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Evidence for Equilibration of 1,3-Alkyl Migration in Silyl(silylene)iron Intermediates

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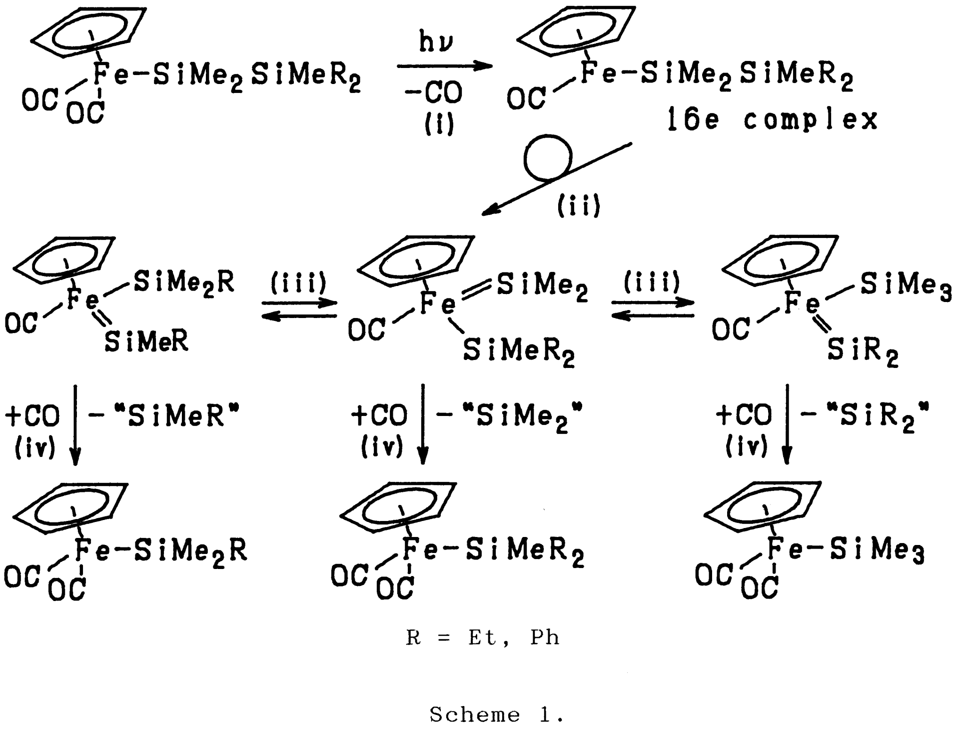
Photolysis of deuteriomethyl-substituted disilanyliron complex $CpFe(CO)_2Si_2Me_{5-m}(CD_3)_m$ (m = 1, 2) resulted in the formation of a mixture of silyliron complexes $CpFe(CO)_2SiMe_{3-n}(CD_3)_n$ (n = 0 - m). Distribution of the produced silyliron complexes indicates that the reaction accompanies alkyl scrambling between two silicon atoms and the scrambling is fast enough to attain an equilibrium.

Photolysis of disilanyliron complexes $FpSi_2Me_{5-n}R_n$ (Fp = $CpFe(CO)_2$; n = 1 - 3; R = Ph, Et) has been proposed to proceed via a mechanism shown in Scheme I,[1-4] (i) photochemically induced loss of a CO ligand to give a coordinatively unsaturated complex; (ii) 1,2-shift of the terminal silyl group to iron atom to form a silyl(silylene)iron intermediate; (iii) [1,3]-sigmatropic methyl and/or R group shift from a silyl group to a silylene ligand; and (iv) ligand substitution of silylene by carbon monoxide. The step (iii) is a unique pathway since the very



Scheme 1.

rapid scrambling of methyl and R groups occurs between the silyl(silylene)iron intermediates. In this paper, an evidence is presented that an equilibrium is attained almost completely in the step (iii).

Pannell's group[1,4)] and we[2,3)] have determined the product distribution in photolysis of complexes $FpSi_2Me_{5-n}R_n$ (n = 1 - 3; R = Ph, Et). In Table 1 (entries 1 - 4), those results are summarized along with the statistically expected values. The latter values were calculated on the assumptions that (1) the ligand substitution of silylene ligand by carbon monoxide (step (iv)) occurs after establishing an equilibrium of the interconversion between silyl(silylene)iron intermediates and (2) methyl and R groups behave identically.

The product ratio in photolysis of $FpSiMe_2SiMeEt_2$ is relatively close to the statistical one. On the other hand, Pannell's results are far away from those expected statistically. Pannell et al. describe in their paper that the nonstatistical distribution of $FpSiMe_{3-m}Ph_m$ complexes suggests either a thermodynamic or kinetic stability difference between the equilibrating silyl(silylene) intermediates.[4)] To minimize the steric and electronic influence of R for the product distribution, we prepared three trideuteriomethyl-substituted complexes, $FpSiMe_2SiMe(CD_3)_2$ (**1**), $FpSiMe_2SiMe_2CD_3$ (**2**), and $FpSiMe(CD_3)SiMe_3$ (**3**), and examined the photolytic product distribution of them.

The bis(deuteriomethyl)disilanyliron complex **1** was prepared by treating dichlorodisilanyliron complex $FpSiMe_2SiMeCl_2$ **4** with CD_3MgI.[5)] The preparative procedures of **4** (Eq. 1) and **1** (Eq. 2) were as follows: **4**: A solution of NaFp (30

$$Na[CpFe(CO)_2] + ClMe_2SiSiMeCl_2 \longrightarrow \underset{\mathbf{4}}{CpFe(CO)_2SiMe_2SiMeCl_2} \qquad (1)$$

$$\underset{\mathbf{4}}{CpFe(CO)_2SiMe_2SiMeCl_2} + 2CD_3MgI \longrightarrow \underset{\mathbf{1}}{CpFe(CO)_2SiMe_2SiMe(CD_3)_2} \qquad (2)$$

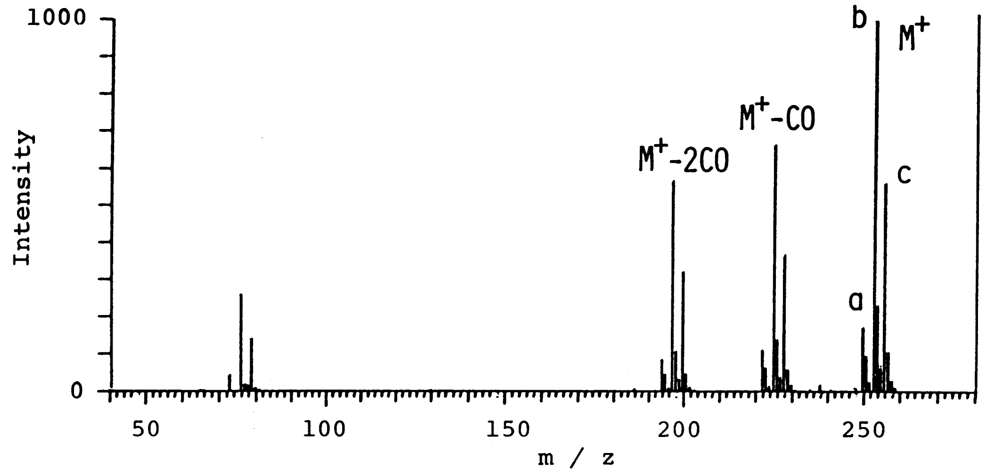


Fig. 1. GC-MS (14 eV) of a mixture of silyliron complexes, $FpSiMe_3$ (a; M^+ = 250), $FpSiMe_2CD_3$ (b; M^+ = 253), and $FpSiMe(CD_3)_2$ (c; M^+ = 256), produced from $FpSiMe_2SiMe(CD_3)_2$ (1).

Table 1. Product distribution in photolysis of disilanyliron complexes $FpSi_2Me_{5-n}R_n$ (R = Et, Ph, or CD_3)

Entry	Disilanyliron complex	Product distribution / %[a]			Ref.
		$FpSiMe_3$	$FpSiMe_2R$	$FpSiMeR_2$	
1	$FpSiMe_2SiMeEt_2$	6(10)	52(60)	41(30)	3
2	$FpSiMe_2SiMePh_2$	1(10)	51(60)	47(30)	4
3	$FpSiMe_2SiMe_2Ph$	7(40)	93(60)		4
4	$FpSiMePhSiMe_3$	8(40)	92(60)		4
5	$FpSiMe_2SiMe(CD_3)_2$	10(10)	57(60)	33(30)	This work
6	$FpSiMe(CD_3)SiMe_3$	41(40)	59(60)		This work
7	$FpSiMe_2SiMe_2CD_3$	39(40)	61(60)		This work

a) The statistically expected value is given in parentheses.

mmol) in 100 ml of THF was added to a solution of $ClMe_2SiSiMeCl_2$ (30 mmol) in 260 ml of THF over 3 h with vigorous stirring at room temperature. The reaction mixture was stirred for additional 20 h, and then the solvent was removed in vacuo. The resulted brown residue was extracted with 110 ml of hexane, and the extract was filtered through a 3 cm of Celite pad. The filtrate was evaporated in vacuo. Molecular distillation of the brown residue (0.007 Torr, 95 °C) afforded orange crystals of **4** in 57% yield. **1**: The dichloro complex **4** (3.2 mmol) was treated with CD_3MgI prepared from Mg (10.7 mmol) and CD_3I (10.3 mmol) in Et_2O (4 ml). The reaction mixture was vigorously stirred for 18 h at room temperature. After workup similar to that of **4** described above, an orange oil of **1** was obtained in 52% yield. Similarly, the mono(deuteriomethyl)disilanyl complexes, **2** and **3**, were obtained by the reaction of the corresponding chloro complexes with CD_3MgI in 68 and 75% yields, respectively.(6)

Photolysis of the disilanyliron complexes was carried out as follows: A C_6D_6 solution of the disilanyliron complex was placed in a Pyrex NMR tube and irradiated with a 450W medium pressure Hg arc lamp in a water-cooled quartz jacket at room temperature. The reaction was periodically monitored by ^1H NMR and gas chromatography (column: SE-30 10% 1m). The gas chromatogram of the reaction mixture showed three peaks. They have been assigned to ferrocene, a mixture of monosilyliron complexes, and the starting material, respectively. The distribution of the silyliron complexes was determined from the intensities of the molecular ion peaks of GC-MS (15 or 20 eV). Figure 1 shows a GC-MS of a mixture of silyliron complexes porduced from **1** as a typical example. Results for the photolyses of the disilanyl complexes, **1** - **3**, are summarized in Table 1 (entries 5 - 7).

The molar ratios of the silyliron complexes produced from the deuteriomethyl-substituted disilanyl complexes, **1** - **3**, are in good agreement with the statistically expected values (entries 5 - 7). Therefore, the alkyl scrambling occurs fast enough to attain an equilibrium in the silyl(silylene)iron intermediates.

Both the monodeuteriomethyldisilanyliron complexes, **2** and **3**, gave the same silyliron complexes $FpSiMe_3$ and $FpSiMe_2(CD_3)$ (entries 6 and 7). The product distribution is comparable with each other and very close to the statistically expected values. These findings again demonstrate that the alkyl scrambling between two silicon atoms in the silyl(silylene)iron intermediates reaches to the equilibrium almost completely. In addition, the good agreement between the product ratios in entries 6 and 7 indicates that the photoinduced conversion from disilanyliron complexes, **2** and **3**, to monosilyliron complexes proceeds via the same intermediates and the fast alkyl migration takes place in them. Thus, the previously proposed mechanism shown in Scheme 1 is reasonable to account for the results in this work.

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5) **1**: Anal. Found: C; 45.76, H; 8.33%. Calcd for $C_{12}H_{14}D_6FeO_2Si_2$: C; 45.87, H; 8.31%.
6) **2**: Exact mass. Found: 311.0539. Calcd for $C_{12}H_{17}D_3FeO_2Si_2$: 311.0539.
3: Exact mass. Found: 311.0537. Calcd for $C_{12}H_{17}D_3FeO_2Si_2$: 311.0539.

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