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Photochemical Conversion of Disilanyliron(II) Complexes to Monosilyliron(II) Complexes

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Photolysis of a C_6D_6 solution of $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_2\text{-}SiMeR_2$ ($Fp\text{-}SiMe_2SiMeR_2$; R=Me, Et) results in the formation of monosilyl-Fp derivatives with the scrambling of alkyl groups. Possible reaction pathways involving silyleneiron intermediates are discussed.

Although photolysis of polysilane derivatives is an important method to generate silicon-containing reactive intermediates,1) there has been no report on the photochemistry of transition metal carbonyl complexes containing disilanyl group(s). Considering that an Si-Si single bond undergoes oxidative addition to various transition metals under very mild conditions,2) the intramolecular oxidative addition of the Si-Si bond in disilanyl-metal complexes is also expected to occur to give silylene-metal complexes. This hypothesis prompted us to investigate the reactivity of disilanyl-metal complexes.

In this paper, we report the photochemical conversion of $(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}SiMe_2SiMeR_2$ ($Fp\text{-}SiMe_2SiMeR_2$; R=Me, Et) (1) producing monosilyliron complexes. The reaction is accompanied by the scrambling of alkyl groups, which is reasonably explained by postulating the formation of silyl(silylene)iron complexes as transient intermediates. Quite recently, Pannell et al. reported independently the photolysis of $Fp\text{-}SiMe_2SiPh_3$ and they also suggested a possible mechanism involving silylene-metal intermediates.3)

When a C_6D_6 solution of $Fp\text{-}SiMe_2SiMe_3$ (1a)4) in a Pyrex tube was irradiated with a 450 W medium pressure mercury arc lamp at room temperature, $Fp\text{-}SiMe_3$ (2)5) was obtained in 64% yield (conversion: 80%) together with ferrocene (Cp_2Fe; 4%) and $Cp_2Fe_2(CO)_4$. The photoreaction was monitored periodically by ^1H NMR

$$\underset{\textbf{1a}}{Fp\text{-}SiMe_2SiMe_3} \xrightarrow[C_6D_6]{h\nu} \underset{\textbf{2}}{Fp\text{-}SiMe_3} + Cp_2Fe + Cp_2Fe_2(CO)_4 \qquad (1)$$

spectroscopy and gas chromatography (column: SE-30 10% 1 m, 100-250 °C). The products were identified by comparing the retention times of their gas chromatography peaks as well as their GC-MS fragment patterns with those of authentic samples. The product 2 can be isolated either by silica gel column chromatography or by molecular distillation from the reaction mixture.

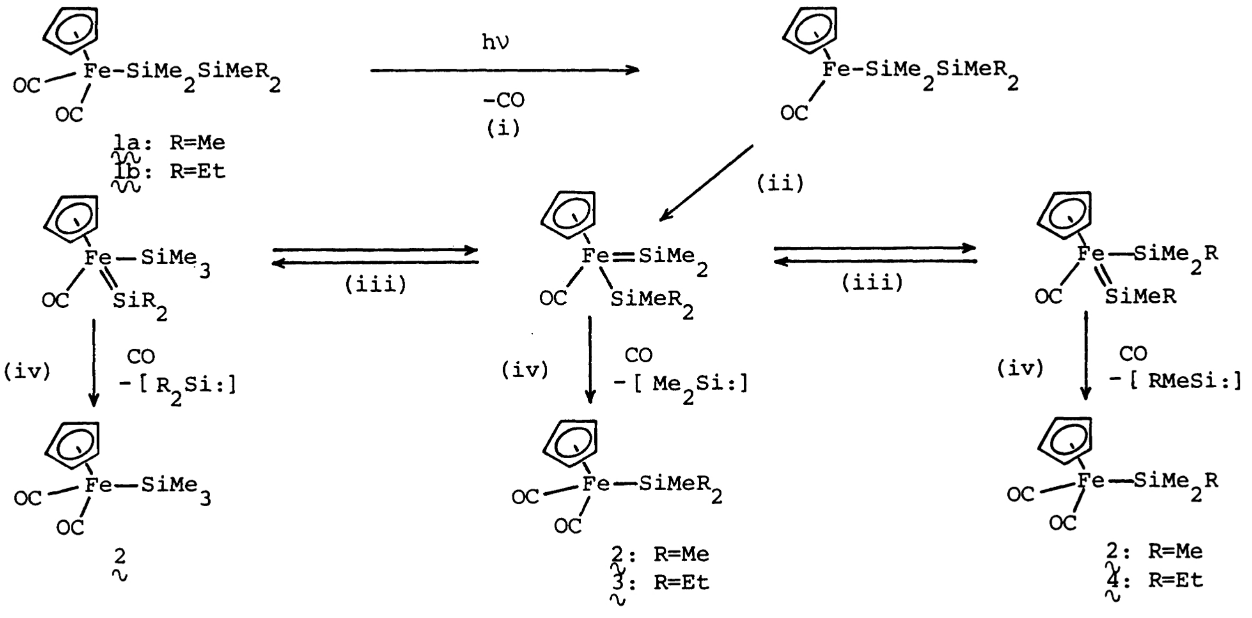
A ^{1}H NMR spectrum of the final reaction mixture (conversion: 98%) showed no strong Si-Me signals except that of **2**. This implies that dimethylsilylene, which is considered to be extruded from **1a**, forms a number of oligomeric and/or polymeric products. The formation of $Cp_2Fe_2(CO)_4$ suggests the existence of a pathway including homolytic cleavage of the Si-Fe bond. When the photolysis of **1a** was performed in a quartz NMR tube with a low pressure mercury arc lamp, more complicated spectral changes were observed: The yield of **2** was low and some other unidentified by-products were formed.

To determine which silicon atom is liberated from the disilanyliron complex **1a**, $Fp\text{-}SiMe_2SiMeEt_2$ (**1b**) was prepared$^{6)}$ and photolyzed. Surprisingly, irradiation of a C_6D_6 solution of **1b** with the 450 W medium pressure lamp afforded a mixture of three monosilyliron complexes, $Fp\text{-}SiMeEt_2$ (**3**),$^{6)}$ $Fp\text{-}SiMe_2Et$ (**4**),$^{7)}$ and $Fp\text{-}SiMe_3$ (**2**) in 26, 33, and 4% yield (conversion: 69%), respectively, and 7% of ferrocene. The formation of **4** (the major product) and **2** can not be explained without

$$\underset{\mathbf{1b}}{Fp\text{-}SiMe_2SiMeEt_2} \xrightarrow[C_6D_6]{h\nu} \underset{\mathbf{3}}{Fp\text{-}SiMeEt_2} + \underset{\mathbf{4}}{Fp\text{-}SiMe_2Et} + \underset{\mathbf{2}}{Fp\text{-}SiMe_3} + Cp_2Fe + Cp_2Fe_2(CO)_4 \qquad (2)$$

considering alkyl migration from one silicon atom to the other. Moreover, it should be noted that the absence of the triethylsilyliron complex in the products may be an evidence for the lack of the intermolecular alkyl transfer mechanism.

A possible mechanism for the photolysis of disilanyliron complexes **1a** and **1b** is outlined in Scheme 1, which is similar to that suggested by Pannell et al. for the photolysis of $Fp\text{-}SiMe_2SiPh_3$.$^{3)}$ The mechanism contains four successive



Scheme 1.

reactions which are as follows: (i) photochemically induced loss of CO to generate a coordinatively unsaturated complex; (ii) 1,2-shift of the terminal silyl group from silicon to iron; the formation of a silyl(silylene)iron complex; (iii) 1,3-alkyl migration from the silyl group to the silylene group, and (iv) ligand substitution of dialkylsilylene by carbonyl.

According to the above mechanism, if the free carbon monoxide formed during the reaction is efficiently removed out of the reaction system, the yield of the monosilyliron complex should decrease significantly. In fact, the photolysis of a vigorously argon purged benzene solution (flow rate > 15 ml/s) of **1a** afforded **2** in a fairly low yield (17%).

Attempts were made to trap dimethylsilylene with hydrosilane and diene, which are regarded as efficient silylene trapping agents.[8] As a result, contrary to our expectations, the photolysis of **1a** in the presence of 10 molar equivalents of Et_2MeSiH afforded, after 90% of **1a** was consumed, Fp-$SiMe_3$(**2**), Fp-$SiMeEt_2$(**3**), and ferrocene in 24, 15, and 11% yields, respectively, whereas $Et_2MeSiSiMe_2H$, the trapped product of dimethylsilylene with Et_2MeSiH, was not detected by means of GC or GC-MS. In a similar manner, the photolysis of **1a** in the presence of two molar equivalents of 2,3-dimethylbutadiene did not give the trapped product, 1,1,3,4-tetramethyl-1-silacyclopent-3-ene.[9] The formation of **3** in the former trapping reaction can be interpreted as a result of the silyl group exchange on iron complexes through successive oxidative addition and reductive elimination of hydrosilanes (Scheme 2).[10] In fact, when **2** was irradiated in the presence of 10 molar equivalents of Et_2MeSiH, **3** was formed in 53% yield (based on 55% conversion of **2**).

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

1a: R=$SiMe_3$, **2**: R=Me

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

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

$$CpFe(CO)SiMeEt_2 + CO \xrightleftharpoons[h\nu]{} \underset{\mathbf{3}}{CpFe(CO)_2SiMeEt_2}$$

Scheme 2.

Silylene-metal complexes have often been invoked as possible intermediates in metal-catalyzed reactions[11] and in the decomposition of silicon-containing organometallic complexes.[12] On the other hand, there is only one isolable silylene complex known so far, i.e., $Me_2SiFeH(CO)_3(SiMe_2R)$ (R=H, Me), which is prepared by the reaction of $Fe_2(CO)_9$ with $RMe_2SiSiMe_2H$.[13] Interestingly, this reaction also involves the 1,2-shift of a silyl group from silicon to iron. The photochemistry of disilanyl-substituted molybdenum, tungsten, and other transition metal carbonyl complexes are currently under active investigation.

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6) **1b** was prepared by the reaction of Na[FeCp(CO)$_2$] with equimolar Et$_2$MeSiSiMe$_2$Cl in THF. Yield: 73% based on Cp$_2$Fe$_2$(CO)$_4$, the precursor of Na[FeCp(CO)$_2$]. The authentic sample of **3** was prepared in a similar manner in 68% yield. **1b**: an orange oil; ^{1}H NMR (C$_6$D$_6$) 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$_6$D$_6$) δ 215.9 (CO), 83.1 (Cp), 8.5 (CH$_3$ of Et), 6.4 (Si-CH$_2$), 4.5 (Si-Me), -5.2 (Si-Me); MS m/e 336 (16; M$^+$), 159 (100; Et$_2$MeSiSiMe$_2$$^+$); IR (neat) 1990, 1934 cm^{-1} (CO); Anal. Found: C, 50.15; H, 7.25%. Calcd for C$_{14}$H$_{24}$FeO$_2$Si$_2$: C, 50.00; H, 7.19%. **3**: an orange oil; ^{1}H NMR (C$_6$D$_6$) δ 4.07 (5H, s, Cp), 1.3-0.7 (10H, m, Et), 0.44 (3H, s, Me); ^{13}C NMR (C$_6$D$_6$) δ 216.2 (CO), 83.2 (Cp), 14.4 (Si-CH$_2$), 9.4 (Me), 2.2 (Me); MS m/e 278 (11; M$^+$), 101 (48; Et$_2$MeSi$^+$); IR (neat) 1988, 1929 cm^{-1} (CO); Anal. Found: C, 52.05; H, 6.58%. Calcd for C$_{12}$H$_{18}$FeO$_2$Si: C, 51.81; H, 6.52%.

7) The authentic sample of **4** was prepared by successive reactions of Me$_2$SiCl$_2$ with slight excess of EtMgBr and then with Na[FeCp(CO)$_2$] in one pot in THF. Yield: 68% based on Cp$_2$Fe$_2$(CO)$_4$ (see Ref. 6). **4**: an orange oil; ^{1}H NMR (C$_6$D$_6$) δ 4.04 (5H, s, Cp), 1.2-0.7 (5H, m, Et), 0.45 (6H, s, Me); ^{13}C NMR (C$_6$D$_6$) δ 216.1 (CO), 83.3 (Cp), 16.4 (Si-CH$_2$), 9.2 (Me), 4.8 (Me); MS m/e 264 (20; M$^+$), 87 (74; EtMe$_2$Si$^+$); IR (neat) 1986, 1925 cm^{-1} (CO); Anal. Found: C, 49.93; H, 6.06%. Calcd for C$_{11}$H$_{16}$FeO$_2$Si: C, 50.02; H, 6.11%.

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