 1.13 (s, 6H, $C\mathit{Me}_2CMe_2H$) 1.14 (d, $J = 6.6$ Hz, 6H, $CMe_2C\mathit{Me}_2H$) 2.16 (sep, $J = 6.6$ Hz, 1H, $CMe_2CMe_2\mathit{H}$) 4.47 (s, 10H, Cp) 7.32 (s, 1H, Si–H)	In C_6D_6 19.6 ($CMe_2C\mathit{Me}_2H$) 23.5 ($C\mathit{Me}_2CMe_2H$) 38.7 ($CMe_2\mathit{C}Me_2H$) 39.1 ($\mathit{C}Me_2CMe_2H$) 84.5 (Cp) 213.5 (CO_{term}) 274.0 (CO_{brid})	In CD_2Cl_2 255.1
$Cp'Fe(CO)_2SiH_2{}^tBu$ (**4a**)	In C_6D_6 1.44 (s, 9H, ^{t}Bu) 1.50 (s, 15H, C_5Me_5) 4.27 (s, 2H, Si–H)	In C_6D_6 9.1 ($C_5\mathit{Me}_5$) 21.5 ($\mathit{C}Me_3$) 30.1 ($C\mathit{Me}_3$) 94.6 (C_5Me_5) 217.7 (CO)	In C_6D_6 38.2

$\mathrm{Cp'Fe(CO)_2SiH_2Tx}$ (**4b**)	In $\mathrm{C_6D_6}$ 1.20 (d, $J = 6.9$ Hz, 6H, $\mathrm{CMe_2C}\mathit{Me}_2\mathrm{H}$) 1.40 (s, 6H, $\mathrm{C}\mathit{Me}_2\mathrm{CMe_2H}$) 1.50 (s, 15H, $\mathrm{C_5Me_5}$) 2.01 (sep, $J = 6.9$ Hz, 1H, $\mathrm{CMe_2CMe_2}\mathit{H}$) 4.27 (s, 2H, Si–H)		
$\mathrm{Cp'Fe(CO)_2SiH_2}$-*p*-Tol (**4c**)	In $\mathrm{C_6D_6}$ 1.52 (s, 15H, $\mathrm{C_5H_5}$) 2.15 (s, 3H, $\mathrm{C_6H_4}\mathit{Me}$) 5.05 (s, 2H, Si–H) 7.08, 7.86 (ABq, $J = 7.6$ Hz, 2H × 2, $\mathrm{C_6}\mathit{H}_4\mathrm{Me}$)	In $\mathrm{C_6D_6}$ 9.3 ($\mathrm{C_5}\mathit{Me}_5$) 21.4 ($\mathrm{C_6H_4}\mathit{Me}$) 94.8 ($\mathit{C}_5\mathrm{Me_5}$) 128.6, 135.6, 136.1 137.9 ($\mathit{C}_6\mathrm{H_4Me}$) 216.5 (CO)	In $\mathrm{C_6D_6}$ 43.2
$\mathrm{CpFe(CO)SiMe_3(H)SiH_2}$-*p*-Tol (**5**)	In $\mathrm{C_6D_6}$ −13.55 (s, 1H, Fe–H) 0.49 (s, 9H, $\mathrm{Si}\mathit{Me}_3$) 2.12 (s, 3H, $\mathrm{C_6H_4}\mathit{Me}$) 4.00 (s, 5H, Cp) 4.26, 4.39 (ABq, $J = 6.9$ Hz, 1H × 2, Si–H) 7.01, 7.65 (ABq, $J = 7.2$ Hz, 2H × 2, $\mathrm{C_6}\mathit{H}_4\mathrm{Me}$)		
$\mathrm{Cp'Fe(CO)SiMe_3(H)SiH_2}$-*p*-Tol (**6**)	In $\mathrm{C_6D_6}$ −12.68 (s, 1H, Fe–H) 0.62 (s, 9H, $\mathrm{Si}\mathit{Me}_3$) 1.48 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$) 2.17 (s, 3H, $\mathrm{C_6H_4}\mathit{Me}$) 5.19, 5.20 (s, 1H × 2, Si–H) 7.06, 7.74 (ABq, $J = 7.5$ Hz, 2H, $\mathrm{C_6}\mathit{H}_4\mathrm{Me}$)	In $\mathrm{C_6D_6}$ 8.1 ($\mathrm{Si}\mathit{Me}_3$) 9.4 ($\mathrm{C_5}\mathit{Me}_5$) 21.4 ($\mathrm{C_6H_4}\mathit{C}\mathrm{H_3}$) 93.5 ($\mathit{C}_5\mathrm{Me_5}$) 128.7, 135.8, 136.0, 138.1 ($\mathit{C}_6\mathrm{H_4CH_3}$) 214.6 (CO)	In $\mathrm{C_6D_6}$ 5.1 30.2

Table 2 (continued)

Compound	^{1}H NMR δ (ppm)	^{13}C NMR δ (ppm)	^{29}Si NMR δ (ppm)
$Cp'Fe(CO)(SiH_2$-*p*-Tol$)_2H$ (**7**)	In C_6D_6 −12.19 (s, 1H, Fe–H) 1.48 (s, 15H, C_5Me_5) 2.12 (s, 6H, C_6H_4Me) 5.22, 5.24 (s, 2H×2, Si–H) 7.00, 7.76 (ABq, $J = 8.1$ Hz, 4H×2, C_6H_4Me)		
$Cp'_2Fe_2(CO)_3SiH$-*p*-Tol (*cis*-**8**) [b]			In C_6D_6 250.4
$Cp'_2Fe_2(CO)_3SiH$-*p*-Tol (*trans*-**8**) [b]			In C_6D_6 235.5
$CpFe(CO)_2SiH_2{}^tBu$ (**9a**)	In C_6D_6 1.24 (s, 9H, ^{t}Bu) 4.17 (s, 5H, Cp) 4.49 (s, 2H, Si–H)	In C_6D_6 22.5 (CMe_3) 30.4 (CMe_3) 83.2 (Cp) 214.7 (CO)	In C_6D_6 21.1
$CpFe(CO)_2SiH_2Tx$ (**9b**)	In C_6D_6 1.04 (d, $J = 7.0$ Hz, 6H, CMe_2CMe_2H) 1.13 (s, 6H, CMe_2CMe_2H) 1.85 (sep, $J = 7.0$ Hz, 1H, CMe_2CMe_2H) 4.11 (s, 5H, Cp) 4.53 (s, 2H, Si–H)		
$Cp_2Fe_2(CO)_3SiCl^tBu$ (**10a**) [a]			In CD_2Cl_2 276.3
$Cp_2Fe_2(CO)_3SiBr^tBu$ (**10b**) [a]			In CD_2Cl_2 284.8
$Cp_2Fe_2(CO)_3SiI^tBu$ (**10c**) [a]			In CD_2Cl_2 289.1

[a] Ref. 21. [b] Ref. 16.

To the dispersion of $LiAlH_4$, a solution of $^tBuSiCl_3$ (29.0 g, 0.15 mol) in dibutyl ether (60 ml) was added dropwise from the dropping funnel over a period of 70 min while stirring. After the addition was completed, the mixture was heated to 80°C and stirred for 2 h. The flask was then cooled in an ice–water bath and 10% sulfuric acid solution (100 ml) was slowly added to the reaction mixture to decompose excess $LiAlH_4$. The precipitate formed was filtered off and washed with a 150 ml portion of dibutyl ether. The aqueous layer of the filtrate was removed using a hypodermic syringe, and the remaining organic layer was dried over anhydrous $MgSO_4$. Fractional distillation afforded $^tBuSiH_3$ (9.67 g, 0.11 mol, 73%) as a colorless oil, b.p. 34°C.

Preparation of (1,1,2-trimethylpropyl)trichlorosilane(thexyltrichlorosilane, $TxSiCl_3$)

A 50 ml stainless steel autoclave equipped with a magnetic stirring bar was charged with 2,3-dimethyl-2-butene (12.5 ml, 0.10 mol), trichlorosilane (40 g, 0.30 mol), and 2,2′-azobis(isobutyronitrile) (AIBN) (3.0 g, 18.3 mmol), and heated to 120°C for 23 h with stirring. The pressure inside the vessel rose to 17 kg cm^{-2} during the reaction. After cooling the reaction mixture, the remaining AIBN was removed by decantation and the supernatant liquid was distilled under reduced pressure to give $TxSiCl_3$ (17.3 g, 78.9 mmol, 77%) as a colorless oil, b.p. 84–86°C/27 Torr. ^1H NMR (90 MHz, $CDCl_3$): δ 1.00 (d, $J = 6.6$ Hz, 6H, CMe_2CMe_2H), 1.12 (s, 6H, CMe_2CMe_2H), 1.87 (sep, $J = 6.6$ Hz, 1H, CMe_2CMe_2H).

Preparation of thexylsilane

In an apparatus similar to that for the preparation of tert-butylsilane, $TxSiCl_3$ (17.2 g, 79.4 mmol) in THF (50 ml) was added dropwise to the dispersion of $LiAlH_4$ (9.0 g, 0.24 mol) in THF (150 ml) over a period of 30 min. The mixture was heated to 65°C for 36 h, and then cooled using an ice-water bath. Water (9.0 ml), 15% NaOH solution (9.0 ml), and water (27.0 ml) were added in this order while stirring vigorously. The precipitate was then filtered from the solution and washed with three 50 ml portions of THF. The filtrate and washings were combined, placed in a separatory funnel, and washed with a dilute NaCl solution and then with water to wash off THF until the volume of the organic layer did not change (13 times). This organic layer was then washed with a saturated NaCl solution and dried over anhydrous $MgSO_4$. The resulting crude product was distilled to give pure $TxSiH_3$ (4.90 g, 42.2 mmol, 54%) as a colorless oil, b.p. 72–73°C. MS: m/z 116 (3%, M^+), 85 (100, $CMe_2CMe_2H^+$).

Preparation of $Cp_2Fe_2(CO)_3SiH^tBu$ (3a)

A deoxygenated solution of $^tBuSiH_3$ (0.53 g, 6.0 mmol) and $CpFe(CO)_2SiMe_3$ (**1**) (2.51 g, 10.0 mmol) in pentane (250 ml) was irradiated with a 450 W medium pressure Hg immersion lamp through a Pyrex sleeve at 0°C with stirring. The pale yellow solution changed to red with evolution of gas, and red crystals separated during irradiation. After the solution had been irradiated for 4 h, the crystals were collected by filtration through a fritted Schlenk funnel and washed with pentane. Concentration of the filtrate to 90 ml followed by cooling to −45°C gave a second crop. Total yield of $Cp_2Fe_2(CO)_3SiH^tBu$ (**3a**) obtained was 1.48 g (3.59 mmol, 69%), red crystals, m.p. 180°C (dec.). MS: m/z 412 (29%, M^+), 384 (51, $M^+ - CO$), 356 (100, $M^+ - 2CO$), 328 (32, $M^+ - 3CO$), 270 (55, $Cp_2Fe_2Si^+$ or $Cp_2Fe_2(CO)^+$).

Preparation of $Cp_2Fe_2(CO)_3SiHTx$ (3b)

$CpFe(CO)_2SiMe_3$ (**1**) (70 mg, 0.28 mmol), $TxSiH_3$ (16 mg, 0.14 mmol), and hexane (3 ml) were placed in a Pyrex tube (8 mm i.d.) and irradiated for 2 h at 0°C. Gas evolution was observed and the solution changed from pale yellow to red. Soon after, red needles precipitated out from the solution. After cooling this mixture to −45°C, the crystals were collected by filtration and washed with pentane to give $Cp_2Fe_2(CO)_3SiHTx$ (**3b**) (40 mg, 0.091 mmol, 65%) as red crystals. MS: *m/z* 440 (69, M^+), 412 (54, $M^+ - CO$), 384 (100, $M^+ - 2CO$).

Photolysis of $Cp'Fe(CO)_2SiMe_3$ (2) in the presence of $^tBuSiH_3$

(i) $Cp'Fe(CO)_2SiMe_3$ (**2**) (128 mg, 0.40 mmol) and $^tBuSiH_3$ (21 mg, 0.24 mmol) in pentane (10 ml) were irradiated at 0°C for 4 h. $Cp'_2Fe_2(CO)_4$ (21 mg, 0.04 mmol, 21%) precipitated from the reaction mixture was filtered off. The filtrate was concentrated and the residue sublimed at 70°C/10^{-3} Torr to give $Cp'Fe(CO)_2SiH_2{}^tBu$ (**4a**) (48 mg, 0.14 mmol, 58% based on $^tBuSiH_3$) as yellow crystals.

Photolysis of a benzene-d_6 solution of **2** and $^tBuSiH_3$ (2:1) in an NMR tube was monitored by ^1H NMR spectroscopy, which showed only growth of the signals due to $Cp'_2Fe_2(CO)_4$ and **4a**.

(ii) **2** (135 mg, 0.42 mmol) and $^tBuSiH_3$ (300 mg, 3.4 mmol) in pentane (25 ml) were irradiated at 0°C for 1 h. Removal of volatile materials *in vacuo* followed by sublimation of the residue (70°C/10^{-3} Torr) afforded **4a** (76 mg, 0.23 mmol, 54% based on **2**).

Preparation of $Cp'Fe(CO)_2SiH_2{}^tBu$ (4a)

A THF (15 ml) solution of $Na[CpFe(CO)_2]$ prepared from $Cp'_2Fe_2(CO)_4$ (2.00 g, 4.0 mmol) and 1% sodium amalgam (Na 0.70 g, 30 mmol) was cooled to −48°C using an acetonitrile/liquid N_2 bath, and $^tBuSiH_2Cl$ (1.97 g, 16.0 mmol) in THF (15 ml) was added over a period of 20 min. After the solution had been stirred at −48°C for 90 h and then at room temperature for 30.5 h, solvent was removed *in vacuo* and the residue was extracted several times with pentane. The extract was filtered through a Celite pad and the filtrate then evaporated to give an orange-yellow oily residue. Molecular distillation of the residue (60°C/0.01 Torr) provided $Cp'Fe(CO)_2SiH_2{}^tBu$ (**4a**) (2.61 g, 6.5 mmol, 81%) as yellow crystals. MS: *m/z* 334 (50%, M^+), 306 (100, $M^+ - CO$), 278 (27, $M^+ - 2CO$).

Photolysis of $Cp'Fe(CO)_2SiMe_3$ (2) in the presence of $TxSiH_3$

$Cp'Fe(CO)_2SiMe_3$ (**2**) (160 mg, 0.50 mmol) and $TxSiH_3$ (407 mg, 3.50 mmol) in pentane (20 ml) were irradiated at 0°C for 1 h. Removal of volatile materials from the reaction mixture *in vacuo* followed by sublimation of the residue (90–100°C/0.01 Torr) gave $Cp'Fe(CO)_2SiH_2Tx$ (**4b**) (90 mg, 0.25 mmol, 50%) as a yellow oil. MS: *m/z* 362 (5%, M^+), 334 (79, $M^+ - CO$), 250 (100, $Cp'SiH_2Tx^+$).

Photolysis of $CpFe(CO)_2SiMe_3$ (1) in the presence of excess p-$TolSiH_3$

$CpFe(CO)_2SiMe_3$ (**1**) (152 mg, 0.61 mmol) and *p*-$TolSiH_3$ (580 mg, 4.8 mmol) in pentane (25 ml) were cooled to 0°C and irradiated for 12 min. After removal of pentane and *p*-$TolSiH_3$ *in vacuo*, the brown residue was chromatographed on a silica gel flash column (15 mm i.d. × 100 mm) under nitrogen pressure. The starting material **1** (27 mg, 0.11 mmol) was recovered first by elution with pentane, then elution with a mixture of pentane and ether (20 : 1) gave a yellowish-brown fraction from which removal of the solvent afforded CpFe(CO)SiMe$_3$(H)SiH$_2$-*p*-Tol (**5**) as a thermally unstable yellowish-brown oil. Crude yield of **5**: 108 mg (0.31 mmol, 52%). MS: m/z 343 (33%, $M^+ - $H), 315 (50, $M^+ - $H $-$ CO), 242 (100, CpFeSiH$_2$-*p*-Tol$^+$).

Photolysis of Cp'Fe(CO)$_2$SiMe$_3$ (2) in the presence of 10 equivalents of p-*TolSiH$_3$*

Cp'Fe(CO)$_2$SiMe$_3$ (**2**) (132 mg, 0.41 mmol) and *p*-TolSiH$_3$ (504 mg, 4.13 mmol) in pentane (30 ml) were irradiated under argon at 0°C for 12 min. After removal of volatile materials *in vacuo*, the residue was subjected to silica gel flash chromatography. Elution with a mixture of hexane and benzene (10 : 1) gave **2** (36 mg, 27% recovery), Cp'Fe(CO)SiMe$_3$(H)SiH$_2$-*p*-Tol (**6**) (65 mg, 0.16 mmol, 39%), Cp'Fe(CO)$_2$SiH$_2$-*p*-Tol (**4c**) (10 mg, 0.027 mmol, 7%), and Cp'Fe(CO)(SiH$_2$-*p*-Tol)$_2$H (**7**) (14 mg, 0.030 mmol, 7%) as pale-yellow crystals. Then elution with a mixture of hexane and ether (4 : 1) afforded a trace amount of *cis*- and *trans*-Cp'$_2$Fe$_2$(CO)$_3$SiH-*p*-Tol (**8**) [16]. MS **6**: m/z 414 (15%, M^+), 413 (38, $M^+ - $H), 385 (12, $M^+ - $H $-$ CO), 340 (50, Cp'Fe(CO)SiH$_2$-*p*-Tol$^+$), 328 (71), 312 (100, Cp'FeSiH$_2$-*p*-Tol$^+$). **4c**: m/z 368 (12%, M^+), 340 (100, $M^+ - $CO), 312 (57, $M^+ - 2$CO). **7**: m/z 462 (20%, M^+), 461 (41, $M^+ - $H), 433 (18, $M^+ - $H $-$ CO), 340 (42, Cp'Fe(CO)SiH$_2$-*p*-Tol$^+$), 313 (58, Cp'Fe(H)SiH$_2$-*p*-Tol$^+$), 312 (100, Cp'FeSiH$_2$-*p*-Tol$^+$).

*Attempted reaction of Cp'Fe(CO)SiMe$_3$(H)SiH$_2$-*p-*Tol (6) with carbon monoxide*

A solution of **6** (20 mg, 0.048 mmol) in C$_6$D$_6$ (0.4 ml) was placed in a 5 mm i.d. NMR tube, and carbon monoxide was bubbled through the solution via a needle at room temperature for 4 h. No change was observed on the ^{1}H NMR spectra periodically recorded during this period.

Photolysis of CpFe(CO)$_2$SiMe$_3$ (1) in the presence of excess ^{t}BuSiH$_3$: isolation of CpFe(CO)$_2$SiH$_2$^{t}Bu (9a)

CpFe(CO)$_2$SiMe$_3$ (**1**) (70 mg, 0.28 mmol) and ^{t}BuSiH$_3$ (250 mg, 2.8 mmol) in pentane (12 ml) were irradiated at 0°C for 10 min. Pentane was removed from the reaction mixture *in vacuo* and the oily residue was subjected to preparative gas chromatography (SE 30, 10%, 1 m). After a small amount of ferrocene and **1** (7 mg, 9% recovery), the third fraction was collected as a yellow oil, which was identified as CpFe(CO)$_2$SiH$_2$^{t}Bu (**9a**) (3 mg, 0.01 mmol, 4%) by comparison of its ^{1}H NMR and IR spectra and GC retention time with an authentic sample prepared by the following procedure.

Preparation of CpFe(CO)$_2$SiH$_2$^{t}Bu (9a)

A THF (60 ml) solution of Na[CpFe(CO)$_2$] prepared from Cp$_2$Fe$_2$(CO)$_4$ (2.00 g, 5.6 mmol) and 1% sodium amalgam (Na 1.03 g, 45 mmol) was cooled to -48°C using an acetonitrile/liquid N$_2$ bath, and ^{t}BuSiH$_2$Cl (2.02 g, 16.5 mmol) in THF (10 ml) was added over a period of 8 min. After the solution had been stirred at -48°C for 1 h and then at room temperature for 16 h, the reaction mixture was worked up in a manner similar to that of the preparation of **4a**. Molecular distillation of the residue (75°C/0.02 Torr) provided CpFe(CO)$_2$SiH$_2$^{t}Bu (**9a**) (2.45

Table 3

Crystal data for $Cp_2Fe_2(CO)_3SiH^tBu$ (**3a**)

Formula	$C_{17}H_{20}Fe_2O_3Si$	$d_{calc.}$ ($g\ cm^{-3}$)	1.54
FW	412.1	$d_{meas.}$ ($g\ cm^{-3}$)	1.52
Crystal system	Triclinic	μ (Mo-K_α) (cm^{-1})	17.5
Space group	$P\bar{1}$	Crystal size (mm)	0.25×0.15×0.1
a (Å)	9.056(2)	Temperature (°C)	23
b (Å)	15.311(3)	2θ range (deg)	3–65
c (Å)	6.769(2)	Scan mode	$\omega-2\theta$
α (deg)	101.84 (2)	ω-scan width (deg)	$1.1+0.50\tan\theta$
β (deg)	104.85(2)	No. of unique data	6483
γ (deg)	85.36(2)	No. of data used with $\lvert F_o \rvert > 3\sigma(F_o)$	4690
V ($Å^3$)	887.5(3)		
Z	2	No. of parameters refined	289
		R [a]	0.035
		R_w [b]	0.036

[a] $R = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$. [b] $R_w = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \Sigma w \lvert F_o \rvert^2]^{1/2}$; $w = [\sigma^2(\lvert F_o \rvert) + aF_o^2]^{-1}$, where $a = 0.005$.

g, 9.3 mmol, 83%) as a yellow oil, m.p. 0°C. MS: m/z 264 (6%, M^+), 236 (100, $M^+ -$ CO), 208 (36, $M^+ -$ 2CO).

Photolysis of $CpFe(CO)_2SiMe_3$ (1) in the presence of excess $TxSiH_3$: isolation of $CpFe(CO)_2SiH_2Tx$ (9b)

In a manner similar to the photolysis of **1** in the presence of $^tBuSiH_3$, **1** (105 mg, 0.42 mmol) and $TxSiH_3$ (248 mg, 2.1 mmol) in pentane (14 ml) was irradiated at 0°C for 15 min. After removal of the solvent, preparative GC of the residue afforded $CpFe(CO)_2SiH_2Tx$ (**9b**) (6 mg, 0.02 mmol, 5%) as a yellow oil. MS: m/z 292 (15%, M^+), 264 (100, $M^+ -$ CO).

Photolysis of a mixture of $CpFe(CO)_2SiH_2{}^tBu$ (9a) and $CpFe(CO)_2SiMe_3$ (1)

$CpFe(CO)_2SiH_2{}^tBu$ (**9a**) (150 mg, 0.57 mmol) and **1** (130 mg, 0.52 mmol) in pentane (10 ml) were irradiated at 0°C for 4.5 h. Crystals precipitated from the reaction mixture were collected by filtration to give red crystals of $Cp_2Fe_2(CO)_3SiH^tBu$ (**3a**) (149 mg, 0.36 mmol, 69%).

X-Ray crystal structure determination of 3a

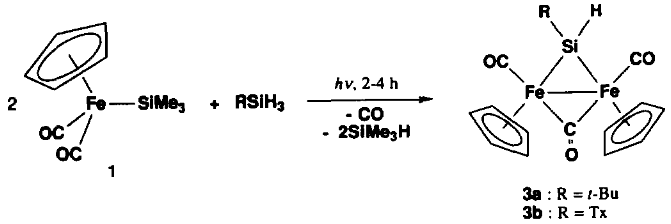
Diffraction measurements were made on a Rigaku AFC-6A four-circle diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) at 23°C. Crystallographic data are listed in Table 3. The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method using individual anisotropic thermal parameters for the non-hydrogen atoms. The positions of all hydrogen atoms were derived by difference-Fourier synthesis and refined applying isotropic thermal parameters. The final atomic parameters and temperature factors of non-hydrogen atoms are listed in Table 4.

The calculations were performed on a Nippon Electric Co. ACOS-2000 computer system at the Computer Center of Tohoku University using the Universal Crystallographic Computation Program System UNICS III [17].

Results and discussion

Synthesis and characterization of silylene-bridged diiron complexes

Irradiation of $CpFe(CO)_2SiMe_3$ (**1**) in the presence of tert-alkyltrihydrosilane, $^tBuSiH_3$ or $TxSiH_3$, in pentane or hexane for several hours afforded a silylene-bridged diiron complex $Cp_2Fe_2(CO)_3SiHR$ (**3a**, R = ^{t}Bu; **3b**, R = Tx) in good yield (eq. 1). When this reaction was traced by ^1H NMR spectroscopy in C_6D_6, a strong doublet and a decet attributable to Me_3SiH were observed. The only known complex with the same framework as **3** is $Cp_2Fe_2(CO)_3SiHMe$ synthesized by Malisch *et al.* via a completely different route [18].



(1)

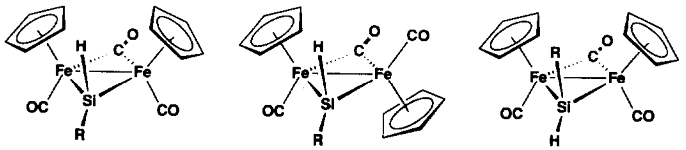
Three geometric isomers are possible for **3** as shown in Fig. 1. In fact, a related complex $Cp_2Fe_2(CO)_3SiHMe$ [18] and its carbon and germanium analogues, $Cp_2Fe_2(CO)_3CHMe$ [19] and $Cp_2Fe_2(CO)_3GeMe_2$ [20], are known to exist as a

Table 4

Final atomic parameters and temperature factors of the non-hydrogen atoms of $Cp_2Fe_2(CO)_3SiH^tBu$ (**3a**) [a]

Atom	*x*	*y*	*z*	B_{eq}
Fe(1)	2330.8(3)	1671.6(2)	3367.9(4)	2.6
Fe(2)	5112.0(3)	2259.9(2)	4539.4(4)	2.5
Si	3082.5(7)	2896.5(4)	2523.5(9)	2.7
O(1)	963(2)	2744(2)	6485(3)	5.2
O(2)	5050(3)	3534(1)	8302(3)	5.3
O(3)	4406(2)	978(1)	6739(3)	3.8
C(1)	1100(4)	503(2)	2682(5)	4.7
C(2)	2386(4)	309(2)	1891(5)	4.6
C(3)	2301(3)	854(2)	431(4)	4.7
C(4)	953(4)	1374(2)	304(5)	4.8
C(5)	209(3)	1162(2)	1725(5)	4.8
C(6)	7372(3)	1769(2)	5313(4)	4.1
C(7)	6555(3)	1199(2)	3545(5)	4.3
C(8)	6026(3)	1699(2)	1966(4)	4.8
C(9)	6526(3)	2577(2)	2759(5)	4.7
C(10)	7333(3)	2615(2)	4829(5)	4.4
C(11)	1541(2)	2342(2)	5262(4)	3.4
C(12)	4999(3)	3037(2)	6765(4)	3.4
C(13)	4085(2)	1437(1)	5478(3)	2.8
C(14)	2167(3)	4072(2)	2902(5)	4.0
C(15)	479(4)	3976(2)	1721(6)	5.7
C(16)	2262(5)	4533(2)	5124(6)	6.0
C(17)	2915(6)	4629(2)	1836(7)	7.0

[a] Positional parameters are multiplied by 10^4. Thermal parameters are given by the equivalent temperature factors ($Å^2$).



cis (H) *trans* *cis* (R)

Fig. 1. Three possible geometric isomers for $Cp_2Fe_2(CO)_3SiHR$ (**3**).

mixture of *cis* and *trans* isomers in solution. In the ^1H NMR spectrum of **3a**, however, only three singlets appear, assignable to ^tBu, Cp, and Si–H groups. Thus it is obvious that **3a** exists as only one geometric isomer in solution. Moreover, this isomer adopts a *cis*-geometry because only one Cp signal is observed both in CS_2 and in C_6D_6. The ^{13}C NMR spectrum and the IR spectrum also supported this identification. In the latter spectrum, as expected, the terminal CO stretching band assigned to the symmetric vibration (1950 cm^{-1}) is stronger than its antisymmetric counterpart. In a similar manner, the ^1H NMR and IR spectra of **3b** indicate that **3b** exists only as the *cis*-isomer in solution. As will be shown below, the X-ray crystal structure analysis of **3a** unambiguously revealed that the exclusive isomer is the least sterically hindered *cis*(H)-isomer.

A notable spectroscopic characteristic of **3a** is that the ^{29}Si NMR spectrum of **3a** shows its signal at remarkably low field (254.4 ppm). This value is in sharp contrast to that for the closely related silylene-bridged diiron complex with no Fe–Fe bond, $[Cp(CO)_2Fe]_2(\mu\text{-}SiHMe)$ (62.8 ppm) [18]. The ^{29}Si signals of halogenated derivatives of **3a**, $Cp_2Fe_2(CO)_3SiX^tBu$ (**10a**, X = Cl; **10b**, X = Br; **10c**, X = I), which we reported previously [21], were found to appear at even lower field (**10a**, 276.3; **10b**, 284.8; **10c**, 289.1 ppm). There are only a few complexes which are known to show signals at a similarly low field, in which, except for Tilley's cationic mononuclear silylene complexes [22], all silicon-containing moieties bridge across metal–metal bonds, *i.e.*, $Cp(CO)_2FeSiCo_3(CO)_9$, 247.8 ppm [5]; $Fe_2(CO)_8(\mu\text{-}SiMe_2)$, 173 ppm [23]; $Cp_2Fe_2(CO)_3SiMe(SiMe_3)$, 232.1–245.5 ppm [24]; $Cp_2Fe_2(CO)_2(\mu\text{-}SiMe_2)_2$, 229.5, 243.8 ppm [24]; and $Cp'_2Fe_2(CO)_3SiH$-*p*-Tol (**8**), *cis* 250.4, *trans* 235.5 ppm [16]. These facts imply that the bonding between the silicon atom and the polynuclear fragment in these complexes is not a combination of simple σ-bonds but a combination of σ-donation from the silicon atom to the polynuclear fragment and a π-interaction between them. The latter bonding model has been developed to explain the bonding in μ-carbene complexes [25].

The ^1H NMR signal for Si–H in **3a** appears at unusually low field (7.23 ppm). Moreover, in the IR spectrum of **3a**, both terminal and bridging carbonyl stretching bands appear at lower wavenumber region (Table 1) than those of $Cp_2Fe_2(CO)_4$ ($\nu(CO_{term})$ 1983, 1958, 1940; $\nu(CO_{brid})$ 1770 cm^{-1}) [26]. These spectroscopic data seem to reflect the very strong σ-donation and relatively weak π-back donation between the μ-silylene ligand and the diiron moiety in **3a**.

Crystal structure of $Cp_2Fe_2(CO)_3SiH^tBu$ (3a)

X-Ray crystal structure analysis was carried out for a crystal formed at 0°C from the photochemical reaction mixture in pentane. The solved structure is shown in Fig. 2. Selected bond distances and angles are listed in Table 5. The two Cp rings

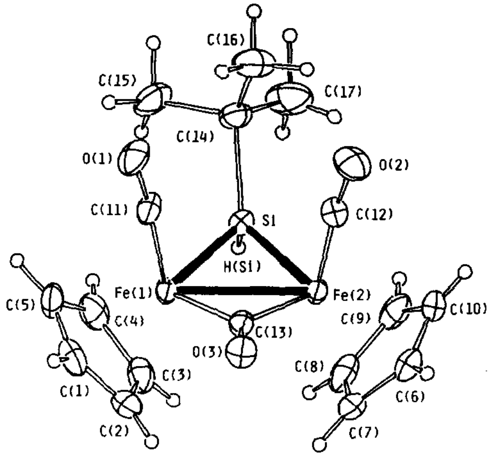


Fig. 2. ORTEP drawing of $Cp_2Fe_2(CO)_3SiH^tBu$ (**3a**) with thermal ellipsoids at the 30% probability level.

are mutually *cis*, and the Cp rings and the bulky ^{t}Bu group are located on the opposite sides of the four-membered ring defined by Fe(1), Si, Fe(2), and C(13). Interestingly, for a closely related complex, $Cp_2Fe_2(CO)_3SiMe(SiMe_3)$, the major isomer was found to be *cis*-($SiMe_3$) [24]. In the latter case, the very long Si–$SiMe_3$ distance (2.371(1) Å) greatly decreases the steric repulsion between the Me_3Si group and the Cp rings. The angle between the C(14)–Si bond and the Fe_2Si plane is markedly enlarged to 140.35(10)° from the calculated value for the ideal tetrahedron (125.27°). This distortion is due to the steric repulsion between the ^{t}Bu group and two terminal CO ligands. In fact, the distances of C(16) ··· O(1)

Table 5

Selected bond distances (Å) and angles (deg) for $Cp_2Fe_2(CO)_3SiH^tBu$ (**3a**)

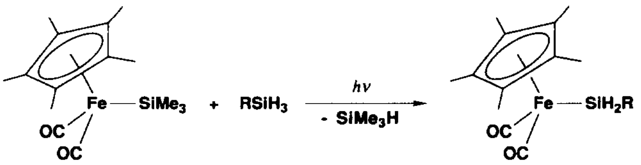
Distances			
Fe(1)–Fe(2)	2.614(1)	Fe(1)–Si	2.270(1)
Fe(2)–Si	2.272(1)	Fe(1)–C(11)	1.738(3)
Fe(2)–C(12)	1.738(2)	Fe(1)–C(13)	1.910(2)
Fe(2)–C(13)	1.918(3)	C(11)–O(1)	1.140(4)
C(12)–O(2)	1.149(4)	C(13)–O(3)	1.180(3)
Si–H(Si)	1.34(4)	Si–C(14)	1.916(3)
C(14)–C(15)	1.536(5)	C(14)–C(16)	1.509(5)
C(14)–C(17)	1.518(6)		
Angles			
Fe(1)–Fe(2)–Si	54.83(2)	Fe(2)–Fe(1)–Si	54.89(2)
Fe(1)–Si–Fe(2)	70.28(2)	Fe(1)–Fe(2)–C(13)	46.79(8)
Fe(2)–Fe(1)–C(13)	47.05(6)	Fe(1)–C(13)–Fe(2)	86.2(1)
Fe(1)–Si–C(14)	126.5(1)	Fe(2)–Si–C(14)	131.4(1)
Fe(1)–Si–H(Si)	114(1)	Fe(2)–Si–H(Si)	117(4)
Fe(1)–C(11)–O(1)	176.0(3)	Fe(2)–C(12)–O(2)	174.3(3)
Fe(1)–C(13)–O(3)	137.1(2)	Fe(2)–C(13)–O(3)	136.7(2)
C(14)–Si–H(Si)	98(1)	Si–C(14)–C(15)	106.2(2)
Si–C(14)–C(16)	116.1(3)	Si–C(14)–C(17)	107.1(3)

and C(16) · · · O(2) (3.443(5) and 3.358(4) Å, respectively) are nearly equal to the sum of the effective van der Waals radii of methyl group and oxygen atom (3.4 Å). The terminal CO groups are bent away from the ${}^tBu$ group (Fe(1)–C(11)–O(1) 176.0(3)° and Fe(2)–C(12)–O(2) 174.3(3)°) owing to this steric repulsion.

The Fe–Si bonds (2.270(1) and 2.272(1) Å) are shorter than normal Fe–Si single bonds in alkyl- or aryl-silyl complexes [27,28], and almost equal to those in halosilyl complexes [28–30]. The Fe–Fe bond (2.614(1) Å) is significantly longer than those in the carbon-bridged analogues $Cp_2Fe_2(CO)_3(\mu\text{-}Y)$ (Y = CO, 2.531(2) [31]; C=N–Ph, 2.530 [32]; CHMe, 2.520(2) [33]; and C=C(Ph)CH_2Ph, 2.5104(5) Å [34]), but slightly shorter than that of $Cp_2Fe_2(CO)_3(\mu\text{-}GeMe_2)$ (2.628(1) Å) [19]. The Fe–Fe distance seems to correlate with the size of the bridging atom, *i.e.*, C < Si < Ge.

Photochemistry of pentamethylcyclopentadienyl derivative Cp′Fe(CO)₂SiMe₃ (2)

In contrast with the reaction of non-substituted Cp complexes, the photolysis of the pentamethylcyclopentadienyl (Cp′) complex $Cp'Fe(CO)_2SiMe_3$ (**2**) in the presence of tert-alkylsilane provided a mononuclear complex, **4**, in fair yield (eq. 2). The reaction was monitored by ${}^1H$ NMR spectroscopy, which showed no signals assignable to dinuclear complexes analogues to **3** even when this reaction was carried out in the molar ratio of **2**/${}^tBuSiH_3$ of 2:1.

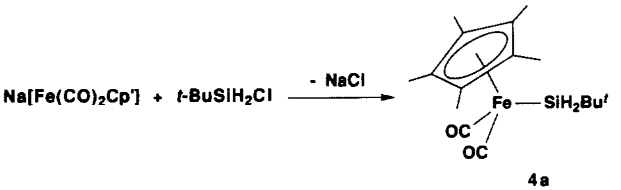


2

4a : R = *t*-Bu
4b : R = Tx

(2)

The products were characterized by usual analytical and spectral data (Tables 1 and 2) and **4a** was further identified by comparison with the authentic sample prepared via the following route (eq. 3).



4a

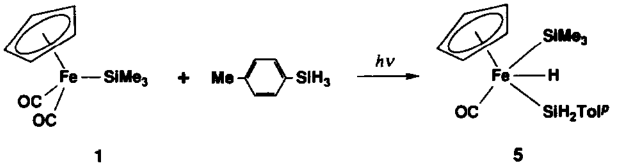
(3)

The exclusive formation of **4** can be ascribed to the bulkiness of the Cp′ ligand and the ${}^tBu$ group which prevents the second Cp′Fe(CO) moiety from being introduced into the same molecule. The isolation of **4a** strongly suggests that **4a** is a kinetically stabilized form of an intermediate in the formation of silylene-bridged diiron complexes.

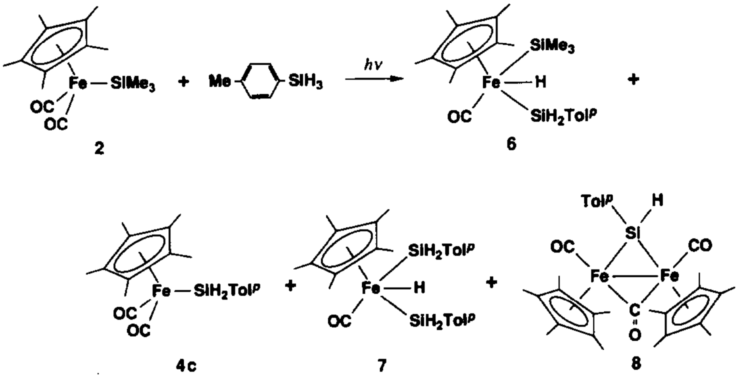
Photochemistry of 1 and 2 in the presence of p-*TolSiH₃*

In order to investigate the influence of the trihydrosilane substituent, we examined the photolysis of **1** and **2** in the presence of excess *p*-$TolSiH_3$, which is significantly different in the steric and electronic properties from tert-alkylsilanes.

In these cases, interestingly, the main product was neither the silylene-bridged dinuclear complex nor the mononuclear monosilyl complex but a hydridobis(silyl) complex Cp*Fe(CO)SiMe$_3$(H)SiH$_2$-p-Tol (**5**, Cp* = Cp; **6**, Cp* = Cp′) (eqs. 4, 5). In the case of the photolysis of **2**, appreciable amounts of **4c**, **7**, and a trace amount of Cp′$_2$Fe$_2$(CO)$_3$SiH-p-Tol (**8**; a *cis–trans* mixture) [16] were isolated in addition to **6** (eq. 5).



(4)



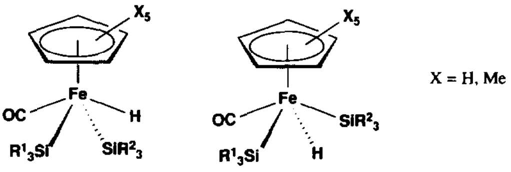
(5)

Surprisingly, **8** became the major product upon decreasing the amount of p-TolSiH$_3$ and making the irradiation time much longer [16]. This result illustrates the importance of steric effects in the selection of final products.

The formation of **5** and **6** can be rationalized by the photodissociation of CO followed by oxidative addition of p-TolSiH$_3$ to the 16-electron intermediate. Then if reductive elimination of Me$_3$SiH occurs subsequently from **6**, another 16-electron intermediate, Cp′Fe(CO)SiH$_2$-p-Tol, would form, and oxidative addition of CO or p-TolSiH$_3$ to this intermediate would give **4c** or **7**, respectively. The low yields of **4c** and **7**, however, suggest that the reductive elimination of Me$_3$SiH from **6** is not very efficient. Furthermore, CO did not react with **6** in the dark at room temperature on the timescale of the photoreaction. Therefore, the formation of **4c** may be accelerated by photoirradiation, a reaction also observed by Maitlis *et al.* who reported an example of photochemically accelerated reductive elimination of hydrosilane from a rhodium complex [35].

In the case of alkylsilyliron complexes, Randolph and Wrighton [9] reported that the photolysis of **2** in the presence of R′$_3$SiH (R′ = Me or Et) yields Cp′Fe(CO)SiMe$_3$(H)SiR′$_3$, but that this complex is labile with respect to loss of R′$_3$SiH in the absence of R′$_3$SiH and converts to Cp′Fe(CO)$_2$SiR′$_3$ (R′ = Me and Et) when treated with CO in the dark. In the photolysis of **2** in the presence of ^{t}BuSiH$_3$ or TxSiH$_3$ (see above), the complexes corresponding to **5** or **6** were not isolated. Obviously, the stability of the complex with structure Cp*Fe(CO)-SiR$^1_3$(H)SiR$^2_3$ is strongly dependent on the electronic properties of the substituents on the silyl groups. There have been three isolated complexes of this type so far, *i.e*, CpFe(CO)(SiCl$_3$)$_2$H [29], CpFe(CO)(SiF$_2$Me)$_2$H [27], and CpFe(CO)(SiMe$_2$Ph)$_2$H [28], all of which have electron withdrawing groups on their silyl groups. It is suggested from thermochemistry [36] and photoelectron spectroscopy [37] that the addition product of R″$_3$SiH to the metal center of certain metal carbonyl complexes becomes more stable when R″ is an electron-withdrawing halogen or aryl group than when R″ is an alkyl group. This effect may be responsible for stabilizing these complexes and also **5**, **6**, and **7**.

For the complex Cp*Fe(CO)SiR$^1_3$(H)SiR$^2_3$, the following two geometrical isomers are possible:

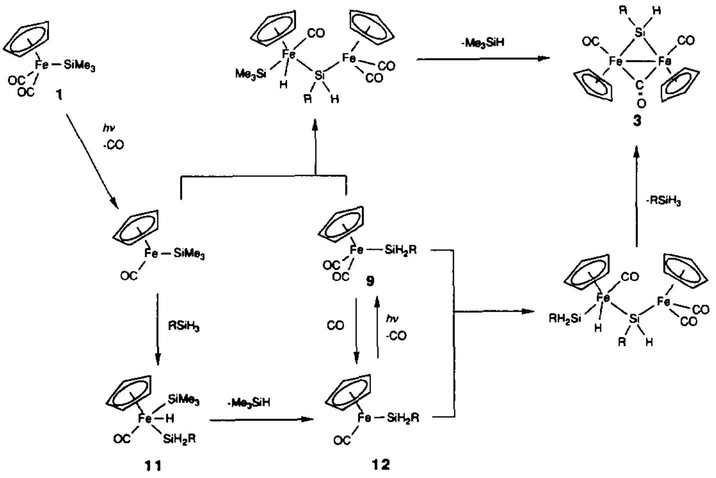


trans *cis*

All of the above-mentioned complexes [9,27–29] are known to be *trans*-isomers. In the cases of **5**, **6**, and **7**, the ^{1}H NMR spectra indicate that each of these complexes exists as only one isomer. The spectrum of **7**, showing only one set of signals for the *p*-tolyl group, is consistent with the formulation of **7** as a *trans* isomer. Taking the bulkiness of two silyl groups into consideration, complexes **5** and **6** are also presumed to be *trans*-isomers. Two sets of Si–H signals are observed in each of the ^{1}H NMR spectra of **5** and **6**, because the two hydrogens on SiH$_2$-*p*-Tol groups in these complexes are diastereotopic.

Mechanism for the formation of silylene-bridged diiron complexes

The silyl group exchange between trialkylhydrosilane and Cp′Fe(CO)$_2$SiR$_3$ or (OC)$_4$CoSiR$_3$ has been thoroughly studied by Wrighton's group [7,9]. They proposed a mechanism involving the following four steps: (1) photoinduced CO loss

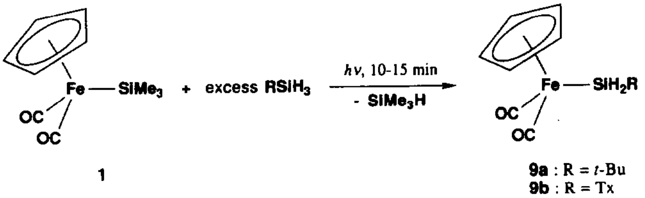


Scheme 1.

from the carbonyl complex to generate a coordinatively unsaturated 16-electron intermediate; (ii) oxidative addition of hydrosilane to the 16-electron intermediate to form a hydridobis(silyl) complex; (iii) reductive elimination of R_3SiH to give a 16-electron intermediate; and (iv) recombination of CO with the intermediate to produce a silyl-exchanged complex.

In the photochemistry of $CpFe(CO)_2SiMe_3$ (**1**) with $^tBuSiH_3$ or $TxSiH_3$, because these silanes have more than one Si–H bond, the above-mentioned process can be repeated twice. A possible mechanism is shown in Scheme 1. It is reasonable to assume that the reaction mechanism would not alter by exchanging **1** for $Cp'Fe(CO)_2SiMe_3$ (**2**) and/or by exchanging $^tBuSiH_3$ and $TxSiH_3$ for *p*-$TolSiH_3$. On this assumption, the isolation of complexes **4a**, **4b**, **5**, **6**, and **7** strongly supports this mechanism. Namely, **4a** and **4b** correspond to **9**, and **5** and **6** correspond to **11**. In addition, **7** can be regarded as the product of oxidative addition of $RSiH_3$ to an intermediate **12**.

This mechanism was further confirmed by the isolation of **9a** and **9b** themselves. Irradiation of **1** in the presence of excess $^tBuSiH_3$ or $TxSiH_3$ for a short time (10–15 min) provided **9a** and **9b** in low yields (eq. 6).



(6)

Furthermore, the photolysis of a mixture of **9a** and **1** gave **3a** in high yield. This result offers good evidence for the intermediacy of **9a** in the formation of **3a**.

Conclusions

Photolysis of $CpFe(CO)_2SiMe_3$ in the presence of tert-alkylsilanes $RSiH_3$ ($R = {}^tBu$, thexyl) afforded silylene-bridged diiron complexes $Cp_2Fe_2(CO)_3(\mu\text{-}SiHR)$ in good yields. The products adopt the least hindered *cis*(H)-form exclusively among the three possible geometric isomers. The crystal structure of $Cp_2Fe_2(CO)_3(\mu\text{-}SiH^tBu)$ was determined for the first time with respect to this type of silylene-bridged diiron complex. The short Fe–Si bonds and the remarkable downfield shift of the ^{29}Si NMR signal suggest that the bridging silylene acts as a σ-donor/π-acceptor ligand in bonding to the Fe_2 moiety.

The photolysis of the bulky pentamethylcyclopentadienyl complex $Cp'Fe(CO)_2SiMe_3$ in the presence of tert-alkylsilanes yielded mononuclear complexes $Cp'Fe(CO)_2SiH_2R$ without the formation of dinuclear complexes. Using *p*-$TolSiH_3$ instead of tert-alkylsilanes, the main photolysis product was $Cp^*Fe(CO)SiMe_3(H)SiH_2R$ ($Cp^* = Cp, Cp'$). A proposed mechanism for the formation of silylene-bridged diiron complex based on these observations (Scheme 1) includes a process of oxidative addition and subsequent reductive elimination of hydrosilane at a coordinatively unsaturated 16-electron species which is repeated twice. This mechanism was further confirmed by the isolation of an intermediate,

$CpFe(CO)_2SiH_2R$, from the photolysis mixture and subsequent conversion to the silylene-bridged diiron complex.

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