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Mechanistic Study on the Photochemical Conversion of Disilanyliron(II) Complexes to Monosilyliron(II) Complexes

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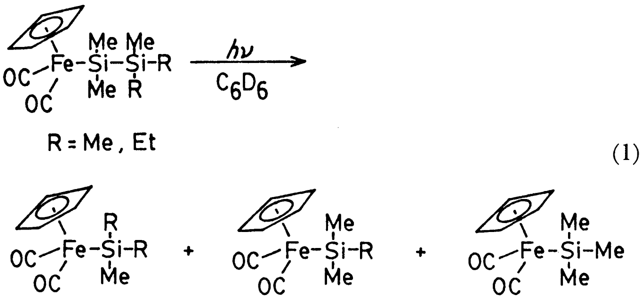
Photolysis of a C_6D_6 solution of $CpFe(CO)_2SiMe_2SiMe_3$ ($Cp=\eta^5$-C_5H_5) or $(MeCp)Fe(CO)_2SiMe_2SiMe_3$ ($MeCp=\eta^5$-C_5H_4Me) resulted in the formation of monosilyl derivative, $CpFe(CO)_2SiMe_3$ or $(MeCp)Fe(CO)_2SiMe_3$ in 64 or 59% yield, respectively, together with small quantities of ferrocene and $Cp_2Fe_2(CO)_4$ or their methylated derivatives. The yield of $CpFe(CO)_2SiMe_3$ increased to 88% when the photolysis was carried out under a carbon monoxide atmosphere, while decreased to 22% when argon was vigorously bubbled through the reaction mixture. These results are consistent with a mechanism involving dissociation and recombination of a carbonyl ligand which are common processes in photoreactions of transition-metal carbonyl derivatives. Dimethylsilylene moiety released during the photolysis was tried to be trapped with a hydrosilane, diene, and cyclotrisiloxane, but none of the expected products from the trapping reactions was detected, even in a trace amount. Photolysis of $CpFe(CO)_2SiMe_2SiMeEt_2$ afforded, accompanying alkyl migration between silicon atoms, $CpFe(CO)_2SiMeEt_2$, $CpFe(CO)_2SiMe_2Et$, and $CpFe(CO)_2SiMe_3$ in 26, 33, and 4% yields, respectively. Photolysis of a 1 : 1 mixture of $CpFe(CO)_2SiMe_2SiMeEt_2$ and $(MeCp)Fe(CO)_2SiMe_2SiMe_3$ provided only products expected from intramolecular alkyl migration mechanism. A possible mechanism involving silyl(silylene)iron intermediates is proposed to explain these results.

Divalent silicon species, silylene, is important as a key intermediate for many reactions containing silicon compounds.[1,2] Its existence is well established by many trapping reactions as well as low-temperature matrix isolation techniques.[3–5] However, the only known divalent silicon species stable at room temperature are decamethylsilicocene, $(\eta^5$-$C_5Me_5)_2Si$,[6] and a metallocarborane, $[(Me_3Si)_2C_2B_4H_4]Si$,[7] and no usual σ-substituted silylene has been isolated so far under normal conditions because of its lability and instability. Carbene is also a very reactive species, but it is well known to be stabilized by coordination to a metal atom and becomes isolable.[8] Therefore, we can expect that silylene is also stabilized as a ligand on a transition metal.

There is no genuine silylene complex isolated at present,[9] although some neutral[10,11] and cationic[12] base-stabilized silylene complexes have been reported. There are also several reactions in which silylene complexes are proposed as reactive intermediates during the courses of reactions; e.g. decomposition reactions of silicon containing organometallic complexes,[13,14] metal-catalyzed reactions of organosilicon compounds,[15] and reactions of transition-metal ions with methylsilanes in gas phase.[16]

Recently, Pannell et al. suggested the formation of novel silyl(silylene)iron complexes as intermediates in the photochemical conversion of $CpFe(CO)_2SiMe_2SiPh_3$ to $CpFe(CO)_2SiPh_nMe_{3-n}$ (n=1—3).[17] Our independent study on the photoreaction of $CpFe(CO)_2SiMe_2SiMeR_2$ (R=Me, Et) (Eq. 1) led us to almost the same mechanism which we reported previously in a preliminary communication.[18] We now give the evidence for the intramolecular mechanism for this reaction as well as the full detail of the mechanistic study.



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Experimental

General Details. All experiments were performed under a nitrogen atmosphere by using standard Schlenk techniques. Hexane, pentane, and tetrahydrofuran (THF) were reagent grade and were freshly distilled from sodium–benzophenone ketyl under nitrogen. Chlorotrimethylsilane, dichlorodimethylsilane, and ethyl bromide were obtained from Wako Pure Chemical Industries, Ltd. and distilled under nitrogen before use. 2,3-Dimethyl-1,3-butadiene was obtained from Tokyo Chemical Industry Co., Ltd. and used after distillation. Chloropentamethyldisilane,[19] 1-chloro-2,2-diethyl-1,1,2-trimethyldisilane,[20] chlorodiethylmethylsilane,[21] diethylmethylsilane,[22] $Cp_2Fe_2(CO)_4$,[23] $(MeCp)_2Fe_2(CO)_4$,[23] $CpFe(CO)_2SiMe_3$ (**2a**),[24] $CpFe(CO)_2SiMe_2SiMe_3$ (**1a**),[25] $(MeCp)Fe(CO)_2SiMe_3$ (**2b**),[26] and hexamethylcyclotrisiloxane[27] were prepared according to the published procedures.

Measurements. Electronic spectra were recorded on a Hitachi 330 or a Shimadzu UV-260 spectrophotometer using a quartz cell of 1 cm optical path length. Infrared spectra were recorded on a JASCO IRA-1 spectrophotometer, and gas chromatography-mass spectra (70 eV) on a JEOL JMS-D300 mass spectrometer. NMR spectra were measured on a JEOL FX-90Q Fourier-transform spectrometer in C_6D_6 at 25 °C. Gas chromatograms were obtained on a Hitachi 263-30 (FID) with a glass column (1 m) packed with 10% SE-30 using nitrogen as a carrier gas. The measurements of HPLC were carried out using a Hitachi 655 with a Gasukuro Kogyo UNISIL Q-30-5 silica-gel column (4.6 mm×250 mm), a

Hitachi 638-41 variable wavelength UV detector, and a Hitachi 655-61 data processor.

Preparation of Compounds. $CpFe(CO)_2SiMe_2SiMeEt_2$ (1c). A solution of $Na[FeCp(CO)_2]$ (5.2 mmol) in 15 cm^3 of THF was added dropwise over 30 min to a solution of 1-chloro-2,2-diethyl-1,1,2-trimethyldisilane (1.05 g, 2.6 mmol) in THF (15 cm^3) with vigorous stirring at room temperature. After the solution was stirred for additional 18 h, solvent was removed from the reaction mixture under reduced pressure and the dark brown residue was extracted with three 10 cm^3 portions of hexane. The extracts were filtered through a Celite pad, and the filtrates were combined and concentrated. Molecular distillation of the dark red residue at 0.15 Torr[†] and 80 °C yielded an orange oil of **1c** (1.29 g, 73%); ^1H NMR (C_6D_6) δ=4.14 (5H, s, Cp), 1.2—0.6 (10H, m, Et), 0.57 (6H, s, Me), 0.14 (3H, s, Me); ^{13}C NMR (C_6D_6) δ=215.9 (CO), 83.1 (Cp), 8.5 (CH_3 of Et), 6.4 (CH_2 of Et), 4.5 (Me), −5.2 (Me); MS *m/z* 336 (M^+, 16.3), 235 (34.0), 207 (15.6), 179 (12.5), 159 (100), 131 (95.2), 121 (24.0). Found: C, 50.15; H, 7.25%. Calcd for $C_{14}H_{24}FeO_2Si_2$: C, 50.00; H, 7.19%.

$CpFe(CO)_2SiMeEt_2$ (2c). In a similar manner, the reaction of $Et_2MeSiCl$ (0.73 g, 5.3 mmol) with $Na[FeCp(CO)_2]$ (5.2 mmol) in THF followed by molecular distillation at 0.02 Torr and 80°C gave an orange oil of **2c** (0.95 g, 68%); ^1H NHR (C_6D_6) δ=4.07 (5H, s, Cp), 1.3—0.7 (10H, m, Et), 0.44 (3H, s, Me); ^{13}C NMR (C_6D_6) δ=216.2 (CO), 83.2 (Cp), 14.4 (CH_2), 9.4 (Me), 2.2 (Me); MS *m/z* 278 (M^+, 10.8), 250 (4.8), 249 (3.6), 220 (9.3), 192 (24.9), 164 (11.6), 121 (11.8), 101 (48.0), 93 (23.3), 73 (100). Found: C, 52.05; H, 6.58%. Calcd for $C_{12}H_{18}FeO_2Si$: C, 51.81; H, 6.52%.

$CpFe(CO)_2SiMe_2Et$ (2d). To a solution of dichlorodimethylsilane (10.9 g, 84.5 mmol) in THF (50 cm^3) was added dropwise over 3 h a solution of ethylmagnesium bromide prepared from magnesium ribbon (2.48 g, 0.102 mol) and ethyl bromide (11.0 g, 0.101 mol) in THF (50 cm^3). After the reaction mixture was stirred at room temperature for 24 h, a solution of $Na[FeCp(CO)_2]$ (56 mmol) in THF (150 cm^3) was added dropwise over 2 h to the reaction mixture. The resulting mixture was stirred at room temperature for additional 12 h and then THF was removed in vacuo. To the reddish brown residue was added 200 cm^3 of hexane and the slurry was filtered through a Celite pad. After evaporation of hexane from the filtrate, the resultant dark red oil was purified by molecular distillation at 0.3 Torr and 90 °C yielding an orange oil of **2d** (10.1 g, 68%); ^1H NMR (C_6D_6) δ=4.04 (5H, s, Cp), 1.2—0.7 (5H, m, Et), 0.45 (6H, s, Me); ^{13}C NMR (C_6D_6) δ=216.1 (CO), 83.3 (Cp), 16.4 (CH_2), 9.2 (Me), 4.8 (Me); MS *m/z* 264 (M^+, 27.1), 236 (16.5), 208 (10.0), 206 (34.5), 180 (41.6), 178 (23.3), 121 (26.6), 93 (27.6), 87 (77.4), 59 (100). Found: C, 49.93; H, 6.06%. Calcd for $C_{11}H_{16}FeO_2Si$: C, 50.02; H, 6.11%.

$(MeCp)Fe(CO)_2SiMe_2SiMe_3$ (1b). This compound was prepared by a procedure similar to that of $CpFe(CO)_2SiMe_2SiMeEt_2$ (**1c**). $Me_3SiSiMe_2Cl$ (1.75 g, 10.5 mmol) and $Na[Fe(MeCp)(CO)_2]$ (5.24 mmol) were used as starting materials, and after the usual work-up, molecular distillation at 0.09 Torr and 65 °C gave an orange oil of **1b** (2.42 g, 72%): ^1H NMR (C_6D_6) δ=4.2—3.9 (4H, m, ring protons of MeCp), 1.52 (3H, s, Me of MeCp), 0.55 (6H, s, Me), 0.23 (9H, s, Me); ^{13}C NMR (C_6D_6) δ=216.3 (CO), 101.0 (ring carbon of MeCp), 13.2 (Me), 3.5 (Me), 0.5 (Me); MS *m/z* 322 (M^+, 11.0), 294 (5.0), 264 (11.4), 249 (45.4), 193 (11.3), 131 (100), 73 (50.0). Found: C, 48.20; H, 6.73%. Calcd for $C_{13}H_{22}FeO_2Si_2$: C, 48.45: H, 6.88%.

The IR and electronic spectral data of all disilanyl- and silyliron complexes which were used in this work were listed in Table 1.

Photolysis. Unless otherwise noted, photolysis was carried out as follows: Iron complex(es) and, in some cases, a trapping agent were placed in a Pyrex NMR sample tube (5 mm o.d.) and dissolved in deoxygenated C_6D_6. It was then immersed in the water at room temperature and irradiated with a 450 W medium pressure Hg arc lamp (Ushio UV-450) placed in a water-cooled, quartz jacket. The distance between the light source and the sample tube was about 3 cm. A ^1H NMR spectrum or gas chromatogram of the reaction mixture was taken periodically to monitor the reaction. Identification of products was accomplished by taking gas chromatograms, gas chromatography-mass spectra, ^1H NMR spectra and, in some cases, high performance liquid chromatograms of the reaction mixture and comparing them with the authentic samples prepared by the independent methods. Yields of products were determined by gas chromatography with dodecane as an internal standard and calculated for the consumed starting materials.

Results and Discussion

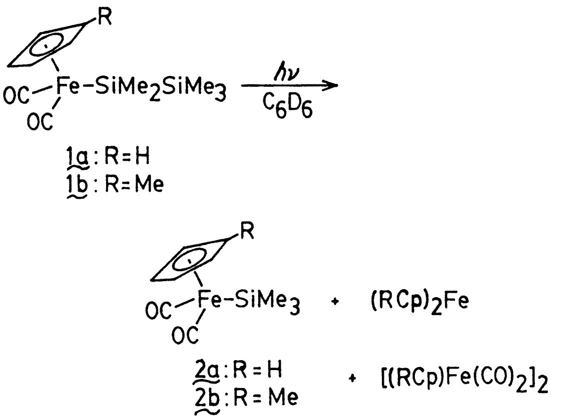
Photolyses of $CpFe(CO)_2SiMe_2SiMe_3$ (1a) and $(MeCp)Fe(CO)_2SiMe_2SiMe_3$ (1b). Irradiation of a solution of disilanyl complex $CpFe(CO)_2SiMe_2SiMe_3$ (**1a**) with a 450 W medium pressure Hg lamp in a Pyrex tube for 7 min at room temperature consumed 80% of **1a** and gave monosilyl complex $CpFe(CO)_2SiMe_3$ (**2a**) in 64% yield together with ferrocene (4%) and $Cp_2Fe_2(CO)_4$.[18] Similarly, the photolysis of methylcyclopentadienyl derivative $(MeCp)Fe(CO)_2SiMe_2SiMe_3$ (**1b**) for 3 min yielded $(MeCp)Fe(CO)_2$-

Table 1. IR and UV-Vis Spectral Data for Relevant Complexes

Complex	ν_{CO}/cm^{-1} (neat)		λ_{max} (hexane)/nm ($\varepsilon/(mol^{-1}\,dm^3\,cm^{-1})$)	
$CpFe(CO)_2SiMe_2SiMe_3$ (**1a**)	1970	1920	284.0 (5000)	330sh (1900)
$CpFe(CO)_2SiMe_2SiMeEt_2$ (**1c**)	1990	1934	285.6 (5100)	330sh (1900)
$(MeCp)Fe(CO)_2SiMe_2SiMe_3$ (**1b**)	1985	1930	285.4 (4900)	330sh (1900)
$CpFe(CO)_2SiMe_3$ (**2a**)	1970	1910	270sh (3700)	322.0 (1600)
$CpFe(CO)_2SiMe_2Et$ (**2d**)	1986	1925		
$CpFe(CO)_2SiMeEt_2$ (**2c**)	1988	1929		
$(MeCp)Fe(CO)_2SiMe_3$ (**2b**)	1990	1932		

[†] 1 Torr≈133.322 Pa.

$SiMe_3$ (2b) (59%), 1,1′-dimethylferrocene (11%) and $[(MeCp)Fe(CO)_2]_2$ after 64% of **1b** was consumed (Eq 2).



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The reactions were monitored either by ^1H NMR spectroscopy or by gas chromatography. Figures 1 and 2 show the changes of ^1H NMR spectrum and gas chromatogram of the reaction mixture of **1a**, respectively. It can be seen that the ^1H NMR signals or the GC peak of **1a** is weakened and those of **2a** newly appear instead. The absence of well-resolved Si-Me signals except that of **2a** on the ^1H NMR spectrum of the final reaction mixture (conversion: 98%) implies that a dimethylsilylene unit, which is considered to be extruded from **1a**, forms a number of oligomeric and/or polymeric products. Results similar to this are also observed for the photolysis of **1b**.

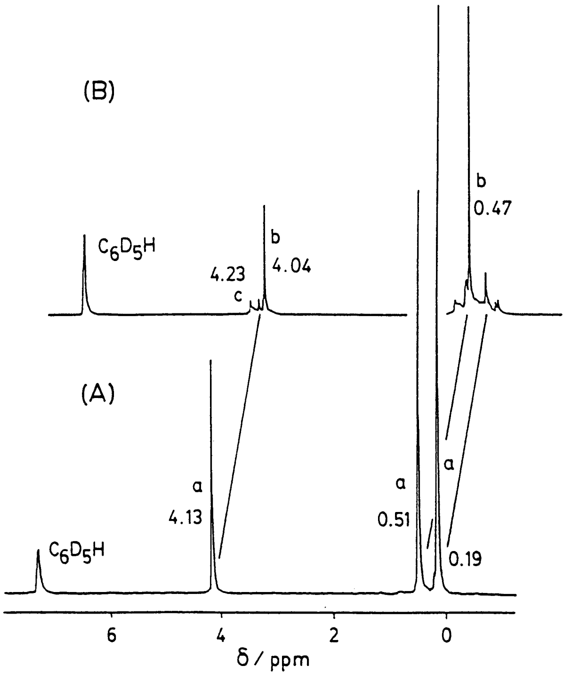

Fig. 1. ^1H NMR spectral change for the photolysis of $CpFe(CO)_2SiMe_2SiMe_3$ (**1a**) in C_6D_6. (A) Before irradiation; (B) after 8 min irradiation. a: $CpFe(CO)_2SiMe_2SiMe_3$, b: $CpFe(CO)_2SiMe_3$, c: $[CpFe(CO)_2]_2$.

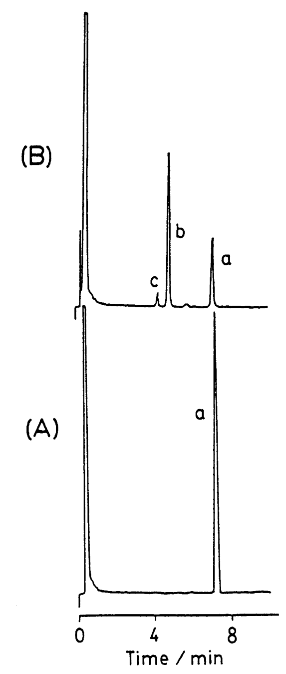

Fig. 2. Change of gas chromatogram for the photolysis of $CpFe(CO)_2SiMe_2SiMe_3$ (**1a**) in C_6D_6. (A) Before irradiation; (B) after 5 min irradiation. a: $CpFe(CO)_2SiMe_2SiMe_3$, b: $CpFe(CO)_2SiMe_3$, c: Cp_2Fe.

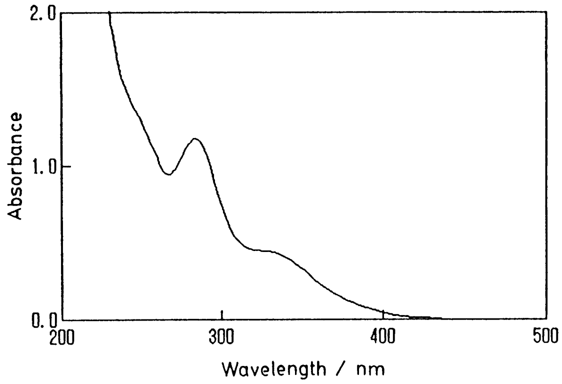

Fig. 3. Electronic spectrum of 2.3×10^{-4} M $CpFe(CO)_2SiMe_2SiMe_3$ (**1a**) in hexane.

Electronic spectra of disilanyliron complexes **1a**—**1c** show two characteristic absorption maxima at ca. 285 nm and ca. 330 nm (Table 1, Fig. 3). This fact suggests that the choice of the light source is critical. In fact, irradiation with a low pressure Hg lamp using a quartz NMR tube as a reaction vessel made the reaction more complicated.

Effect of CO Concentration on the Photoreaction of $CpFe(CO)_2SiMe_2SiMe_3$ (1a). $CpFe(CO)_2SiMe_3$ (**2a**) is known to lose one of the coordinated carbonyl ligands by near UV irradiation. Thus, the irradiation of **2a** in the presence of PPh_3 forms $CpFe(CO)(PPh_3)SiMe_3$ as a main product (Eq. 3).[24] By analogy with this reaction, the initial step of the photoreaction of **1a** is likely to be

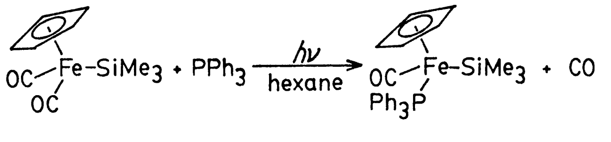

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Table 2. Photolysis of $CpFe(CO)_2SiMe_2SiMe_3$ (**1a**) under a Nitrogen Atmosphere, a Carbon Monoxide Atmosphere, and with a Vigorous Argon Bubbling

Entry	Reaction condition	Conversion/%	Product and yields/%	
			(**2a**)	ferrocene
1	N_2 atmosphere, 7 min	80	64	4
2	CO atmosphere, 4 min	73	88	9
3	Ar bubbling,[a] 5 min	83	22	3

a) Dry argon saturated with benzene vapor was bubbled through the reaction mixture. Flow rate $>15\ cm^3\,s^{-1}$.

the loss of CO.

The effect of CO on the photoreaction of **1a** was investigated by the following two experimental procedures: In the first procedure a solution of **1a** was saturated with CO before irradiation. In the second procedure CO which was considered to be liberated from **1a** was efficiently removed from the system by vigorous argon bubbling through the reaction mixture.[28] The results of these experiments along with that of photolysis under nitrogen atmosphere are summarized in Table 2.

The large decrease of the yield of **2a** in entry 3 is in accord with the light-induced CO loss mechanism. In a preliminary experiment, irradiation of vigorously argon bubbled solution of **2a** in the same conditions as in entry 3 caused decomposition of only 14% of **2a**. Therefore the decrease of **2a** during the photolysis in entry 3 is considered to be almost negligible. The substantial increase of the yield of **2a** in entry 2 comes from the efficient bimolecular CO recombination process. An analogous photochemical behavior including dissociative loss and following recombination of CO is reported with respect to the photolyses of $Me_3SiCo(CO)_4$[29] and $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$[30] in the presence of R_3SiH by Wrighton et al.

Photolysis of $CpFe(CO)_2SiMe_2SiMe_3$ (1a) in the Presence of Silylene-Trapping Agents. As mentioned above, the formation of monosilyl complex **2a** from disilanyl complex **1a** must be a result of expulsion of Me_2Si moiety. Thus, in hopes of trapping this Me_2Si moiety, we employed three different types of silylene-trapping agents, i.e., 2,3-dimethyl-1,3-butadiene (**3**),[31] diethylmethylsilane (**4**),[1] and hexamethylcyclotrisiloxane (**5**).[32] It is known that each of them undergoes a certain type of reaction with dimethylsilylene to give a specific product, **6**, **7**, or **8**, respectively (Eq. 4).

A benzene solution of $CpFe(CO)_2SiMe_2SiMe_3$ (**1a**) and two- to twenty-fold excess of a silylene-trapping agent was irradiated under conditions similar to those of the simple photolysis of **1a**. Contrary to our expectations, no silylene-trapped product was detected from each of those reaction mixtures by means of GC and GC-MS.

From the photolysis of **1a** in the presence of **3** or **5**, formation of a reasonable amount of **2a** was observed. On the other hand, the photolysis of **1a** in the presence of eighteen-fold excess of **4** provided significant amount of $CpFe(CO)_2SiMeEt_2$ (**2c**) (15%) besides **2a** (24%) (conversion: 90%). The formation of **2c** can be interpreted as a result of the silyl group exchange on iron complexes through successive oxidative addition and reductive elimination of hydrosilanes (Scheme 1).[29,30] In fact, when **2a** was irradiated in the presence

$$CpFe(CO)_2SiMe_2R \overset{h\nu}{\rightleftarrows} CpFe(CO)SiMe_2R + CO$$

1a: $R{=}SiMe_3$

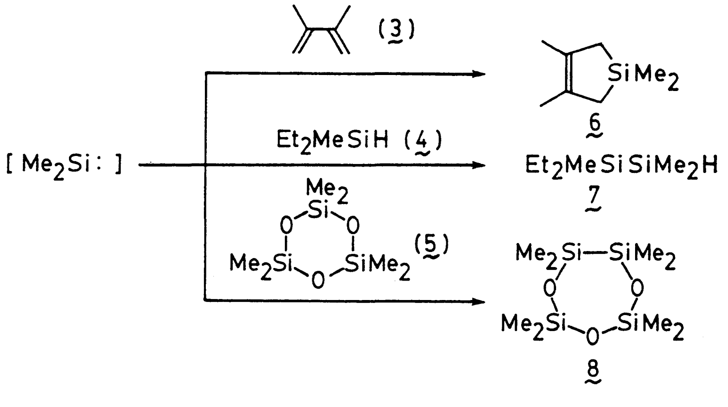
2a: $R{=}Me$

$$CpFe(CO)SiMe_2R + Et_2MeSiH \rightleftarrows CpFe(CO)H(SiMe_2R)(SiMeEt_2)$$

$$CpFe(CO)H(SiMe_2R)(SiMeEt_2) \rightleftarrows CpFe(CO)SiMeEt_2 + RMe_2SiH$$

$$CpFe(CO)SiMeEt_2 + CO \overset{h\nu}{\rightleftarrows} \underset{\mathbf{2c}}{CpFe(CO)_2SiMeEt_2}$$

Scheme 1.



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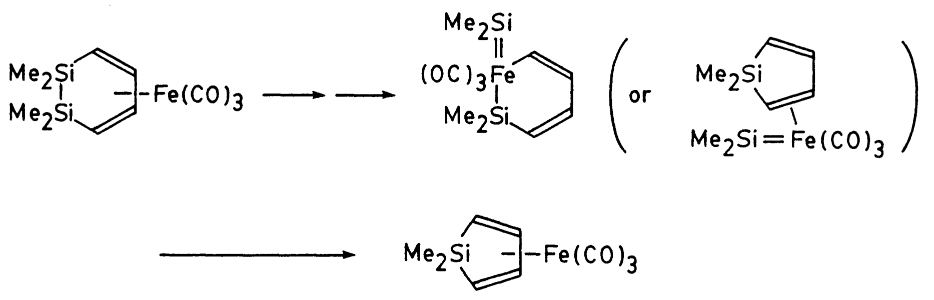
of 10 mol equiv of Et_2MeSiH, **2c** was formed in 53% yield based on 55% conversion of **2a**.

Carbon monoxide generated during the photolysis might be a silylene trapping agent. However, the following two respects seem to make this possibility unlikely: (a) The concentration of free carbon monoxide in the reaction mixture is thought to be extremely low compared with that of added trapping agent throughout the reaction; (b) since the yield of **2a** is 64% under a nitrogen atmosphere, the amount of extruded dimethylsilylene exceeds that of carbon monoxide liberated into the solution. This means that all dimethylsilylene can not be trapped by carbon monoxide if one carbon monoxide reacts with one dimethylsilylene. Therefore these results suggest the existence of some unknown route of excluding Me_2Si unit without generating free dimethylsilylene. Loss of Me_2Si unit from silylene-metal intermediate without being trapped with some trapping agents are also reported by Pannell et al. in the photolysis of $CpFe(CO)_2SiMe_2SiPh_3$[17] and by Sakurai et al. in the pyrolysis of disilacyclohexadiene iron complexes (Eq. 5).[13]

Photolysis of $CpFe(CO)_2SiMe_2SiMeEt_2$ (1c). The fact that Me_2Si unit is extruded from **1a** without being trapped suggests the complexity of the mechanism of photochemical conversion from **1a** to **2a**. To probe the structure and reactivity of intermediates in this reaction, two methyl groups on **1a** was changed to ethyl groups and the diethyl derivative **1c** was photolyzed under the same reaction conditions. Surprisingly, after 69% conversion of **1c**, three monosilyliron complexes, $CpFe(CO)_2SiMeEt_2$ (**2c**), $CpFe(CO)_2SiMe_2Et$ (**2d**), and $CpFe(CO)_2SiMe_3$ (**2a**) were obtained in 26, 33, and 4% yields, respectively, together with 7% of ferrocene (Eq 6). Monosilyl complexes **2d** and **2a** can not be formed by only the cleavage of relatively weak Si–Si and Si–Fe bonds of **1c**. Therefore it is necessary to postulate the alkyl migration between silicon atoms, although that type of reaction is very rare. To our knowledge, there are two sorts of reactions accompanying alkyl migration between two silicon atoms: The one is the 1,3-migration of a methyl group between the two silicon atoms in a cationic intermediate generated in the reaction of $(Me_3Si)_3CSiR_2I$ with silver salts,[33] and the other is the [1,3]sigmatropic shifts of methyl and phenyl groups from a saturated Si atom to an unsaturated one in dimethyl[bis(trimethylsilyl)methylene]silane or its phenyl- or *t*-butyl-substituted derivatives.[34–37] Particularly, the degenerate [1,3]-sigmatropic shift of the methyl group in dimethyl[di-*t*-butylmethylsilyl(trimethylsilyl)methylene]silane (**9**) is fast enough even at 30°C to broaden the peaks in the ^1H NMR spectrum (Eq. 7).[37]

Concerted, symmetry-allowed reaction mechanism undoubtedly plays an important role for these systems to decrease the activation energy of alkyl migration. A



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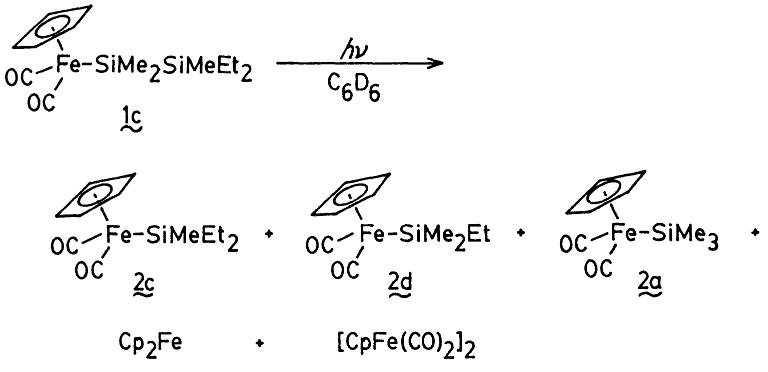

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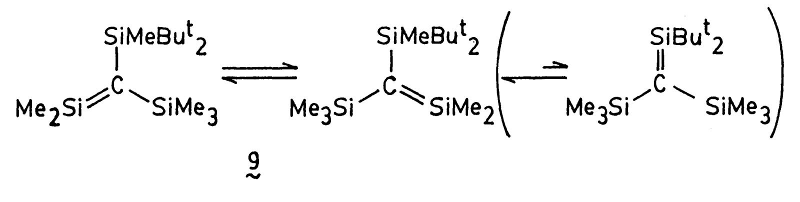

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similar concerted mechanism and perhaps a similar structure of intermediates involving an unsaturated silicon atom seem to be necessary to explain the unusually fast shift of alkyl groups in the photoreaction of **1c**. A possible mechanism will be discussed later in datail.

Photolysis of a 1 : 1 Mixture of $(MeCp)Fe(CO)_2SiMe_2SiMe_3$ (1b) and $CpFe(CO)_2SiMe_2SiMeEt_2$ (1c). It is important to determine whether the photochemical conversion from disilanyl complex to monosilyl complex proceeds intramolecularly or intermolecularly. If only an intramolecular mechanism is operative in the reaction, we can discard some mechanisms including split intermediates such as radicals, solvent separated ion pairs, etc., and possible mechanisms can be greatly limited. The lack of triethylsilyl derivative $CpFe(CO)_2SiEt_3$ in the products of the photolysis of **1c** as shown in the previous section is suggestive of the intramolecular mechanism. Thus, to obtain more reliable answer to this question, we performed the cross reaction of two substrates, **1b** and **1c**, in which the former has an iron atom labeled with methylcyclopentadienyl ligand and a disilanyl group labeled with five methyls, while the latter has an iron atom labeled with unsubstituted cyclopentadienyl ligand and a disilanyl group labeled with two ethyls and three methyls. It is apparent from the result mentioned above that a methyl group on the cyclopentadienyl ligand has almost no effect on the photoreaction (Eq 2).

When a benzene solution of a 1 : 1 mixture of $(MeCp)Fe(CO)_2SiMe_2SiMe_3$ (**1b**) and $CpFe(CO)_2SiMe_2SiMeEt_2$ (**1c**) was irradiated under a nitrogen atmosphere, ferrocene, 1-methylferrocene, 1,1′-dimethylferrocene, $CpFe(CO)_2SiMe_3$ (**2a**), $(MeCp)Fe(CO)_2SiMe_3$ (**2b**) (39%), $CpFe(CO)_2SiMe_2Et$ (**2d**) (28%), and $CpFe(CO)_2SiMeEt_2$ (**2c**) (21%) were detected by GC-MS. Yields of ferrocenes and $CpFe(CO)_2SiMe_3$ (**2a**) were not determined because the GC peaks of them were not fully separated (Fig. 4).

Scheme 2 shows the products expected from intramolecular and intermolecular alkyl migrations. Here, the intermolecular alkyl migrations include not only the intermolecular migration of an alkyl group itself but also that of silyl groups, e.g., $SiMeEt_2$, $SiMe_2Et$, etc. None of the products which are expected only from intermolecular alkyl migrations was detected in the reaction mixture by GC-MS. Therefore the possibility of intermolecular alkyl migration mechanisms is effectively ruled out.

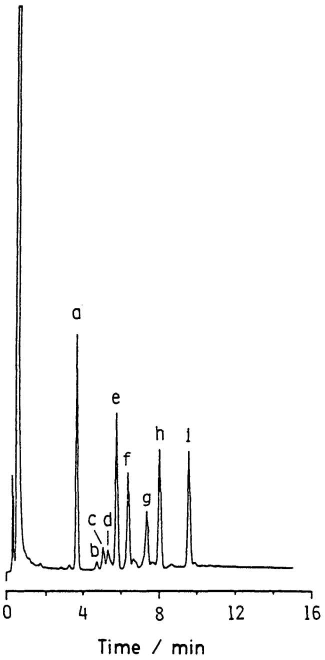
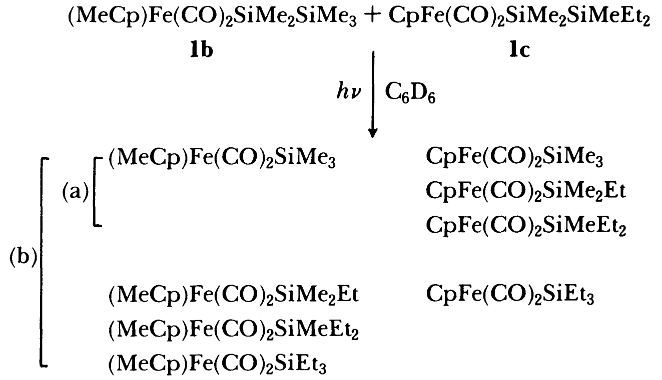


Fig. 4. Gas chromatogram after a 1:1 mixture of **1b** and **1c** was photolyzed for 8 min. a: dodecane, b: $FeCp_2$, c: $FeCp(MeCp)$, d: $Fe(MeCp)_2$+$CpFe(CO)_2SiMe_3$, e: $(MeCp)Fe(CO)_2SiMe_3$, f: $CpFe(CO)_2SiMe_2Et$, g: $CpFe(CO)_2SiMeEt_2$, h: $(MeCp)Fe(CO)_2SiMe_2SiMe_3$, i: $CpFe(CO)_2SiMe_2SiMeEt_2$.



$$\underset{\textbf{1b}}{(MeCp)Fe(CO)_2SiMe_2SiMe_3} + \underset{\textbf{1c}}{CpFe(CO)_2SiMe_2SiMeEt_2} \xrightarrow[C_6D_6]{h\nu}$$

(b) [(a) [$(MeCp)Fe(CO)_2SiMe_3$ — $CpFe(CO)_2SiMe_3$, $CpFe(CO)_2SiMe_2Et$, $CpFe(CO)_2SiMeEt_2$]

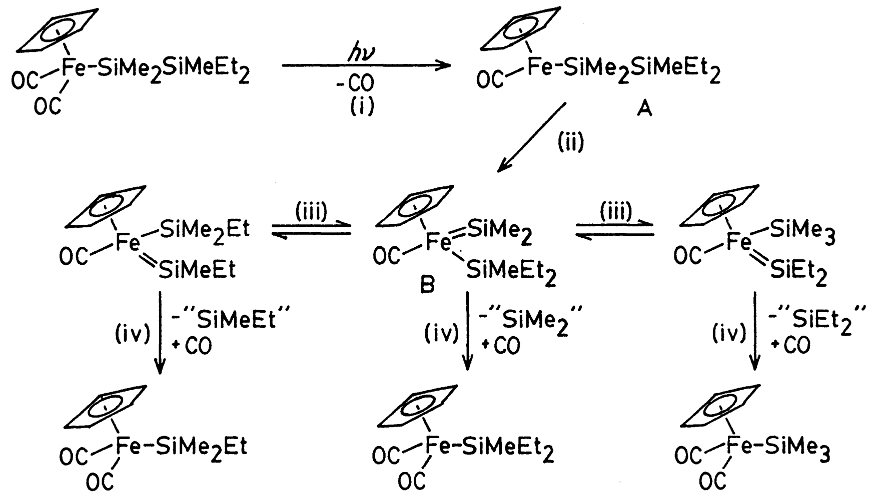
$(MeCp)Fe(CO)_2SiMe_2Et$, $(MeCp)Fe(CO)_2SiMeEt_2$, $(MeCp)Fe(CO)_2SiEt_3$ — $CpFe(CO)_2SiEt_3$]

(a) Products expected from an intramolecular alkyl migration mechanism.
(b) Products expected from an intermolecular alkyl migration mechanism.

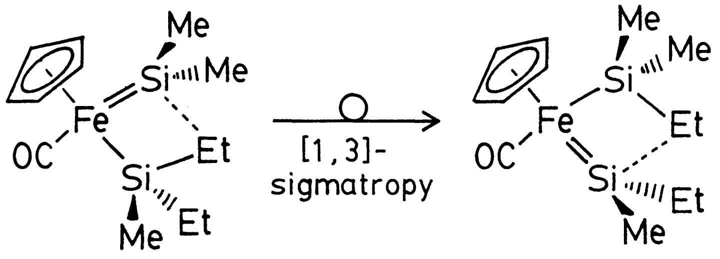
Scheme 2.

Mechanism of Photochemical Conversion from Disilanyliron Complexes to Monosilyliron Complexes. The following points were revealed in this study: (1) The reaction may be initiated by a light-induced CO loss and completed by a CO re-coordination; (2) unusually fast intramolecular alkyl migration from one silicon atom to the other occurs during the photoreaction, and the existence of concerted process such as the sigmatropic shift is suggested; (3) The R_2Si unit extruded in this photochemical conversion could not be trapped with usual silylene trapping agents. This fact implies the existence of some unknown route of excluding R_2Si unit without generating free silylene.

Although the third point is still obscure, we can construct the principal framework of the possible mechanism as shown in Scheme 3. The key intermediate is silyl(silylene)iron complex **B** which is very likely to be formed by 1,2-migration of the terminal silyl group to the 16e metal center of intermediate **A**. Moreover, it is worth noticing that this intermediate **B**



Scheme 3.



Scheme 4.

takes an ideal geometry for [1,3]sigmatropic shift of an alkyl group from a saturated Si atom to an unsaturated one as depicted in Scheme 4.

The mechanism contains four successive reactions which are essentially similar to those proposed by Pannell et al. for the photoreaction of $CpFe(CO)_2SiMe_2SiPh_3$:[18] (i) Photochemically induced loss of CO to generate a coordinatively unsaturated complex A; (ii) 1,2-shift of the terminal silyl group to the Fe atom; the formation of a silyl(silylene)iron complex B; (iii) [1,3]sigmatropic alkyl shift from a saturated Si atom to an unsaturated one; and (iv) ligand substitution of dialkylsilylene by carbonyl.

The product ratio in the photolysis of $CpFe(CO)_2SiMe_2SiMeEt_2$ turned out to be $CpFe(CO)_2SiMe_3$: $CpFe(CO)_2SiMe_2Et$: $CpFe(CO)_2SiMeEt_2$=0.7 : 6 : 4.7. Therefore interconversion between three silyl(silylene)iron complexes (iii) seems to be quicker than the ligand substitution of dialkylsilylene by carbonyl, since the observed product ratio is relatively close to the statistically predicted product ratio after reaching an equilibrium of the interconversion: $CpFe(CO)_2SiMe_3$: $CpFe(CO)_2SiMe_2Et$: $CpFe(CO)_2SiMeEt_2$=1 : 6 : 3 on the assumption that methyl and ethyl groups behave identically.

Low-temperature photolysis of **1a** was carried out in hopes of observing the silyl(silylene)iron complexes. However, irradiation in a methylcyclohexane matrix at 77 K resulted in little net photoreaction. In comparison with the efficient photochemical conversion of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ to $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ at 77 K,[38] this low efficiency may be attributable to the difficulty of migration of bulky trimethylsilyl group in a relatively hard methylcyclohexane matrix.

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20) This compound was prepared owing to standard procedures shown in the following equation.

$$\mathrm{PhMe_2SiLi{+}Et_2MeSiCl} \xrightarrow[\mathrm{THF}]{} \mathrm{PhMe_2SiSiMeEt_2}$$

$$\xrightarrow[\text{benzene}]{\text{HCl, cat. AlCl}_3} \mathrm{ClMe_2SiSiMeEt_2}$$

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